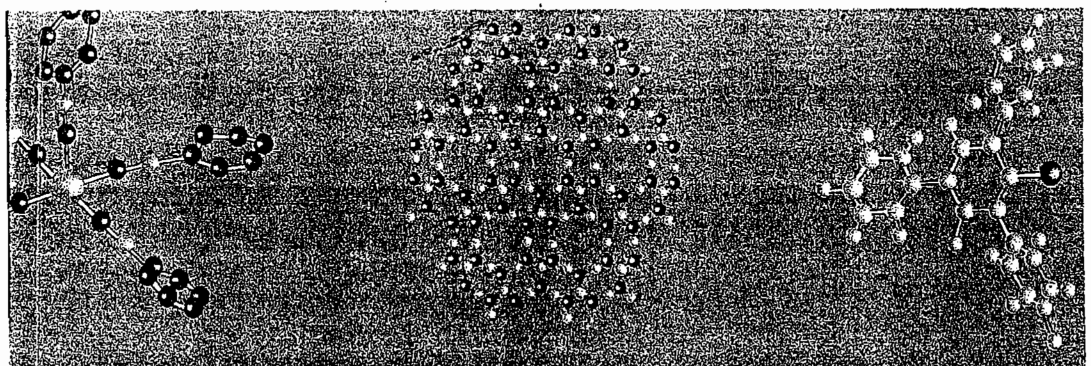

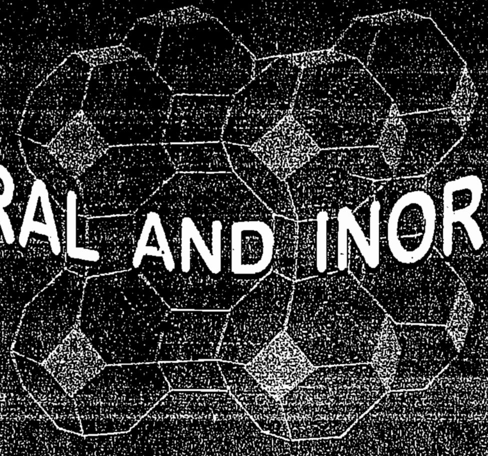

GENERAL AND INORGANIC CHEMISTRY

[Part II]

R. Sarkar

An advanced level text for BSc (Hons/Major) students,
also helpful to students of environmental science, marine science etc.
and candidates of NET/SLET and other competitive examinations

General and Inorganic CHEMISTRY

In SI Units

Part II

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to
my parents

Preface

No lame excuse would suffice to justify the long gap in the publication of this second part of General and Inorganic Chemistry, specially in view of the warm reception which the Part I of the book had received from teachers and students throughout India. The author would instead submit his unconditional apology to the readers for the immense inconvenience caused.

This part of the book deals mainly with chemistry of the elements meant for the 3-year degree students. In keeping with recent revisions in the syllabii of different universities, organometallic chemistry and bioinorganic chemistry have been included in separate chapters though in an extremely elementary manner to cope with the suggested time schedule. The treatments provided in the descriptive inorganic chemistry portions have been rather lengthy, but this was unavoidable to maintain a balance between facts and interpretations both of which have expanded by leaps and bounds in the recent past. The approach has been rather classical but the objective was to provide a single one volume source for the inquisitive learners most of whom do not have proper access to the costly books and periodicals on the subject. As before, in-chapter exercises, problems and summaries at the end of each chapter have been added to assist the students.

This book is essentially a compilation of the facts and interpretations available in standard texts and in doing so I have drawn freely from works of eminent authors in the subject to whom I am greatly indebted. I gratefully acknowledge the resources available in their texts and convey my sincerest thanks to all of them. A list of sourcebooks has been added separately. To quote poet Kalidasa in *Raghuvamsam*, my role has been like a thread passing through jewels pierced by drills as has been done by my predecessors in this discipline :

Athavā kṛtāvāgdvāré vaṃśésmin pūrvasūriviḥ
Maṇau vajrasamutkirṇé sūtrasyévāsti mé gatiḥ.

I am grateful to Prof. Nityananda Saha who had kindly edited the part one of the book and also few initial chapters of this part. His continuous encouragement has been a source of inspiration to me though I failed to keep in touch with him owing to my protracted illness. The work could not have been completed but for the untiring help rendered by some of my friends, colleagues and ex-students. I gratefully acknowledge the meticulous efforts of Dr. Rupendranath Bandyopadhyay (Jadavpur University), Dr. Gourgopal Basak (New Alipore College) and Dr. Arindam Rana (City College) who read several parts of the manuscript and offered many valuable suggestions for which I shall remain indebted to them forever. I am also thankful to Dr. Ramsundar Bandyopadhyay (Calcutta University), Dr. Subhendu Gupta (Raja Peary Mohan College), Sri Tilak Dutta, Dr. Bhaskar Ghosh and Dr. Kakali Das for various helps; to Sri Amritendu Mukherjee, Sri Rupanjan Bhattacharyya and Sm Basudha Sarkar who prepared the index with utmost care; to Mr. Uday Guha who spared no pain in preparing the typescript flawlessly and to Sri Shyamal Bhattacharya, computer operator of Books and Allied Pvt. Ltd for his untiring effort in reproducing the computer diagrams and typesetting the book. Last, but not least, I am also grateful to Mr. Jogendranath Sen and Mr. Arunabha Sen of the New Central Book Agency for their extreme patience throughout all these years.

In spite of my best efforts, this first edition may not be found without a number of mistakes, misconceptions and misprints for which I beg to be pardoned by the learned teachers and beloved students. My efforts will not go in vain if I am regarded by my readers as one who dreams to remain a garland-maker in the garden of Goddess Saraswati—*"ami tabo malancher habo malakar."*

Sripanchami, 1407 Bangabda
January 29, 2001

R. Sarkar

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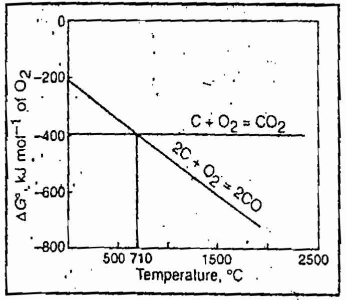

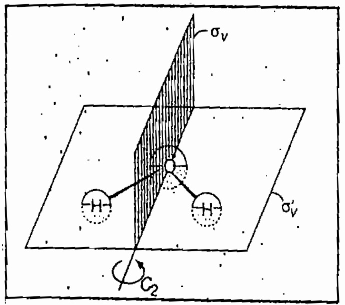

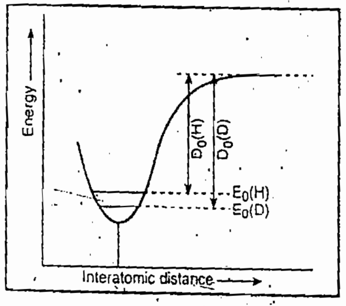

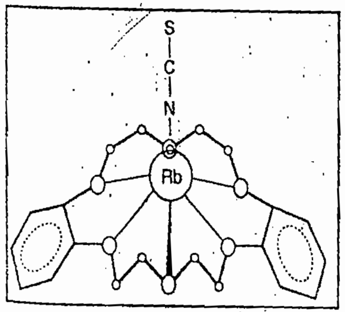

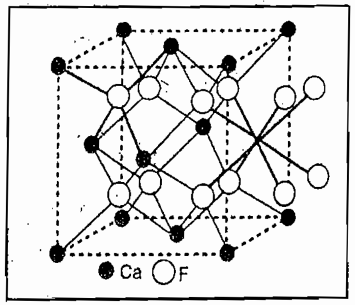
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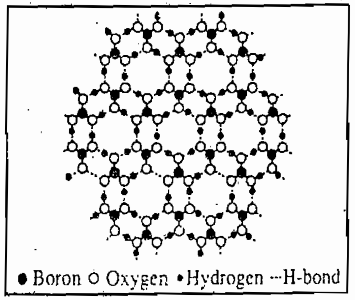
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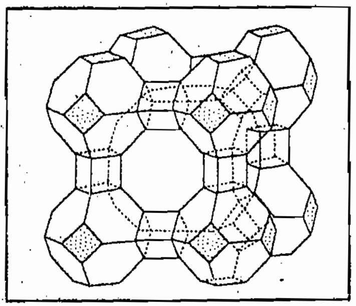

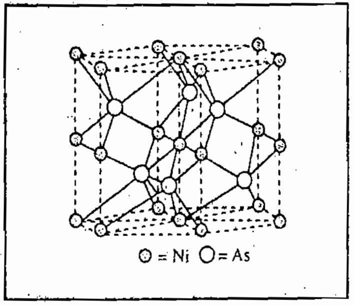
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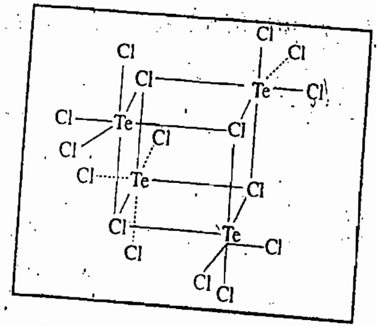
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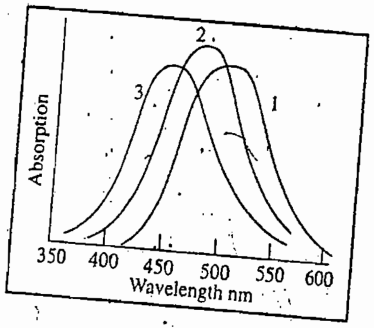
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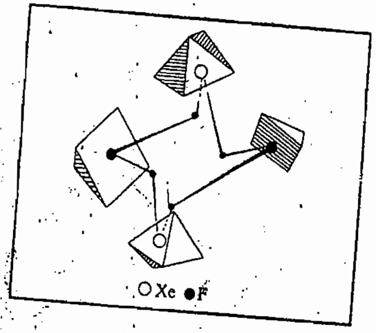
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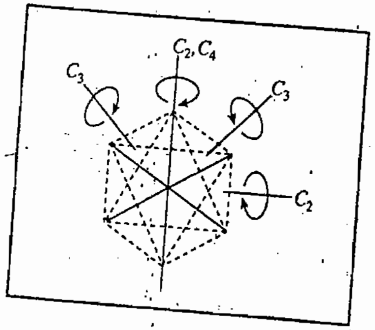
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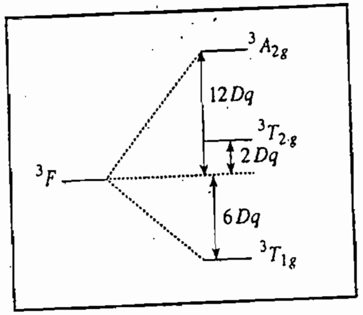
C_2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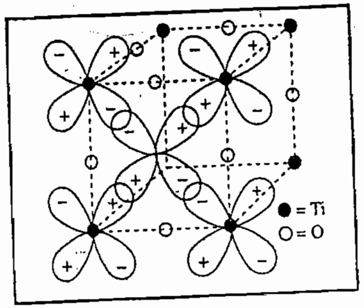
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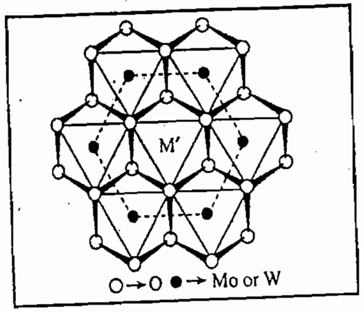
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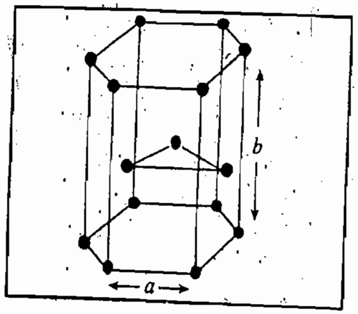
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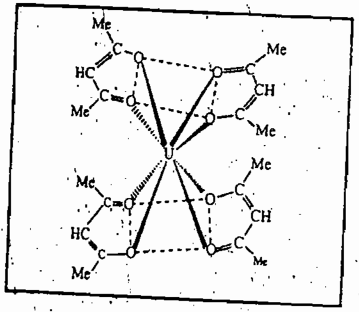
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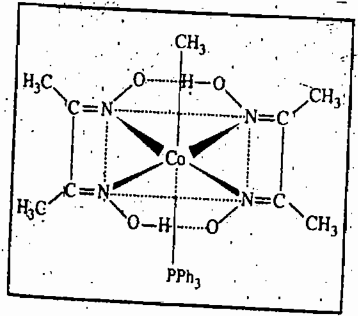
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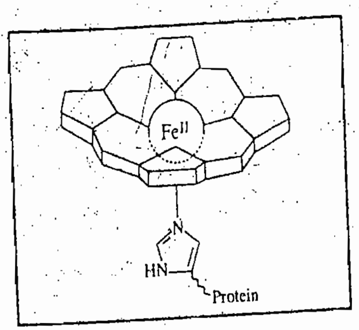

General & Inorganic
CHEMISTRY

Part II

CHAPTER FIFTEEN

UNDERSTANDING CHEMICAL REACTIONS

OBJECTIVES

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15.2. Chemical Energetics
  - Enthalpy [15.2.1]
  - Entropy [15.2.1]
  - Gibbs energy [15.2.3]

15.3. Kinetics and Mechanism
  - The rate of a chemical reaction [15.3.1]
  - Theories of rate processes [15.3.2]
  - Reaction Mechanism [15.3.3]

15

15.1. INTRODUCTION

Why do chemical reactions occur? This leading question in chemistry cannot be answered in a simple sentence. Detailed investigations reveal that two factors primarily determine the feasibility of a chemical reaction under a given set of conditions :

Energy and Rate

(1) The potential energy of the reacting system must be lowered by the reaction. This criterion is the same as the criterion of spontaneity of any physical process in the universe. (2) Even when the reactants possess the "potentiality" to react, they must find a suitable path to react at a perceptible rate under the specified conditions. The first aspect concerns thermodynamics and is often discussed under the sophisticated name: "chemical energetics". The second one constitutes the study of chemical kinetics. We shall briefly survey these two aspects of chemical reactions in the following discussion.

15.2 CHEMICAL ENERGETICS

All natural processes follow a general trend—they take place in the direction which results in an ultimate decrease of the energy of the universe. Chemical reactions are also governed by this general rule. The release of energy in a chemical reaction is readily demonstrated by the exothermic reactions. Side by side, there are endothermic reactions which are accompanied by an absorption of heat. In fact, many exothermic reactions are reversible and the reverse process must be endothermic in nature. The synthesis of ammonia provides a ready example:

Forward: $1/2\,N_2 + 3/2\,H_2 \longrightarrow NH_3 + 46.0$ kJ.

Reverse: $NH_3 + 46.0\text{ kJ} \longrightarrow 1/2\,N_2 + 3/2\,H_2$

So, evolution of heat cannot be considered to be the only way to attain a state of lower energy and provide the necessary driving force for a reaction. Careful consideration of a large number of spontaneous processes has now established that two factors control the ultimate energy change during a chemical process. These are: (1) the enthalpy change (ΔH) and (2) the entropy change (ΔS). These two changes collectively determine the change of another fundamental property of the system, the Gibbs energy (also free energy; ΔG). Thorough acquaintance of these factors is possible only through an adequate course on thermodynamics; only a brief review of the important aspects of these properties will be taken up in the following sections:

15.2.1 Enthalpy

The enthalpy (H) of a system is an extensive state property defined as

$$H \equiv U + PV$$

[U = internal energy; P = pressure and V = volume of the system].

From the first law of thermodynamics, for any process at constant pressure,

$$\Delta H = \Delta U + P\Delta V = Q_p$$

[Q_p = heat change at constant pressure.]

Chemical reactions are generally carried out at constant pressure. The corresponding heat change is thus given by ΔH, the change in enthalpy of the system. If heat is evolved in a reaction (i.e. exothermic reactions) ΔH is negative; if heat is absorbed, ΔH is positive:

$$1/2N_2 + 3/2H_2 \longrightarrow NH_3 \qquad \Delta H = -46.0\text{ kJ mol}^{-1}$$

$$NH_3 \longrightarrow 1/2N_2 + 3/2H_2 \qquad \Delta H = +46.0\text{ kJ mol}^{-1}$$

Standard heat of formation

Heats of reaction can be measured experimentally (for example, in a bomb calorimeter). But no means is available for the determination of the absolute value of the enthalpy of an element. Therefore, the enthalpy of an element in its standard state (i.e. its most stable physical form; conventionally at 1 atm. pressure and at 25°C) is arbitrarily fixed at zero. Accordingly, the heat evolved in the formation of 1 mole of a compound from its elements under standard conditions gives its **standard heat of formation,** $\Delta H^\circ_{f\,298}$

$$C(s;\text{ graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ_{298} = -393.5\text{ kJ mol}^{-1}.$$

The enthalpy values may be algebraically added in accordance with the Hess's law of constant heat summation: the overall heat change involved in a chemical reaction is the same irrespective of the number of steps involved. This enables us to calculate the standard enthalpy change for any reaction if the standard heat of formation, ΔH°_f (or ΔH°) of each reactant and product is known. So, it is useful to have a table of ΔH°_f values. In Table 15.1 are given the standard heats of formation of a few substances (in alphabetical order of their formula), together with other thermodynamic properties (ΔG° and S°, see later).

In addition to their importance in furnishing standard heats of formation and reaction, enthalpy data for specific processes are also helpful to the chemist. Enthalpies of ionization (Ionization Potential), electron attachment (Electron Affinity), solvation and neutralization are very common examples of such classified enthalpy data. The additivity of such enthalpy values provides a ready method for the computation of enthalpy changes of processes which cannot be carried out directly.

Estimation of bond energy

A specially useful application of enthalpy data is found in the estimation of bond energies. A chemical reaction is essentially a process of bond breaking and bond making. Bond breaking requires energy (endothermic process), while bond making is accompanied by liberation of energy (exothermic process). If the bonds formed in a chemical reaction are more stable than the bonds broken, the extra energy is obtained in the form of heat—this constitutes the heat of reaction for the given process. The following example will be illustrative:

		ΔH° (kJ mol^{-1})
Bond breaking:	$H_2(g) \longrightarrow 2H(g)$	+435·9
	$Cl_2(g) \longrightarrow 2Cl(g)$	+241·8
Bond making:	$2H(g) + 2Cl(g) \rightarrow 2HCl\,(g)$	-2×431kJ.

Therefore, the overall reaction is exothermic to the extent of $(-2 \times 431 + 435.9 + 241.8)$ kJ, i.e. -184.3 kJ.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad \Delta H^\circ_f = -92{\cdot}15\text{ kJ mol}^{-1}.$$

Enthalpy data for known bonds and known compounds may be used to calculate unknown bond energies, as illustrated in the problems below.

Problem 15.1. Calculate the heat of formation of methane from the following heats of combustion:

	ΔH°, kJ mol^{-1}
$C(s;\text{ graphite}) + O_2(g) \rightarrow CO_2(g)$	−393·4
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−285·8
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	−890·2

Solution: We want ΔH° for the process $C(s;\text{ graphite}) + 2H_2(g) \rightarrow CH_4(g)$.

This can be arrived at from the given processes via the following manipulations:

$$\begin{array}{llll}
 & & & \Delta H^\circ \text{ kJ} \\
 & 2H(g) + O_2(g) & \rightarrow 2H_2O(l) & -2\times285{\cdot}8 \\
 & C(s) + O_2(g) & \rightarrow CO_2(g) & -393{\cdot}4 \\
\hline
\textit{Add} & C(s) + 2H_2(g) + 2O_2(g) & \rightarrow CO_2(g) + 2H_2O(l) & -965 \\
 & CH_4(g) + 2O_2(g) & \rightarrow CO_2(g) + 2H_2O(l) & -890{\cdot}2 \\
\hline
\textit{Subtract, Rearrange} & C(s) + 2H_2(g) & \rightarrow CH_4(g) & -74{\cdot}8
\end{array}$$

Note: Similarly, we can evaluate the heat of formation of ethane from the heats of combustion of C (graphite), hydrogen and ethane.

Problem 15.2. Calculate the C–C bond energy from the following standard enthalpy data:

$$\begin{array}{ll}
 & \Delta H^\circ 298 \\
C(s;\text{ graphite}) \rightarrow C(g) & 712.9 \text{ kJ mol}^{-1}. \\
H_2(g) \rightarrow 2H(g) & 435.9 \quad ,, \\
CH_4(g) \rightarrow C(g) + 4H(g) & 1660 \quad ,, \\
2C(s;\text{ graphite}) + 3H_2(g) \rightarrow C_2H_6(g) & -79.9 \quad ,,
\end{array}$$

Solution. Methane has four C–H bonds. The data on methane will give us the C–H bond energy: ($1660 \div 4 = 415$ kJ mol^{-1}). Now, ethane has six C–H and one C–C bond energy. If we can calculate the enthalpy change for breaking of all these bonds, subtraction of the 6 C–H bond energies will give us the C–C bond energy. We require ΔH° for the process:

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g).$$

We may arrive at this process by manipulating the supplied processes as:

$$\begin{array}{lll}
 & & \text{Heat change} \\
 & 2\,C(s) \rightarrow 2C\,(g) & 2 \times 712.9 \text{ kJ mol}^{-1}. \\
 & 3H_2\,(g) \rightarrow 6H\,(g) & 3 \times 435.9 \quad ,, \\
\hline
\textit{Add} & 2C\,(s) + 3H_2\,(g) \rightarrow 2C\,(g) + 6H(g) & 2733.5 \quad ,, \\
 & 2C\,(s) + 3H_2\,(g) \rightarrow C_2H_6\,(g) & -79.9 \quad ,, \\
\hline
\textit{Subtract, rearrange} & C_2H_6\,(g) \rightarrow 2C\,(g) + 6H\,(g) & 2813.4 \quad ,,
\end{array}$$

From this, we subtract 6 × 415 kJ for the breaking of 6 C – H bonds. Hence

$$\text{C – C bond energy} = 2813.4 - (6 \times 415) \text{ kJ mol}^{-1}. \doteq 323.4 \text{ kJ mol}^{-1}.$$

Problem 15.3. Calculate the O – O bond energy in H_2O_2 from relevant ΔH° values taken from the following:

Enthalpy of formation (kJ mol^{-1}), *heat evolved*, $H_2O(g)$: 241.83; $H_2O(l)$: 285.77; $H_2O_2(g)$: 136.3; $H_2O_2(l)$: 187.8.

Enthalpy of bond breaking (kJ mol^{-1}), heat required; $H_2(g)$: 436, $O_2(g)$ 496.

Solution: H_2O_2, H – O – O – H, contains two O – H bonds and one O – O bond. To estimate the O – O bond energy we should know the O – H bond energy and the enthalpy change for the process

$$H_2O_2(g) = 2H(g) + 2O(g).$$

Estimation of O – H bond energy :

This can be done with the data given for $H_2O(g)$, $H_2(g)$ and $O_2(g)$ as follows (including proper sign to the enthalpy values):

$$\begin{array}{lll}
 & & \Delta H^\circ \\
 & H_2O(g) = H_2(g) + \tfrac{1}{2}O_2(g) & +241.83 \text{ kJ} \\
 & H_2\ (g) = 2H(g) & +436 \quad ,, \\
 & \tfrac{1}{2}O_2(g) = O(g) & + \tfrac{1}{2} \times 496 \quad ,, \\
\hline
\textit{Add,} & H_2O(g) = 2H(g) + O(g) & +925.83
\end{array}$$

This is the energy required to break the two O – H bonds in water. Half of this quantity gives the *average* O – H bond energy (see section 5.3.1).

Estimation of O – O bond energy

The necessary enthalpy value may be calculated as follows:

$$\begin{array}{lll}
 & H_2O_2(g) = H_2(g) + O_2(g) & +136.3 \text{ kJ.} \\
 & H_2\ (g) = 2H(g) & +436 \quad ,, \\
 & O_2(g) = 2O(g) & +496 \quad ,, \\
\hline
\textit{Add:} & H_2O_2(g) = 2H(g) + 2O(g) & +1068.3 \text{ kJ.}
\end{array}$$

This is the energy required to break two O – H and one O – O bond. We get the O – O bond energy by subtracting the energy required for the two O – O bonds:

$$E_{O-O} = (1068.3 - 925.83) \text{ kJ mol}^{-1}. = 142.47 \text{ kJ mol}^{-1}.$$

We shall soon appreciate that the driving force for a chemical process is determined by the combined effect of enthalpy and a new property, the entropy. However, we shall also find that at ordinary temperatures, the major contribution to the driving force comes from the enthalpy term.

TABLE 15.1

Chemical Thermodynamic Properties of few substances at 298.15K and 1 Bar (elements arranged in the alphabetical order of their symbols)

Substance	ΔH_f° kJ mol^{-1}	ΔG_f° kJ mol^{-1}	S° JK^{-1}mol^{-1}
Ag^+ (*aq*)	105.579	77.107	72.68
AgCl (*cr*)	−127.068	−109.789	96.2
Ag_2O (*cr*)	−31.05	−11.20	121.3
Al (*cr*)	0	0	28.33
Al_2O_3 (*cr*)	−1675.7	−1582.3	50.92
$AlCl_3$ (*cr*)	−704.2	−628.8	110.67
Al^{3+} (*aq*)	−531.37	−485.34	321.75
$B(OH)_3$ (*aq*)	−1072.32	−968.85	162.34
BF_3 (*g*)	−1137.00	−1120.35	254.01
Ba^{2+} (*aq*)	−537.64	−560.74	9.62
$BaCl_2$ (*cr*)	−858.56	−810.44	123.68
$BaCO_3$ (*cr*)	−1216.29	−1137.63	112.13
Be^{2+} (*aq*)	−382.84	−379.7	−129.7
BeF_2 (*cr*)	−1026.7	−979.47	−53.35
Br^- (*aq*)	−121.55	−103.96	82.4
C (*graphite*)	0	0	5.74
C (*diamond*)	1.895	2.900	2.377

Substance	ΔH_f^o kJ mol^{-1}	ΔG_f^o kJ mol^{-1}	S^o JK^{-1}mol^{-1}
CO (*g*)	−110.525	−137.168	197.674
CO_2 (*g*)	−393.509	−394.359	213.74
CO_3^{2-} (*aq*)	−677.14	−527.81	−56.9
CaO (*cr*)	−635.09	−604.03	39.75
$CaCl_2$ (*aq*)	−877.13	−816.01	59.8
$CaCO_3$ (*calcite*)	−1206.92	−1128.79	92.9
CH_4 (*g*)	−74.81	−50.72	186.26
C_2H_6 (*g*)	−84.68	−32.82	229.60
C_2H_2 (*g*)	226.73	209.20	200.94
C_2H_4 (*g*)	52.26	68.15	219.56
C_6H_6 (*g*)	82.93	129.72	269.31
Cl_2 (*g*)	0	0	223.07
Cl^- (*aq*)	−167.16	−131.23	56.5
ClO_3^- (*aq*)	−99.16	−3.35	162.34
ClO_4^- (*aq*)	−129.33	−8.62	182.00
Cu (*cr*)	0	0	33.15
Cu^+ (*aq*)	71.67	49.98	40.6
Cu^{2+} (*aq*)	64.77	65.49	−99.6
$CuSO_4$ (*cr*)	−771.36	−661.91	108.78
F_2 (*g*)	0	0	202.78
F^- (*aq*)	−332.63	−278.79	−13.8
Fe (*cr*)	0	0	27.28
Fe^{2+} (*aq*)	−89.1	−78.90	−137.7
Fe^{3+} (*aq*)	−48.5	−4.7	−315.9
H_2 (*g*)	0	0	130.684
H^+ (*aq*)	0	0	0
HBr (*g*)	−36.4	−53.45	198.69
HCl (*g*)	−92.32	−95.299	186.91
HF (*g*)	−271.1	−273.2	173.78
HF (*aq*)	−320.08	−296.855	88.70
HI (*g*)	26.48	1.70	206.594
HNO_3 (*l*)	−174.10	−80.71	155.60
HNO_3 (*aq*)	−207.36	−111.25	146.4
H_2O (*l*)	−285.83	−237.129	69.91
H_2O (*g*)	−241.82	−228.57	188.57
H_2O_2 (*l*)	−187.78	−120.35	109.6
H_2S (*g*)	−20.63	−33.56	205.79
H_2SO_4 (*l*)	−813.989	−690.00	156.90
H_2SO_4 (*aq*)	−909.27	−744.53	20.1
I_2 (*cr*)	0	0	116.135
I_2 (*g*)	−62.438	−19.359	260.58
I^- (*aq*)	−55.187	−51.59	111.29
K^+ (*aq*)	−252.38	−283.27	102.5
KOH (*aq*)	−482.37	−440.50	91.6
KCl (*cr*)	−436.747	−409.14	82.59
KCl (*aq*)	−419.53	−414.49	159.0
Li^+ (*aq*)	−278.44	−293.80	14.22
Li_2CO_3 (*cr*)	−1215.62	−1132.44	90.62
MgO (*cr*)	−601.70	−569.43	26.94
$MgCl_2$ (*aq*)	−801.15	−717.1	−25.1
Mg^{2+} (*aq*)	−466.85	−454.8	−138.1
N_2 (*g*)	0	0	191.61
NH_3 (*g*)	−46.11	−16.45	192.45
NH_3 (*aq*)	−80.29	−26.50	111.3
NH_4^+ (*aq*)	−132.51	−79.31	113.4
N_2O (*g*)	82.05	104.20	219.85
NO (*g*)	90.25	86.57	210.76
NO_2 (*g*)	33.18	51.31	240.06
NO_3^- (*aq*)	−205.0	−108.74	146.4
N_2H_4 (*l*)	50.63	149.24	121.21
Na^+ (*aq*)	−240.12	−261.90	59.0
NaCl (*cr*)	−411.15	−384.138	72.13
NaCl (*aq*)	−407.27	−393.13	115.5
NaOH (*aq*)	−470.114	−419.15	48.1
O_2 (*g*)	0	0	205.138
O_3 (*g*)	142.7	163.2	238.93
OH^- (*aq*)	−229.99	−157.24	−10.75
P (*cr, white*)	0	0	41.09
P_4 (*g*)	58.91	24.44	279.98
PCl_3 (*g*)	−287.0	−267.8	311.78
PCl_5 (*g*)	−374.9	−305.0	364.58
P_4O_{10}	−2984.03	−2697.84	228.86
Pb^{2+} (*aq*)	−1.674	−24.393	10.46
S (*rhombic*)	0	0	31.8
SF_6 (*g*)	−1209.18	−1105.41	291.71
SO_2 (*g*)	−296.83	−300.194	248.22
SO_3 (*g*)	−395.72	−371.06	256.76
SiO_2 (*quartz*)	−910.94	−856.67	41.84
Zn^{2+} (*aq*)	−153.89	−147.06	−112.1
ZnO (*cr*)	−348.28	−318.30	43.64

15.2.2. Entropy

Entropy and Probability

The first law of thermodynamics helps up to identify the permissible changes of a system. But it does not tell us whether these changes would occur spontaneously or not. Our experience shows that certain processes take place spontaneously, while some others do not. A gas always fills the total available space, but it does never contract spontaneously, though this would not change the total energy of the gas molecules in an isolated system. Similarly, coal burns in oxygen to carbon dioxide, but the reverse has never been observed to take place spontaneously. Generalization of our observation leads to the fact that in an isolated system, spontaneous changes are always accompanied by an increase in the *mode* of distribution of the total energy of the system. Changes take place in an isolated system in a direction in which the total energy of the system can be distributed in the maximum number of ways; the number is maximum when the system reaches equilibrium. In thermodynamics, this is described in terms of the thermodynamic probability (W) of the system: this is the number of ways in which the molecules (or other constituent particles) of the system can be arranged to produce the same system. A new property of the system, the entropy (S), is then defined as

$$S = k \ln W \ (k = \text{Boltzmann constant})$$

This entropy of a system is a state function, that is, its change is determined only by the initial and final states of a system. It measures the chaotic dispersal of energy and hence the randomness of a system. The natural tendency of any spontaneous change is towards states of higher entropy (ΔS + ve). The calculation of entropies for a system is somewhat complicated; that requires a detailed knowledge of the structure, properties and interactions of the constituent particles. We avoid that at present and attempt at a qualitative insight into the nature of entropy from some familiar system.

Entropy increases solid—liquid—gas

The energy of a molecule is distributed among various quantized energy levels—translational, rotational and vibrational. For a given energy range, there are more translational energy levels than rotational energy levels; the vibrational energy levels are still less. The constituent particles of a solid has vibrational energy levels only. In the liquid and gaseous states, the molecules have all three kinds of energy levels. But there are more translational energy in the gaseous state. As the number of energy levels increases, the energy of the molecules can be distributed in a greater number of ways. Hence, the entropy increases from the solid state to the liquid state to the gaseous state.

Entropy changes in dissolution

Now let us consider a simple system—the dissolution of solid potassium nitrate in a beaker of water *in an isolated system.* As the system is isolated, the total energy of the system remains constant. The temperature of the system is lowered, showing that the process is an endothermic one. We apply our nascent ideas of entropy to this system. After dissolution, the crystal structure of potassium nitrate is broken down— the potassium and nitrate ions are hydrated by water molecules. The hydration energy is certainly insufficient to overcome the lattice energy (Lattice energy of $KNO_3 = -684.5$; Hydration energy: $K^+ - 339$; $NO_3^- - 310$; all values in kJ mol^{-1}). Heat energy is therefore abstracted from the system itself—water and the air molecules enclosed within the system. The entropy of the system may now be considered in parts as follows:

(i) In solid potassium nitrate, only vibrational energy levels were present. As the ions (hydrated) pass into solution, a large number of translational energy levels are provided. This will increase the entropy of the system.

(ii) As some water molecules orient themselves around the ions, their translational and rotational motion is restricted. This causes a decrease in the entropy of the system.

(iii) The air above the solution is cooled—the molecules move slower, their kinetic energy decreases. Less energy is distributed among the various energy levels (particularly translational) and the entropy decreases.

But the decrease in entropy in (ii) and (iii) is more than compensated by the increase in entropy in (i). Therefore, the process takes place spontaneously.

At this point, a student often raises the case of the spontaneous crystallization of sodium chloride on the sea-shore. It is no problem—the decrease in entropy on crystallization is more than compensated by the increase in entropy of the evaporated water molecules.

Following the same line of argument, it is possible to appreciate that all spontaneous processes take place toward increasing entropy. However, in the next section, we shall find that the enthalpy and entropy terms jointly determine the course of a reaction.

Meanwhile, it is essential to know the magnitude of entropy change accompanying any process. It can be shown that this magnitude (ΔS) is given by the thermodynamic relationship

$$\Delta S = \frac{Q_{rev}}{T}$$

where Q_{rev} is the *reversible* heat change involved in the transfer of the system from one equilibrium state to another,

Entropies of different substances may be calculated using the third law of thermodynamics. The standard entropy of a substance, S°_{298} is the entropy of the substance at 25°C and 1 atm pressure. Unlike enthalpies, the standard entropy of an element is not assigned the conventional value of zero. As a consequence, the entropy of a compound is *not equal to* its entropy of formation. The standard entropy change in a chemical reaction is obtained by the relation:

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}).$$

The value of ΔS at temperatures T_1 and T_2 are related as

$$\Delta S^\circ_{T_2} = \Delta S^\circ_{T_1} + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT$$

The standard entropies of some selected substances are given in Table 15.1. The values are in Joules; the values of ΔH° and ΔG° are given in kilo Joules.

Useful generalizations regarding entropy

Certain generalizations regarding the entropies of different substances may be made as follows:

(i) Entropies of liquids are greater than those of the solids; entropies of gases are still higher.

(ii) Entropy increases with molar mass (M). For a series of compounds with similar formula, the plot of entropy against log M is mostly linear (Fig. 15.1).

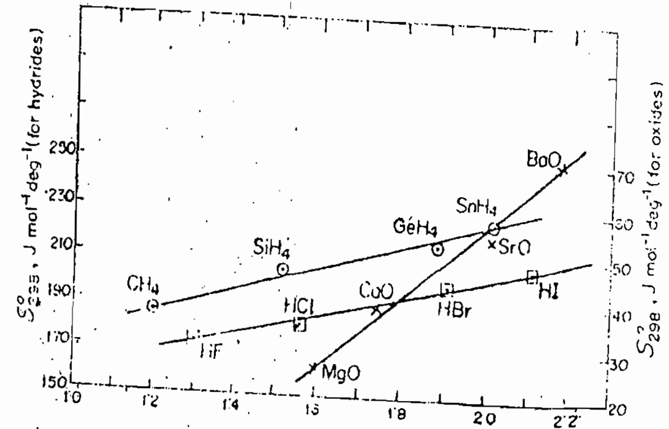

Fig. 15.1. Entropies of some compounds as a function of molar mass (M).

The size of the rotational and vibrational quanta depend inversely on the mass of the atoms involved. Hence, for a given total energy, the number of available energy states becomes greater as mass increases. This leads to an increase in entropy with molecular weight.

(iii) Hydrides have low reduced mass and hence, high vibrational frequencies. Other things being equal, hydrides therefore have a lower entropy. This is reflected in the following entropy data (J mol^{-1} deg^{-1}) for pairs of molecules with same number of atoms and nearly same M:

H_2Se(g) 218.9 vs. Cl_2O(g) 266.1 ; HI(g) 206.48 vs. BrCl(g) 239.91.

(iv) Entropy increases with increasing complexity of a molecule, e.g. Ne < HF < H_2O (nearly same mass) since the degrees of rotational freedom increase in the same order. At the same time, an increase in symmetry (see next chapter) results in a decrease in entropy (e.g. N_2 vs. CO). Again, entropies of H_2O, NH_3 and CH_4 are nearly same in spite of an increase in the number of atoms in the molecules (with nearly equal M). Increasing symmetry of the molecules appear to counteract the rise in entropy.

(v) Solids with strong binding energies have low entropy, e.g. diamond and silicon. Graphite has a relatively higher entropy due to its lower cohesive energy. Similarly, entropies of $KClO_3$, NH_4Cl etc. are higher than those of MgO, NaCl etc. due to greater complexity of the units involved.

$\Delta S°_{298}$ for some common reactions are given below (J mol^{-1} K^{-1})

(i) $C\,(graphite) + O_2\,(g) = CO_2(g)$ 2.86.

(ii) $\frac{1}{2}C\,(graphite) + \frac{1}{2}CO_2\,(g) = CO\,(g)$ 87.93

(iii) $CaCO_3 = CaO(s) + CO_2(g)$ 160.5

(iv) $\frac{3}{2}H_2(g) + \frac{1}{2}N_2\,(g) = NH_3$ – 103.1

We observe that (i) the change in entropy is very small when the number of moles of gaseous substances remains the same. (ii) The entropy increases when the number of moles of gaseous substances in the system increases, and hence, the volume increases at constant pressure. (iii) Entropy decreases when the number of moles of gaseous products is reduced, i.e. $\Delta V_P < 0$.

However, these examples do not help us in finding an ultimate single criterion for the spontaneity of a process. We find that the decomposition of solid calcium carbonate is accompanied by a large increase in entropy (reaction iii), though the process does not take place spontaneously at ordinary temperature. On the other hand, the reverse process, i.e., combination of calcium oxide with carbon dioxide takes place readily, though it results in a lowering of the entropy of the system ($\Delta S = -160.48$ J/K).

Entropy vs Enthalpy

Clearly, two opposing factors are operating on the system. One factor tends to separate the constituents of the system, thereby increasing its disorder and entropy; this factor favours the decomposition of solid calcium carbonate. The second factor tends to keep calcium oxide and carbon dioxide together in the form of solid calcium carbonate. Obviously, the second factor predominates at ordinary temperatures. At higher temperatures, the first factor must be dominating as we find calcium carbonate to decompose readily on heating to calcium oxide and carbon dioxide. This first factor may be measured by the tendency of the system to increase its entropy and is called the *entropy factor*; this increases rapidly with temperature and is given by the product $T\Delta S$. The second factor, which tends to unite the constituents of a system through the formation of stable bonds and to lower its potential energy is called the *enthalpy factor*, ΔH, as discussed earlier.

15.2.3 Gibbs Energy.

The Gibbs energy* (G) of a system is a property of the state of the system defined as

$$G = H - TS$$

For a finite change at constant T,

$$\Delta G = \Delta H - T\Delta S.$$

It can be easily shown that the decrease in Gibbs energy of a system for any transformation at constant temperature and pressure ($-\Delta G_{T,P}$) is equal to the maximum available work from the process, i.e. the net available work other than expansion work.

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*Previously known as Gibbs function, Gibbs free energy or simply free energy; also represented by F. The IUPAC agreement is to use the term **Gibbs energy** and the symbol G.

As in the case of enthalpy and entropy, the Gibbs energy change during the formation of one mol of a substance in standard conditions from the elements in their standard states is termed the standard Gibbs energy of formation of that substance ($\Delta G°$). Values for some selected substances are given in Table 15.1.

From the very definition of the function G, it is clear that it combines the effects of the enthalpy and entropy factors of the process. The ultimate sign of ΔG, the change in Gibbs energy of a system accompanying any given process, determines the thermodynamic feasibility of the process to take place. The standard Gibbs energy change, $\Delta G°$, is related to the equilibrium constant K:

$$\Delta G° = -RT \ln K, \quad R = 8.314\ JK^{-1}\ mol^{-1}.$$

At equilibrium, $K = 1$, if $\Delta G° = 0$. For any spontaneous process, $\Delta G°$ should be negative. (The converse is however not true. A system with a negative value of $\Delta G°$ may *not* occur spontaneously, though it has the thermodynamic potentiality to do so. See later).

We may proceed a bit further to examine the contributions of the ΔH and ΔS terms to make the overall ΔG term negative for a chemical process. We recall the relation $\Delta G = \Delta H - T\Delta S$ and consider three ways to attain a negative ΔG.

Case I. Both ΔH and ΔS make ΔG negative. This occurs when $\Delta H < 0$ and $\Delta S > 0$.

A large number of combustion reactions illustrate the case, e.g.,

	$C(s)$	$+\ \frac{1}{2}O_2(g)$	$=\ CO(g)$	
$\Delta H°$	0	0	–110.5	kJ mol^{-1}
$S°$	5.7	205	197.67	J mol^{-1} K^{-1}.

$$\Delta G° = -110.5 - 298 \times [197.67 - (5.7 + \tfrac{1}{2} \times 205)] \times 10^{-3}\ kJ\ mol^{-1}$$
$$= -137.16\ kJ\ mol^{-1}.$$

Case II. ΔS is negative, so that the $T\Delta S$ term opposes ΔH. But ΔH is more negative to give an overall negative ΔG. For example,

	$SO_2(g)$	$+\ \frac{1}{2}O_2(g)$	$=\ SO_3(g)$.	
$\Delta H°$	–296.8	0	–395.7	kJ mol^{-1}.
$S°$	248.2	205	256.76	J mol^{-1} K^{-1}.

$$\Delta G° = [-395.7 - (-296.8 + 0)] - 298\,[256.76 - (248.2 + \tfrac{1}{2} \times 205)] \times 10^{-3}\ k$$
$$= -70.9\ kJ\ mol^{-1}$$

Case III. The reaction is endothermic i.e., $\Delta H > 0$, But ΔS is positive so that the $T\Delta S$ term makes ΔG negative. Examples of such processes at room temperature are not very common. The endothermic dissolution of many crystalline salts in water (e.g. NaCl, KNO_3 etc.) provide such examples. The following endothermic reaction reportedly occurs at ordinary temperature due to the large positive ΔS term accompanying the formation of a large number of gaseous products:

$$CoCl_2,\ 6H_2O(s) + 6SOCl_2(l) \rightarrow CoCl_2(s) + 6SO_2(g) + 12HCl(g)$$

But we note with interest that many endothermic processes are favoured at higher temperatures when the $T\Delta S$ term outweighs the ΔH term. We consider the reaction

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

$$\Delta H^\circ = +178\ \text{kJ mol}^{-1};\ \Delta S^\circ = 160.48\ \text{J mol}^{-1}\ \text{K}^{-1}.$$

At 1500°K, $\Delta G = 178 - 1500 \times 160.48 \times 10^{-3}$ kJ mol^{-1}.

$$= -62.6\ \text{kJ mol}^{-1}.$$

So, one should expect solid calcium carbonate to decompose at high temperatures. At 25°C, however, the *reverse process* has a large negative ΔG°:

$$CaO(s) + CO_2(g) = CaCO_3(s).$$

$$\Delta G^\circ = -178 - (298 \times -160.48) \times 10^{-3}\ \text{kJ mol}^{-1}.$$

$$= -130.18\ \text{kJ mol}^{-1}.$$

The variation of ΔG with temperature and its applications will be discussed further in due course.

Some generalizations from bond strength

While considering the reactions under cases i – iii, we observe that the contribution of the entropy term is usually small (in Joules) in comparison to the enthalpy term (in kilo Joules). This is particularly true for reactions at lower temperatures. So, we may reasonably expect that the course of a reaction at ordinary temperatures is largely controlled by the enthalpy term (ΔH). This, in turn, is determined by the relative bonding strengths in the reactants and products. So a useful generalization of reaction principles may be laid down from the criterion of bond strengths.

(i) For ionic compounds, the principal energy term involved is the lattice energy. This has been discussed earlier (Chapter six).

(ii) For reactions involving rearrangement of covalent bonds, it is logical to expect that reactions should proceed in the direction of stronger bond formation. The criterion of bond strength may be summarily recapitulated as follows.

The strength of a covalent bond tends to be greater,

(a) the shorter the bond length

(b) the higher the extent of overlap between the bonding orbitals, and

(c) the greater the bond polarity.

Thus, phosphorus reacts readily with oxygen and the halogens to form binary oxides and halides in which the bonds are stronger than the bonds present in the reactants. But it does not react readily with nitrogen since the bonds between nitrogen and phosphorus are not strong enough (low polarity, inadequate overlap due to large energy difference) to overcome the strong binding already present in the reactants, specially N_2.

On the other hand, there are reactions in which the principal driving force is provided by the ΔS term:

$$BBr_3(g) + BCl_3(g) = BBr_2Cl(g) + BCl_2Br(g).$$

Reactions driven by entropy

Here the sum of the bond energies of the reactants is practically equal to the sum of the bond energies of the products. But the products have lower symmetry than the reactants; so their entropies are higher. A net positive ΔS drives the reaction to right. The same thing happens in the racemization reactions where $\Delta H = 0$:

$$2d\text{-}[Co(en)_3]^{3+} = d\text{-}[Co(en)_3]^{3+} + l\text{-}[Co(en)_3]^{3+}.$$

Problem 15.4. Is it thermodynamically meaningful to attempt at the preparation of hydrazine by oxidizing aq. ammonia by NO? Given the ΔG° values: $H_2O(l)$: – 237.13; N_2H_4 *(aq)*: 128.03; NO*(g)*: 86.57; NH_3 *(aq)* – 26.50 kJ mol^{-1}.

Solution: The reaction involved would be

$$8NH_3(aq) + 2NO(g) \rightarrow 5N_2H_4(aq) + 2H_2O(l).$$

$$\Sigma\Delta G^\circ = 5 \times 128.03 + 2 \times (-237.13) - 8 \times (-26.50) - 2 \times 86.57\ \text{kJ}.$$

$$= +204.75\ \text{kJ}.$$

The large positive value of ΔG° suggests that the reaction would not be favoured thermodynamically. Also,

$$\Delta G^\circ = -RT \ln K, \text{ when at } 298\ \text{K}.$$

$$\log K = -204{,}750 \div (8.314 \times 298 \times 2.303) = -35.88.$$

$$K = 1.3 \times 10^{-36}$$

Comment. The conclusion reached here should not be generalized too far. See section 15.2.4.

Variation of ΔG with temperature

We have already seen how the free energy change of a reaction changes its sign with temperature. The underlying reason is also clear. Accordingly, we expect that for reactions with very small values of ΔS, ΔG will not change appreciably with temperature. The reactions of carbon (graphite) with oxygen are illustrative:

$$C + O_2(g) = CO_2(g)\quad \Delta H^\circ = -393.5\ \text{kJ mol}^{-1};\ \Delta S^\circ = 2.9\ \text{JK}^{-1}.$$

$$2C + O_2(g) = 2CO(g)\quad \Delta H^\circ = -221\ \text{kJ mol}^{-1};\quad \Delta S^\circ = 178.56\ \text{JK}^{-1}.$$

In the first reaction, one mol of CO_2 is formed for each mol O_2 consumed and the entropy changes very little. But the second reaction produces two mols of gaseous CO for each mol of O_2 consumed and ΔS° is consequently very large. Neglecting the changes of ΔH and ΔS with temperature, we may conclude that the magnitude of ΔG for the first reaction will change very little with temperature, while for the second reaction it will rise sharply. The ΔG vs T curves for the two reactions are shown in Fig. 15.2. We find that the two curves intersect one another at about 700°C. Below this temperature, the first reaction results in a greater decrease of free energy and hence carbon dioxide is the stable reaction product. But above 700°C, carbon monoxide becomes the thermodynamically favoured product. This fact is utilized in the reduction of metal oxides.

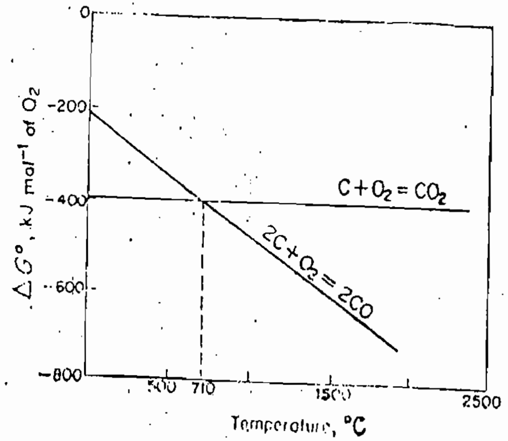


Fig. 15.2 ΔG° *vs* T for carbon monoxide and carbon dioxide.

The reduction of metal oxides

The formation of an oxide by reactions like

$$2M(s) + O_2(g) = 2MO(s)$$

Ellingham diagram

is accompanied by a drop in entropy (consumption of gaseous oxygen). Therefore ΔG becomes less negative as T increases. As shown in Fig. 15.3, this change in ΔG per mol of O_2 may be plotted as a function of T for different oxides. Such graphs are called Ellingham diagrams. Similar plots may be obtained for the various sulfides and halides.

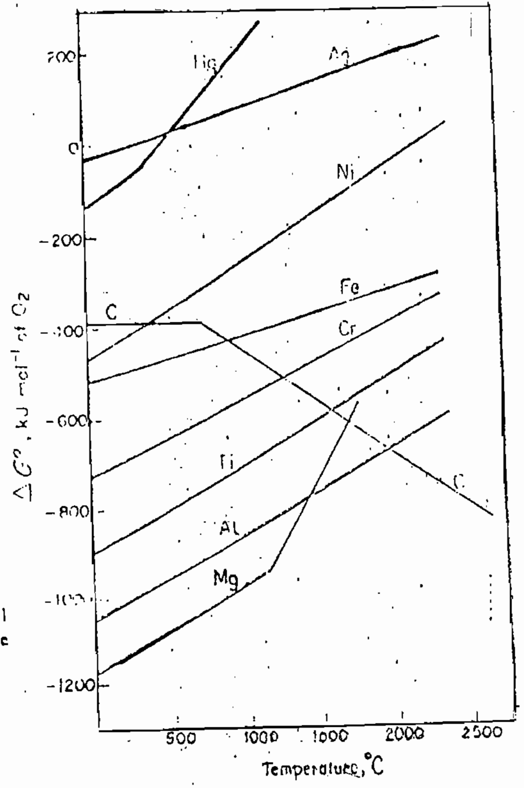


Fig. 15.3 ΔG *vs* T for some metal oxides with the resultant curve for carbon.

An examination of these graphs reveals some interesting features: (**a**) all the graphs except that of carbon slowly rise upward except when a phase change affects the entropy term and alters the slope. This is reflected in the curves for mercury and magnesium; mercury boils at 356°C, so does magnesium at 1120°C.

(**b**) The formation of an oxide becomes thermodynamically unfavourable when the corresponding ΔG value becomes positive, i.e. the ΔG vs T curve rises above the $\Delta G = 0$ line. The curves for silver, gold and mercury lie in this range around normal temperatures or slightly above it. Consequently their oxides are easily decomposed to the free metals. Theoretically, of course, any metal oxide can be decomposed by heat at a sufficiently high temperature.

(**c**) The diagram also reveals that the oxide of any metal (M) can be reduced by a second metal (M^1) lying *below* it in the Ellingham diagram: the driving force for the process will be supplied by the difference of free energy of the two oxides at that temperature. Thus, magnesium will reduce the oxides of all metals lying above it in the diagram. Aluminium will reduce the oxides of Ti, Cr, Fe and Ni, (but not MgO below ~ 1500°C).

(**d**) Since the resultant curve for carbon slopes downward, it intersects and ultimately falls below the curves for most metals. Clearly, the oxides of these metals will be reduced by carbon at the appropriate temperatures. One may conclude that, in principle, carbon will reduce any metal oxide if a high enough temperature is used. In practice, however, there may be many limitations to this, e.g., (a) operations at such high temperatures may not be economical in all cases and (b) the metal may form carbides with carbon (Cr, Ti).

15.2.4 Limitations of thermodynamic analysis

Conclusions drawn from thermodynamic considerations alone are often inadequate to describe the actual fate of a chemical system. For example, free energy changes (ΔG) for both the processes,

$$C + O_2(g) = CO_2(g): \qquad H_2(g) + \tfrac{1}{2} O_2(g) = H_2O(g)$$
$$\Delta G^\circ = -394.36 \text{ kJ mol}^{-1}. \qquad \Delta G^\circ = -228.57 \text{ kJ for } H_2O(g)$$

are largely negative at ordinary temperature. But our common experience shows that both carbon and hydrogen may be kept indefinitely in contact with oxygen at ordinary temperature. The reactions do not proceed perceptibly inspite of favourable free energy changes. This is because thermodynamics merely points out the conditions *necessary* for a process to occur but those conditions may not be sufficient. It just states the feasibility of a process but does not state anything about the rate at which the process will take place. In fact, both the above mentioned processes proceed imperceptibly slowly. When initiated by a suitable catalyst or high enough temperature, the reactions take place readily.

The converse conclusion should also be used with caution. In problem 15.4 we concluded that the preparation of hydrazine from ammonia and nitric oxide would not be favoured thermodynamically. This, however, does not imply that all reactions with $\Delta G^\circ \gg 0$ would be impractical to be carried out. If one of the products of a reaction can be continuously removed (for example, by volatilisation or condensation), it may be possible to obtain an appreciable yield of the product from such reactions.

Another limitation of such conclusions is that the system is supposed to be in equilibrium which is far from reality. However, such thermodynamic analysis are often helpful in understanding the ultimate feasibility, and hence, the direction of a process.

15.3 KINETICS AND MECHANISM

The preceding discussion was primarily developed around the question: why do chemical reactions occur? The question that follows logically is: **how** do chemical reactions occur? It is a hard task for a chemist to answer this question. In fact, the ultimate answers to the "how"s of majority of reactions are not known with certainty. It has been found that a reaction seldom occurs in a single step. Several steps are involved even for an apparently "simple" reaction; each step may involve different chemical species. Many of them are produced and consumed as intermediates. A knowledge of the sequence of the elementary steps i.e., the processes taking place at the molecular level, of an observed overall reaction is called the mechanism of the reaction. In a broader sense, a reaction mechanism should provide a detailed account of how the chemical bonds, or the electrons and the nuclei in the reactants rearrange themselves to form the ultimate product (the intrinsic mechanism). However, such finer details of a mechanism are often lacking for want of suitable experimental techniques.

What is mechanism?

In any case, the available mechanisms are merely guessed on the basis of experimental facts at hand. Often these "mechanisms" have to be changed to accomodate new experimental findings. At the same time, one should remember that the same reaction may take place through a number of probable mechanisms. For example, the conversion of glucose to carbon dioxide and water by oxygen certainly occurs by different mechanisms in the laboratory and in an animal body.

There are several methods by which one may attempt to understand the mechanism of a reaction. Some of them are (i) ascertaining the stoichiometry of a reaction, (ii) isolation of intermediate products wherever possible, (iii) study with isotopes, (iv) interpretation of the stereochemistry of the reactants and products and (v) measurement of rates of reactions under suitably designed conditions. It is the last method which constitutes the study of kinetics and provides the most valuable informations regarding the path of a chemical reaction. We shall have only a very brief introduction to the topic assuming a fair degree of familiarity through physical chemistry classes. Other methods of studying mechanism will be mentioned wherever appropriate. (e.g. The use of isotopes has been mentioned earlier in part I.)

15.3.1 The Rate of a Chemical Reaction

The rate of a chemical reaction is expressed in terms of its advancement with time. The extent of advancement may be followed by studying the rate of consumption of a particular reactant or the rate of formation of a particular product. At constant volume, it is convenient to express these rates in terms of the respective concentrations. Thus, for the reaction

$$A + 2B \longrightarrow 3C + 4D$$

the rate may be expressed in terms of the rate of change of concentration of any of the species A, B, C or D with time, (dc_i/dt). Denoting decreases of concentration by a negative sign, and remembering the stoichiometry of the reaction,

$$\text{Rate} = -\frac{dc_A}{dt} = -\frac{1}{2}\frac{dc_B}{dt} = \frac{1}{3}\frac{dc_C}{dt} = \frac{1}{4}\frac{dc_D}{dt}$$

A general reaction

$$\nu_A A + \nu_B B + \ldots \longrightarrow \nu_M M + \nu_N N + \ldots \quad \text{may be briefly expressed as}$$

$$\Sigma \nu_i A_i = 0$$

with the convention that stoichiometric mole numbers (ν_i) are positive for the products and negative for the reactants. The advancement of the reaction is conventionally expressed by ξ (*zeta*), called the **extent of reaction.** The number of moles of any species is now given as

$$n_i = n_i^\circ + \nu_i \xi$$

where n_i° is its initial number of moles. A change from ξ to $\xi + d\xi$ means that $\nu_A\, d\xi$ moles of A, $\nu_B\, d\xi$ moles of B etc. have reacted to form $\nu_M\, d\xi$ moles of M etc. Since n_i° is independent of time, we have

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}.$$

The rate is now defined as, $\text{rate} = \dfrac{d\xi}{dt} = \dfrac{1}{\nu_i}\dfrac{dn_i}{dt} \quad \left[\equiv \dfrac{1}{\nu_i}\dfrac{dc_i}{dt} \text{ at constant volume}\right]$

Measurement of rate

The rate of a reaction may be followed by measuring, at constant temperature, a suitably selected property of the reaction system at various time intervals. Changes in pressure, volume, pH, refractive index, absorbance, thermal and electrical conductivity etc. may be tactfully utilized for the purpose. A small portion of the reaction mixture may also be taken out of the system, the rate quenched by a sharp lowering of temperature and analyzed quickly to obtain the composition of the mixture.

Apart from such studies of a reaction mixture at constant volume and temperature, (i.e. in a **static system**), rate studies are also carried out by **flow techniques.** Here the reactants enter continuously into the reaction vessel through an inlet and the product(s) are withdrawn through an outlet. The reaction mixture *may* or *may not* be stirred according to the technique adopted.

Such techniques are useful in the study of transient intermediates. For example, the addition of Fe^{3+} to a solution of $Na_2S_2O_3$ produces a transient violet colour. In a stirred-flow reactor, conditions may be adjusted to maintain the colour and study the intermediate by absorption spectrometry. The intermediate appears to be $FeS_2O_3^+$.

An improvement of the flow techniques is the *stopped-flow technique.* Small amounts of the reacting solutions are mixed very rapidly by injecting them into a cavity. The flow is now stopped and the progress of the reaction with time is studied, mostly by spectroscopic methods.

In **Relaxation methods** developed for the study of very fast reactions, a reaction system at equilibrium is suddenly subjected to an external influence that quickly changes the position of equilibrium (e.g. the temperature is raised). The course of the system to the new equilibrium position is then studied. The *temperature-jump method* (T-jump) is a very important relaxation technique in which the equilibrium of a system is changed by causing a sudden jump of temperature. One common method is to send an electric discharge through the system. T-jumps of between 5 and 10K can be achieved in about 10^{-7}s. The rate of the reaction

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

has been studied by this method. This is one of the fastest reactions in solution, with a rate-constant of the order of 10^{11} $dm^3 mol^{-1} s^{-1}$ at room temperature.

In the **Flash photolysis** technique a flash of light for a very short duration (10^{-6}s, or even 10^{-9}s using lasers) is used to initiate a bond cleavage (photolysis) in the reactants and the subsequent course of the reaction is followed spectroscopically.

Ultra modern techniques for rate studies are based on quite different aspects. Instead of following the dependence of the rate on concentration, these methods aim at following the dependence of rate on molecular encounters, e.g., (i) the state of vibrational excitation of molecules (ii) the energy with which molecules collide, (iii) the rate at which energy is changed from one form to another, e.g. vibrational to rotational. **Molecular beam** techniques have been designed to examine collisions between molecules in preselected energy levels and to study the energy states of the products of a reactive collision.

The Rate Constant

The rate of a reaction depends variously on the temperature, pressure and concentrations of the reactants; it may also depend on the concentrations of catalysts (or inhibitors) or on the area of the active surface (for reactions occurring on surfaces). For reactions occurring in one phase only (homogeneous reactions), it is often possible to correlate (at constant temperature and pressure) the experimental rate with the concentrations of the various reactants (A, B, C .. etc) as

$$\text{Rate} = k\, C_A^{\alpha} . C_B^{\beta} \ldots .$$

The constant k is called the rate constant or the specific rate constant of the reaction : it is the rate if all the concentrations are unity. For reactions taking place in several steps, each elementary step is marked by a different rate constant. The unit of k depends on the units of concentrations used and the numerical values of α, β, .. etc.

The magnitude of the rate constant is determined by the form of rate expression. For the process

$$A + 2B \longrightarrow 3C + 4D$$

the various rate expressions may be written as

$$-\frac{dC_A}{dt} = k_1 . C_A^{\alpha} . C_B^{\beta} \;;\quad -\frac{dC_B}{dt} = k_2 . C_A^{\alpha} . C_B^{\beta} \text{ etc.}$$

Obviously, $k_2 = 2k_1$, and so on.

The Order of a reaction

The order of a reaction is given by the sum of the powers of the concentrations of a reactants in an *experimentally established* simple rate expression. If the rate of a reaction *can be* expressed in terms of the concentrations C_A, C_B .. as

$$\text{Rate} = k . C_A^{\alpha} . C_B^{\beta} \ldots\ldots$$

the overall order of the reaction is given by $(\alpha + \beta + \ldots .)$. The reaction is of order α with respect to A, order β with respect to B and so on.

It is not possible to assign a simple order to reactions whose rates cannot be followed experimentally (e.g. very slow or very fast reactions) or where a simple rate expression connecting the concentration terms cannot be arrived at. Reactions may be of zero or fractional orders as well.

The molecularity of a reaction

The molecularity of a reaction is the number of reacting species (atoms, molecules, ions or radicals) involved in each step of a reaction. For elementary reactions, that is reactions that take place in a single act, the order and molecularity are often identical but they are not synonymous. Thus the thermal decomposition of dinitrogen (V) pentaoxide, N_2O_5, is represented as

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g).$$

The experimental rate equation is

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

Thus the order is 1.

But the reaction is believed to consist of three elementary steps having different molecularities

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \qquad \textit{fast, unimolecular}$$
$$NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2 \qquad \textit{slow, bimolecular}$$
$$NO + NO_3 \longrightarrow 2NO_2 \qquad \textit{fast, bimolecular}$$

The overall rate of the reaction is naturally determined by the rate of the slowest process. (See p. 23).

Since collisions between three or more particles become increasingly less probable, reactions of higher molecularities are very uncommon.

Effect of temperature

The rates of chemical reactions increase with increasing temperature. On an average, the rates usually double themselves for every 10K rise in temperature. The variation of the rate constant k with temperature T (kelvin) is expressed by the Arrhenius equation

$$k = A\,e^{-E_a/RT}$$

The coefficient A, the pre-exponential factor, has the same units as k. For a first order reaction, the usual unit is s^{-1}, which is the unit of a frequency. Accordingly, A is called the *frequency factor*. E_a is the *energy of activation*; this is the minimum energy the reacting species must possess to be able to react on encounter. A higher activation energy at a given temperature indicates a slower reaction rate. E_a (as well as A) may be evaluated by plotting $\log_e k$ against T.

15.3.2 Theories of rate processes

Two main theoretical approaches have been developed to interprete the observed rates of chemical processes. These are mostly oriented around reactions in the gaseous phase, since the statistical mechanics and the kinetic theory of gases are sufficiently advanced to tackle such situations. But the statistical mechanics of liquid solutions is not yet competent enough to lead to satisfactory quantitative predictions regarding reactions in the liquid phase.

The theories may be broadly classified into two main branches—(1) **the collision theory** and (2) **the activated complex theory.**

The collision theory proposes that the rate of a chemical reaction depends on the frequency of *effective collisions* between the fundamental particles of the reacting substances. The number of collisions is obtained from the kinetic theory of gases while the criterion of effective collisions is principally determined by two main factors: (i) the particles must possess a minimum energy, called the energy of activation. The fraction of such particles is satisfactorily given by the Boltzmann distribution function. (ii) the particles must have proper orientation before they can form the product. But there has been no satisfactory theoretical approach to calculate this probability. The success of the theory is very limited.

The activated complex theory, also known as the theory of absolute reaction rate, assumes that in passing from the reactants to the products, the reactants have to pass through a crucial configuration of highest energy. In this transition state, the reactants form an activated complex whose concentration is determined by the concentration of the reactants. Thus two reactants A and B may be supposed to form the activated complex $AB^{\ddagger}$:

$$A + B \longrightarrow AB^{\ddagger} \longrightarrow \text{Products},$$

$[AB^{\ddagger}] = K^{\ddagger}[A][B]$, $K^{\ddagger}$ = equilibrium constant for the formation of $AB^{\ddagger}$.

The rate of the reaction is now dependent on the concentration of the activated complex and the frequency ($\nu^{\ddagger}$) of its passage over the barrier. This frequency is equal to the frequency with which a complex flies apart into products. This takes place when one of its vibrations fail to provide little or no restoring force. This mode is transformed into one translational degree of freedom; a bond holding the complex is ruptured and the direction of the bond becomes the direction of translation of the separated fragments.

Equating the vibrational energy $h\nu^{\ddagger}$ to the thermal energy kT, we have,

$$\text{rate} = -\frac{d[A]}{dt} = \nu^{\ddagger}[AB^{\ddagger}]$$
$$= \frac{kT}{h}\cdot K^{\ddagger}[A][B].$$

The measurable rate constant k' is defined as

$$-\frac{d[A]}{dt} = k'[A][B]$$

This gives, $k' = \dfrac{kT}{h}\cdot K^{\ddagger}$

Thermodynamic considerations similar to those of ordinary chemical equilibria give the relations

$$\Delta G^{\ddagger} = -RT\ln K^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger}$$

Hence, $k' = \left(\dfrac{kT}{h}\right) e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT}$

Substituting $\Delta H^{\ddagger}$ by $E_a - RT$ from somewhat more involved thermodynamic considerations,

$$k' = \left(\frac{ekT}{h}\right) e^{\Delta S^{\ddagger}/R}\, e^{-E_a/RT}$$

The resemblance of this expression for the rate constant with the Arrhenius equation is remarkable; the frequency factor (A) of the latter is now found to be a function of the entropy of activation.

The idea of the activated complex in the transition state may be understood with an example: Suppose a hydrogen atom approaches a halogen molecule, say iodine (I_2), along the I – I bond direction. When the two are far apart, the energy of the system is equal to the sum of individual energies. As the hydrogen atom gets sufficiently close to the iodine molecule, the orbitals of the two begin to overlap. Side by side, the I – I bond begins to stretch. The energy of the system now tends to increase. We may think of the activated complex as the highest energy composite species in which the I — I bond is stretched to its maximum limit while a new H — I bond is on the verge of completion. An infinitesimal compression of the H — I bond now stretches the I — I bond further, and it breaks.

The whole set of events from reactants to products is often conveniently represented in a reaction profile. This represents the potential energy of the reacting system at different stages of the interaction. (Fig. 15.4).

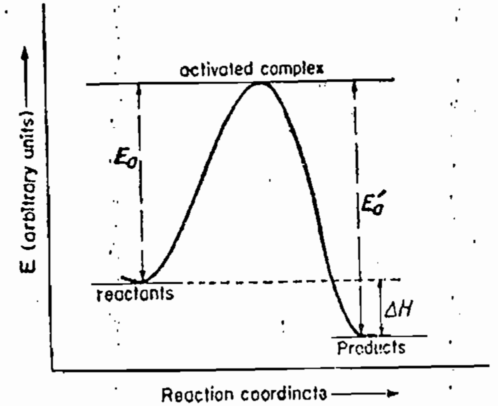


Fig. 15.4. The energy profile for a simple reacting system.

In terms of the absolute reaction rate theory, a catalyst functions by lowering the free energy of activation, $\Delta G^{\ddagger}$. The corresponding energy-profile is moderated accordingly. This is illustrated in Fig. 15.5.

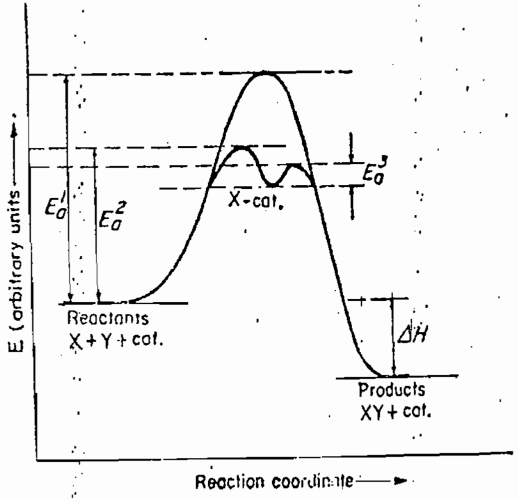


Fig. 15.5. E_a^1: Energy of activation for the uncatalyzed reaction.
E_a^2: Energy of activation for the process X + cat → X-cat.
E_a^3: Energy of activation for the process X-cat + Y → XY + cat.

15.3.3 Reaction Mechanism

The mechanisms of most inorganic reactions are still in the speculative stage. This is because most of them are so fast that suitable kinetic data are not available. Nevertheless, the rate at which interests are growing around a mechanistic approach to the subject is certainly noteworthy. It is not unlikely that the undergraduate course of inorganic chemistry in the twenty-first century (if not earlier) will be oriented more on reaction types than on the element types.

In correlating observed kinetic data with a number of possible elementary steps, we first conclude logically that in any process involving several steps the slowest step will be the rate determining step. Secondly, we use the *steady state approximation*: in the steady state of a reaction the rate of formation of any intermediate is equal to the rate at which it is consumed. Let us consider the thermal decomposition of N_2O_5: it is believed to proceed in the following steps,

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \qquad \text{(fast)}$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO \quad \text{(slow)}$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2 \qquad \text{(fast)}$$

The intermediates are NO and NO_3.

Rate of formation of NO $= k_2\,[NO_2]\,[NO_3]$.

Rate of consumption of NO $= k_3\,[NO]\,[NO_3]$.

$\therefore \quad k_2\,[NO_2]\,.\,[NO_3] = k_3\,[NO]\,.\,[NO_3]$ at steady state.

i.e. $\quad k_2\,[NO_3] = k_3\,[NO]$

Similarly, for NO_3,

$$k_1\,[N_2O_5] = k_1\,[NO_2]\,[NO_3] + k_2\,[NO_2]\,[NO_3] + k_3\,[NO]\,[NO_3].$$

$$\therefore \quad [NO_3] = k_1\,[N_2O_5]/(k_{-1}\,[NO_2] + k_2\,[NO_2] + k_3\,[NO])$$

$$= k_1\,[N_2O_5]/(k_{-1} + 2k_2)\,[NO_2]$$

Now, $\quad \text{rate} = -\dfrac{d\,[N_2O_5]}{dt} = k_1\,[N_2O_5] - k_{-1}\,[NO_2]\,[NO_3]$

$$= k\,[N_2O_5].$$

where $\quad k = 2k_1k_2/(k_{-1} + 2k_2)$.

Thus, the result agrees with the experimental order of unity.

However, kinetic data alone may not be sufficient to suggest a unique set of elementary steps. To illustrate, we consider the reaction

$$2Fe^{III} + U^{IV} \longrightarrow 2Fe^{II} + U^{VI}.$$

The observed rate follows the equation

$$\frac{d\,[U^{VI}]}{dt} = k\,[Fe^{III}]\,[U^{IV}]$$

Now, two sets of mechanisms would give this same rate expression:

Set I

$$Fe^{III} + U^{IV} \longrightarrow Fe^{II} + U^{V} \quad \textit{(slow)}$$

$$Fe^{III} + U^{V} \longrightarrow Fe^{II} + U^{VI} \quad \textit{(fast)}$$

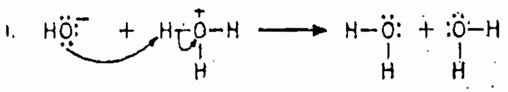
Set II

$$Fe^{III} + U^{IV} \longrightarrow Fe^{I} + U^{VI}$$

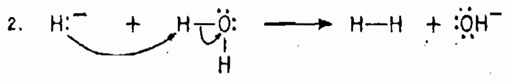
$$Fe^{III} + Fe^{I} \longrightarrow 2Fe^{II}.$$

A choice might be possible if one could detect the small amounts of U^V or Fe^I, if formed. Lacking that, one may simply argue that U^V is known and hence the first mechanism is valid.

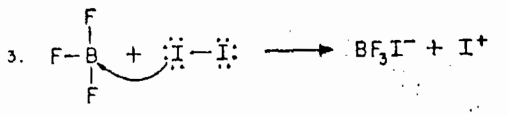
Chemical reactions have been conveniently classified as substitution, addition or elimination, exchange, solvolysis and redox types. But such labels do not directly convey anything regarding the mechanism of the reaction. Rather, the classification used by organic chemists based on electrophilic or nucleophilic nature of a process appears to be equally applicable to inorganic reactions. The following examples are self-explanatory:

1. 

Nucleophilic displacement of water by hydroxide on hydrogen

2. 

Nucleophilic displacement of hydroxide ion by hydride ion on water

3. 

Electrophilic displacement of iodine by boron on iodine

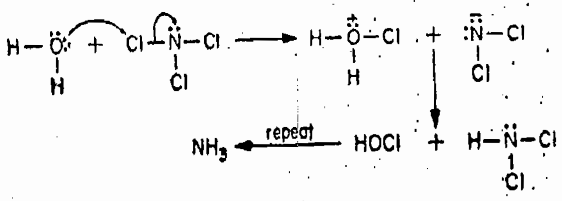
4. $Ti^{3+} + HO—OH \longrightarrow [Ti(OH)]^{3+} + {}^{\cdot}OH$

Radical displacement of hydroxyl radical by Ti(III) on H_2O_2.

The initial mode of attack is always important in determining the course of a reaction. This, in turn, depends on several factors, like (i) steric requirements at the attacking site, (ii) possibility of establishing new interactions (octet expansion), (iii) bond strengths etc. The following hydrolytic reactions present some typical illustrations.

Hydrolysis of NCl_3

Let us first consider the hydrolysis of nitrogen trichloride, NCl_3. We note that (i) electronegativities of chlorine and nitrogen are equal. Nucleophilic attack by a molecule of water can take place at either site. (ii) But the nitrogen is sterically shielded and practically inaccessible to nucleophilic attack. (iii) The high electronegativity of the NCl_2 fragment to which each chlorine is bound renders the chlorine more electrophilic than normal. (iv) Chlorine can expand its valence shell by accepting a pair of electrons in the vacant 3d orbitals. All these points suggest high electrophilicity of the chlorine. The actual reaction product confirms nucleophilic attack on chlorine.



The resistance of NF_3 to hydrolysis is understandable from the same set of reasonings when we remember that the N — F bonds are stronger than the N — Cl bonds and fluorine cannot expand its valence shell.

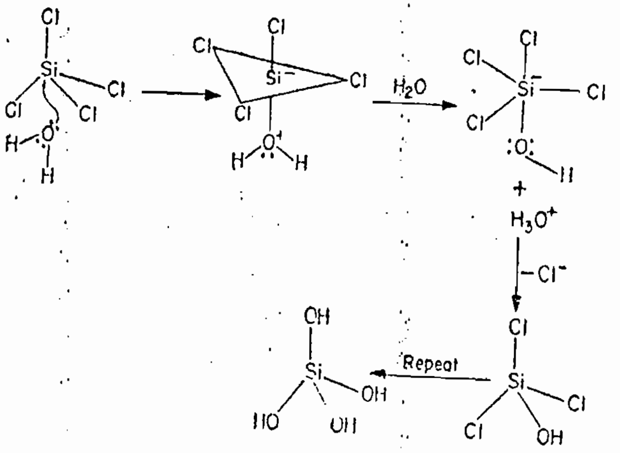
The carbon halides are also notably reluctant to hydrolysis. Thermodynamically, however, the reactions

$$CX_4(g) + 2H_2O(g) = CO_2(g) + 4HX(g)$$

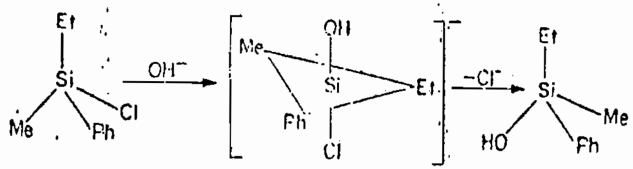
are accompanied by large negative free energy changes (CF_4 : $\Delta G° = -150$: CCl_4 : $\Delta G° = -250$ kJ mol^{-1}). In these cases also, the reluctance may be assigned to the absence of suitable reaction paths. This is probably due to the fact that carbon is both coordinately saturated and sterically protected while the halogens are more negative and hence less electrophilic than in NCl_3.

Hydrolysis of $SiCl_4$ and PCl_3

Hydrolysis of the halides of silicon and phosphorus is interpreted by nucleophilic attack on the Si/P atoms, to the exclusion of the halogens. This may be attributed to (i) the more "open" structures of PX_3 (or SiX_4) (ii) the lower electronegativity of the PCl_2 group in PCl_3 (or $SiCl_3$ in $SiCl_4$) and (iii) the ability of phosphorus and silicon to expand their valence shell. The reactions probably follow an S_N2 route.



This agrees with the observed inversion of many optically active silicon compounds (comparable to Walden inversion).



Similarly, reduction of an asymmetrically substituted silicon chloride, $R_1R_2R_3Si^*Cl$, with lithium aluminium hydride to $R_1R_2R_3Si^*H$ also results in an inversion of structure.

However, retention of configuration and racemization is also observed in many cases:

$$R_1R_2R_3Si^*H \longrightarrow R_1R_2R_3Si^*Cl \text{ (retention)}$$

$$R_1R_2R_3Si^*Cl \xrightarrow[\text{or } CCl_4]{Et_2O} R_1R_2R_3Si^*Cl \text{ (retention)}$$

but, $$R_1R_2R_3Si^*Cl \xrightarrow{CH_3CN} R_1R_2R_3Si^*Cl \text{ (racemization)}$$

also, $$R_1R_2R_3Si^*F \xrightarrow{CH_3OH} R_1R_2R_3Si^*F \text{ (racemization)}$$

These observations are also interpreted in terms of the five coordinate intermediate shown above, but with the introduction of an additional idea of **Berry pseudorotation, BPR.** (R. S. Berry, 1960). This suggests that in a TBP arrangement two equatorial groups may get interchanged for two axial groups via a transition through a square pyramid arrangement. The changed configuration of the intermediate may now lead to retention of the original tetrahedral configuration. The details of the process are beyond the scope of the present treatment. BPR also explains the equivalence of the five fluorine atoms in PF_5. Similar mechanisms for changing the configurations of molecules without breaking bonds have also been suggested for other coordination numbers. We shall find such an example for C.N. 6 with trisethylenediamminecobalt (III) ion ("Bailar twist") later on.

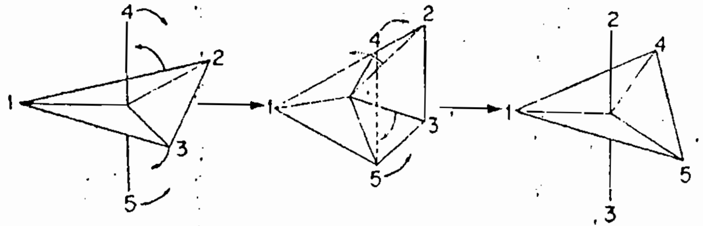
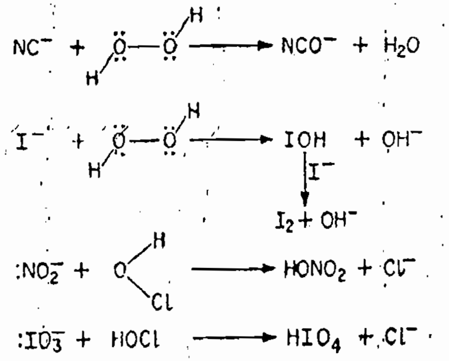


Fig. 15.6. Schematic representation of Berry Pseudorotation.

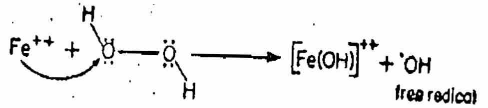
In the reactions considered above, the oxygen atom in H_2O acts as a nucleophile. There are also examples in which oxygen acts as an electrophile: the reactions of peroxides, peroxoacids and hypohalites are good examples:



The reactions are also interesting as they represent **atom transfer oxidation** reactions. Use of tracer oxygen (O^{18}) in the reaction of nitrite confirms that the third oxygen actually comes from the hypochlorous acid:

$$:NO_2^- + HO^*Cl \longrightarrow HO^*NO_2 + Cl^-$$

However, it should be remembered that such reactions may also take place by alternative mechanisms. In presence of trace metal ions, for example, these reactions occur through free radical intermediates; the metal ion catalyzes the free radical decomposition of the peroxides and the hypochlorous acid: for example,



Rate studies on oxoanions

Rate-studies on the reactions of the oxyanions (ClO_3^-, BrO_3^-, SO_4^{2-}, OCl^- etc.) are specially interesting as they reiterate the importance of kinetic factors over and above the thermodynamic gate pass of a reaction. Reactions like

$$NO_2^- + OCl^- \longrightarrow NO_3^- + Cl^-$$

and $$ClO_3^- + I^- \longrightarrow ClO_3^- + OI^-$$

are usually very slow but they are catalysed by H^+. For example, the reactions

$$XO_3^- + 5X^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$$

show a rate-law:

$$\text{Rate} = k\,[XO_3^-]\,[X^-]\,[H^+]^2.$$

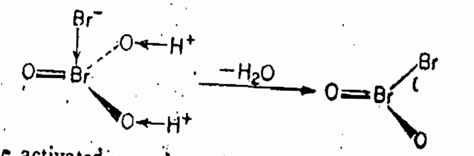
The reaction may proceed as:

$$2H^+ + XO_3^- \rightleftharpoons H_2OXO_2^+ \quad \text{(fast)}$$

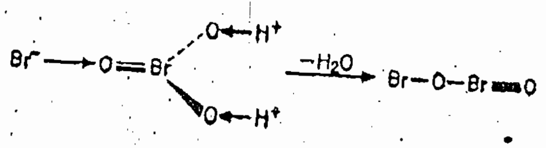
$$X^- + H_2OXO_2^+ \longrightarrow X_2O_2 + H_2O \text{ (slow)}$$

$$X_2O_2 + X^- \longrightarrow X_2 + XO_2^- \quad \text{(fast)}$$

Subsequently, the XO_2^- ion gets reduced to X^- by a series of fast reactions. The rate law suggests that the activated complex may have the composition $[XO_3^- . X^- . H^+ . H^+]$. A trigonal pyramidal structure is most likely:



Alternatively, the activated complex might have a planar structure, but that would involve more electrostatic repulsion. Also, removal of a molecule of H_2O does not yield a stable structure:



Similar studies on different oxyanions reveal that

(i) lower the charge on the central atom, higher is the reactivity. For the oxyanions of chlorine, rates increase in the order

$$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$$

The rate of exchange of oxygen with water similarly follows the order

$$ClO_4^- < SO_4^{2-} < HPO_4^{2-} < H_2SiO_4^{2-}$$

(ii) The larger the size of the central atom, the higher will be the rate of reaction. The rate order observed is

$$ClO_3^- < BrO_3^- < IO_3^-.$$

Besides such classifications in terms of electrophilic, nucleophilic and free radical reactions, certain broader generalizations have also been suggested for chemical reactions. Reactions accompanied by changes of oxidation number are called electron-transfer reactions; others may be classified as atom-transfer or group-transfer reactions. In this second category, reactions may be further subdivided into different classes according to the process involved: substitution, decomposition, addition, proton transfer or neutralization etc. Among these, substitution mechanisms appear to be most widely studied. The examples mostly involve coordination compounds and so their mention is deferred till their presentation. In general, the conversion of two reactants R_1 and R_2 to products P_1 and P_2 (say) may take place in one of the following ways:

1. **Associative** or **A**-mechanism: In the rate-determining step, R_1 and R_2 transform into a new species $R_1 - R_2$ which subsequently gives rise to the products (P_1 and P_2). $R_1 - R_2$ is termed an intermediate. The energy profile diagram is similar to that shown for a catalyzed reaction (Fig. 15.5). The first activated complex is formed by an associative activation mode, *a*: in this the reactants form a bond creating the intermediate $R_1 - R_2$. The second step requires a much smaller activation energy for conversion of $R_1 - R_2$ to the product $P_1 : P_2$. This implies a bimolecular step and the rate expression should be second order:

$$\text{Rate} = k\,[R_1]\,[R_2].$$

2. **Dissociative** or **D**-mechanism. In this process, a reactant, say, R_1, unimolecularly dissociates into a product (P_1) and an intermediate X in the rate-determining step. X can then recombine with P_1 or may diffuse into a solvent cavity with R_2 where it reacts to form the product. The energy profile diagram is the same as before, but the initial activation involves a dissociative activation mode, *d*. This leads to complete fragmentation of one of the reactants (R_1) into one of the products (P_2) and an intermediate X for kinetically significant stability. X then reacts rapidly with the other reactant R_2 to give the product. This suggests a unimolecular process characterized by a first order rate expression:

$$\text{Rate} = k\,[R_1].$$

3. **Interchange** or **I**-mechanism: The slowest step involves smooth transformation of the reactants R_1 and R_2 into the products P_1 and P_2 via a single, unstable high energy activated complex. The energy profile diagram is similar to Fig. 15.4 and involves only one energy of activation. No reactive intermediate is formed. On the micropicture, however, the transition state may involve fragmentation or dissociation of one of the reactants, (R_1, say), with practically no bond formation between R_1 and R_2. This is referred to as an I_d process. Alternatively, the transition state may involve an association between R_1 and R_2, when it is referred to as an I_a process. A bimolecular process with a second order rate expression in R_1 and R_2 is expected in either case.

4. **Diffusion controlled reaction.** In this case, the reaction may proceed by any of the above processes but the rate of the reaction is determined by the rate of diffusion of the reactants R_1 and R_2 into a solvent cavity or cage to form a cage complex $R_1 : R_2$. Obviously, this constitutes the slowest step. The neutralization of a proton by a hydroxyl ion (both aquated) is a common example of this type.

But how do we categorize a reaction into one of these different types? There are several paths to tackle this problem. For a D or A mechanism, direct observation of the intermediate will provide the conclusive evidence. The distinction between an I or A process is somewhat more involved. Rate-studies with designed variations in the reactants R_1 and R_2 with selected substituents are one of the major steps. Rates of I_d and D-processes are largely influenced by substituents which favour bond-breaking and the rate constants show large dependence on the nature of the leaving group. On the other hand, A or I_a processes are based on bond-making, and so their rate constants are significantly altered by the nature of the entering group. The electron configuration of the central atom(s) in the reacting species may also be used as a predictive tool : an I or A mode is expected when the central atom bears significant valence unsaturation. The final decision between I and A is determined by several factors like energy of activation, strength of bonds formed, etc. Usually, compounds of elements which can expand their valence shell and form stable adducts, are found to react by A – mechanism. If the reagent is valence saturated; the expected path is either D or I. The ultimate choice of mechanism does always rest on a delicate balance of several factors all of which cannot be properly discussed in this short span. Nevertheless, this discussion will help us to identify such labels as A, D or I when used in appropriate cases in the text.

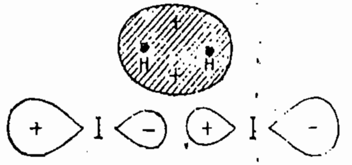
In recent years, kinetic-mechanistic studies have been further developed in terms of symmetry considerations for the molecular orbitals involved. We shall confine our discussion to bimolecular reactions only. The energies and shapes of the **highest occupied molecular orbital, HOMO** and the **lowest unoccupied molecular orbital, LUMO** of the reacting molecules are important in such cases. These terms are self-explanatory. Referring to the m.o. energy level diagrams (Chapter Seven) we readily understand that in O_2 and F_2, the HOMO would be the antibonding π_{2p}^* m.o. while the LUMO would be the antibonding σ_{2s}^* m.o. For N_2, the HOMO would be the σ_{2s}^* m.o. (actually σ_{sp}), the LUMO would be the π_{2p}^* m.o. When a chemical reaction takes place between the two molecules, electrons flow from the HOMO of one molecule to the LUMO of the other. This is equivalent to the attack of a nucleophile (HOMO) on an electrophile (LUMO). The following conditions are to be fulfilled for a reaction to occur:

(i) The HOMO and LUMO must have a net non-zero overlap permitted by their symmetry.

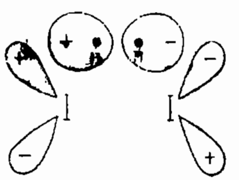
(ii) The energy of the LUMO should preferably be lower than that of the HOMO; in any case, the LUMO should not be more than ~ 6 eV higher than the HOMO.

(iii) The HOMO must be either a bonding m.o. of a bond to be broken or an antibonding m.o. of a bond which is going to be formed. The LUMO must conform to the converse conditions.

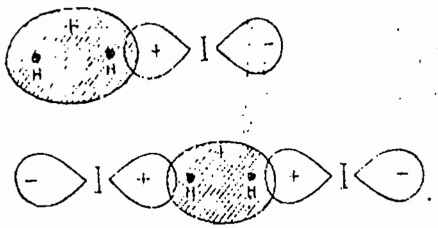
The application of these rules to the familiar $H_2 - I_2$ reaction is illustrated below:



Case I: Broadside approach between H_2 and I_2: **HOMO** of $H_2(\sigma_s)$ and **LUMO** of $I_2(\sigma_p{}^*)$. Net overlap zero, hence forbidden.



Case II: Broadside approach between H_2 and I_2: **HOMO** of I_2 (π *) and **LUMO** of H_2 (σ_s*). Symmetry permitted but electron flow from the antibonding m.o. of I_2 will actually strengthen the I − I bond. Hence unlikely.



Cases III and IV: End-on approach of the HOMO of H_2 molecule by (III) one or (IV) two I-atoms: Both are symmetry-and energy allowed.

Conclusion. It must be confessed at this point that the foregoing discussion on kinetics and mechanism cannot make a student self-sufficient to apply such principles. In fact, this may at best serve as an appetizer, or as an attempt to familiarise them with various terminologies. This will be supplemented in the text matter whenever feasible. Most extensively studied are reaction mechanisms for coordination compounds; they deserve special attention and will be mentioned in relevant context.

SUMMARY

The thermodynamic criterion for the feasibility of a reaction may be understood in terms of the thermodynamic functions **enthalpy** (H), **entropy** (S) and **Gibbs energy** (G) of the system. The changes in these functions accompanying a chemical process (ΔH, ΔS and ΔG) are significant:

$\Delta H = Q_p$ (heat involved at constant pressure).

ΔH negative = exothermic process; ΔH positive = endothermic process.

The enthalpy of an element in its standard state is arbitrarily fixed at zero. Accordingly, the heat evolved in the formation of 1 mol of a compound from its elements under standard conditions gives its **standard heat** of formation, ΔH°_{298}.

In a chemical reaction, if the bonds formed are more stable than the bonds broken, the extra energy is obtained in the form of heat, a negative ΔH results (exothermic process). *At ordinary temperatures*, reactions usually proceed towards a negative ΔH unless other factors, like entropy, interfere.

The **entropy** (S) of a system is a thermodynamic state function whose change ΔS in a process is given by $\Delta S = Qrev/T$, where $Qrev$ is the reversible heat change involved in the transfer of the system from one equilibrium state to another. S is also related to the thermodynamic probability (W) of a system by the relation $S = k \ln W$. (W is

the number of ways in which the molecules, or other constituent particles, of the system can be arranged to produce the same system; k = Boltzmann constant). Clearly, entropy is a measure of the randomness or disorder of a system. Our experience shows that **spontaneous processes** take place in the direction of greater disorder, that is, in which ΔS is positive. The entropy of substances at 25°C and 1 atm pressure, the *standard entropy*, S°, is obtained from the third law of thermodynamics.

The **Gibbs Energy** (G, Gibbs function, Gibbs free energy or simply **Free energy**) of a system is defined as $G = H - TS$. For a spontaneous process, ΔG, the change in Gibbs energy, must be negative. The converse, however, may not be true—a process with a negative ΔG has the thermodynamic potentiality to take place, but it may not occur at a perceptible rate.

The magnitude of ΔG for any process is determined by the ΔH and $T\Delta S$ terms. The contribution of the entropy term is usually small (in Joules) in comparison to the enthalpy term (in kilo Joules). So at ordinary temperatures, the enthalpy term is the primary deciding factor for a chemical process. This, in turn, depends on the relative strengths of the bonds broken and bonds formed and a reaction is generally favoured in the direction of stronger bond formation. However, with rise in temperature, the $T\Delta S$ term may dominate in determining the sign of ΔG. So, reactions with a positive ΔS are favoured at high temperatures. This has been applied to the reduction of metal oxides by carbon and aluminium.

The mechanism of a chemical reaction provides information regarding the nature of elementary steps involved in an observed overall reaction. Ideally, it should furnish a detailed account of how the chemical bonds, or the electrons and the nuclei in the reactants rearrange themselves to form the ultimate product. Among the several established methods for the study of reaction mechanisms, (i) isotopic studies, (ii) isolation of intermediates where possible and (iii) kinetic studies are important.

The rate of a chemical reaction is generally referred to as the variation of concentration of the reactants or product with time. For homogeneous reactions, it is often possible to correlate, at constant T and P, the experimental rate with the concentrations of the various reactants A, B, C etc. as

$$\text{Rate} = k \,.\, C_A{}^\alpha \,.\, C_B{}^\beta \ldots\ldots,$$

The constant k is called the specific rate constant, or simply the rate constant of the reaction. The reaction is said to be of order α with respect to A, β with respect to B .. and so on. The overall *order of the reaction* is $(\alpha + \beta + \ldots\ldots)$.

The **molecularity of a reaction** is the number of reacting species involved in each step of a reaction.

The rate of a chemical reaction increases markedly with temperature according to the relation $k = A \,.\, e^{-E_a/RT}$, where A is a constant for a particular reaction, called the frequency factor. E_a is called the **energy of activation** for the reaction—it is the minimum energy which the reacting species must possess to be able to react on encounter. A higher energy of activation indicates a slower reaction rate. A catalyst accelerates the rate of a reaction by providing an alternative path with a lower energy of activation.

Chemical reactions may be classified according to their nature as substitution, addition or elimination, exchange, solvolysis and redox types. Labels illustrating nucleophilic, electrophilic or radical nature of the reaction are also useful.

Recent kinetic-mechanistic studies are being developed in terms of symmetry considerations for the molecular orbitals involved in a chemical process. The **highest occupied molecular orbital** (HOMO) and the **lowest unoccupied molecular orbital** are most important in this connection. For any reaction between two molecules, electrons will flow from the HOMO of one to the LUMO of the other. The conditions necessary are:

(i) The HOMO and LUMO must have a net non-zero overlap permitted by their symmetry.

(ii) The energy of the LUMO should preferably be lower than that of the HOMO.

(iii) The HOMO must be either a bonding m.o. of a bond to be broken or an antibonding m.o. of a bond which is going to be formed. The LUMO must conform to the converse conditions.

EXERCISE

1. *What is the standard enthalpy of formation of a compound?*
   Calculate the heat of combustion of ethyne (C_2H_2) *from the following heats of formation* ($kJ\ mol^{-1}$).
   $C_2H_2(g)$ 226.7; CO_2 − 393.5; $H_2O(g)$ − 241.8.

2. *Use the following bond energies* ($kJ\ mol^{-1}$) *to predict whether* C_2H_2, C_2H_4, N_2, NH_3, PH_3 *and* P_2 *should form polymers (containing single bonds).*

$C-H$: 414 ;	$C-C$: 347 ;	$C=C$: 611 ;	$C\equiv C$: 837.
$N-H$: 391 ;	$N-N$: 160 ;	$N=N$: 418 ;	$N\equiv N$: 946.
$P-H$: 322 ;	$P-P$: 209 ;	$P=P$: 335 ;	$P\equiv P$: 485.

3. *If chemical changes always proceed in the direction of greater stability, why do endothermic reactions occur at all?*

4. *Calculate the* $N-H$ *and* $N-N$ *single bond energies from the following enthalpy data:*
   Enthalpy of formation ($kJ\ mol^{-1}$): $NH_3(g)$ − 46; $N_2H_4(g)$ + 95.4; *Enthalpy of bond breaking* ($kJ\ mol^{-1}$) H_2 : 436; N_2 : 945.6.

[**Hints:** See problem 15.3). **Ans.:** $E_{N-H} = 391\ kJ\ mol^{-1}$.
$E_{N-N} = 158.2\ kJ\ mol^{-1}$.

4. *Comment on the following absolute entropies at 298K* ($J\ mol^{-1}\ deg^{-1}$):
   (i) $I_2(g)$ 260.6; $I_2(s)$ 116.1.
   (ii) $N_2(g)$ 191.6. $H_2(g)$: 130.68. $NH_3(g)$ 192.4.
   (iii) $H_2O(g)$: 188.6 $H_2S(g)$: 205.8. $H_2Se(g)$: 221.4. $H_2Te(g)$: 234.3.

5. *State, with reasons, whether you expect* $\Delta S°$ *for the following processes to be +ve or −ve.*
   (i) ice ⟶ water
   (ii) $P_4(g) + 10F_2(g) = 4PF_5(g)$.
   (iii) $I_2(s) + Cl_2(g) = 2ICl(g)$.
   (iv) $BF_3(g) + NH_3(g) = H_3NBF_3(g)$.

6. *What should be the main thermodynamic reasons that the following processes take place from left to right?*
   (i) $NH_4NO_3(s)$ + water ⟶ solution.
   (ii) $BCl_3(g) + BBr_3(g) \longrightarrow BCl_2Br(g) + BClBr_2(g)$.
   (iii) $3C_2H_2(g) \longrightarrow C_6H_6(g)$.
   (vi) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$.
   (v) $SnCl_2 + Cl_2 \longrightarrow SnCl_4$.
   (vi) $LiI + CsF \longrightarrow LiF + CsI$.

7. *The neutralization of aqueous solutions of strong acids by strong alkalies can be represented by the equation:*
   $H^+(aq) + OH^-(aq) \longrightarrow H_2O$. $\Delta H° = -56.1\ kJ\ mol^{-1}$.
   Calculate $\Delta S°$ *and* $\Delta G°$ *at 298K. Given standard entropies* ($J\ mol^{-1}\ deg^{-1}$):
   $H^+(aq)$: 0; $OH^-(aq)$: − 10.5; $H_2O(l)$: 69.9.

8. *For the reaction* $2NO + O_2 = 2NO_2$, *the rate is found to increase by a factor of eight if the concentrations of both the reactants are doubled. When only the concentration of oxygen is doubled, the rate increases by a factor of two. Write down the rate eqn. What will be the effect of doubling the concentration of* NO?

9. *The heat of vaporization of liquid hydrogen peroxide is 51.6* $kJ\ mol^{-1}$ *while its heat of decomposition into liquid water and oxygen is* − 98 $kJ\ mol^{-1}$. *Calculate* $\Delta H°_f$ (H_2O_2, g). *Given* $\Delta H°_f$ (H_2O, l) = − 285.77 $kJ\ mol^{-1}$.

10. *It is proposed to synthesize compounds of the type* N_2X_4 (X = *halogen*). *The structures are similar to that of* N_2H_4. *With which halogen would you suggest starting? On a purely thermochemical basis, would you expect the synthesis to be feasible?*

CHAPTER SIXTEEN

A PRELUDE TO THE CHEMISTRY OF THE ELEMENTS

OBJECTIVES

16.1. Introduction

16.2. Origin of the elements

16.3. Abundance of the elements

- Cosmic Abundance [16.3.1]
- Terrestrial Abundance [16.3.2]
- Occurrence of the elements [16.3.3]
- The Formation of Minerals [16.3.4]

16.4. Major Periodic Trends

16.5. The forthcoming elements

16.6. An introduction to symmetry

- Symmetry operations and Symmetry elements [16.6.1]
- Point Groups [16.6.2]

16

16.1. INTRODUCTION

The roll strength of the elements in the periodic table now extends upto 112, with scopes for further addition. However, only 75 elements occur in the earth's crust in concentrations greater than 10^{-4} ppm. Their abundances show wide variations in the earth as well as in the universe as a whole. A study of this abundance of the elements in various isotopic compositions present an interesting starting point for the study of their origin and chemical behaviour. We begin this chapter with a brief introduction to the origin of the elements and their abundances, followed by a brief survey of the major periodic trends in their properties. We conclude with glimpses of symmetry elements, symmetry operations and point group symbols which are becoming unavoidable in any modern approach to the subject.

16.2. THE ORIGIN OF THE ELEMENTS

Origin of the universe—the hot big bang

The origin of the elements must be traced back to the origin of the universe itself. Regarding the latter, the Big Bang theory seems to be the most dominant one at present. According to this theory, the entire matter and energy of the universe was cumulated in the form of a cosmic egg of very high density ($\sim 10^{96}$ g cm^{-3}) and temperature (10^{32}K). It is not clear how this nucleus was formed. Perhaps the "matter" present in it was actually in the form of radiations. Now, a tremendous and sudden explosion (big bang) occurred approximately 1.8×10^{10} years ago*. The universe started to expand after this explosion and the temperature began to fall very rapidly. For example, after one second of the explosion, the temperature is supposed to have fallen to $\sim 10^{10}$K. From this stage onward, the universe was densely populated by the elementary particles like neutrons, protons and electrons. During the next 10 – 500 seconds, these particles started to condense, like nuclear fusion reactions, into the nuclei of different elements. It is further estimated that ${}^4_2$He was the principal product at this stage ($\sim 25\%$ of the total mass of the universe), together with small amounts of deuterium ($\sim 10^{-3}\%$). The heavier nuclei were then formed by several series of thermonuclear reactions. The early stars condensed at this stage and the process continued to give new elements.

Experimental support: 2.7K radiation

The hot Big Bang theory is supported by the existence of 2.7 K radiation, experimentally verified in 1965 (Penzias and Wilson; Nobel Prize 1978 for this discovery). The universe must have been filled initially with radiation corresponding to its very high temperature, $\sim 10^{10}$K. As the universe expanded, its temperature came down. It has been estimated that after 18×10^9 years, the temperature of the universe should be around 3K. In 1965, Penzias and Wilson built a highly sensitive horn-shaped radio-receiver for use in a space program. While testing it, they discovered a faint whisper of radio noise coming from all directions in outer space. This was actually a microwave radiation of wavelength 1.285 cm. This wavelength corresponds to isotropic thermal black body radiation at a temperature of 2.7K. Hence the cosmic microwave background radiation can be considered as a remnant of the hot Big Bang.

Formation of the elements—thermonuclear reactions

Whatever be the origin of the universe in its earliest form, our knowledge about the formation of the elements is more compact in terms of the series of thermonuclear reactions just mentioned. The distribution of the various elements throughout the entire universe and their isotopic compositions have been estimated by wide range spectroscopic studies on the sun and the solar system, as well as on the stars, galaxies, nebulae and interstellar space. The estimated abundances of different nuclides can be understood through anticipated thermonuclear reactions of various kinds. We are already familiar with the processes of fusion of hydrogen nuclei into helium. The process occurs in a number of stars at about 10^7K. As the process continues, the outward thermal pressure of radiation counteracts the gravitational force on the gaseous mass. But when approximately 10% of the hydrogen in a star of about the same size as the sun has been used up, the thermal pressure of radiation becomes insufficient to counteract the gravitational pull. As a consequence the star contracts and the temperature rises. When the temperature reaches $\sim 2 \times 10^8$K, helium-burning starts forming heavier nuclei:

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* Estimated from the observed present rate of expansion of the universe, 18 km s^{-1} per 10^6 light years; the rate is supposed to have remained constant from the beginning.

$${}^4_2\text{He} + {}^4_2\text{He} \rightleftharpoons {}^8_4\text{Be}$$

$${}^8_4\text{Be} + {}^4_2\text{He} \rightleftharpoons {}^{12}_6\text{C} + \gamma$$

The process of contraction and temperature rise may be repeated, providing scopes for a wide variety of nuclear reactions. A few schematic nuclear reactions leading to the formation of different nuclides are given below:

Process	Typical Reaction	Temp. °K. (approx.)
H-burning	${}^1H + {}^1H \longrightarrow {}^2H + e^+ + \nu$	10^7
	${}^2H + {}^1H \longrightarrow {}^3He + \gamma$	,,
	${}^3He + {}^3He \longrightarrow {}^4He + 2\,{}^1H$	,,
He-burning	$3\,{}^4He \longrightarrow {}^{12}C + \gamma$	10^8
	${}^{12}C + {}^4He \longrightarrow {}^{16}O + \gamma$	,,
	${}^{16}O + {}^4He \longrightarrow {}^{20}Ne + \gamma$	,,
	${}^{20}Ne + {}^4He \longrightarrow {}^{24}Mg + \gamma$	,,
C-burning	${}^{12}C + {}^{12}C \longrightarrow {}^{24}Mg + \gamma$	10^9
	$\longrightarrow {}^{23}Na + {}^1H$	,,
	$\longrightarrow {}^{20}Ne + {}^4He$	,,
O-burning	${}^{16}O + {}^{16}O \longrightarrow {}^{28}Si + {}^4He$	,,
	$\longrightarrow {}^{31}P + {}^1H$	,,
	$\longrightarrow {}^{31}S + {}^1n$	,,
α-process	${}^{20}Ne + \gamma \longrightarrow {}^{16}O + {}^4He$	$> 10^9$
	${}^{20}Ne + {}^4He \longrightarrow {}^{24}Mg + \gamma$	,,
	${}^{24}Mg + {}^4He \longrightarrow {}^{28}Si + \gamma$	,,
Neutron absorption		
slow ($s-$) and	${}^{56}Fe + {}^1n \longrightarrow {}^{57}Co + \beta^-$	10^9
rapid ($r-$) processes	${}^{57}Co + {}^1n \longrightarrow {}^{58}Ni + \beta^-$	,,

Note 1. ^{4}He may also result as the net product from a cycle consisting of C, N and O as (Bethe and Weizsacker);

$${}^{12}C + {}^1H \longrightarrow {}^{13}N + \gamma$$
$${}^{13}N \longrightarrow {}^{13}C + e^+ + \nu$$
$${}^{13}C + {}^1H \longrightarrow {}^{14}N + \gamma$$
$${}^{14}N + {}^1H \longrightarrow {}^{15}O + \gamma$$
$${}^{15}O \longrightarrow {}^{15}N + e^+ + \nu$$
$${}^{15}N + {}^1H \longrightarrow {}^{12}C + {}^4He.$$

It has been estimated that about 10% of the energy of the sun comes from this process. Most of the rest comes from the straightforward H-burning.

2. Besides the processes mentioned above, rapid proton capture by heavier nuclides (*p*-process) may lead to proton-rich nuclei.

Spallation

3. Spallation reactions also give rise to some light elements. Cosmic rays consist of a wide variety of atomic particles, from hydrogen to uranium. While travelling great distances in the galaxies, the heavier particles occasionally collide with atoms of the interstellar gas—largely ^1H and ^4He. As a result, fragmentation occurs and the lighter elements are formed. High speed α-particles may also collide with interstellar iron group elements, inducing spallation. Such processes, together with $^{13}C\ (p, \alpha)^{10}B$ and $^{14}N\ (p, \alpha)\ ^{11}C$ reactions, followed by β-decay of ^{11}C to ^{11}B, account for the abundance of the lighter isotopes of Li, Be and B.

Neutron absorption:

4. Neutron absorption β emission processes are most significant for the elements beyond iron. The reactions are primarily (n, γ) type, the unstable nuclide formed subsequently undergoing β-decay. In the *s*-process, neutron capture is slow compared with β-emission while in the *r*-process, neutron capture is rapid. The nuclides formed by the *s*-process are controlled by the neutron capture cross-section of the precursor nuclide. The stable nuclei corresponding to neutron magic numbers 50, 82 and 126 have very low neutron capture cross-sections. This explains the relatively high abundances of $^{89}_{39}Y$, $^{90}_{40}Zr$, $^{138}_{56}Ba$, $^{140}_{58}Ce$, $^{208}_{82}Pb$ and $^{209}_{83}Bi$. In the *r*-process, a large number of neutrons are added successively into a single nucleus in a very short time; for example, some 200 neutrons might be added to an iron nucleus in 10—100s. Eeventually the product becomes excessively neutron-rich and a cascade of 8—10 β-emissions result in the formation of a stable nuclide. The abundances of nuclides of mass numbers 80, 130, 194 as well as ^{36}S, ^{46}Ca, ^{48}Ca are explained in this manner.

Such schemes of proposed nuclear reactions have been considerably developed to account for the observed abundances of different nuclides throughout the universe. Let us now have a glance at the abundances of the elements.

16.3. ABUNDANCE OF THE ELEMENTS

The average relative content of an element in any natural system is called its abundance. Spectroscopic analysis of the celestial bodies and analysis of meteorites provided knowledge about the abundance of the elements over the whole universe, or the cosmos; this is often referred to as the cosmic abundance of the elements. Abundances of the elements on the earth are somewhat different and are referred to as the terrestrial abundance of the elements. For this, analysis is based primarily on the crust of the earth (about 36 km. depth), together with the atmosphere and the surface water. Each abundance data is helpful in providing a systematic generalization of the elements with respect to their formation, stability and occurrence.

16.3.1 Cosmic Abundance

A plot of the abundances of chemical elements (in terms of number of atoms per 10^6 atoms of silicon) against their atomic numbers is shown in Fig. 16.1. Certain selected values (A. Cameron) are also given in Table 16.1. The values are approximate and disputed. Yet the general features presented by them are interesting:

(i) Hydrogen and helium are most abundant of all elements. Carbon and oxygen come next in the sequence.

(ii) Abundances show a rapid exponential decrease from elements of small atomic number to molybdenum (Z = 42). After this, abundances remain more or less constant.

Certain generalizations on cosmic abundance

(iii) The abundance data may be clearly divided into two separate curves, one lower and one upper, as shown. The upper curve (solid line) connects the nuclides of even atomic number which are clearly more abundant than the nuclides of neighbouring elements with odd Z. This was expressed earlier in the empirical rules of Harkins. (See below).

(iv) The abundances of lithium, boron (both with odd Z) and also beryllium are unusually low. These nuclides are easily transmuted by nuclear bombardment.

(v) Nuclides whose mass numbers are multiples of 4 (e.g. ^{16}O, ^{20}Ne, ^{24}Mg, ^{28}Si, ^{32}S, ^{36}Ar, ^{40}Ca, ^{48}Ti) are more abundant than their immediate neighbours (rule of Oddo). This shows the stability of the 2-proton-2-neutron combination ("alpha-particle nuclides").

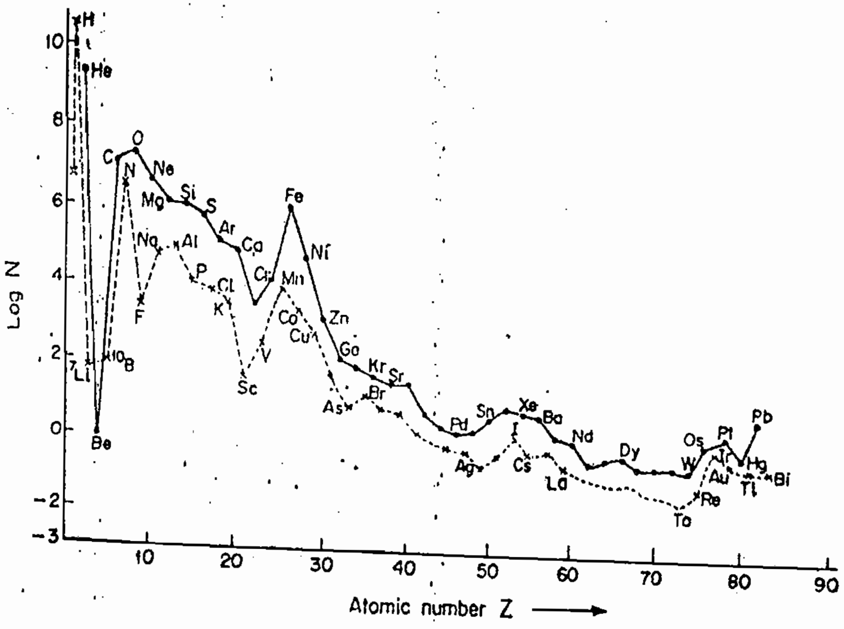

Fig. 16.1 Cosmic abundance of elements. N=no. of atoms per 10^6 atoms of Si.

(vi) Atomic numbers 23—28 are marked by a peak in the curve, ^{56}Fe being remarkably abundant in comparison to its immediate neighbours (~ 10^4 times). We recall that this nuclide occurs at the maxima of the nuclear binding energy curve.

(vii) Most of the peaks in the curve correspond to the magic numbers of protons and neutrons: ^4_2He, $^{16}_8O$, $^{40}_{20}Ca$, $^{90}_{40}Zr$, $^{118}_{50}Sn$, $^{138}_{56}Ba$, $^{208}_{82}Pb$.

Detailed study of abundance data further shows:

(viii) The commonest isotope of a given element is that with an even number of neutrons. Isotopes containing protons and neutrons in odd numbers are less abundant, e.g. ^2_1H, $^{40}_{19}K$.

(ix) Plot of abundances against mass numbers (not shown here) further reveals that: (a) Atoms of heavy elements tend to be rich in neutrons; heavy proton-rich nuclides are rare. This lends support to the hypothesis of primordial elemental synthesis by neutron absorption. (b) Among the heavier elements, abundance maxima occur in pairs for mass numbers 80, 90; 130, 138; 196, 208. This shows the stability of magic numbers of nucleons.

Study of the abundances of elements throws light on the mode of formation of the elements (nucleogenesis) as outlined in the last section. The ultimate abundance of an element depends on several factors, particularly the probability of the nuclear process involved and the stability of the various isotopic species.

The "rules" of Harkins (1928) :

1. No common nucleus except hydrogen contains fewer neutrons than protons.

2. Elements with even number of nuclear charge are more abundant and more stable than those with odd charges. They are also richer in isotopes.

3. Nuclei with even numbers of neutrons are more abundant and more stable than nuclei having odd numbers of neutrons.

4. Nuclei with even mass numbers are more abundant than nuclei having odd mass numbers.

The applicability of these generalizations may be readily appreciated with reference to any table of isotopic abundance. The numbers of stable nuclides known for different odd and even combinations of atomic number (Z) and neutron number (N) are also noteworthy: (also see section 14.2.3)

Combination	Number (approx.)
Z even, N even	163
Z even, N odd	56
Z odd, N even	50
Z odd, N odd	5

TABLE 16.1

Relative Abundances of some elements (approx)

(atoms per 10^6 atoms Si)

Element	Abundance	Element	Abundance
1. H	2.7×10^{10}	27. Co	2200
2. He	1.8×10^{9}	28. Ni	4.8×10^{4}
3. Li	60	29. Cu	540
4. Be	1.2	30. Zn	1260
5. B	9	31. Ga	38
6. C	1.11×10^{7}	32. Ge	115
7. N	2.31×10^{6}	33. As	6.2
8. O	1.84×10^{7}	34. Se	67
9. F	780	35. Br	9.2
10. Ne	2.6×10^{6}	36. Kr	41.3
11. Na	6.0×10^{4}	37. Rb	6.1
12. Mg	1.06×10^{6}	38. Sr	22.9
13. Al	8.5×10^{4}	39. Y	4.8
14. Si	1.00×10^{6}	40. Zr	12
15. P	6500	41. Nb	0.9
16. S	5×10^{5}	42. Mo	4.0
17. Cl	4740	47. Ag	0.46
18. Ar	1.1×10^{5}	50. Sn	3.7
19. K	3500	52. Te	6.5
20. Ca	6.2×10^{4}	53. I	1.27
21. Sc	31	54. Xe	5.84
22. Ti	2400	56. Ba	4.8
23. V	254	78. Pt	1.41
24. Cr	1.27×10^{4}	79. Au	0.21
25. Mn	9300	80. Ag	0.21
26. Fe	9×10^{5}	82. Pb	2.6

16.3.2. Terrestrial Abundance

A very small fraction of the mass of the Earth is available for direct analysis and study—the crust*, the hydrosphere and the atmosphere. They make up less than 1 per cent of the Earth by mass. Obviously, indirect methods have to be used to estimate the composition of the earth. One may reasonably assume that the Sun, and the planets and meteorites of the solar system were derived via the same set of nucleosynthetic events. Hence the abundances of the non-volatile elements are in the same proportion in the Earth as they are in the Sun or meteorites. Related arguments and studies have led to several estimates of the abundances of the elements in the crust of the earth. The estimates differ considerably from one another, but their overall trend is not very different from the cosmic abundance of the elements. Some approximate figures are given in Table 16.2

TABLE 16.2

Abundance of some elements (approximate) in Crustal Rocks

(grams per metric Ton or ppm.)

Element	Crustal average	Element	Crustal average
1. H	1500	22. Ti	4300
2. He	0.003	23. V	135
3. Li	20	24. Cr	120
6. C	200	25. Mn	1000
7. N	20	26. Fe	52,000
8. O	466,000	27. Co	29
11. Na	28,000	28. Ni	100
12. Mg	20,900	29. Cu	68
13. Al	81,300	30. Zn	75
14. Si	277,000	47. Ag	0.08
15. P	1100	78. Pt	0.01
16. S	340	79. Au	0.004
19. K	25,900	80. Hg	0.08
20. Ca	36,500	87. Pb	13

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* Seismic data and other studies primarily suggest that the earth consists of several zones based on density and perhaps chemical affinity: (a) **the crust** (~ 36 km. in depth), (b) **the mantle** (36 –2900 km), and (c) **the core** (2900 km. to center). Primarily, the crust consists of a heterogeneous layer of silicates and oxides of different elements; the mantle has a fairly homogeneous combination of different silicates, mainly of magnesium and iron. Geophysical evidence indicates that the core should contain elements with the properties of molten iron (and some nickel); a mean atomic number of 22 is explained by the supposed presence of some lighter element like sulfur; carbon, silicon, and oxygen may also be present.

Certain features of the table are interesting:

(i) Eight elements constitute the major part of the crust—O, Si, Al, Na, Fe, Ca, Mg and K. They make nearly 98.5% of the total.

(ii) Of these eight elements, oxygen is the most predominant. The crust consists almost entirely of oxygen compounds—mainly silicates of the six metals out of these eight elements. In terms of volumes of the atoms, oxygen alone occupies more than 90% of the total volume occupied by the elements. The crust may thus be considered as a packing of oxygen anions—bonded by silicon and the common metals.

(iii) The abundance of certain common elements are much lower than or comparable to those of many less familiar elements; for example (crustal abundances in ppm in parenthesis):

Cu (68) < **Zr** (162) ; **Pb** (13) < **Ga** (19)

Hg (0·08) << **La** (35) or **Tb** (1·2); **Zn** (75) ≃ **Rb** (78)

or any "rare earth"

Sn (2) << **V** (135) ; **As** (1·8) < **Sc** (25)

I (0·5) < **Hf** (2·8)

The abundance of an element in terms of its average percentage in the crust of the Earth is expressed in **clarke** (symbol C). The clarke of oxygen is ~46, that of silicon ~28.

16.3.3. Occurrence of the Elements

Dispersed elements

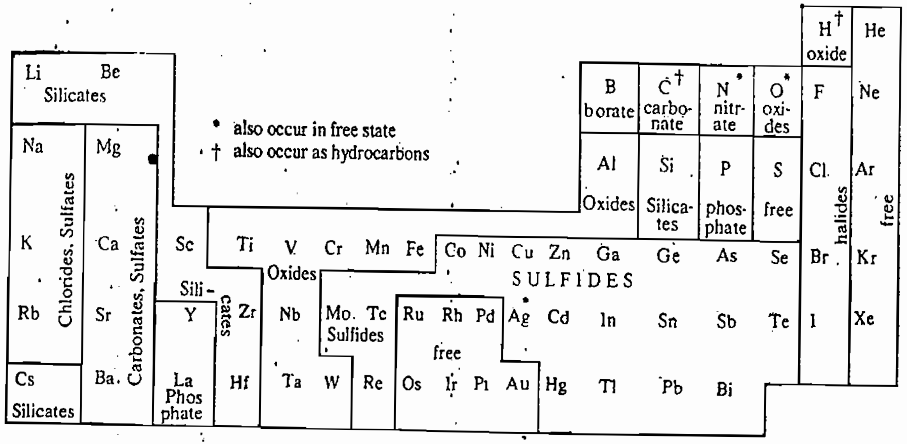
The abundance of an element is different from its mode of occurrence, or availability. Some elements present in the crust in considerable amounts never occur in any concentrated form; they are dispersed in common minerals and are called *dispersed elements*. Thus, copper, much less abundant than rubidium, forms rich ore deposits. On the other hand rubidium is found dispersed in potassium minerals. Similarly gallium is dispersed in aluminium minerals; but chromium and lead, both comparatively less abundant metals, are known to form large scale ores. Indium, hafnium, and rhenium are similarly dispersed elements.

The availability of an element depends largely on its ability to form concentrated mineral sources. Even then, elements with rich "ore deposits" also have a larger fraction unavailable as dispersed amount. Extraction of the element from such dispersed states is impractical for technical and economic reasons. Thus magnesium in large quantities (~30%) is present in vast deposits of olivine. But it is extracted from sea-water, where it is present only to the extent of 0.13%. Sometimes a relatively rare element gains importance due to its usefulness, e.g. Be (see text). Sometimes, a rare element may be obtained as an industrial by-product. Electrolytic refining of copper can provide large quantities of tellurium; about 1000 tons of gallium and germanium may be obtained annually from the ashes of certain coals. It is time that we should explore possibilities of utilising these elements on a commercial scale.

The main forms of existence of the common elements on the Earth is shown in Table 16.3. It appears that oxygen compounds, mainly in the form of silicates, predominate on the Earth's crust. Carbonates, sulfides and sulfates occur in gradually decreasing quantities.

TABLE 16.3

Common Forms of Occurrence of The Elements



Geochemical classification

According to Goldschmidt, distribution of the elements in the crust, mantle and the core of the earth was initiated by formation of different layers of varying densities during the solidification of the earth. Different elements were then distributed among these layers according to their affinity. On this basis he classified the elements into four groups according to their relative affinities for metallic, sulfidic, silicate and gaseous phases. These are

(a) Siderophilic or iron-loving: These elements are believed to occur free in the core of the earth together with iron. However, many of them occur in the crust in other combined forms. Except Ru, Rh, Pd, Os, Ir, Pt, Au and C, the remaining elements occur in combination with sulfur in the crust of the earth (chalcophilic). Ru, Rh, Pd and Os also show some affinity for sulfur. Carbon occurs as carbonates in rocks (lithophilic). Some elements, viz., Fe, Co, Ni, Cu, Ga, Ge and Sn are also found as their oxides in rocks (lithophilic).

This group includes elements which have incompletely filled outermost shells of electrons. They are relatively chemically inert—the triads of group VIII are the most important in this category (Table 16.3).

The siderophilic elements have high negative potentials and they occur near the minima in the atomic volume (vs. atomic no) curve. The heats of formation of oxides of these elements are lower than that of FeO.

(b) Chalcophilic or copper loving. This group generally contains elements whose ions contain 18 electrons in the outer shell and whose ionization energies are greater than about 600 kJ (6—7 eV) and which form covalently bonded sulfides. Since copper is chiefly found as its sulfide mineral, these elements are also found principally as sulfides (Table 16.3). These elements have intermediate potentials in the electrochemical series. In the atomic volume curve, they occupy sections in which the atomic volume increases with the atomic number.

(c) Lithophilic or stone-loving. These elements readily form ions with an octet in the outermost shell. They have low ionization energies (< ~600 kJ mol^{-1}) and high positive potentials (1–3 volts). They combine strongly and ionically to oxygen—the heats of formation of these oxides are greater than that of FeO. The difference between the two heats of formation is a measure of the intensity of the lithophile character. In the atomic volume curve, they appear near the maxima and on the declining parts.

When sufficiently basic, the oxides of the lithophilic elements combine with silica to form silicates. Hydrogen and the halogens, however, occur in different forms: hydrogen as oxide and the halogens as their halides.

(d) **Atmophilic or vapour loving.** These are the elements which are gaseous at ordinary temperatures. Hydrogen and oxygen are included in this group as members showing secondary affinity.

The distribution of any element depends on the temperature, pressure and the chemical environment of the system as a whole. As a result, some elements may show affinity for more than one group. Thus chromium is a strongly lithophile element in the crust of the Earth; but it becomes chalcophilic in an oxygen-deficient atmosphere, as is found in some meteorites. Carbon and phosphorus become siderophilic under strongly reducing conditions.

TABLE 16.4

Geochemical classification of Elements according to Goldschmidt

Siderophilic	Chalcophilic	Lithophilic	Atmophilic
Fe$^{c\ l}$, **Co**$^{c,\ l}$, **Ni**$^{c,\ l}$	**Cu, Ag**	**Li, Na, K, Rb, Cs**	H, N, O
Ru, Rh, Pd	**Zn, Cd, Hg,**	**Be, Mg, Ca, Sr, Ba**	**He, Ne, Ar,**
Os, Ir, Pt	**Ga, In, Tl**	**B, Al, Sc, Y, La-**	**Kr, Xe.**
Cu$^{c,\ l}$, **Au**	Gc, Sn, **Pb**	**Si, Ti, Zr, Hf, Th**	
C^{l}, **Ga**$^{c,\ l}$, **Ge**$^{c,\ l}$, **Sn**$^{c,\ l}$,	**As, Sb, Bi**	**P, V, Nb, Ta**	
As^{c}, **Sb**^{c}, **Mo**^{c}, **W**^{c},	**S, Se, Te**	**O, Cr, U.**	
	Fe, Mo, Os	**H, F, Cl, Br, I.**	
	Ru, Rh, Pd, Pt.	**Fe, Mn,** Zn, Ga	

c → chalcophilic in the crust of the earth. l → lithophilic in the crust of the earth.

In the last three groups, the affinity is much less pronounced for the elements in normal (not bold) types.

The above geochemical classification of an element refers to its behaviour in liquid phase equilibria in melts. The actual mineralogy of an element is somewhat different because there are many secondary factors responsible for mineral formation. Thus, thallium, a chalcophile element, forms sulfide minerals. But the greater part of the thallium in the earth's crust is found in potassium minerals where Tl^+ ions replace K^+ ions (p. 44). In the following section, we shall briefly survey the principal factors responsible for mineral formation.

16.3.4 The Formation of Minerals

What are minerals

Minerals are naturally occurring substances, generally solid and inorganic, whose atoms and ions are arranged in regular, three-dimensional patterns that give each mineral a characteristic set of physical properties. A mineral may be composed of either a single element (graphite) or of several elements. Minerals may have widely different chemical compositions and structures. They present a great diversity of forms, structures and physical and chemical properties. We identify a mineral by its form, color, transparency, hardness, lustre, etc.

About 3300 different kinds of minerals have been known to be present in nature—of which only a few hundred are common.

A mineral rarely exists alone in the crust. Usually two or three are combined in regular pattern and definite proportion to form different rocks. According to their origin of formation we group various rocks into igneous, sedimentary and metamorphic rocks. The mother of these rocks may be identified as the magma.

What is magma?

Magma may be roughly defined as molten rock material, mainly silicate. Temperature in the crust increases at the rate of about 1°C for each 33m depth and it does not become steady until the depth is very great. From 60 km. onward, the temperature ranges from 500—1200°C, or even 2000°C. This temperature is sufficient to melt any rock. But at the very high pressure of the upper crust (~ 500,000 atmosphere), rocks do not melt entirely but turn into a thick fluid, the magma.

Igneous rocks. Igneous rocks result from freezing of magma. They may be of two types—intrusive rocks and extrusive rocks. The magma intrudes upward through cracks into surrounding rocks—with a sharp fall in temperature and pressure it differentiates and crystallizes to form minerals. The "frozen" magma now becomes a body of intrusive rocks. The lava poured out from a volcano solidify into extrusive rocks.

Almost all igneous rocks are crystalline. Intrusive rocks are formed by slow cooling and are usually coarse-grained. But extrusive or volcanic rocks are formed by rapid cooling—and so large crystals cannot be formed; they are either fine-grained or glassy.

Granites and basalts are common examples of igneous rocks. Chemically, silicates are the main constituent of these rocks. An average composition is:

SiO_2	Al_2O_3	$FeO + Fe_2O_3$	MgO	CaO	Na_2O	K_2O	H_2O	TiO_2
59.1	15.3	6.8	3.5	5.1	3.8	3.1	1.15	1.05

Pegmatites are another kind of igneous rock which crystallize during the last stages of cooling and solidification of magma. They consist of coarser grains than granites and contain many rare elements (see Li). Igneous rocks are the major kinds of rocks in the crust, making up about 65 per cent of the total by weight.

Sedimentary rocks. Sedimentary rocks are formed by the erosion of igneous rocks by exogenic forces. Rocks exposed on the surface are acted upon by sun rays, ice freezing, wind, rains, plant roots etc. With this sort of continuous weathering they get transformed into debris, sand and soil. These are then carried out by water current, wind, glacier etc. and get deposited in rivers, lakes, sea-beds and the like. The sediments grow in thickness over years. As the pressure and temperature increase, water is squeezed out of the pores in the sediments and the pores are filled by silica, iron oxide or carbonates from solution. Their cementing action converts the loose grainy sediment to sedimentary rocks. Thus the four steps in the formation of sedimentary rocks are (i) weathering, (ii) transportation, (iii) deposition and (iv) diagenesis. Most sedimentary rocks are hydrogenic in nature and water plays a vital role in their formation. Some sedimentary rocks may also be formed by the agency of air, glacier or volcanoes.

Mudstone, sandstone, limestone, dolomite etc. are examples of sedimentary rocks. Such rocks can be readily identified by their layer structure or stratification. These strata are subsequently deformed by crustal movement giving rise to faults and folds.

Sedimentary rocks are nearly 8% of the total weight of the crust. But they are widely distributed over continental surfaces and sea-beds. Almost 75% of the continental surfaces are covered by them.

Metamorphic rocks. These rocks are formed by the transformation of igneous and sedimentary rocks. The latter, buried at great depths in the crust, get heated by intruding hot magma. At the high temperature and pressure, the rocks undergo a change of structure, texture and ingredients, too; ultimately they are converted to metamorphic rocks. Slate and marble are common examples of such rocks. They make up about 27% of the whole crust.

The background of mineral formation

The actual processes involved in the formation of rocks are a series of complicated chemical reactions taking place over a very long period of time under varying external conditions. As stated earlier, the elements may be broadly classified according to their geochemical affinity into lithophilic, siderophilic etc. groups. This classification may be used as a rough starting point for the formation of minerals.

As the earth gradually attained its present form, a phase differentiation was brought about by gravity. The compositions of these phases were determined by the most abundant elements — Fe, Mg, Si, O, S and Al. The amount of oxygen was evidently more than that of sulfur; again the total oxygen plus sulfur was insufficient to combine with the entire amount of electropositive elements. Among them, iron was more abundant than magnesium and silicon and possessed the greatest affinity for sulfur. At the same time, it was most easily reduced to the free metal. As a consequence, three distinct phases were formed —free iron (left uncombined), iron sulfide and iron-magnesium silicate. Elements more electropositive than iron displaced iron from the silicates. The less electropositive elements were displaced *by* iron from the silicate phase. Elements which form essentially homopolar bonds with sulfur—the sulfide group metals in analytical chemistry and the metalloids—were accommodated in the sulfide phase.

This interpretation is also in keeping with the classification of elements as class-a and class-b (see hard and soft acids and bases). The class-a metals are usually found associated with oxygen and oxoanions such as phosphates, silicates and carbonates. The class-b metals are usually found as their sulfides, e.g., zinc, cadmium and mercury. It is likely that in the reducing atmosphere prevailing when the earth's crust solidified, these and other chalcophilic metals separated out in the sulfide phase. Subsequently, as rocks were weathered, some of the sulfides were leached out and eventually precipitated as carbonate, silicate or phosphate. This idea appears to be very much applicable to the minerals of zinc.

Further insight into the process of mineral formation involves detailed consideration of the various factors determining the formation and stability of compounds in general. The atoms and ions are striving toward stability through stages of redistribution and recombination under different prevailing conditions. The principal controlling factors for such changes may be broadly generalised in terms of our discussions in chapter 15 : (i) structural control (ii) thermodynamic control and (iii) kinetic control. Even one can smell an essence of biological control in the lower abundance of potassium in sea-water owing to greater absorption by plants or in the occurrence of large deposits of sodium nitrate (Chapter 18)

Ionic size, ease of packing and electrical charge balance are the most important structural factors in the formation of minerals. Thus ions of similar radii but *different chemical character* often occur together in silicate minerals. We have already mentioned the existence of thallium in potassium minerals which may be attributed to similar ionic radii (K^+ 0.14 nm; Tl^+ 0.15 nm). Some other examples are shown in Table 16.5.

TABLE 16.5

Ions occurring together on the basis of similarity in ionic radius

Ionic radius (nm)	**Ions**
0.05 — 0.07	Li^+, Mg^{2+}, Al^{3+}, Fe^{3+}, Ti^{4+}, Mo^{6+}, W^{6+}
0.07 — 0.09	Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Zr^{4+}, Sn^{4+}, Nb^{5+}
0.09 — 0.11	Na^+, Ca^{2+}, Cd^{2+}, Ce^{4+}, Th^{4+}, U^{4+}
0.11 — 0.14	K^+, Sr^{2+}, La^{3+} — Eu^{3+}.

Some examples of structural control in mineral formation

The ease of packing of cations and anions in a particular mineral is largely determined by radius-ratio effects. When a cation has a radius-ratio lying near the boundary between two types of coordination, it may occur in both coordination numbers. The temperature and pressure at which crystallization took place gains importance in such cases. High temperature and low pressure favour the lower coordination number. Thus aluminium has a radius-ratio value 0.38 with oxide ion. It assumes C.N. 4 in typically high-temperature minerals and substitute silicon (e.g., feldspars). In minerals formed at lower temperatures, it tends to attain C.N.6.

The importance of electrical stability in crystals is nicely summarised in the following rule of Pauling : "In a stable structure the total strength of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge on the anion." Thus feldspars (see silicates) contain 4-coordinated Si or Al with oxide ions. Only one-fourth of the valency of an oxygen atom is left unsatisfied by the Si or Al. Mg or Fe in sixfold coordination would contribute at least 2/6 or one-third unit of charge. This would be greater than the "charge-requirement" of the oxygen atom and hence Mg or Fe cannot enter such structures. But Na, K etc. univalent ions and large bivalent cations like Ca^{2+} have radius-ratios (with the oxide ion) greater than 0.71, nearly that required for C.N. 8. They can meet the residual charge requirement of the oxide ion. So we find feldspars with Ca, Na and K but not with Mg or Fe in their structures.

Formation of isomorphous crystals or solid solutions and atomic substitution are other examples of structural control on the formation of minerals. Examples of isomorphism are already well-known. Solid solution formation is independent of isomorphism, e.g. between FeS and ZnS. In atomic substitution, atoms or ions replace others of similar size and charge. Sometimes the charge may be balanced by the inclusion of an additional ion, or by way of coupled substitution : $Mg^{2+} - Si^{4+}$ ion-pairs in diopside ($CaMgSi_2O_6$) are replaced in part by $Al^{3+} - Al^{3+}$. Substitution does not usually occur when the ionic charges differ by more than unity : Y^{3+} not by Na^+; nor Zr^{4+} by Mn^{2+}. The presence of iron and manganese in dolomites (Calcium magnesium carbonate) is now interpreted in terms of atomic substitution of magnesium. This is often referred to as **diadochy**, the ability of different elements to occupy the same lattice position.

Crystal field stabilization energy provides another interesting illustration of various stabilizing factors involved in mineral formation. Pending our introduction to the nature of this energy in the chapter on coordination chemistry, we simply accept that certain ions are preferentially stabilized in octahedral sites, e.g. the divalent ions of Ti, V, Cr, Fe, Co, Ni and Cu. The non-transition elements and Mn(II), Zn(II) ions lack this stabilization. The orders of decreasing octahedral site preference energy for some of the + 2 and + 3 transition metals are

$$+\mathbf{2} : \mathrm{Ni} > \mathrm{Co} > \mathrm{Mn} : \quad +\mathbf{3} : \mathrm{Cr} > \mathrm{V} > \mathrm{Sc}$$

This order suggests that Ni^{2+} would be more readily depleted from the magma during crystallization of olivine and pyroxene than would Co^{2+}. The structures of inverse spinels also point out the importance of crystal field stabilization (see text).

16.4. MAJOR PERIODIC TRENDS

The challenging diversity of inorganic chemistry could not be tackled but with the surprising generalizations made possible through the periodic table of the elements. Nevertheless, one should remember that the periodic variations of properties of the elements are not smooth—a fact which is largely understandable in terms of the outer electron distributions in the elements. Here we make a general survey of the major periodic trends which will be supplemented in the discussions on the detailed chemistry of the elements by groups, or in deserving cases, individually.

The fundamental trends apparent from the periodic table have been discussed in chapter 4. They may be summarized as follows:

Trends in Electro-negativity

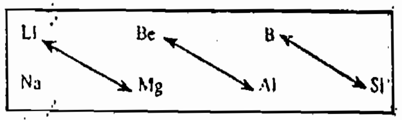
(a) Descending down any group, the size of an atom and its electropositive character increases. The ionization potential usually decreases, but may increase when the effective nuclear charge actually increases for a lower member, e.g. Ag – Au, Cd – Hg. Similarly, electronegativity and electron affinity also generally decrease, but with certain *apparent* anomalies. The electron affinity of the second row elements are usually lower than the corresponding third row elements in the same group: the pairs F – Cl and N – P are illustrative. The reason is assigned to the enhanced repulsion from the nonbonding electrons in the smaller second row elements. The electronegativity also decreases from the second row to the third row elements in each group, but then it does not decrease remarkably—rather it shows a tendency to increase in the fourth row (first series of post-transition elements: Ga – Ge – As – Se – Br) and in the sixth row (first series of post-inner-transition elements: Tl – Pb – Bi etc.). The reason for such *apparent amomalies* may be traced to poor shielding by the 3*d* and 4*f* electrons. This imparts a higher effective nuclear charge in the elements just following the 3*d* and 4*f* series. On the basis of reaction patterns and bond energy data, it has been suggested that the electronegativities of these elements should be higher than those quoted conventionally. (For example, the Ge – X bonds are found to be 21 – 113 kJ mol^{-1} weaker than Si – X bonds. This difference in energy can be related to the differences in electronegativity only when we assign a higher electronegativity to Ge). In fact, Allred and Rochow suggested the values 1.91, 2.00, 1.94 and 2.23 for Si, **Ge**, Sn and Pb respectively. The higher electronegativity of Ge may be understood from the decrease in size accompanying incomplete shielding by the *d*-shell (Allred-Rochow or Sanderson scale) and the consequent increase in ionization energy (Mulliken-Jaffe scale). Similar reasons apply to other fourth row elements.

The higher electronegativity values of the sixth row elements can be similarly explained as the result of the addition of 14 poorly shielded protons across the lanthanide series.

Further consequences of the poor shielding by the d- and f-shells will be discussed in the next topic (innert pair effect). It may be noted here that the apparent "exceptions" to the general periodic trends for ionization energy, electron affinity, size etc. are not exceptions at all; they fill our reasonable expectations from the very nature of orbitals involved.

Besides these broad generalizations some more points of related interest are noteworthy.

(i) **The diagonal relationship:** It has been observed that a number of pairs of elements related diagonally (left to right downward) in the periodic table exhibit close resemblance in chemical porperties:



For an account of such resemblances, we shall wait till the respective chemistry is dealt with. However, we can interprete this relationship in terms of the idea of ionic potential developed earlier (chapter six). We recall that the polarizing power of a cation depends directly on its charge and inversely on its size. Accordingly, one would expect the diagonal elements to have similar charge-size ratios since size increases to a lower period while charge increases to the right. This simple interpretation, however, fails to survive quantitative verifications.* But the involvement of size-charge effect in the diagonally related elements cannot be ruled out completely. The relationship loses prominence for elements on the right side of the periodic table (e.g. C and P, N and S) where metallic character is practically absent so that the ionic potential becomes insignificant. However, these elements show some proximity in their electronegativity values, which, in turn, is again related to size-charge effects. The resemblance is also difficult to be established among the lower periods of the periodic table owing to the involvement of higher orbitals, including d- and f-.

(ii) The first ten elements (H to Ne) show little resemblance to their followers

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*Taking *r* in nm, calculation of z^+/r shows that Li$^+$ (17) should be closer to Ca^{2+} (20) than Mg^{2+} (31). [The ionic potentials are given in parentheses.] Be^{2+} (61.5) is, however, closer to Al^{3+} (60). Some authors suggest the use of z^+/r^2. The values for Li$^+$ and Mg^{2+} are 278 and 473 respectively (*r* in nm). Clearly, screening affects the effective nuclear charge.

in respective groups of the periodic table. The case of hydrogen is unique while the difference is no less remarkable for the remaining elements from lithium to fluorine. The unusually small size, high electronegativity and ionization enthalpy and absence of d-orbitals - all are primarily responsible for such deviations. Specific examples of such departures from the group trend will be mentioned in respective groups.

(iii). **The inert pair effect:** This label is assigned to describe the observed reluctance of heavier post-transition metals (p-block elements) to exhibit the highest oxidation state or greatest covalence characteristic of their groups. Thus thallium ($6s^26p^1$), lead ($6s^26p^2$) and bismuth ($6s^26p^3$) prefer oxidation states of +1, +2 and +3 respectively (examples in text). We recall that the early members in each group, B, C, P and others, readily form compounds by unpairing and promotion of the *s*-pair (or by ionization of the *s*- and *p*-electrons *together*, if ionic). Therefore it appears that *as if* the *s*-electron pairs of the heavier members have become inert towards bonding; hence this has been referred to as the inert pair effect, or sometimes as the "inert *s*-pair effect". However, we shall presently appreciate that this is a misnomer.

This inert pair effect is not an abrupt development for the sixth row elements. The oxidation state of two units below the group valence becomes progressively more stable as each group is descended (examples in text).

In reality, the "inert pair effect" serves merely as a label the *s*-pair of electrons in the heavier elements are *not* inert in that way. The stability of the lower valent states of these elements cannot be directly ascribed to the intrinsic inertness, that is, unusually high ionization energy of the *s*-pair of electrons. This may be understood with reference to the ionization energies of the *s*-electrons of the valence shell of the elements of main groups III and IV.

TABLE 16.6

Ionization Energies of s-electrons (kJ mol^{-1})

Element	**Ionization Energy** $(I_2 + I_3)$	**Element**	**Ionization Energy** $(I_3 + I_4)$
Al	4550	Si	7580
Ga	4940	Ge	7710
In	4520	Sn	6870
Tl	4840	Pb	7160

We find that

$$(I_2 + I_3)_{Ga} > (I_2 + I_3)_{Tl} \quad \text{and} \quad (I_3 + I_4)_{Ge} > (I_3 + I_4)_{Pb}$$

If the inert-pair effect were a direct consequence of the stability of the *s*-pair, one should expect Ga and Ge to be more susceptible to this effect. Our experience is contradictory.

The ultimate reason

The ultimate reason responsible for the "inert pair effect" seems to be the gradual weakening of bonds formed by heavier elements. Two factors are primarily responsible for this bond weakening: (i) poorer overlap of the orbitals of larger atoms and (ii) increased repulsion from inner shell of electrons. As expected, factor (ii) is most pronounced (a) in Ga and Ge, which are the first metals to come after completing the 3*d* shell and also (b) in Tl and Pb, the first metals coming after the lanthanides. As a consequence of this bond weakening, the promotion energy ($s^2p^n \rightarrow s^1p^{n+1}$) cannot be ultimately compensated for by the energy released in the formation of two extra bonds. That is, for a series of reactions like

$MX_n + X_2 = MX_{n+2}$, decreasing M – X bond energy eventually fails to provide the energy for the process $M^n \longrightarrow M^{n+2}$. This is illustrated by the decreasing ease with which chlorine adds in the following reactions:

$$GeCl_2 + Cl_2 \longrightarrow GeCl_4 \text{ (rapid at 25°)}.$$

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4 \text{ (slow at 25°)}.$$

$$PbCl_2 + Cl_2 \longrightarrow PbCl_4 \text{ (reversed st 25°)}.$$

Sufficient weakening of the M – X bond will thus favour the reverse reaction leading to the lower valent state of M :

$$MX_{n+2} \longrightarrow MX_n + X_2.$$

This will be further aided by the X – X bond energy. The enhanced lattice energy expected for the higher oxidation state of M is partly cancelled by greater polarization effects.

The inert pair effect has also been extrapolated to explain the observed inertness of elemental mercury which contains only an "inert" $6s^2$ configuration in the valence shell. Here the term seems to have some relevance, since both the first and second ionization energies of Hg are higher than those of Zn and Cd. This may be ascribed to the poor nuclear shielding afforded by the 4f shell. In addition, the large Hg^{2+} ion has a very small hydration energy and hence E^0 (Hg^{2+} + Hg) has a positive value, placing it below hydrogen in the electrochemical series.

The marked instability of $AsCl_5$ in comparison to PCl_5 and $SbCl_5$ may also be correlated to the inert pair effect. (In fact, $AsCl_5$ was first prepared in 1976; see text.). The effect of incomplete sheilding of the nucleus by the d-shell. as observed in the high ionization energies of Ga and Ge (Table 16.3), continues to As. Consequently the energy of the 4s orbital in As and $AsCl_3$ is considerably lowered, so that promotion of the $4s^2$ electrons for the formation of $AsCl_5$ becomes extremely difficult. A similar effect probably operates in bismuth following the filling of the 4f shell, explaining the non-existence of $BiCl_5$.

The same state of affairs is repeated in Gr. VIA. SeO_3 is thermodynamically unstable relative to SO_3 and TeO_3. In the hexafluorides also, S – F and Te – F bonds are more stable than Se – F bonds.

In essence, therefore, the reluctance for highest oxidation states shown by the fourth row post-transition elements (Ga – Ge – As – Se) and the sixth row post lanthanide elements (Tl – Pb – Bi – Po?) rests on the common ground= incomplete shielding of nuclear charge by the *d*- or *f*- shells. The label "inert pair effect" is however reserved for the sixth row elements.

We may proceed one step more to include the p-orbitals and generalize our observations as : elements which follow the first filling of a given type of sublevel (*p*, *d* or *f*) will be marked by a decreased tendency to attain the highest oxidation state; the stability of compounds formed in such oxidation states would be obviously lower. The elements appearing after the first completion of the *p* subshell (i.e. Ne) are sodium and magnesium. It is found that their compounds are less stable than those formed by the elements just above or below in respective groups (Li, K; Be, Ca). Of course, the effect of incomplete shielding is much less pronounced in this case.

(iv) The elements following the completion of d- and f-shells present some apparent "anomalies", some of which we have just noticed in the preceding discussion. We shall encounter further examples in the text.

(v) **Participation of outer nd orbitals in bonding**

In the directed valence model, it is necessary to consider participation from one or more outer *d* orbital in bonding where the central atom has more than four electron pairs in its valence shell. We encountered such examples in the proposed hybridization schemes for XeF_2, PF_5, SF_6, ICl_4^{2-} etc. But different experimental and theoretical considerations reveal that such full-fledged participation by the d-orbitals in bonding is open to question. Orbitals mix effectively with each other forming hybrids and hence strong bonds only when they are of similar size. But it is now known that in the excited atoms the occupied *d*-orbitals (as for example in the excited configurations $3s^1\,3p^3\,3d^1$ of P or $3s^1\,3p^3\,3d^2$ of S) are very much larger in size than the corresponding *s*- or *p*-orbitals. The *d*-orbitals therefore have to contract appreciably to form effective hybrids with the *s*- and *p*-orbitals. Theoretical calculations show that such contractions of the *d*-orbitals do really take place in compounds like PF_5, SF_6, ClF_3 etc. Contraction is most marked when (a) more than one *d*-electron is promoted from lower-energy orbitals and (b) when the central atom bears high formal charge. Point (a) suggests that the 3*d* orbitals of S in the sp^3d^2 configuration will contract more than the *d*-orbital of P in the sp^3d configuration. Point (b) signifies that the contraction of *d*-orbitals would be greater when highly electronegative atoms are attached to the central atom (because that imparts greater formal charge). Thus the *d*-orbitals of phosphorus would contract more in PF_5 than in PCl_5. Such contractions are least likely in SH_6 or PH_5– and the compounds are non-existent. Direct experimental evidence (nuclear quadrupole resonance studies) shows that *d*-orbital participation is indeed very small in ICl_2^- and ICl_4^-. It is greater in compounds like SF_6 or $Te(OH)_6$ but to a smaller extent than the *s*- or *p*-orbitals.

Contraction of d-orbital

The bonding in PF_5, SF_6, ICl_4^{2-} etc., can also be explained *without* the involvement of *d*-orbitals. In the Three-Center Bond Model, linear three-center molecular orbitals formed by *p*-orbitals only may account for such species; in addition to usual 2*c*-2*e* (2 center– 2 electron) bonds, they involve 3*c*– 3*e* and 3*c*– 4*e* bonds as well (see structures of XeF_2 and PF_5, for example).

Though the role of *d*-orbitals in σ-bond formation is controversial, their participation in π-bond formation is more generally accepted. This has been discussed below.

(vi) **pπ– pπ bonding:** The effect of multiple bonding on the chemistry of the nonmetals is noteworthy. C, N and O in the second row form stable multiple bonds between themselves using available p-orbitals (for O_2, we need the MO description). This tendency to form homonuclear π-bonds practically disappears from the third row onward; we do not have stable S = S or P ≡ P molecules, nor do we have silicon analogs of ethylene, acetylene or benzene. The π-bonds are sacrificed for the sake of stronger σ-bonds (see the elemental forms of S and P).

Two factors may be mainly responsible for this:

(a) For elements with $n>2$, the valence shell *p*-orbitals (*np*) are much larger than the 2*p* orbitals and hence their π-overlap becomes poorer. If the bonded atoms tend to approach closer for appreciable π-interaction, strong repulsions would occur between the inner electron cores and also between the nuclei. In the first short period the relatively compact 1*s* core does not exert such strong repulsions.

(b) For $n>2$, the node(s) in the *np* orbitals largely reduce the extent of π-interaction

Elements having $n>2$ do not form stable *p*π – *p*π bonds with the elements in the first short period, viz., C, N and O. The *np* ($n>2$) orbitals are much larger than the 2*p* orbitals and the node(s) in the *np* orbitals again reduce the effective overlap. The symmetry of the wave functions also do not match completely for a bonding overlap. As illustrated in Fig. 16.2, a bonding π-overlap with the outer lobe of a 3*p* a.o. is largely opposed by an antibonding overlap with its inner core. As a consequence of such weak π-bonding, we find Si– O σ bonds to make the sole structural unit in the polymerized silica, SiO_2, and in the silicones; in sharp contrast to discrete CO_2 and the ketones. The differences of the oxides and oxyacids of phosphorus from those of nitrogen and many similar observations may be explained from this consideration.

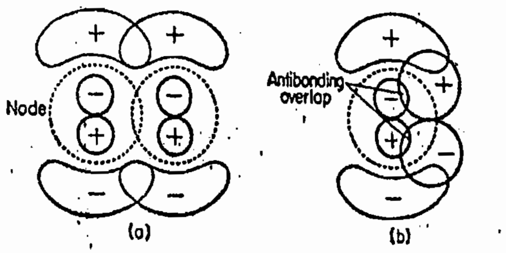

Fig. 16.2. Schematic representation of π-interaction between (a) two 3*p* orbitals and (b) a 3*p* and a 2*p* orbital.

In recent years, however, a number of compounds containing $Si=Si$ (1981) and $C \equiv P$ (1961, 1978) have been synthesized, as also a number of heterocyclic compounds containing P, As, Sb or Bi (1966-1972). Nevertheless, the stabilities of such compounds are very poor and the general comment made above is not ruled out. (For examples, see text).

(vii) **dπ—pπ bonding:** In sharp contrast to what has been said above, multiple bonding involving *d*-orbitals play a vital role in the chemistry of many nonmetals. Of the numerous examples to be found later in the text starting with Si — X bonds in silicon halides, we may just mention the P = O bonds in phosphoryl compounds and phosphine oxides, P = N bonds in cyclic conjugated systems like the phosphazenes and the S = N bonds in cyclic sulfur nitrides.

In tetrahedral AB_4 species like SiF_4, SiO_4^{4-}, PO_4^{3-} etc, each A atom may be assumed to form σ-bonds with its *s*- and *p*-orbitals. The *d*-orbitals of A (empty) are now available for π-bonding. Each B-atom has two filled *p*-orbitals available for π-bonding—these are perpendicular to the A—B bond axis. (One such *p*-orbital is shown in Fig. 16.3. The other *p*-orbital would be perpendicular to this one). All the *d*-orbitals of A may now undergo π-overlap with the *p*π orbitals on B. But detailed examination shows that the $d_{x^2-y^2}$ and d_{z^2} are particularly suitable for this purpose—they are expected to have $\sqrt{3}$ times as much π-interaction than the other *d*-orbitals. The π-overlap of the $d_{x^2-y^2}$ orbital on A with one *p*π orbital is shown in Fig. 16.3.

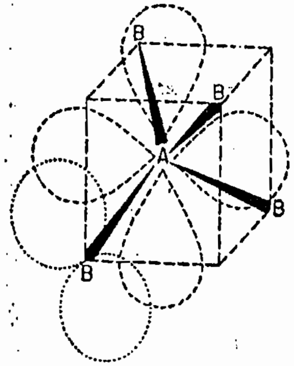

Fig. 16.3. *d*—*p* π-overlap in a tetrahedral AB_4 species.

π-bonding in oxo-anions

As we move from left to right along any period, the effective nuclear charge increases. This results in gradual contraction of the diffuse *d*-orbitals and consequently stronger π-overlap. Accordingly we find the strength of π-bonds among the tetrahedral AO_4^{n-} oxo anions to increase with A as Si<P<S<Cl. This is reflected in the gradually greater shortening of A—O distances with respect to estimated A—O single-bond distances (Table 16.7).

TABLE 16.7

Bond lengths in some oxo anions involving dπ-pπ bonding: (pm)

Ion (AO_4^{n-})	Observed A—O distance	Estimated A—O single bond distance	Shortening
SiO_4^{4-}	163	176	13
PO_4^{3-}	154	171	17
SO_4^{2-}	149	169	20
ClO_4^{-}	146	168	22

This observation is in harmony with the observation that the silicates form the most extensive polymeric species; the tendency drops sharply to P and then to S; we have an extensive series of polyphosphates—though not as extensive as the polysilicates. With sulphur, the pyrosulphate and trisulphate only are known ($S_2O_7^{2-}$ and $S_3O_{10}^{2-}$), while the perchlorate ion is extremely stable toward polymerization. Even in molecules containing Si—O—Si units, *p*π→*d*π bonding reduces the Si—O bond lengths significantly.

The formation of *p*π—*d*π bonds may even dictate the geometry of a molecule. $(CH_3)_3N$ is pyramidal, while $(SiH_3)_3N$ and $(GeH_3)_3N$ are planar: the planar Si_3N and Ge_3N arrangement permits appreciable $N(2p_z)$—Si(3*d*) or Ge(4*d*) π-overlap. The bonds are really 5 to 15 pm shorter than estimated single bond lengths.

(viii) The trends set by the transition and inner transition elements have patterns of their own. As expected, these are marked by a delicate balance of size and charge which becomes most pronounced in the 4f- and 5f- series of elements. Obviously, the expectations based on a flat and gradual periodic trend are not fulfilled at this extreme of the periodic table; but we have already learnt to treat such apparent "exceptions" as reasonable expectations!

16.5. THE FORTHCOMING ELEMENTS

16.5.1. Prediction of Missing Elements

A historical survey

Chemists have not satisfied themselves merely with the study of the available elements and their compounds. Their attempts to systematize the chemistry have always inspired them to predict missing elements which would fill certain gaps in their generalization. The monumental work of Mendeleev in this connection is already known to us (the periodic table, chapter 4). The first credit of correctly predicting a missing element, however, seems to go to Newlands, who predicted (1864) a missing element of atomic weight 73 between silicon and tin (Germanium). In the following eighty years, a large number of "missing" elements were predicted and discovered. The discovery of the noble gases (1894-98) is remarkable as their existence was not "predicted" from the periodic table of Mendeleev. Moseley's work on the characteristic X-rays of elements and the determination of their atomic number (1913) provided a direct method of ascertaining the actual number of missing elements between hydrogen and uranium. A significantly new step in the prediction of missing elements was taken by Seaborg in 1944, (eighty years after Newlands and seventyfive years after Mendeleev) when he forwarded his actinide hypothesis and predicted the existence of 14 elements upto $Z = 103$.

Some important achievements concerning the prediction and discovery of elements upto this point have been summarized in Table 16.8.

TABLE 16.8

Major events in the prediction and synthesis of elements (upto Z = 103)

1864	Prediction of a missing element between silicon and tin with at wt = 73.	**Newlands**
1869—71	Prediction of Ge, Ga, Sc, Tc, Re, Po, Fr, Ra, Ac, Pa.	**Mendeleev**
	Surprisingly correct predictions for Ge, Ga, Sc and their compounds.	
1894—98	Noble gases: (He), Ne, Ar, Kr and Xe discovered.	**Lord Rayleigh, W. Ramsay, M. W. Travers.**
1898	Discovery of Po, then Ra.	**Marie Curie** **Pierre Curie**
1899	Actinium discovered	**Debierne**
1900	Radon discovered	**Dorn**
1913	Explanation of the periodic table on the basis of atomic structure	**Bohr**
	Work on characteristic X-rays and atomic number.	**Moseley**
1917—45	Discovery of Pa (1917), Hf (1923), Re (1925), Tc (1937), Fr (1939) and Pm (1945).	**Hahn, Meitner, Coster, Hevesy, Noddack, Segre and others**
1940	Synthesis of the first trans-uranium element ^{93}Np.	**McMillan** and **Abelson**
1944	The actinide hypothesis—prediction of 14 elements upto Z = 103.	**G. T. Seaborg**

16.5.2. The Trans-actinide Elements

The last actinide element with Z = 103 (lawrencium, Lr*) was synthesized in 1961. Attempts to synthesize elements beyond lawerncium continued and elements 104 and 105 have been reported by two groups of workers—A. Ghiorso (and others) in Berkeley, California and G. N. Flerov (and others) in Dubna, near Moscow (1970). Priority in these discoveries is disputed, so also are the names of these elements. Elements 106—109 are also claimed to have been synthesized recently. Element 106 has been detected by both the American and Russian groups of scientists, while element 107 has been claimed singly by the Russians. Element 108 has been claimed on the basis of three decay events from long-term bombardment of Pb with ^{58}Fe. An isotope of mass number 265 has a half-life of 3 minutes. Element 109 has been similarly claimed from a single decay event after bombarding a bismuth target with ^{58}Fe for three weeks. An isotope of mass number 226 has a half-life of about 5 minutes.

The elements 104 to 112 are members of the 6d transition series. They have been dicussed in chapter 29 (section 29.8).

The dispute in naming

The problem of naming these elements deserves special mention. In fact, controversies on naming a newly synthesized element initiated since element 102. An international team of scientists working at the Nobel Institute for Physics in Stockholm claimed to have synthesized the element in 1957. But their results were not reproducible. The same synthesis was reported to have been carried out in 1958 by Ghiorso and others. The earlier name Nobelium was however retained. But Soviet workers later claimed that this element was rightly characterized by them (1963-66). They suggested the parallel name joliotium (in honour of F. Joliot-Curie). The wave of priority controversy and disputed naming continued to the next elements to be discovered. The name lawrencium for element 103 seems to have been accepted by both group of workers.

IUPAC recommendations

The IUPAC (1977) suggested a new method of naming these elements from atomic number. The digits appearing in the atomic number of an element are serially expressed using the following numerical roots :

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

The roots are put together and the name is completed by adding *ium* (irrespective of whether the element is expected to be a metal or a nonmetal). To avoid repetition, the final '*i*' of *bi* and *tri* are dropped when they appear before *ium*; similarly, the final '*n*' of *enn* is dropped when it occurs before *nil*.

The symbol of an element is also derived from its name using the initial letters of the numerical roots in the proper sequence. The following examples will be illustrative :

TABLE 16.9

Proposed nomenclature of elements based on atomic number

Atomic number	Numerical roots	Name	Symbol
101	un, nil, un	unnilunium	**Unu**
102	un, nil, bi	unnilbium	**Unb**
103	un, nil, tri	unniltrium	**Unt**
104	un, nil, quad	unnilquadium	**Unq**
105	un, nil, pent	unnilpentium	**Unp**
106	un, nil, hex	unnilhexium	**Unh**
107	un, nil, sept	unnilseptium	**Uns**
111	un, un, un	unununium	**Uuu**
190	un, enn, nil	unennilium	**Uen**
200	bi, nil, nil	binilnilium	**Bnn**

Names of elements 104-109 have been finalised by the IUPAC 1997 (see section 29.8).

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* Formerly Lw. Lr was adopted by the IUPAC in 1965.

16.6. SYMMETRY

Consciously or unconsciously, we encounter numerous examples of symmetry in nature and in our daily life—small plants, leaves, flowers and fruits, all possess some sort of symmetry in their appearance. Our appreciation of a thing of beauty is often associated with an inherent sense of symmetry in our subconscious mind: just think about the spider's web! In chemistry also, we have encountered different types of symmetry in the angular distributions of atomic orbital wave functions and in the shapes of various molecules. A systematic study of such symmetry properties lead to certain important generalizations and hence, attractive simplifications. Therefore, such generalizations have become indispensable in the study of the everexpanding field of inorganic chemistry. Accordingly, we shall develop here the preliminary line of approch for the application of the ideas of symmetry in chemistry. To appreciate the utility of taking this additional "trouble", one may have a look at the following list of applications of the principles of symmetry and its direct outcome, the group theory.

1. Classification of molecular orbitals.
2. Classification of molecular structure.
3. Prediction of splitting of electronic levels in electric fields of various symmetry.
4. Construction of hybrid orbitals.
5. Classification of electronic states of molecules.
6. Classification of the normal modes of vibration.
7. Prediction of allowed transitions in spectra.

However, within the limited scope of this book we shall restrict ourselves to a mere familiarity with the symmetry operations and symmetry elements which is likely to provide a better starting point for the study of group theory in the next higher course of study.

16.6.1. Symmetry Operations and Symmetry Elements

What is symmetry?

A molecule (or any chemical species) is said to possess symmetry if it has two or more orientations in space which cannot be distinguished from one another. We may go from one orientation to the other by different processes like reflection on a mirror plane, rotation about an axis, or a combination of these. Each such process is called a symmetry operation. *A symmetry operation is a process (real or imaginary) which when carried out on an object leaves that object in an indistinguishable spatial arrangement of the atoms (not necessarily identical) with respect to its initial arrangement.*

Symmetry operation

Each symmetry operation is associated with a corresponding *symmetry element*, about which the symmetry operation is carried out. These may be a point, line or plane containing the molecule. Five symmetry elements and operations are important for single molecules:

1. The Identity. This symmetry element is included for theoretical interest only. The identity operation corresponds to doing nothing to a molecule so as to leave it unchanged. At best this may be described as a rotation by 360° about some symmetry axis. It is represented by *E*. All molecules possess this symmetry element.

2. Center of symmetry, or inversion center, symbolized by *i*. If one starts from any atom of a chemical species, moves in a straight line to this center, and then proceeds an equal distance on the other side of the center, one encounters a similar atom. The square planar $PtCl_4^{-2}$ ion, the benzene molecule and SF_6 (octahedral) possess centre of symmetry.

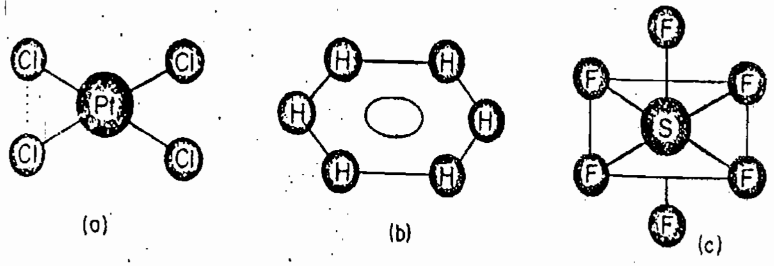

Fig. 16.4. Species containing center of symmetry

The inversion operation transforms the coordinates x, y, z of each point into their respective negatives: $-x$, $-y$ and $-z$. This may be represented by

$$i\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

Two successive applications of i (or any even number of times) reproduce the original configuration:

$$i \cdot i\begin{bmatrix} x \\ y \\ z \end{bmatrix} = i\begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

This is equivalent to the *identity operation*, *E*, which leaves the orientation unchanged. We may write $i^k = E$ when k is even. For k odd, $i^k = i$,

3. Proper axis of rotation. If a molecule assumes an indistinguishable appearance by rotation about an axis through an angle of $2\pi/n$, (counter-clockwise by convention), the molecule is said to possess an n-fold rotational axis of symmetry. It is represented by C_n. The water molecule possesses one two-fold axis of symmetry. The highest-fold rotation axis of a molecule is conventionally taken as the vertical Z-axis. A C_2 operation about the z-axis transforms the coordinate x, y, z of a point into $-x$, $-y$, z, i.e.

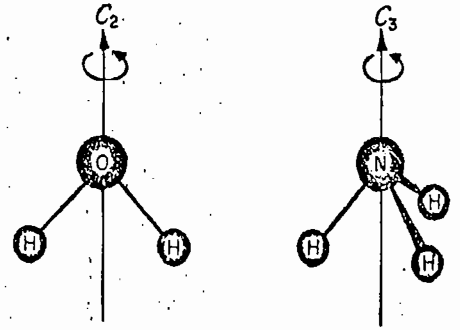

Fig. 16.5. Rotational axis of symmetry in H_2O and NH_3

$$C_2\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

Two successive applications of the C_2 operator or three successive applications of the C_3 operator will bring a molecule back to its original position (equivalent to the identity operation, E). Symbolically,

$$C_2^2 = C_3^3 = E$$

For a fourfold symmetry axis (C_4 operator), it is easy to realize that $C_4^2 = C_2^1$ and $C_4^4 = E$. The operators of a fourfold axis may be represented as

$$\begin{array}{cccc} C_4^1 & C_4^2 & C_4^3 & C_4^4 \\ & C_2^1 & & E \end{array}$$

4. The plane of symmetry (mirror plane). If reflection of all atoms of a molecule through a plane in it gives an indistinguishable configuration, the molecule is said to possess a symmetry plane. Both the symmetry plane and the reflection operator are represented by σ. Two successive application of σ, (or any even number of times) gives back the original configuration. Hence, $\sigma^k = E$, k even and $\sigma^k = \sigma$, k odd. The water molecule possesses two planes of symmetry. One plane bisects the HOH angle and another plane contains the three atoms.

If there are several rotational axes of the same highest symmetry, e.g. three two fold axes, the z-axis is so chosen that it passes through the greatest number of atoms.

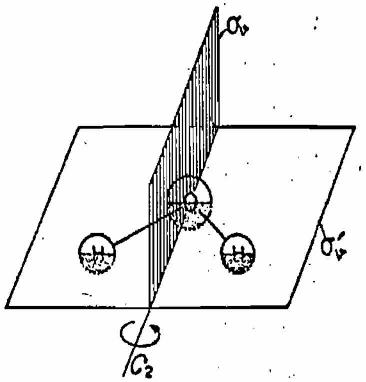

Fig. 16.6. Planes of symmetry in H_2O

Symmetry planes containing the principal C_n axis are called vertical symmetry planes, usually symbolized as σ_v. The particular symmetry planes which bisect the angles between successive twofold axis are usually called diagonal planes σ_d. A mirror plane perpendicular to the vertical axis is the horizontal plane, σ_h. (e.g. BCl_3, Fig. 16.12). The symmetry planes of the water molecule contain the C_2 symmetry axis and may be represented by σ_v and σ_v' (Fig. 16.6). The ammonia molecule has three σ_v containing the C_3 axis.

5. The Improper axis of rotation (S_n). The operation of improper rotation consists of a rotation by an angle of $2\pi/n$ about an axis, followed by reflection through a plane perpendicular to the axis. When this yields an indistinguishable configuration, the species is said to possess an n-fold improper rotational axis or rotation-reflection axis, S_n. The staggered configuration of ethane contains an S_6 axis coincident with the C_3 axis. The methane molecule has three S_4 axis coincident with the C_2 axis.

The operation of improper rotation consists of two successive operations, rotation (C_n) followed by reflection (σ). Hence

$$S_n = \sigma C_n.$$

But we shall see that to have the S_n symmetry element, a molecule need not possess the symmetry elements σ and C_n. It is further interesting to note:

An S_1 element is equivalent to a plane of symmetry (σ).

An S_2 element is equivalent to a centre of symmetry (i).

When n is odd, $S_n^{2n} = E$; for n even, $S_n^n = E$.

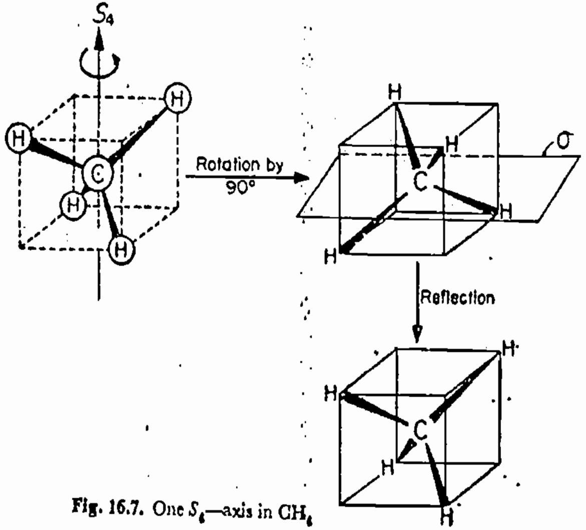

Fig. 16.7. One S_4—axis in CH_4

16.6.2 Point Groups

The complete set of symmetry operations that can be carried out on a molecule constitutes a mathematical group*. These are called symmetry groups or sometimes point groups. All the operations leave the molecule fixed at a certain point in space—hence the name point group.

Thus, no translational motions are considered in point groups. There may be other groups of symmetry operations, such as those applied to crystal structures. There the individual units/molecules move from one location to another (translate) to generate a space lattice.

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*A set of operations belong to a mathematical group only when they are interrelated by the following conditions:

(i) If A and B are two symmetry operations of the same group, their product AB (equal to F, say) will also be an operation of the group. Operation AB means operation B followed by A. This leads to the idea of multiplication of operations. A multiplication table may be prepared for each symmetry group, the one for the C_{2v} group being given on p. 58 (footnote). In this particular group, the product AB is always equivalent to BA, i.e. when the order of application of the operators is reversed. Here the operators are said to commute, they are *commutative* : $AB = BA$. In other cases, $AB \neq BA$.

(ii) Each group will have an identity operator E. For any other operation A,

$$AE = EA = A.$$

(iii) For each operation A, there will be an inverse operation A^{-1} which will return the object to its original arrangement: $A^{-1}A = AA^{-1} = E$. The inverse of a C_2, σ or i operation is the operator itself. The inverse of C_3^1 is C_3^2; the inverse of S_4^1 is S_4^3.

(iv) The associative law of multiplication will hold.

$$A\,(BC) = AB\,(C).$$

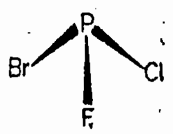
Two systems of notation for point groups are in use. The international system, also called the *Herman-Mauguin System*, is however used almost exclusively in connection with crystal symmetry. Individual molecules are more conventionally treated by the *Schoenflies system*. We discuss only the latter. The major point group systems and their symbols are given below:

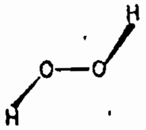
Systems of notation for Point Groups

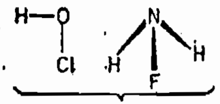
1. C_n, C_{nh} and C_{nv} Groups:

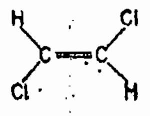
The groups generated by repetition of C_n operation are termed C_n point groups, n repetitions of this operation gives back the starting configuration, i.e. $C_n^n = E$. Hence the order of the group is n and it has n operations.

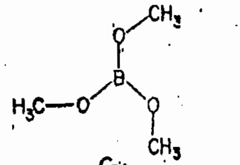
If a horizontal mirror plane, σ_h is added to the C_n operation, we get C_{nh} groups. The C_{1h} group is called C_s.


C_1


C_2

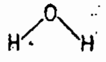

$C_{1h} \equiv C_s$

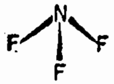

C_{2h}

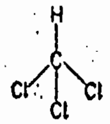

C_{3h}

Addition of a vertical mirror plane (σ_v) to the C_n group gives a C_{nv} group.

Both C_{nv} and C_{nh} groups have $2n$ elements or operations.


C_{2v}


C_{3v}


C_{3v}

(continued from p. 57)

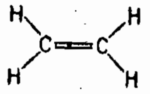
Multiplication Table for the group C_{2v}

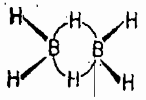
		Operation B			
		E	C_2^1	σ_v	σ_v'
	E	E	C_2^1	σ_v	σ_v'
Operation A:	C_2^1	C_2^1	E	σ_v'	σ_v
	σ_v	σ_v	σ_v'	E	C_2^1
	σ_v'	σ_v'	σ_v	C_2^1	E

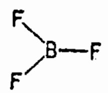
2. D_n, D_{nh} and D_{nd} Groups

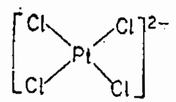
When a vertical C_n axis is accompained by a set of n C_2 axes perpendicular to it, we get a *dihedral group*, D_n. There are $2n$ symmetry elements in this group. Molecules in this group are optically active and have a zero dipole moment. Examples of D_n symmetry are rare; we shall get some examples later in coordination compounds (in $[Co(NH_2C_2H_4NH_2)_3]^{3+}$ e.g.).

Addition of a σ_h operation (reflection in a horizontal plane of symmetry) to a D_n group generates a D_{nh} group, with $4n$ symmetry elements.

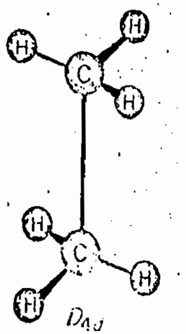

D_{2h}

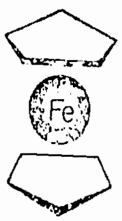

D_{2h}


D_{3h}


D_{4h}

Addition of vertical mirror planes to a D_n group which bisects the angles between pairs of C_2 axes generates a D_{nd} group. Such groups have no σ_h. The mirror planes are referred to as σ_d, dihedral planes, which are n in number. There are $4n$ symmetry elements in a D_{nd} group.


D_{4d}


D_{5d}

3. The S_n Groups

The S_n groups are generated by the S_n operation. For odd values of n, $S_n^{2n} = E$; in such cases the S_n group is the same as the C_{nh} group. When n is even, new groups may arise, though they may be written in another way, e.g. $S_4^2 \equiv C_2$, $S_2 = i$. Molecules of S_n symmetries are not very common.

4. The $C_{\infty v}$ and $D_{\infty h}$ Groups

Linear molecules possess an ∞-fold axis of rotation passing through the nuclei. Simultaneously there are an infinite number of reflection planes (σ_v) passing through the atoms. If no horizontal mirror plane (σ_h) is present (*alternatively*, no C_2 axis perpendicular to the C_∞ axis), the molecule belongs to the $C_{\infty v}$ group: HCl, HCN, CO etc. When a C_2 axis is present perpendicular to the C_∞ axis, the species belongs to the $D_{\infty h}$ group: N_2, O_2, CO_2 etc.

Assigning Molecules to Symmetry Groups

Several schemes have been suggested for assigning molecules to their respective symmetry groups. The following outline may be helpful:

(i) Linear molecules (C_∞) may be easily classified as $C_{\infty v}$ (no i) or $D_{\infty h}$ (i present).

(ii) For others, try to locate a C_n axis. *If there is none*, the molecule belongs to

C_s, if a σ element is present.
C_i, if no σ, but an i is present.
C_1, if neither σ nor i is present.

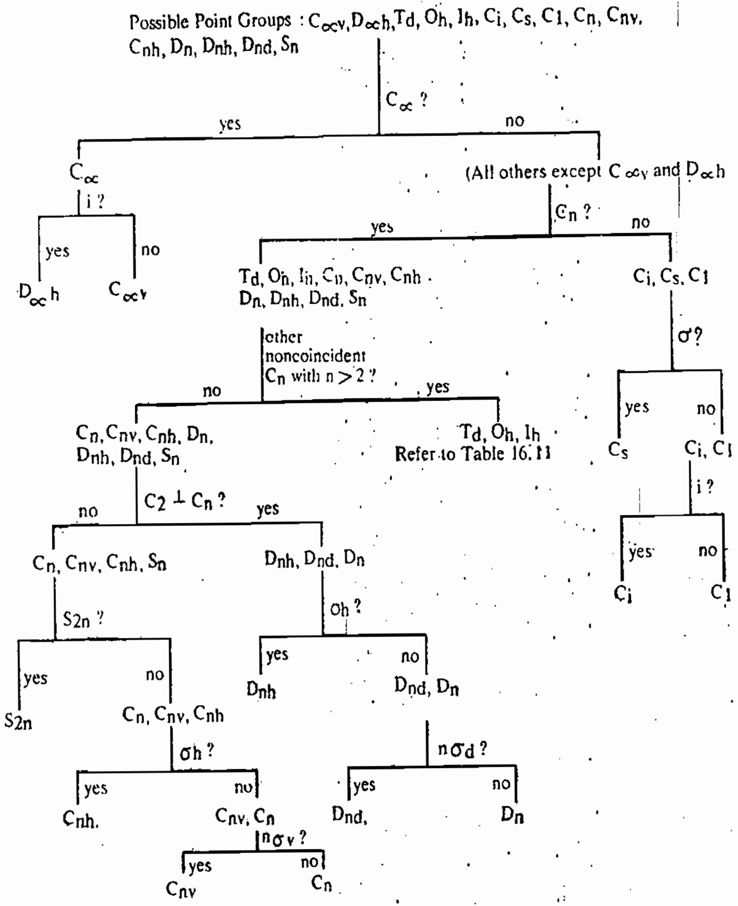
(iii) If a C_n axis is present, find the highest order. Then look for other non-coincident C_n axes with $n > 2$. If they are present, refer to Table 16.11 for point groups of higher symmetry. Otherwise proceed as follows:

(iv) If there is a C_2 axis perpendicular to the C_n axis, the molecule goes to the D_n group. (There will be n C_2 axis). Proceed as shown in, Table 16.10.

(v) If there is no other noncoincident axis of rotation, the molecule belongs to the C_n group. Then proceed as shown in Table 16.10.

TABLE 16.10

Scheme to select point-group symbol



5. The cubic and Icosahedral Groups (T, O, I and their derivatives):

Many common chemical species possess more than one principal axis of symmetry. For example, the ammonium ion possesses four C_2 axes, one along each $N-H$ bond (Fig. 16.8). The methane molecule also possesses the same

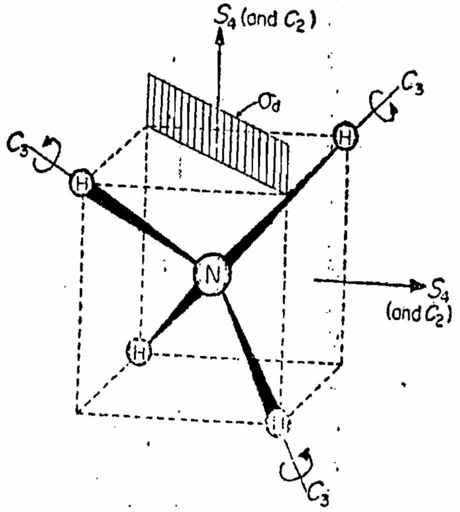


Fig. 16.8. Some of the symmetry elements of the NH_4^+ ion (T_d point group). There are three S_4 axes at right angles to one another, but the third one (projected to the reader) has not been shown. Similarly, there are four C_3 axes (at angles of 109°28′) along each N – H bond, but only three are shown. Also there are six vertical σ_d planes, each of which passes through the nitrogen and two hydrogens and relates the other two hydrogens to each other. Only one is shown.

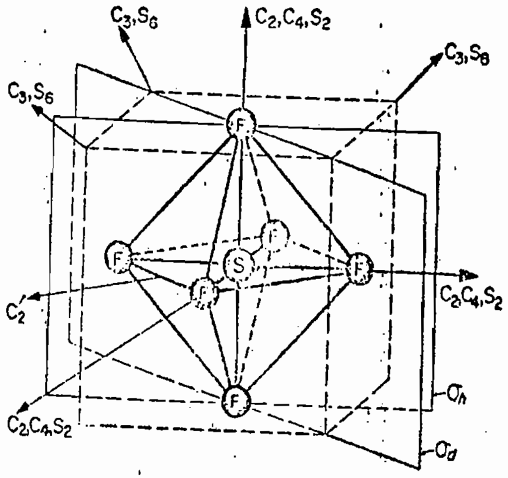


Fig. 16.9. The symmetry elements of SF_6 (O_h group). The octahedron is inscribed in a cube to show that both have the same elements of symmetry. There are three C_4 axes at right angles to one another: three S_4 and three C_2 axes are coincident with the C_4 axes. Four C_3-axes (and four coincident S_6 axes) are situated along the body-diagonals. There are six C_2' axes bisecting opposite edges, three planes of σ_h type and six of of the type σ_d.

symmetry elements. Such molecules (or species) belong to groups of very high symmetry. The group T_d is the group of the regular tetrahedron and the group O_h is the group of the regular octahedron. The regular icosahedron belongs to the I_h group. The actual evaluation of all the symmetry operations belonging to each such group is a bit complicated and is not given here.

[For example, the T_d group has three S_4 axes, four C_3 axes and six reflection planes. These symmetry elements give rise to the following symmetry operations:

Each S_4 axis gives rise to the operations S_4, $S_4^2 = C_2$, S_4^3 and $S_4^4 = E$. Neglecting S_4^4, we have 3 operations for each of the three S_4 axis, making a total of $3 \times 3 = 9$ operations.

Each C_3 axis gives rise to the operations C_3, C_3^2 and $C_3^3 (= E)$. Neglecting the last, we have, for the four C_3 axes, $4 \times 2 = 8$ operations.

Each reflection plane gives rise to a σ_d operation, contributing $6 \times 1 = 6$ operations.

Thus we have a total of $9 + 8 + 6$ + one identity operation = 24 operations.

Similarly the O_h group has 48 operations. The I_h group (icosahedron and pentagonal bipyramid) has 120 operations].

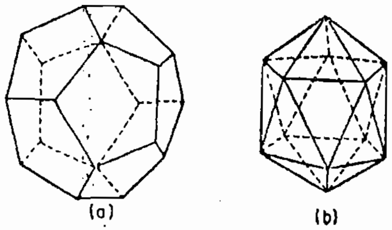


Fig. 16.10. (a) Pentagonal bipyramid and (b) icosahedron.

However, it is possible to classify a molecule (or any species) into its point group formalism from the following scheme Table 16.11:

(i) Find the highest C_n axis.

(ii) See if there are other noncoincident C_n with $n > 2$. n may be equal to 3, 4 or 5.

(iii) $n = 3$: It belongs to the tetrahedral (T) group. If there is an i or σ_h symmetry element, the point group is T_h.

If there is no i or σ_h but 6 σ_d elements, the group is T_d.

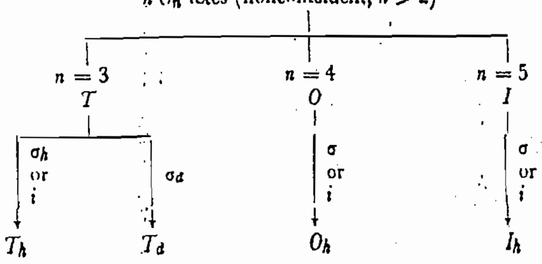
If there is none of the i or σ elements, the point group is simply T.

(iv) $n = 4$. The point group belongs to the O category. If there is a σ or i element, the point group will be O_h, otherwise simply O.

(v) $n = 5$. The point group belongs to the icosahedron, I. Again, if there is a σ or i element, the point group will be I_h, otherwise simply I.

TABLE 16.11

Classification of T, O and I point group



The point group symbols of some common molecules are mentioned below.

1. HCl. A linear molecule, hence an ∞-fold axis of rotation (C_∞). No inversion center. $C_{\infty v}$.

2. H₂. Linear molecule, C_∞. Inversion plane perpendicular to the C_∞. Hence $D_{\infty h}$.

3. BFClBr. The molecule is planar triangular. There is no proper axis of rotation (C_n). The only symmetry element is the plane of symmetry (σ) in which the atoms lie. Hence the point group is C_s.

4. HOCl. Here also, no C_n, only the mirror plane (σ) containing the atoms. Hence C_s.

5. H₂O. One C_2 axis, two mirror planes (σ_v and σ_v') [Fig. 16.11a]. Hence point group symbol C_{2v}.

6. NH₃. There is only one C_3 axis and three mirror planes containing this axis [Fig. 16.11(b), σ_v, σ_v' and σ_v'']. Point group symbol C_{3v}.

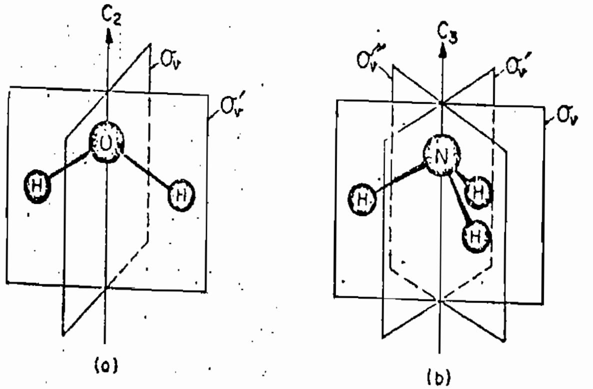


Fig. 16.11. Symmetry elements in the (a) H_2O and (b) NH_3 molecules.

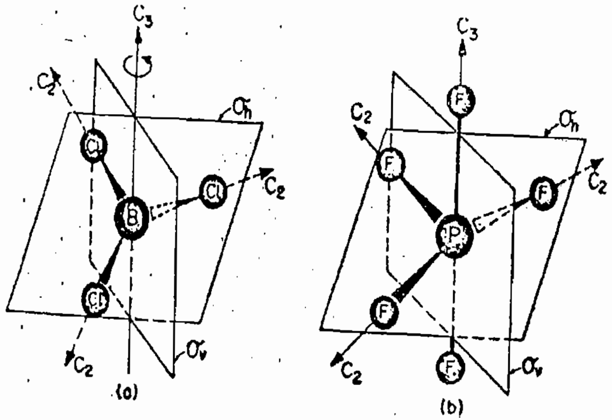


Fig. 16.12. Some of the symmetry elements in (a) the BCl_3 molecule (D_{3h}). (b) the PF_5 molecule (D_{3h})

7. BCl₃. There is a C_3 axis. Three C_2 axes lie perpendicular to this C_3 axis, one along each B – Cl bond. There is also a mirror plane containing the atoms

(σ_h), and perpendicular to the C_3 axis. In addition there will be three mirror planes
perpendicular to the σ_h plane, one along each B – Cl bond. Only one such σ_v
plane is shown in the figure, others being excluded for clarity. The total symme-
try elements are then C_3, $3C_2 \perp C_3$, $\sigma_h \perp C_3$, and $3\sigma_v \perp \sigma_h$. Point group symbol D_{3h}.

8. PF$_5$. The molecule is trigonal bipyramidal (Fig. 16.12(b)). There is a
C_3 axis and perpendicular to this are three C_2 axes. There is a mirror plane in the
equatorial plane containing three P – F bonds, and perpendicular to the C_3 axis
(σ_h). Three vertical mirror planes are present perpendicular to this σ_h ($3\sigma_v$), one
along each equatorial P – F bond. Only one such plane is shown. The point-
group symbol will be D_{3h}.

SUMMARY

Abundance of the Elements. The average relative content of an element in any natural system is called its abdundance. The abundance of the elements over the whole universe, or the cosmos is often referred to as the **cosmic abundance**, while the abundance of the elements on the earth (crust upto about 36 km. depth, the atmosphere and the surface water) is called the **terrestrial abundance.** Cosmic abundance data are estimated from spectroscopic analysis of the celestial bodies while terrestrial abundances are based on actual analysis on a statistical basis.

A systematic study of the abundance of various elements (both cosmic and terrestrial) reveal certain general trends:

(i) Hydrogen and helium are most abundant of all elements (cosmic abundance). Carbon and oxygen come next in the sequence.

(ii) Nuclides of even atomic number are more abundant than the nuclides of neighbouring elements having odd atomic number.

(iii) Nuclides whose mass numbers are multiples of 4 are more abundant than their immediate neighbours.

(iv) The crust of the earth is mainly composed of the eight elements (decreasing order of abundance): oxygen, silicon, aluminium, iron, calcium, sodium, potassium and magnesium. They make about 98.5% of the mass of the crust.

(v) Geochemically, the elements may be classified into four categories depending on their primary affinity of occurrence:

(a) **siderophilic or iron-loving:** Mainly the elements of the periodic group VIII and gold. However, many of them are also chalcophilic in the crust.

(b) **chalcophilic or copper loving:** Elements having ionization energies greater than about 600-700 kJ mol^{-1} and which form covalently bonded sulfides; e.g. Cu, Ag, Zn, Cd, Hg, Pb, Fe and others.

(c) **lithophilic or stone loving:** Elements having low I.P. (<600 kJ mol^{-1}) which combine strongly and ionically to oxygen. These occur mostly as oxides and silicates, e.g. Li, Na, K, Mg, Ca, Al, etc.

(d) **atmophilic or vapour loving.** The gaseous elements like H_2, He, Ne, etc.

Major Periodic Trends: (a) Descending along any group in the periodic table, the size of an atom generally
increases while electronegativity, ionization energy and electron affinity usually decreases. But electron affinity
increases from a 2nd row element to the corresponding third row element in a group (F – Cl, N – P) as the
smaller atoms exert greater repulsion from the nonbonding electrons. Electronegativity first decreases down a
group but then remains steady or slightly increases in the fourth and sixth periods. This is due to an increased
effective nuclear charge caused by poor shielding by the *d* and *f* electrons.

(b) The **diagonal relationship** in the periodic table relates to the chemical resemblance of diagonally related
pairs of elements (left to right downward) like Li – Mg, B – Si etc. The reason lies mostly in an increase in
size going downward matched by an increase in charge in moving towards right.

(c) **The inert pair effect** describes the observed reluctance of heavier p-block elements to attain the highest oxida-
tion state characteristic of their respective groups. Tl ($6s^2 6p^1$), Pb ($6s^2 6p^2$) and Bi ($6s^2 6p^3$) prefer oxidation
states of I, II and III respectively, as if the *s* pair of electrons have become inert. The reason for this behaviour
may be traced to the intrinsic weakness of the bonds formed by these elements. This, in turn, is, related to the
very poor shielding by the f-electrons and consequent increase in effective nuclear charge.

(d) C, N and O in the second row form stable homonuclear π-bonds using available *p*-orbitals (for O_2, we need the MO description). This tendency practically disappears from the second row onward as the π-bonds are energetically less favourable in comparison to σ-bonds (c.f. N_2 vs. P_4 and O_2 vs S_8). Pi bonds to other elements also become less favourable e.g. CO_2 vs. SiO_2 and CO vs. SiO. But multiple bonding involving *d*-orbitals play a vital role in the chemistry of many nonmetals like P, S, Si etc.

A symmetry operation is a process which when carried out on an object leaves that object in an indistinguishable spatial arrangement of the atoms with respect to its initial arrangement.

Each symmetry operation is associated with a corresponding *symmetry element* about which the symmetry operation is carried out. For a discrete object like a molecule, five symmetry elements are found to be significant.

(i) **the axis of symmetry,** *C*, (ii) **the plane of symmetry,** σ, (iii) **the center of inversion,** *i*,
(iv) **the improper axis of rotation,** *S* and (v) **the identity** *E*.

The corresponding symmetry operations are

(i) **C$_n$**, rotation of the molecule through an angle 360°/*n* about a symmetry axis. *n* is called the *order* of rotation. The highest order rotation axis is called the principal axis of rotation; it is usually placed vertically along an imaginary *Z*-axis.

(ii) σ, reflection of all atoms through a mirror plane.

(iii) **i**, inversion of all atoms through a point of the molecule.

(iv) **S$_n$**, rotation of the molecule by 360°/*n*, followed by reflection in a plane perpendicular to the axis.

(v) **E**, the identity operation which leaves the molecule unchanged.

Planes of reflection which are perpendicular to the principal axis are called horizontal planes (*h*). Similarly, planes of reflection containing the principal axis are called vertical planes (*v*) or dihedral planes (*d*) when they bisect two 2-fold axes.

The complete set of symmetry operations that can be performed on a molecule is called the *symmetry group* or *point-group* of the molecule.

EXERCISE

1. *What are the important generalizations by which one may rationalize the following observations?*
   (i) *Lithium does not occur with sodium and potassium though it belongs to Group I in the periodic table.*
   (ii) *Potassium and strontium are sometimes found to occur together in minerals.*
   (iii) *Thr isotope ^{39}K is more abundant than the isotope ^{40}K.*
   (iv) *Abundance of the isotopes of hydrogen fall sharply from protium to deuterium to tritium.*
2. *Give examples of the so-called inert-pair effect.*
   How is this observation rationalised in terms of the very electronic configuration of the atoms?
3. *Suggest probable interpretations.*
   (a) *At 25°C, $GeCl_2$ reacts rapidly and $SnCl_2$ reacts slowly with chlorine giving $GeCl_4/SnCl_4$: but $PbCl_4$ loses chlorine to form $PbCl_2$.*
   (b) *$AsCl_5$ is remarkably less stable than either PCl_5 or $SbCl_5$.*
   (c) *$BiCl_5$ is nonexistent.*
   (d) *Mercury is an inactive metal in spite of being liquid at ordinary temperature.*
4. *What are point groups?*
5. *Determine the point groups of the following molecules*
   (i) *SiFClBrI (tetrahedral)* (ii) *H_2S.* (iii) *PCl_3.* (iv) *FeF_6^{3-}.* (v) *CHClBr(CH_3).* (vi) *CCl_4.*

Ans. : (i) C_1. (ii) C_{2v}. (iii) C_{3v}. ((iv) O_h. (v) C_1. (vi) T_d.

CHEMISTRY OF THE ELEMENTS

SECTION—I : THE S-BLOCK ELEMENTS

CHAPTER SEVENTEEN

HYDROGEN

OBJECTIVES

17.1 Introduction
  - Abundance and Isotopes (17.1.1)
  - Nuclear Spin isomers (17.1.2)
  - Use (17.1.3)
  - Atomic and ionized forms (17.1.4)

17.2 Preparation
  - Small and Large scale (17.2.1—17.2.2)
  - Preparation of $D_2|D_2O$ (17.2.3)
  - Preparation of T_2 (17.2.4)

17.3 Properties and Bonding
  - **The Hydrogen ion** : Acidity in gas phase; H^+ ion in solution; strength of protonic acids; the Hammett acidity function (17.3.1)
  - The ionic hydrides (17.3.2)
  - The covalent hydrides (17.3.3)
  - Hydrides of the transition elements (17.3.4)
  - The Hydrogen bridge bond (17.3.5)
  - The Hydrogen bond (17.3.6)
  - Ice, Water, Hydrates, Clathrates (17.3.7)
  - Cluster and encapsulated hydrides (17.3.8)
  - Co-ordination compounds (17.3.9)

17

HYDROGEN

17.1 INTRODUCTION

The element hydrogen has several characteristics of its own.

(i) It is the only element in which the valence electron is under direct influence of the nucleus—there is no screening by any other electron. (Even in helium, the electrons mutually screen one another). With its single 1s electron, hydrogen presents a wide range of bonding modes (section 17.3) in its compounds. Besides normal covalent bonds and hydride ion formation, it also forms a wide range of nonstoichiometric compounds and interesting bridges between other atoms.

(ii) Hydrogen forms more chemical compounds than any other element, including carbon. In fact, it forms compounds of one kind or another with nearly every other active element.

(iii) The position of hydrogen in the periodic table is often disputed.

Position in the periodic table

Its ns^1 electron configuration justifies its position in Gr Ia with the alkali metals. But the alkali metals are highly electropositive with very low ionization energies (520 – 375 kJ mol^{-1}; $I_H = 1310$ kJ mol^{-1}). Also, the H^+ ion does not exist as such in any compound.

Considered otherwise, the electron configuration of hydrogen is just one electron short of the next noble gas (He) and so it may be placed in group VIIb with the halogens. The ionization energies are comparable (e.g. $I_{Cl} = 1250$ kJ mol^{-1}); the H^- ion in ionic hydrides (e.g. NaH) is formally similar to the halide ions. Nevertheless, the dissociation energy of H_2 (436 kJ mol^{-1}) is considerably higher than those of the halogens (e.g. F_2 : 155 kJ mol^{-1}, Cl_2 : 240 kJ mol^{-1}); its electron affinity is also very low (H : 73; F : 322; Cl : 348 kJ mol^{-1}). The H^- ion is highly polarizable, too.

With its half-filled valence shell, hydrogen is also comparable to the group IV element C, forming covalent bonds with a wide range of polarities. Some of the similarities are presented by (i) metal hydrides and metal alkyls, e.g. $Na^+ H^-$ and $Na^+ CH_3^-$ (ii) electron deficient Al. . H. . Al bridge and Al. . CH_3. . Al bridge (iii) formation of covalent compounds SiR_4 to PbR_4, R = H or alkyl group; stability decreasing as Si > Ge > Sn > Pb. (iv) formation of unstable σ-bonds to transition metals like $RCo(CO)_4$, R = C or H.

However, there is no reason to bother much about the position of hydrogen in a particular group. As an extreme element it is quite natural for it to have some peculiar character. Consistent with its electron configuration, it may be just included in the s-block of elements.

(iv) Being very light, addition of one or two neutrons to the nucleus of hydrogen produces relatively large mass difference and associated variations in the properties of the isotopes.

(v) The existence of the ortho-and para-forms (17.1.) of hydrogen molecule similarly gains importance due to the very small mass of the hydrogen atom. (Though the ortho-and para-forms are equally feasible for all diatomic molecules in which the atoms have an odd number of nucleons e.g. F_2, I_2, HF etc.)

(vi) The establishment of the hydrogen bond and its crucial role in the structure of many living and non-living systems also seems to be unique for hydrogen though it cannot be considered impossible for other elements.

The chemistry of hydrogen has, of late, gained fresh importance in view of its probable role as fuel in the hydrogen-oxygen fuel cells. The immense potentiality of this alternative energy source sounds logical when we remember the huge stock of hydrogen in the earth as surface water. Recent development of several organometallic compounds as efficient catalysts in the hydrogenation of different unsaturated organic compounds has also added to the industrial importance of hydrogen. So, before we actually start with the conventional chemistry of the element, let us have a brief look at the abundance of the element and its uses in the near future.

17.1.1 Abudance and Isotopes

Hydrogen is the most abundant element in the universe (p. 36). But it does not occur free in the earth's atmosphere—the speed of the molecules at the temperature of the atmosphere is sufficient to enable them to escape from the earth's gravitational field. On the earth's surface, however, it is the third most abundant element (after O and Si). In the combined form in the earth's crust and oceans, its abundance is nearly 0.9% by weight (ninth position).

Isotopes of hydrogen with mass numbers 2 and 3 (i.e. ^2_1H and ^3_1H) are given separate names and symbols, deuterium (D) and tritium (T) respectively. This is more a matter of convention than of principle though the distinct names are justified on the basis of large isotope effects in the light hydrogen atom.

Terrestrial hydrogen contains about 0.0156% of deuterium atoms. Tritium occurs naturally only in traces, ~ 1 in 10^{17}. But tritium is being continuously formed in the upper atmosphere by nuclear reactions induced by cosmic rays, e.g. $^{14}N\ (n, ^3_1H)\ ^{12}C$. Tritium is β^--active ($t_{\frac{1}{2}} = 12.4$ y).

Due to the presence of three isotopes, hydrogen molecules may be depicted as H_2 (dihydrogen), D_2 (dideuterium), T_2 (ditritium) as well as HD, HT and DT. The chemical properties of all these molecules are basically the same; but they differ considerably in their physical properties and on the rates of reaction. Table 17.1 shows a number of such properties for H_2, D_2 and T_2. The properties of HD etc. may be supposed to be intermediate. Some values are given in the Table also.

TABLE 17.1

Physical Properties of H_2, D_2 and T_2.

	H_2	D_2	T_2	(HD)
MP (K)	13.957	18.73	20.62	16.60
BP(K)	20.39	23.67	25.04	22.13
Critical temperature (K)	33.19	38.35	40.6(cal.)	35.91
ΔH_{diss}(298K) (kJmol^{-1})	435.88	443.35	446.9	439.3

Note: Hydrogen occurs in the atmosphere of the sun and the *heavier* planets e.g. Jupiter.

17.1.2 Nuclear Spin Isomers : ortho- and para-Hydrogen

When the nucleus of an atom contains an odd number of nucleons, the nucleus has a resultant spin. If two such atoms combine to form a diatomic molecule, the nuclei may have their spins parallel or antiparallel. This is called nuclear spin isomerism. The molecule in which the two nuclei have parallel spins are conventionally termed the *ortho-* form and the molecule with antiparallel nuclear spins is called the *para*-form. Both the forms exist in a temperature dependent tautomeric equilibrium. Such nuclear spin isomerism has been established for H_2, D_2, T_2, $^{14}N_2$, $^{15}N_2$, $^{17}O_2$ etc.

The hydrogen nucleus has a single proton whose spin may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. In *ortho*-hydrogen, parallel spin of the two protons gives a resultant nuclear spin quantum number (S) equal to 1 ($2 \times \frac{1}{2}$). This gives rise to a three fold degeneracy ($2S+1$), called a triplet state. In *para*-hydrogen, the opposing nuclear spins make $S = 0$, giving rise to a singlet state ($2 \times 0 + 1$). Now, there are three different ways in which $S = 1$ may be coupled vectorically with the total angular momentum of the molecule, J, but only one way in which $S = 0$ may be so coupled. Accordingly, the first type of molecules ($S = 1$, *ortho*-hydrogen) would occur statistically three times as often as the second type of molecules ($S = 0$, *para*-hydrogen). It can further be shown that *ortho*-hydrogen has rotational energy-states corresponding only to odd numbers of J while *para*-hydrogen has rotational energy-states corresponding only to even values for J. This gives rise to slight differences in the hyperfine structure of the electronic band spectrum of the two forms; the presence of the two forms is seen as an alternation in the intensities of successive rotational lines in the fine structure.

Relative abundance

When hydrogen gas is cooled to very low temperatures, its molecules tend to occupy the lowest possible energy state. For *para*-H_2, this corresponds to $J = 0$, while for *ortho*-H_2, the lowest state has $J = 1$. Therefore the *para*-form is more stable at lower temperature (e.g. 99.8% at 20K). If the mixture is heated (with catalysts, see below), the *ortho*-content rises gradually and at about 273K, it reaches the statistically weighted proportion of 3 *ortho* : 1 *para*, i.e., 75% o–H_2 and 25% p–H_2. Fig. 17.1 shows the variation of o–H_2 : p–H_2 with temperature. It may be noted that almost pure *para*-H_2 may be obtained at low temperature (0.2% *ortho* content) but pure *ortho*-H_2 cannot be obtained. The maximum *ortho*-content is 75%.

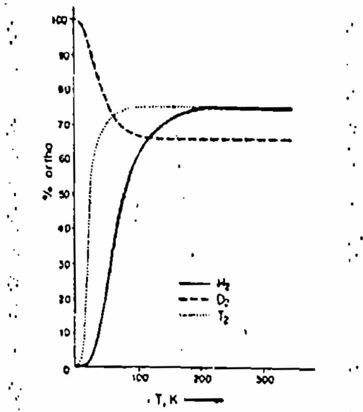


Fig. 17.1. Variation of *ortho* : *para* forms with temperature.

ortho- and para- deuterium

The deuterium atom has two nucleons, making its nuclear spin quantum number 1. The system will follow Bose-Einstein statistics instead of the Fermi-Dirac statistics applicable to the proton. This gives the total possible nuclear spin for D_2 as 2, 1 and 0. Their respective statistical weights (given by the multiplicities) are 5, 3 and 1.

This leads to the conclusion that for D_2, the *ortho*-D_2 will be the more stable form at low temperature. The statistical weights at equilibrium will be 6 *ortho* : 3 *para*. This is revealed in Fig. 17.1 where the equilibrium value of 66.67% *ortho*-D_2 is reached above ~190K. Tritium has an half-integral spin; hence *ortho*-T_2 and *para*-T_2 resemble H_2 (Fig. 17.1).

Conversions

The conversions *para*–H_2 → *ortho*–H_2 and vice versa are normally very slow as they involve a forbidden transition between two energy states of different spin-multiplicity. Introduction of atomic hydrogen or use of catalysts like O_2, NO, NO_2, Mn^{2+}(aq.), Fe^{3+}(aq), Pt, Pd and charcoal accelerates the attainment of equilibrium. Most of these catalysts are paramagnetic. They either break the H – H bond, or at least weaken it or effect some sort of magnetic perturbations.

Consistent with this, the rate of conversion of $p-H_2$ to $o-H_2$ is proportional to $[p-H_2]$ [total $H_2]^{\frac{1}{2}}$ at high temperature.

Properties

Nuclear spin isomerism does not effectively influence the bond between the atoms and so the chemical properties of *ortho*- and *para*- hydrogen (or any other element) are alike. Most physical properties are also little affected. However, the heat capacities of the two forms differ appreciably and so also do the thermal conductivities, which are proportional to the heat capacities (Fig. 17.2). Thus, the thermal conductivity of $p-H_2$ is more than 50% greater than that of $o-H_2$. (This is used to estimate the $o : p$ content). The melting and boiling points differ slightly as shown in Table 17.2. Note that the trend is reversed with D_2 and the difference also becomes smaller (increase of mass). For other elements, the differences are expected to be still smaller.

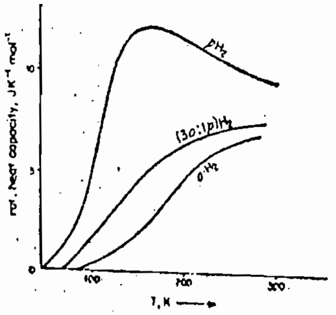


Fig. 17.2. Variation of rotational heat capacities of *ortho*, *para* and *normal*-hydrogen with temp.

TABLE 17.2

Certain Physical Properties of o- and p- H_2 and D_2

	$o-H_2$*	$p-H_2$	$o-D_2$	"normal" D_2 (66.7% o)
M.P. (K)	14.05	13.81	18.70	18.73
B.P. (K)	20.45	20.29	23.63	23.67
Rotational specific heat (J mol⁻¹ K⁻¹)				
50 K	0.00	0.167		
100 K	0.305	6.276		
298 K	7.690	9.146		

* Extrapolated value.

17.1.3 Uses of Hydrogen

Uses of H_2

The chief uses of hydrogen are in the

(i) Manufacture of ammonia.

(ii) Manufacture of hydrochloric acid and other chemicals, particulary methanol by the oxo process:

$$CO + 2H_2 \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH$$

[This is subsequently oxidized to formaldehyde which is used in other synthesis and in the manufacture of plastics.]

(iii) In hydroformylation reactions, i.e. the addition of H_2 and the formyl group CHO into alkenes (also known as the oxo process as it introduces oxygen):

$$R\,CH = CH_2 + H_2 + CO \xrightarrow{\text{Catalyst*}} R\,CH_2CH_2CHO.$$

The aldehydes are subsequently changed to alcohols; these are used in the production of PVC resin and detergents.

* $[Rh(CO)H(PPh_3)_3]$ and $[HCo(CO)_4]$. (See chapter 32.)

(iv) Hydrogenation of oils.

(v) Welding by atomic hydrogen torches.

(vi) Reduction of metal oxides. Direct reduction of iron ore has now been developed on a commercial basis.

(vii) Propulsion of rockets (liquid hydrogen used in Saturn-V).

(viii) Bubble chambers (liquid hydrogen) to study high energy particles.

Uses of D_2

Deuterium is largely used in the form of D_2O or heavy water. It is now largely used as a moderator in nuclear power plants. D_2O is also used as a source of other deutero-compounds which are used in the study of reaction mechanisms.

Uses of Tritium

Tritium is widely used as a tracer element due to its radioactivity. It is extensively used (i) in hydrological studies to follow the movement of ground water, (ii) to study the absorption of hydrogen in metals and multiphase alloys (autoradiography) (iii) in the study of reaction mechanism, kinetics and homogeneous catalysis.

Future uses of hydrogen

The chief importance of hydrogen in the near future lies as an alternative source of energy. When our reserves of coal and oil will get exhausted, nuclear power and liquid hydrogen seem to be the most promising alternatives. Since electricity cannot be stored as such and its transmission from a nuclear power plant may involve large costs, liquid hydrogen may become the media for the transport and storage of energy. The hydrogen will be obtained from the electrolysis of water. The method will be practicable only when electricity will be available at a much cheaper rate. In that case internal combustion engines may also be run on liquid hydrogen and such automobiles have already been designed. They have a greater energy release per unit weight of fuel.

The great advantage of liquid hydrogen as a fuel is that it is free from the pollution hazards of conventional fuels. The only problem lies with the storage and transmission of bulk quantities of liquid hydrogen. But vacuum insulated cryogenic tanks have been successfully used to store huge quantities of liquid hydrogen for US space programmes. Pipeline (~ 200 km) and road-transmission by tankers are also in use without any reported accident.

Hydrogen may also be stored as certain metallic hydrides, for example $FeTiH_{1.95}$. It is possible to store more hydrogen in this form (density of hydrogen 0.096 g cm^{-3}) than in the same volume of liquid H_2 (density = 0.07 g cm^{-3}). These hydrides can be reversibly decomposed to give H_2 and the metal.

Fuel cells using liquid hydrogen for the regeneration of electric power have been operated on a commercial basis with conversion efficiency as high as 70%. Non-electrolytic methods of producing cheap hydrogen from water are also under extensive search and research activity.

17.1.4. Atomic and Ionized forms

The hydrogen molecule is a very stable species:

$$H_2 = 2H \qquad \Delta H = 434.1 \text{ kJ mol}^{-1}.$$

Even at 2000°K, there is only 1% of atomic hydrogen in hydrogen gas at 1 atm. pressure. (This accounts for the observed lack of reactivity of hydrogen at ordinary temperature). It is possible to obtain atomic hydrogen in appreciable concentrations by several methods, e.g.

Atomic Hydrogen

(i) By forcing a jet of H_2 through an electric arc struck between tungsten electrodes in an atmosphere of hydrogen.

(ii) By passing H_2 (below 0.01 mm pressure) over heated Pt or Pd wire at ~ 2000°K.

(iii) By exposing a mixture of mercury vapour and hydrogen (upto 0.5 atmosphere pressure) to the resonance radiation of a mercury lamp (253.7 nm).

(iv) Photolysis of thiols : $RSH \rightarrow RS. + H.$

Once produced, the hydrogen atoms in atomic hydrogen tend to recombine to the molecules, but the heat liberated causes them to separate again. The half-life of atomic hydrogen is nearly 1 second at 0.2 mm pressure. Recombination is rapid in presence of other gases and certain metals.

Atomic hydrogen is highly reactive in nature; obviously a strong reducing agent. Some of its reactions may be summarily represented as:

Oxygen, ethylene:	$O_2 \longrightarrow H_2O_2$; $C_2H_4 \longrightarrow C_2H_6$.
Metal ions (aqueous)	$Cu^{2+} (Ag^+, Hg^{2+}) \longrightarrow Cu (Ag, Hg)$
Oxidizing Agents	$CrO_4^{2-} (MnO_4^-) \longrightarrow Cr^{3+} (Mn^{2+})$
	$H_2O_2 \longrightarrow H_2O$.
Oxides of metal	$AgO (CuO, HgO, PbO_2) \longrightarrow Ag (Cu, Hg, Pb)$
Nonmetals	$S (Cl, Br, I) \longrightarrow H_2S (HCl\ etc)$.

Elements which form very unstable hydrides (e.g. Pb, Bi) will naturally appear unreactive towards atomic hydrogen.

Atomic hydrogen is used in the high temperature welding of metals like tantalum and tungsten using the atomic hydrogen torch. Atomic hydrogen formed in an arc is allowed to recombine on the metal surface—the large amount of heat released in the recombination of hydrogen atoms raises the temperature to about 4000K.

Among the various ionized forms of hydrogen, the proton H^+, the hydride ion H^-, the hydrogen molecule ion H_2^+, and the trihydrogen cation H_3^+ appear well characterized. The first two species have been covered extensively in section 17.3.

H_2^+ and H_3^+: Both the species are highly unstable, detected only in low pressure gas discharged tubes (mass spectrometry). They are valuable as model systems in chemical bonding theories. In H_2^+, the removal of one bonding electron from H_2 results in a lower bond dissociation enthalpy and increased bond length (values in parenthesis are for H_2 molecule):

$$\Delta H = 255\ (436) \text{ kJ mol}^{-1} \qquad d_{H-H} = 106\ (74) \text{ pm}.$$

The triatomic hydrogen molecule ion (trihydrogen cation) H_3^+ is different from the tritium atom as their relative atomic masses differ (H_3^+ : 3.027 ; ${}^3_1T$: 3.016). A linear 3-center 2-electron structure has been suggested for it on theoretical grounds, but recent studies are mostly in favour of a bent structure. The ion is energetically somewhat stable :

$$H(g) + H(g) + H^+(g) = H_3^+(g) \qquad \Delta H = -770 \text{ kJ mol}^{-1}.$$

$$H_2(g) + H^+(g) = H_3^+(g) \qquad \Delta H = -337 \text{ kJ mol}^{-1}.$$

17.2 PREPARATION

Hydrogen may be prepared by the action of metals on water and acids, by the electrolysis of water or by the reforming of hydrocarbons by steam. It is also obtained as a byproduct in the electrolytic manufacture of caustic alkalis from brine.

17.2.1 Small Scale Preparations

The alkali and alkaline earth metals react with water in the cold evolving hydrogen (eqn. a, b)—the vigour may be controlled through amalgamation. Magnesium, aluminium (or their alloys) and zinc-copper couple react with boiling water giving hydrogen and the hydroxide of the metal (Eqn. c, d). Red hot metals like Zn, Mg, Fe, Co, Ni and Mn decompose steam (eqn. e, f).

(a) $2Na + 2H_2O = 2NaOH + H_2$ (b) $Ca + 2H_2O = Ca(OH)_2 + H_2$.

(c) $Zn + 2H_2O = Zn(OH)_2 + H_2$. (d) $2Al + 6H_2O = 2Al(OH)_3 + 6H_2$.

(e) $3Fe + 4H_2O = Fe_3O_4 + 4H_2$. (f) $Ni + H_2O = NiO + H_2$.

Zinc, aluminium, tin and silicon evolve hydrogen when treated with hot, concentrated (20-30%) caustic alkali:

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$$

Ferrosilicon containing 80% Si (Silicol process) reacts similarly. A mixture of silicon, caustic soda and slaked lime (Hydrogenite) evolves hydrogen on ignition leaving sodium and calcium silicates.

Hydrolysis of calcium hydride is also a convenient method:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

17.2.2 Large Scale Production

(A) Very pure (99.9%) hydrogen and oxygen are obtained from the electrolysis of 20% caustic soda (or potash) solution in steel cells using iron electrodes. The anodes are nickel plated to prevent oxidation. The anodes and cathodes are separated by porous diaphragms to prevent diffusion and mixing of hydrogen with oxygen (the mixture is explosive). The cells may be operated at atmospheric pressure (Knowles cells) or at higher pressure (e.g. Lorentz cells use 30 atm pressure).

(B) Steam may be decomposed by coke at high temperature to give water gas:

$$C + H_2O \xrightarrow{1000°C} CO + H_2$$

The carbon monoxide may be made to reduce more steam in presence of iron oxide (or cobalt oxide or a mixture of zinc oxide and chromium (III) oxide) catalyst at 400°C.

$$CO + H_2O \xrightarrow{\text{Catalyst}} CO_2 + H_2 \quad \Delta H = -42 \text{ kJmol}^{-1}.$$

This is known as the water gas shift reaction. A homogenous catalyst in aqueous solution (platinum chloride-tin chloride) has recently been reported to effect the same reaction at low temperature.

From Natural gas

(C) Large amounts of hydrogen are now obtained from the reforming of hydrocarbons (in natural gas) by steam in presence of a nickel catalyst at ~900°C.

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n+1)\,H_2$$

Some CO_2 and CH_4 are also formed:

$$CO + H_2O \rightleftharpoons CO_2 + H_2; \quad CO + 3H_2 \rightleftharpoons CH_4 + H_2O.$$

The mixture of gases is cooled to ~ 350°C and entered into a shift converter. Here most of the CO is catalytically converted to CO_2 by steam (Shift reaction'; the exothermic reaction soon raises the temperature of the gas mixture to 400°C). Often a second stage shift reaction at 200°C is carried out. The CO content is reduced to about 0.2% by volume. The gas is ultimately cooled and CO_2 is removed by absorption (water under pressure or ethanolamine at ~ 70°C).

The last traces of CO (and CO_2) can be removed by *methanation*, i.e. conversion to methane at ~ 300°C by Ni-catalyst:

$$CO + 3H_2 = CH_4 + H_2O \qquad \Delta G = -96.22 \text{ kJ mol}^{-1}.$$

The methane is harmless in most synthetic use. The purity of the hydrogen is high (99.9%).

17.2.3 Preparation of D_2 (and D_2O)

Deuterium is prepared from heavy water, D_2O, by the action of sodium metal or by the electrolysis of D_2O containing dissolved phosphorus pentoxide. D_2O as such is more useful industrially as moderator. Other deuterium compounds are also made readily from it.

Production of heavy water

Heavy water, D_2O is produced by enrichment of ordinary water (0.0156% deuterium) by repeated electrolysis. The overvoltage for the discharge of D^+ ions is higher than that for H^+ ions. Hence the hydrogen gas evolved in electrolysis contains a higher ratio of H : D, while the residual water becomes gradually richer in deuterium. (i.e., lower H : D ratio). The enrichment is expressed as a separation factor (s) between the gaseous and liquid phases:

$$s = (H/D)_g/(H/D)_l$$

The separation factor depends on the metal used as the electrodes; it is very high for platinum and gold ($\geqslant 14$) in alkaline solutions. With $s = 10$, 99% deuterium can be obtained by electrolytic reduction of volume by a factor of 22,000.

At present, the starting water is enriched to ~ 15% deuterium content by chemical exchange. This utilizes the small differences in free energies of the H and D forms of different compounds:

$$HOH\,(l) + HSD\,(g) = HOD\,(l) + HSH\,(g) \qquad K = 1.01$$

The $H_2O - H_2S$ exchange has been used successfully on a large scale and the enriched water produces ~ 99% D_2O on much lower reduction of volume on electrolysis (~ fortyfold only).

Estimation of deuterium content

The deuterium content of water may be determined from measurement of density or refractive index or by infrared spectroscopy. Mass spectrometry, thermal conductivity and gas chromatography (alumina activated by $MnCl_2$) are useful to study the deuterium content of a gaseous $H_2 - D_2$ mixture.

Preparation of deutero-compounds

D_2O may be used as the starting material for other deuterium compounds as illustrated below:

$$\begin{array}{llll} D_2O + Al_4C_3 \longrightarrow CD_4 & & D_2O + CaC_2 \longrightarrow C_2D_2 \\ \quad + Mg_3N_2 \longrightarrow ND_3 & & \quad + P_4O_{10} \longrightarrow D_3PO_4 \\ \quad + LiH \longrightarrow HD & & \quad + SO_3 \longrightarrow D_2SO_4 \end{array}$$

17.2.4 Preparation of T_2 (and its compounds)

Tritium is made artificially by bombarding ^6_3Li with neutrons:

$$^6_3Li + ^1_0n = ^4_2He + ^3_1T$$

The lithium is usually taken in the form of an aluminium- or magnesium-alloy. Some tritium is retained by these metals which may be released by the action of an acid.

Alternatively, LiF may be irradiated with neutrons in vacuum at 450°. The gaseous product contains helium, tritium, fluorine and tritium fluoride, TF. Isolation is achieved through gas diffusion.

Tritium is β-active ($t_{\frac{1}{2}} = 12.3$y) and cannot be stored for a long time.

It is often kept in the form of UT_3 (formed by reacting finely divided uranium). It releases tritium when heated above 400°C.

Preparation of tritium compounds

1. T_2O can be prepared by either of the reactions:

(i) $2T_2 + O_2 \xrightarrow{Pd} 2T_2O$ (ii) $T_2 + CuO \longrightarrow T_2O + Cu$.

Pure T_2O is highly radioactive (1 cm³ ≡ 2650 Ci). In chemical exchange reactions, tritiated water with 1% tritium abundance is often satisfactory.

2. Useful synthetic reagents containing tritium can be prepared from T_2 or T_2O. Exchange reactions occur readily:

$$LiH + T_2 \xrightarrow{350°C} LiT + HT. \qquad B_2H_6 + T_2 \longrightarrow B_2H_5T + HT.$$
$$LiT + AlCl_3 \longrightarrow LiAlT_4 + LiCl. \qquad Mg_3N_2 + T_2O \longrightarrow NT_3 + Mg(OH)_2$$
$$NH_3 + T_2 \longrightarrow NH_2T + HT. \qquad NH_4^+(aq) + HTO \longrightarrow (NH_3T)^+(aq) + H_2O.$$

Non-labile hydrogen atoms may be exchanged using catalysts like Pd or Pt.

3. Tritium-labelled organic compounds may be prepared by merely storing a compound under tritium gas—the β^- radiation inducing the exchange. The compounds may be purified by chromatography.

17.3 PROPERTIES AND BONDING OF HYDROGEN

The important physical properties of hydrogen are given in Table 17.1. Chemically, molecular hydrogen is rather unreactive at ordinary temperature—a fact attributed to the high bond dissociation energy of 434 kJ mol⁻¹. It combines only with fluorine even in the dark and reduces aqueous solutions of palladium (II) chloride:

$$PdCl_2 + H_2 \longrightarrow Pd + 2HCl.$$

However, many transition metal complexes are able to cleave this bond at low temperature and pressure, forming two metal-hydrogen bonds

$$RhCl(PPh_3)_3 + H_2 \rightleftharpoons Rh(H)_2Cl(PPh_3)_3$$

Nascent hydrogen is an active reducing agent even at ordinary temperature. Under the action of light, heat or catalysts, hydrogen reacts readily with many metals and nonmetals. Combination with the strongly electropositive metals effectively reduces the hydrogen to the H^- ion and in such reaction hydrogen may be considered as an oxidising agent. In other cases, hydrogen behaves mainly as a reducing agent. The unique features of the electron configuration of the hydrogen atom have already been discussed. Accordingly, its mode of bonding may be classified as follows:

1. Loss of the valence electron.

The proton, H^+, has been recognized as a fundamental particle and may be produced by (i) ionizing molecular hydrogen by an electric arc or by a radio-frequency discharge.

(ii) bombardment of solid paraffin by neutrons (or deuterons).

(iii) artificial nuclear reactions, e.g. $^{14}_{7}N\,(\alpha, p)\,^{17}_{8}O$.

The formation of a proton from the hydrogen atom involves very high ionization energy:

$$H(g) - e = H^+(g) \qquad \Delta H = 569\ \text{kJ mol}^{-1}.$$

The size of the proton is very small, $r \simeq 1.5 \times 10^{-3}$ pm. This is roughly 1/50,000 that of the Li^+ ion. Consequently the field strength at the boundary of the H^+ ion would be very high, more than 10^9 times as great as that of the Li^+ ion for example. This implies that the proton will not be a stable species chemically; whenever in contact with other atoms, it will pass into the covalent state.

But the proton may be stabilized when bonded to other species. For example, its union with a molecule of water (g) to form the oxonium ion (g) as also its hydration to aquated oxonium ion, are both highly exothermic:

$$H^+(g) + H_2O(g) \longrightarrow H_3O^+(g) \qquad \Delta H = -720\ \text{kJ mol}^{-1}.$$
$$H^+(g) + nH_2O \longrightarrow H_3O^+(aq) \qquad \Delta H = -1090\ \text{kJ mol}^{-1}$$

The chemistry of the oxonium ion deserves special attention.

The ability of a chemical species to furnish a proton has given rise to the very important aspect of acid-base behaviour, both in the gaseous phase and in solution. These have been discussed in section 17.3.1.

2. Gain of an electron.

Addition of an electron to the 1*s* orbital of hydrogen produces the hydride ion; the process is slightly exothermic (E.A. = 67 kJ mol⁻¹). But the overall energetics from $H_2(g)$ to $H^-(g)$ is not encouraging, as shown below. The values for corresponding steps with $Cl_2(g)$ and $Br_2(g)$ are also given. It appears that the formation of the H^- ion is much less favourable than the formation of halide ions due mainly to (i) the low electron affinity and (ii) high bond dissociation energy of H_2.

Process	ΔH (kJ mol⁻¹)	$\Delta H(Cl_2)$ (kJ mol⁻¹)	$\Delta H(Br_2)$ (kJ mol⁻¹)
$\frac{1}{2}H_2(g) \longrightarrow H(g)$	218	121	113
$H(g) + e \longrightarrow H^-(g)$	−67	−364	−345
$\frac{1}{2}H_2(g) + e \longrightarrow H^-(g)$	+151	−243	−232

Owing to this endothermic character of the hydride ion, only the strongly electro-positive metals form ionic hydrides. One might expect highly charged metal ions to form ionic hydrides with high lattice energy, but the high polarizability of the H^- ion make such hydrides mainly covalent. Since two electrons are present under the influence of a single proton, the H^- ion is highly compressible. Its radius is estimated at 208 pm, but the observed radii in different ionic hydrides vary from 134 to 155 pm. The chemistry of such hydrides has been discussed in section 17.3.2.

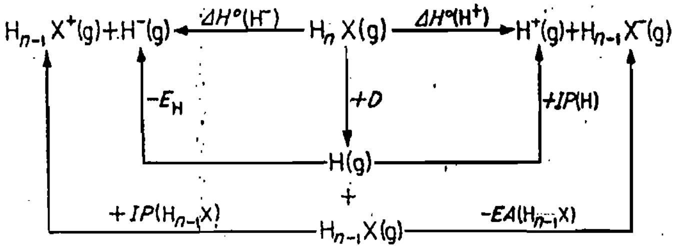
The general tendency of binary hydrogen compounds to exhibit protonic or hydridic character is considered below.

3. Formation of an electron pair bond

It has already been mentioned that hydrogen forms more compounds than any other element. The majority of such compounds contain covalently bonded hydrogen involving an electron pair bond (exception: electron-deficient hydrides e.g. boranes; see later). The actual nature of such compounds is determined primarily by the polarity of bond holding the hydrogen. We have already discussed some typical cases in connection with acid-strengths. Further study of these hydrides will be taken up in section 17.3.3 of this chapter and again under individual group study. Here we shall make a general survey of the periodic table with respect to the binary hydrogen compounds.

Hydridic and protonic character of gaseous hydrides

Let us first consider the thermo-dynamic aspects of hydridic and protonic character of binary hydrides in general. For simplicity, we first restrict ourselves to gase-phase behaviour. The dissociation of a gaseous hydride H_nX to furnish a hydride ion, $H^-(g)$ or a proton, $H^+(g)$ may be treated by appropriate Born-Haber cycles as shown:



where D = dissociation energy ; E or EA = electron affinity and IP = ionization energy.

Clearly,

$$\Delta H^\circ(H^-) = D + IP(H_{n-1}X) - E_H \ ; \ \Delta H^\circ(H^+) = D + IP(H) - EA(H_{n-1}X)$$

General survey of the periodic table

Hydridic Character. Clearly, the change in hydridic character from one compound to another will be determined by the sum of the bond dissociation energy (D) and the ionization potential of $H_{n-1}X$ [IP ($H_{n-1}X$)]. We expect that both these quantities will generally decrease in the periodic table (i) down any vertical group of elements and (ii) from right to left along any horizontal series of elements. Such decreases should favour the formation of the hydride ion (gaseous). Hence we may conclude that the greatest hydridic character will be found in the (gaseous) hydrides of the elements in the bottom left corner of the periodic table. This trend is reflected in the values of $\Delta H^\circ(H^-)$, heat of reaction for hydridic dissociation (Table 17.3).

TABLE 17.3

Some Thermochemical Data for Gaseous Hydrides. All values* are in kJ mol^{-1}.

$\Delta H^\circ(H^-)$	690	1305	1460	1690	2180
	LiH	**CH_4**	**NH_3**	**H_2O**	**HF**
D	243	435	430.9	497.9	566
EA	59.6	8.4	71.1	175.7	328.3
$\Delta H^\circ(H^+)$	1494.4	1737.6	1670.8	1633.2	1548.7
$\Delta H^\circ(H^-)$	623	1088	1213	1318	1615
	NaH	**SiH_4**	**PH_3**	**H_2S**	**HCl**
D	200.8	380.7	351	389.1	431
EA	52.7	138.1	121.3	225.9	348.8
$\Delta H^\circ(H^+)$	1459.1	1553.6	1740.7	1474.2	1393.2
$\Delta H^\circ(H^-)$	468				1439
	KH	**GeH_2**	**AsH_3**	**H_2Se**	**HBr.**
D	184.1	364	305.4	313.8	366
EA	48.4	167.4	121.3	213.4	324.8
$\Delta H^\circ(H^+)$	1446.7	1507.6	1485.1	1411.4	1352.2
					HI
D					297.1
EA					295.3
$\Delta H^\circ(H^+)$					1312.8

* The values are approximate, only showing the general trend in the periodic table.

Protonic Character. The energy terms differentiating between two gaseous hydrides are D and EA ($H_{n-1}X$). As usual, D tends to increase toward the upper right-hand corner of the periodic table. The trend of EA ($H_{n-1}X$) for LiH .. NaH and HF .. HI is the same as the trend of atomic electron affinities. For others, EA($H_{n-1}X$) cannot be guessed directly. Since the electron affinity of a species should be numerically equal to the ionization potential of the corresponding negative ion, we may expect EA($H_{n-1}X$) to increase with increase in nuclear charge and electronegativity of the atom X. Accordingly EA ($H_{n-1}X$) should also increase toward the upper right corner of the periodic table. Again, the trend in protonic character depends on the difference D − EA ($H_{n-1}X$). This makes our task a bit complicated, since the two terms do not vary uniformly. From Table 17.3, we find that

(i) along a horizontal period from left to right, the increase in electron affinity (EA) is slightly more rapid than the change in the bond-dissociation energy D, particularly for the nonmetals. This should give rise to some increase in acidity from left to right.

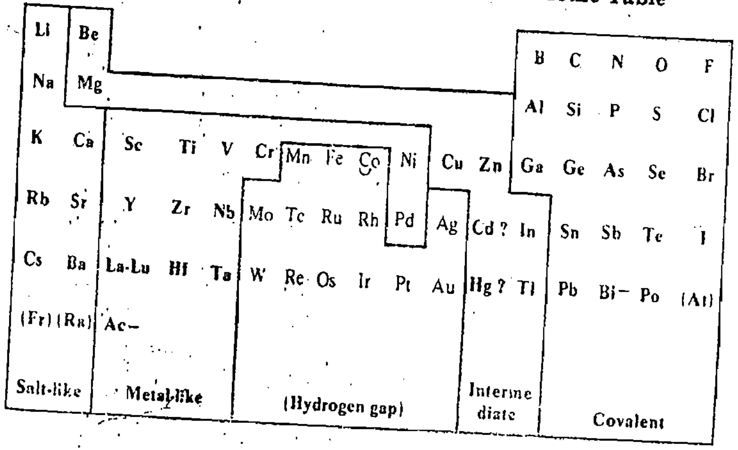
(ii) In any vertical group in the periodic table, the dissociation energy D decreases downward more rapidly than the electron affinity. This favours acid character.

While considering the data in Table 17.3, we should remember that they refer to hydridic or protonic behaviour in the gas phase only. For example, the data shows that NaH(g) should be more acidic than HF(g). At the same time, we observe that the dissociation to H^-(g) ion is energetically favourable in the alkali metal hydrides and also to some extent for the nonmetal hydrides of group IV and V. Of course, we reasonably expect that these behaviours will be largely modified in presence of solvents—as illustrated for the hydrogen halides (Section 10.2.4).

The binary hydrogen compounds in the periodic table may also be classified roughly as shown in Table 17.4.

TABLE 17.4

Classification of the hydrides in the Periodic Table



4. Formation of bridge between two atoms. Hydrogen bridge bonds are observed in (i) the hydrides of boron, aluminium and beryllium and (ii) in transition metal complexes, particularly some carbonyl hydrides. Such bridge formation between two atoms by a hydrogen atom deserves special mention as the hydrogen atom, with its single 1*s* orbital, cannot be expected to form two normal two-electron covalent bonds simultaneously. Special bonding picture involving delocalization of the 1*s* a.o. with appropriate orbitals and corresponding formation of three-center m.o.-s has been invoked to explain such bridge bonds (Section 17.3.5).

5. Formation of the hydrogen bond. This is another interesting aspect of the small hydrogen atom. It is surprising that such hydrogen bonds involve far too small energy in comparison to energies involved in other bond types and yet they dominate the structure and properties of a vast majority of hydrogen compounds and bear crucial importance in biological systems. A brief survey of this has already been done earlier (Chapter 7); few supplementary examples will be given in section 17.3.6. The structures of ice, water, and some hydrates dominated by H-bond will be discussed in section 17.3.7.

Besides, hydrogen forms a number of nonstoichiometric compounds. These have been discussed in connection with the hydrides of transition metals (17.3.4).

"Compounds" containing loosely held hydrogen atoms in clusters or capsule like environments are discussed in section 17.3.8.

6. Formation of complex compounds. Complex compounds of transition metals with both atomic and molecular hydrogen have been established. Some examples have been given in section 17.3.9.

Slower reaction-rate for deuterium compounds

The isotopes of hydrogen are chemically identical. But they differ widely in the rates of reactions as the zero-piont vibration energy of any X – D (or X – T) bond is lower than that of an X – H bond. Accordingly, the bond dissociation energy for an X – D bond (or X – T) becomes higher, i.e. $E_{X-D} > E_{X-H}$. This results in a higher energy of activation for compounds of the heavier isotopes —hence a slower rate. As an example, reactions involving C – D bonds are nearly seven times slower than with C – H bonds.

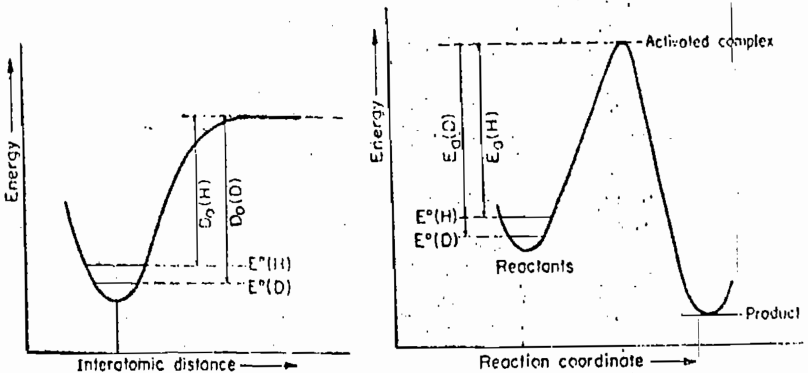


Fig. 17.3.

(a) Potential energy of X–H and X–D bonds. E° represent resepective zero-point energy; D° = respective bond dissociation energy. (b) Potential energy diagram for a reaction involving cleavage of a bond to hydrogen or deuterium. E_a = respective activation energy.

17.3.1 The Hydrogen Ion

As already explained (p. 76), the energy required in the formation of the hydrogen ion is very high and the proton cannot exist as such except in ion beams. Our discussion on the proton will therefore mostly involve the hydrated or solvated proton. However, considerable advancement has recently been made in the study of gas phase proton affinities, particularly due to rapid development in highly sophisticated experimental techniques like electron impact and photo-ionization mass spectrometry (for IP's), high-pressure mass spectrometry, flowing afterglow and ion cyclotron resonance spectrometry (for study of ion-molecule interactions). Study in such gas-phases has the advantage that it enables a comparison of acid-base behaviour independent of the effect of solvents. We shall briefly touch some of the interesting features of such gas-phase study.

Acidity In the Gaseous Phase

We have already considered (p. 77-78) the thermodynamic aspects of the release of a proton by a molecule of a binary hydride in the gas phase. The heat of ionization of H_nX to a proton (Table 17.3), $\Delta H°$ (H^+), is actually the proton affinity* of the corresponding anion, $H_{n-1}X^-$. As already mentioned, such proton affinity data are now available with a fair dgree of accuracy to enable a good comparison of relative acid-strengths in the gas-phase. Some selected data are given in Table 17.5A. Side by side, we may also consider the energy required to separate a proton from a cationic species in the gas phase :

$$BH^+(g) \longrightarrow H^+(g) + B(g).$$

This energy is actually the proton affinity of the corresponding base B. Some selected values are given in Table 17.5B.

TABLE 17.5A.

Heats of ionization to furnish a proton (Proton affinity of the anion); kJ mol⁻¹.

Acid	Anion	ΔH°
CH_4	CH_3^-	1737·6
H_2	H^-	1675·3
NH_3	NH_2^-	1670·8
H_2O	OH^-	1633·2
CH_3OH	CH_3O^-	1586·6
C_2H_5OH	$C_2H_5O^-$	1573·6
CH_3SH	CH_3S^-	1502·1
C_6H_5OH	$C_6H_5O^-$	1470·2
CHF_3	CF_3^-	1571·5
$CHCl_3$	CCl_3^-	1514·6
CH_3NO_2	$CH_2NO_2^-$	1500·8
HF	F^-	1548·7
HCl	Cl^-	1393·2
HBr	Br^-	1352·2
HI	I^-	1312·8
H_2S	HS^-	1474·2
PH_3	PH_2^-	1740·7
SiH_4	SiH_3^-	1553·6
CH_3COOH	CH_3COO^-	1458·1
CF_3COOH	CF_3COO^-	1350·2
HNO_3	NO_3^-	1358·1

TABLE 17.5B.

Proton affinity of some molecules; kJ mol⁻¹.

Base	PA
LiOH	1008·3
NaOH	1037·6
KOH	1100·4
CsOH	1125·5
NH_3	866·1
PH_3	801·6
AsH_3	700·7
$(CH_3)_3N$	954·8
$(CH_3)_3P$	957·7
CH_3NH_2	906·2
$C_6H_5NH_2$	894·1
CH_3PH_2	864·0
NF_3	610·9
NCl_3	790·8
H_2O	723·4
CH_3OH	776·5
CH_3SH	793·3
C_6H_6	773·2
C_2H_4	669·4
C_2H_2	636·0

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* See section 6.6.2.

The appropriate Born-Haber cycle for the gas phase ionization of an acid H_nX to furnish H^+ (g) has already been discussed. Likewise the proton affinity of a base B, PA(B), may be expressed in terms of the bond dissociation energy D_{H-B^+}, ionization potential of the base B, *IP*(B) and ionization potential of hydrogen I_H as

$$PA(B) = D_{H-B^+} + I_H - IP(B).$$

The trends of gas-phase acidic (and basic) character (in terms of proton) apparent from Tables 17.3 and 17.5 are interesting, for example, *NaH* > *HF* in acid strength. Further interesting features are presented by the effect of substitution on acidity trends, for example:

(i) $C_2H_5OH > CH_3OH$.
(ii) $CHCl_3 > CHF_3$
(iii) $CH_3SH < H_2S$ but $CH_3OH > H_2O$.
(iv) $ClCH_2COOH > FCH_2COOH$.

To a first approximation, we may expect the acidity to increase with substitution by a more electron withdrawing group. For a species HXR_n (R = substituent), the process

$$HXR_n(g) \longrightarrow H^+(g) + XR_n^-(g).$$

Electronic Relaxation Energy

should be favoured by increasing electronegativity of R-groups, i.e. increasing positive charge on X. But this consideration alone cannot explain the acidity trends mentioned above. The energy of the ionization process, as written above, is merely the coulombic interaction energy between the proton and the anion. The actual energy term, however, involves a second (hypothetical) factor—electronic relaxation of the anion XR_n^-; this involves redistribution of charge within the anion. The more readily the substituents can delocalize the negative charge on the anion, the greater will be its stability. This electronic relaxation, usually exothermic, will make a definite contribution to the total energy of the ionization process. Combination of these two effects now help us to understand the acidity trends given above.

(i) **$C_2H_5OH > CH_3OH$.** As the size of the alkyl group increases, so also increases its polarizability. This releases higher electronic relaxation energy and acidity increases.

(ii) **$CHCl_3 > CHF_3$.** There is greater delocalization of the negative formal charge on the carbon in case of $:CCl_3^-$. This increases the electronic relaxation energy and offsets the trend expected from electronegativity alone.

[**Note:** CH_3NO_2 is a still stronger acid as the carbon lone pair in the $:CH_2NO_2^-$ anion can be extensively delocalized into the π^* orbital of the NO_2 group. (Draw resonance structures).]

(iii) **$CH_3OH > H_2O$ and $CH_3SH < H_2S$:** In CH_3OH, we expect a greater electronic relaxation energy of CH_3O^- by way of hyperconjugation:

$$H_3C - O^- \longleftrightarrow H^-H_2C = O.$$

This effect must overcome the greater inductive effect of the methyl group, as evident from the acidity trend.

But for CH_3SH, the sizes of carbon and sulfur are greatly dissimilar, and the delocalization is not sufficient to overcome the greater electron donating ability of the methyl group. Therefore the electrostatic energy term dominates over the small electronic relaxation energy.

(iv) **$ClCH_2COOH > FCH_2COOH$.** The relaxation energy and the stability of the anion increase as the polarizability of the halogen atom increase from fluorine to chlorine.

A third process involving stereochemical rearrangement of the anion may also contribute to the energy of the ionization process. However, this energy is likely to be relatively small except in some unusual cases.

The Hydrogen Ion in Solution

When a hydrogen compound is dissolved in a medium that solvates the proton and the solvation energy is sufficient to overcome the bonding energy of the hydrogen atom in the compound, solvated hydrogen ions will be furnished in solution. In water, the solvation (hydration) energy of the proton is very high (− 1090 kJ mol⁻¹); this causes a good number of compounds to exhibit acid-base character in water in the protonic sense.

Water itself is weakly ionized; the process of self-ionization results from the solvation of a proton from one water molecule by the other water molecule:

$$H_2O + H_2O = H_3O^+ + OH^-$$

or, simply

$$H_2O = H^+ + OH^-$$

The ions may undergo further hydration, as discussed later. Such ionization is also known in other solvents like pure sulfuric acid and pure liquid ammonia:

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-;$$
$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

The hydrated hydrogen ion is usually represented as H_3O^+—the hydroxonium or the oxonium ion. It is also found in many solid acid hydrates:

$$HClO_4, H_2O \equiv H_3O^+ ClO_4^-$$
$$HCl, \quad H_2O \equiv H_3O^+ Cl^-$$
$$HNO_3, 3H_2O \equiv H_3O^+ NO_3^-, 2H_2O.$$

The oxonium ion

The protons in the oxonium ion are all equivalent and the ion is a rather flat pyramid with HOH bond angle of approximately 115°. (A planar or nearly planar oxonium ion from sp^2 hybridized oxygen has also been suggested recently (1979) from ^{17}O nmr spectrum). $H_3O^+ClO_4^-$ and $NH_4^+ClO_4^-$ are isomorphous.

In a classical proof of the existence of the oxonium ion (Bagster and Cooling), H_2O and HBr were mixed with anhydrous liquid sulfur dioxide. The two compounds dissolved in equimolar proportions—indicating an 1 : 1 interaction. On electrolysis, the solution yielded water and hydrogen at the cathode and bromine at the anode. The proportion of the products were in strict accordance with Faraday's laws applied to the composition $H_3O^+Br^-$ for the 1 : 1 product.

The oxonium ion may attach to itself further water molecules through hydration or hydrogen-bonding. H_3O^+, H_2O or $H_5O_2^+$; H_3O^+, $2H_2O$ or $H_7O_3^+$; H_3O^+, $3H_2O$ or $H_9O_4^+$ and H_3O^+, $5H_2O$ or $H_{13}O_6^+$ ions have been characterized in solution as well as in crystalline hydrates.

Whatever be the fate of the hydrogen ion in solutions, it can be simply represented by H^+ or H_3O^+ just as we write Fe^{3+} for the ferric ion in aqueous solution, though $[Fe(H_2O)_6]^{3+}$ would have been a more justified representation.

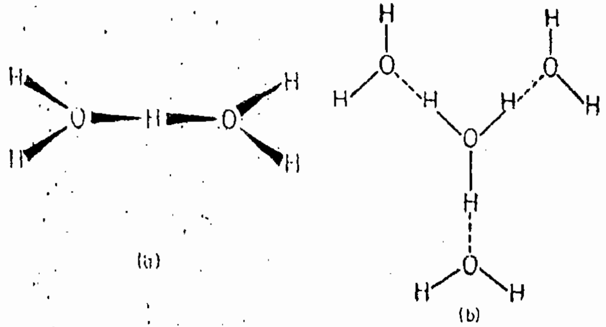

(a) (b)

Fig. 17.4. The structure of (a) $H_5O_2^+$ and (b) $H_9O_4^+$ ions.

The hydroxide ion OH^- is similarly expected to be hydrated, though much less is known in detail. A bifluoride analog of the hydroxide ion, $H(OH)_2^-$, has been characterized as the symmetrical $[H-O-H-O-H]^-$ species. This central $H_3O_2^-$ ion is then surrounded by four extra water molecules via hydrogen bonding (Fig. 17.5).

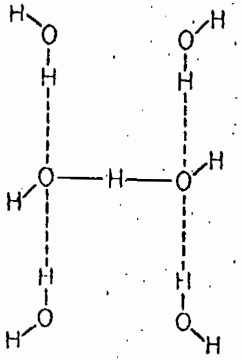


Fig. 17.5. The ion $H_3O_2^-, 4H_2O$.

Several aspects of ionic equilibrium in solutions containing hydrogen ions have already been discussed (Chapters 10 and 11). The main points of interest are just mentioned here:

1. The autoprotolysis constant, K_w.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}\ M^2 \text{ at } 25°C.$$

The value of K_w increases with temperature: 60°C, $K_w = 9.6 \times 10^{-14}$; 100°C, $K_w = 5.6 \times 10^{-13}$.

2. The pH scale.

$$pH = -\log [H^+].$$

For operational difficulties, the scale is practically limited to the range 0 – 14 in dilute aqueous solutions of acids and bases. (See Hammett Equation).

3. The standard hydrogen electrode:

$$H^+ (aq) + e = \tfrac{1}{2}H_2(g). \quad E° = 0.000V.$$

4. The potentials of hydrogen and oxygen evolution from aqueous solutions. The half-cell e.m.f. of the standard hydrogen electrode refers to unit activity of hydrogen ion. In pure water,

$$[H^+] = 10^{-7} \text{ mol. dm}^{-3}. \text{ Hence at } 25°C.$$

$$E_{red} = 0.00 - 0.05915 \log \frac{1}{10^{-7}}.$$

$$= -0.414V.$$

The negative value of the potential indicates that hydrogen becomes a stronger reducing agent in pure water than in a solution with $[H^+] = 1M$. This suggests that systems whose electrode potentials (reduction) are more negative than −0.414V will be oxidized by water, liberating hydrogen. However, overvoltage, insolubility etc. may interfere with normal expectations. Thus U^{3+} is oxidized by water with the liberation of hydrogen ($E°_{red} = -0.61V$ for U^{3+}—U^{4+}).

In alkaline solutions, evolution of hydrogen is guided by the half-cell e.m.f.

$$2H_2O(l) + 2e \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E° = -0.828V.$$

Similarly, the evolution of oxygen in aqueous systems is dependent on the half-cell e.m.f.'s.

Acid: $O_2(g) + 4H^+(aq) + 4e \rightleftharpoons 2H_2O(l) \quad E° = 1.229V.$

Alkali: $O_2(g) + 2H_2O(l) + 4e \rightleftharpoons 4OH^-(aq) \quad E° = 0.401V.$

Clearly, the potentials associated with the evolution of hydrogen or oxygen from aqueous solutions are dependent on pH. This may be represented graphically as shown in Fig. 17.6 (p_{H_2} or p_{O_2} = 1 atm). However, kinetic factors influence the potentials significantly. The actual potentials thus differ by about 0.5V, as shown by the dashed curves.

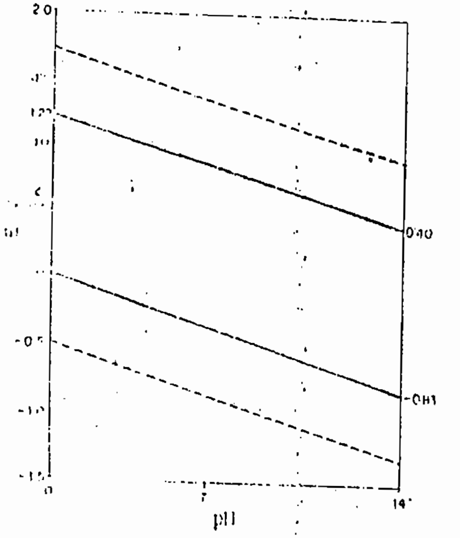


Fig. 17.6. pH—dependence of potentials for hydrogen and oxygen evolution.

5. Strength of Protonic Acids in Aqueous Solutions

The strength of protonic acids in aqueous solutions is expressed in terms of their acid dissociation constants, K, or pK values, $pK = -\log K$. These pK_a values may be obtained from e.m.f. studies or from kinetic, thermodynamic and other indirect methods (specially for very weak acids like the covalent hydrides). We note that a higher pK value corresponds to a weaker acid character. The pK value for common strong acids are usually less than zero. For acids containing more than one ionizable hydrogen, the successive dissociation constants are lowered usually by a factor of 10^{-5} owing to increasing negative charge on the corresponding anion; the pK values therefore increase by about 5.

Aqueous acidity of the binary hydrides within a vertical group of the periodic table increases on descending the family. As discussed earlier (Chapter 10), several factors interplay, but the decrease in X – H bond energy (X = the element other than hydrogen) dominates, together with hydration energy of the anions (the hydration energy of the proton remains constant).

[However, dissociation may not be the only factor controlling aqueous acidity, as exemplified by recent (1976) studies on HF. From thermodyanmic data we found that the HF bond is so strong that its rupture is not compensated by the hydration energies of H^+ and F^- ions (though the latter is exceptionally above the other halogens). So we were led to believe that most dissolved HF molecules remain undissociated. But now it has been suggested that *HF is dissociated*, but it remains as tight ion-pairs: $F^- \ldots . H^+$ (aq). This extremely strong hydrogen-bonding, unique to F^-, therefore, reduces the thermodynamic activity coefficient of H_3O^+. (In any case, the ultimate cause is the very strong binding, if not the bond, between hydrogen and fluorine).]

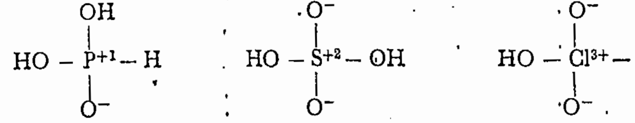
In any case, the trend parallels the trend shown by gas-phase acidity (Table 17.5). But the horizontal trend of aqueous acidity in the perioidic table is different from that in the gas phase. There is a marked trend toward greater acidity from left to right, detectable acidity being found only in groups VI and VII. This may be assigned to the decreasing size of the anion, with consequent increase in hydration energy. The effects of electronegativity and other substituents on the central atom affect acidity as usual.

Approximate pK value for oxo-acids

Compounds with X – OH groups form the most important family of acids in aqueous solutions. These are called oxo acids or hydroxy acids. The formal charge of the central atom seems to be the most important factor in determining acidic dissociation. For an oxo acid H_nXO_m, the formal charge may be computed by assuming the structure to be $O_{m-n}X(OH)_n$ (exceptions: H_3PO_2 and H_3PO_3; see later). Each X – OH bond is formally nonpolar (as it is formed by sharing one electron from X and one electron of the oxygen). Each X – O bond may be represented by two electrons from X being coordinated to oxygen, contributing +1 to the formal charge of X. Therefore, for non-π-bonded hydroxy acids covered by the Lewis octet theory, the formal charge on the central atom X will be simply equal to the number of nonhydroxyl oxygen, i.e. $m - n$. ($= n_o$, say). The pK of the neutral hydroxy acid molecule is then approximately given by the relation

$$pK = 8 - 5n_o.$$

Some applications of this rule are shown below



$$\mathrm{HO-\overset{\displaystyle OH}{\underset{\displaystyle O^-}{P^{+1}}}-H} \qquad \mathrm{HO-\overset{\displaystyle O^-}{\underset{\displaystyle O^-}{S^{+2}}}-OH} \qquad \mathrm{HO-\overset{\displaystyle O^-}{\underset{\displaystyle O^-}{Cl^{3+}}}-O^-}$$

H_3PO_3; $n_o = 1$; p$K \simeq 3$. H_2SO_4; $n_o = 2$; p$K \simeq -2$ $HClO_4$; $n_o = 3$; p$K \simeq -7$

Several other pK values are listed in Table 17.6. The agreement is usually satisfactory, within ±1. For H_3PO_3, $n_o \neq m - n$, for its particular structure supported by other evidence. Similarly, H_3PO_2 has the structure $OPH_2(OH)$, and hence $n_o = 1$ ($\neq m - n$). For H_2CO_3, HNO_2 and HNO_3, the formal charges are calculated for structures ignoring π-bonding in which the central atom lacks an octet. For H_2CO_3, the measured pK_1 is ~ 6.38. But it does not correspond to the equilibrium

$$H_2CO_3 = H^+ + HCO_3^-$$

Most of the CO_2 are only loosely hydrated. Relevant correction gives p$K_1 = 3.6$, as given in the table.

The large separation of successive pK values for polybasic oxo acids may be attributed to the electrostatic effect of the negative charge left by the dissociation of the proton in the first step (or in an immediately preceding one). For H_2O and H_2S, separation of K_1 and K_2 is unusually high: H_2O : $K_1 = 10^{-14}$, K_2 (estimated) $< 10^{-38}$; H_2S : $K_1 \simeq 10^{-7}$, $K_2 \simeq 10^{-14}$. This is because the negative charge caused by the removal of the first proton is solely concentrated on the O or S atom to which the second proton is linked.

The effect of substituents on aqueous acidity is sometimes quite different from the trend shown in gas phase acidity. For example the haloacetic acids show the following trend of aqueous acidity: $FCH_2COOH > ClCH_2COOH \ldots\ldots$

TABLE 17.6

pK values of aqueous oxo acids, $H_n OX_m$ or $O_{m-n}X(OH)_n$

$n_o = (m-n)$	**Examples**	**pK_1**	**pK_2**
0	HOCl	7.2(7.5)	
	HOBr	8.7	
	HOI	11.0	
	H_3AsO_3	9.2	
	H_6TeO_6	8.8	
	H_3BO_3	9.2	
+1	H_2CO_3	3.6	10.3
	HNO_2	3.2	
	H_3AsO_4	2.3	7.0
	H_3PO_4	2.2	7.1
	H_3PO_3	1.8	6.2
	H_3PO_2	2.0	
	H_2SO_3	1.9	7.2
+2	HNO_3	< 0	
	H_2SO_4	< 0	1.9
+3	$HClO_4$	$<< 0$	
	$HMnO_4$	$<< 0$	

(The gas phase acidity was reverse). Here the electronic relaxation is affected by the polarization of the solvent as well as of the halogen atom. For the smallest halogen atom, the solvent molecules are closest to the center of the negatively charged halogen. In fact, the polarization of the solvent dominates over the polarization of the halogen atom and explains the observed acidity trend.

Aquated metal ions may also be treated as oxo acids (the so-called hydrolysis).

$$[Fe\,(H_2O)_6]^{3+} = [Fe\,(H_2O)_5\,OH]^{2+} + H^+ \quad K = 10^{-3}.$$

The ferrous ion will be less acidic owing to its lower positive charge.

Some transition metal carbonyl hydrides in which the metal atoms have high positive charges (back bonding; see carbonyls) exhibit acidic character in aqueous and alcohol solutions. Thus in methanol solution, $HCo(CO)_4$ has a pK value less than zero, and $HMn(CO)_5$ has a pK value of ~ 7. However, their acidity does not convey that the hydrogen atoms in these compounds are positively charged. Rather, X-ray photoelectron spectroscopic studies show that the hydrogen atoms are actually negatively charged.

6. Rates of acid-base reactions in water

All the protons in water are undergoing rapid migration from one oxygen atom to another. This makes the life of an individual H_3O^+ (or similar) ion very small, of the order of 10^{-13} seconds. When a H_3O^+ ion diffuses close to a base, (e.g. the OH^- ion, also solvated), the proton is transferred readily to the base by concerted shifts across the solvent molecules (Fig. 17.7).

The critical distance for proton-transfer to take place has been estimated at 6 to 8 A°, equivalent to 2 or 3 hydrogen bond lengths. The transfer of a proton from an acid (H_3O^+) to a base may thus be considered to take place in the following sequence.

(i) Diffusion of the acid and base to close proximity and formation of a "collision complex".

(ii) Transfer of a proton through the hydration structure of the complex from the acid to the base (Fig. 17.7).

(iii) Breakup of the hydration structure.

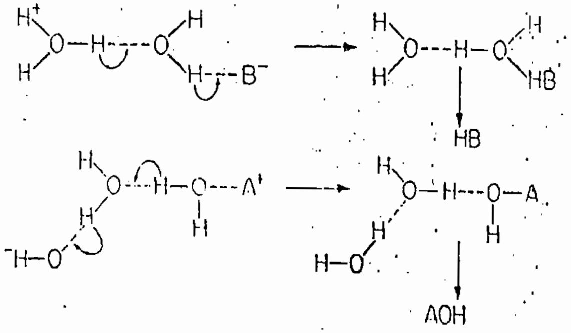


Fig. 17.7. Transfer of proton by concerted shift across water molecules : combination of (i) H_3O^+ with a base B^- (ii) OH^- with an acid A^+.

The first process is the rate-determining step and is controlled by the rates of diffusion of the ions. Such processes are very fast and accordingly acid-base reactions in water have high specific rate constants (measured by relaxation methods), as given in Table 17.7. The values are approximate.

TABLE 17.7

Specific rate constants for acid base reactions in water at 25°C.

Reaction	k, $dm^3\ mol^{-1}s^{-1}$.
$H_3O^+ + OH^- \rightarrow H_2O + H_2O$	1.4×10^{11}
$H_3O^+ + SO_4^{2-} \rightarrow H_2O + HSO_4^-$	1×10^{11}
$H_3O^+ + H_2BO_3^- \rightarrow H_2O + H_3BO_3$	1.2×10^{10}
$H_3O^+ + NH_3 \rightarrow H_2O + NH_4^+$	4.0×10^{10}

It may be recalled in this connection that the very high electrical conductivity of H^+ and OH^- ions in aqueous solution is also attributed to such proton exchange between neighbouring water molecules across the hydrogen bonded structure (Grotthus type of conduction).

7. The Hammett Acidity Function.

The concentration of the hydrogen ion in aqueous solution is expressed by the pH-scale and the relative acid dissociation constants are expressed by the pK-values (Chapter 10-11). But these concepts are satisfactory only for dilute aqueous solutions of acids (and bases). For concentrated solutions, for example those not covered by the pH scale 0 – 14, and in nonaqueous media, an "acidity function" H_0, also called the **Hammett acidity function** has been defined. The definition is based on the protonation equilibrium of an indicator base B (e.g. picramide or *p*-nitroaniline)

$$B + H^+ \rightleftharpoons BH^+$$

By definition, $H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$.

In dilute aqueous solution of a protonic acid, H_0 becomes synonymous with pH since $K_{BH^+} = [B][H^+]/[BH^+]$. In concentrated solutions upto the pure acid, H_0 can be estimated by determining the ratio $[BH^+]/[B]$ spectrophotometrically. The more negative the value of H_0, the larger the acidity, or strength, of the acid that transfers its proton to the base B.

For a system buffered with a base B^- and its neutral conjugate acid HB, the function H^- is defined as

$$H_- = pK + \log \frac{[B^-]}{[HB]}.$$

H_0 and H_- values for some acids and bases are given in Table 17.8.

TABLE 17.8

Some values of the Hammett acidity functions H_0 and H_-.

Solution	$-H_0$	Solution	H_-
100% H_2SO_4	12	5M KOH (aq)	15.4
98% H_2SO_4 (aq)	10.4	10M KOH (aq)	16.9
60% H_2SO_4 (aq)	4.5	15M KOH (aq)	18.2
HF	11		
H_3PO_4	5		
HCOOH	2.2		

For a number of strong acids in aqueous solution upto about 8M concentration, the acidity is found to be independent of the anion. The rise in acidity with concentration can be explained by assuming that the hydrogen ion exists as $H_9O_4^+$:

$$H_9O_4^+ + B \rightleftharpoons BH^+ + 4H_2O.$$

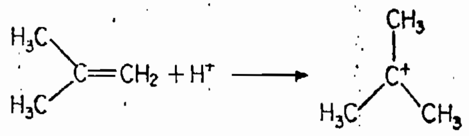
Superacids Acid media with $-H_0$ values greater than ~6 are often referred to as superacids as they are nearly 10^6 times as strong as 1M aqueous solution of a strong acid. (Some authors set the boundary of $-H_0$ at 11 – 12 for superacid designation). Thus, in addition to HF and H_2SO_4, we have $H_2S_2O_7$ ($-H_0$ =.15) and HSO_3F ($-H_0$=15) in our list of superacids. The addition of a Lewis acid like SbF_5, BF_3, NbF_5 and TaF_5 to HF or HSO_3F remarkably raises the $-H_0$ value by equilibria of the type

$$2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^-$$

Such systems have $-H_0$ values as high as 21 or even greater. The HCl – Al_2Cl_6 pair provides another superacid system.

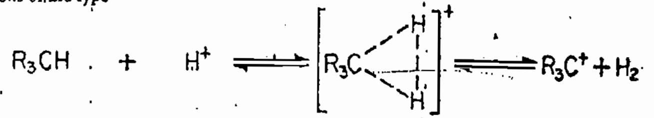
A superacid medium permits a number of interesting reactions:

(A) Protonation of very weak bases such as acetamide, acetic acid, aromatic species and biological systems. A variety of organic carbonium ions, oxonium ions, acyl cations etc. may be stabilized which are too reactive to exist in less acidic solutions:



There are also evidences of protonation of H_2, CH_4, Cl_2, Br_2, CO and Xe in SbF_5 –HF media.

Interestingly, a "*pentacoordinate*" carbonium ion is probably formed as an intermediate in reactions of the type



(B) Oxidation of molecular halogens and interhalogens give rise to interesting cations:

$$2I_2 + S_2O_6F_2 \longrightarrow 2I_2^+ + 2SO_3F^- \text{ (in } HSO_3F\text{; blue solution):}$$

peroxodisulfuryl-difluoride

(C) Elemental sulfur, selenium and tellurium give condensed coloured cations:

$$2S_8 + S_2O_6F_2 \longrightarrow S_{16}^{2+} + 2SO_3F^- \text{ (in } HSO_3F\text{; yellow-orange).}$$

$$8Se + 6H_2S_2O_7 \longrightarrow Se_8^{2+} + HS_3O_{10}^- + 5H_2SO_4 + SO_2 \text{ (in oleum; green).}$$

Such superacid systems may prove to be of potential industrial value in carrying out many organic reactions such as isomerization of straight chain to branched chain alkanes, or vice versa and acetylation and alkylation reactions of hydrocarbons.

17.3.2 The Ionic Hydrides; (The Saline Hydrides)

The energy factors involved in the formation of the hydride ion were mentioned earlier (p. 77). As such, definitely stoichiometric salt-like hydrides containing the H^- ion are formed only by the alkali and alkaline earth metals. MgH_2 is intermediate between ionic hydrides and solid covalent hydrides like AlH_3. The two lanthanide elements, europium and ytterbium, form hydrides EuH_2 and YbH_2, which are isomorphous with CaH_2 and are probably ionic.

Preparation The saline hydrides are generally formed by direct combination at 200 – 700°.

$$2Na + H_2 = 2NaH \quad > 200°.$$

$$2\,Li + H_2 = 2LiH \quad > 700°.$$

The reactions are generally slow, presumably due to an inert coating of the inert hydride on the metal surface. Better results are obtained when the metal is dispersed in an inert solvent like tetrahydrofuran (THF) or kerosene in the presence of a surface active agent like magnesium stearate. NaH can be prepared at room temperature by reacting hydrogen with sodium and naphthalene ($Na^+C_{10}H_8^-$) in THF; titanium isopropoxide is used as a catalyst.

Sodium azide yields NaH on heating in hydrogen: $NaN_3 + 5H_2 \rightarrow NaH + 3NH_3$.

Properties: The saline hydrides are crystalline solids—white when pure but often greyish due to traces of the metal. Their melting points are high but only LiH is sufficiently stable to be melted (688°C). The densities of the saline hydrides are much higher than those of the metals (~50% increase for the alkali metals). Strong coulombic interaction between the metal and the hydride ions results in close packing and relatively dense crystal.

High density

The saline hydrides conduct electricity in the molten state or in solution in molten alkali halides. Electrolysis of such solutions yield hydrogen at the anode in quantitative agreement with Faraday's laws for the H^- ion.

The ionic radii of H^- and F^- ions are roughly equal, 140 and 136 pm respectively (see later). Accordingly, the physical properties of the saline hydrides are similar to those of the corresponding fluorides.

Thermal stability The hydrides decompose at high temperatures giving the metal and hydrogen. Thermal stability decreases from LiH to CsH and from CaH_2 to BaH_2 but MgH_2 decomposes at a much lower temperature (greater covalent character). Thermal stability of the alkaline earth metal hydrides is appreciably higher than the alkali metal hydrides. Lattice energy seems to be the main controlling factor.

Chemical Reactivity The saline hydrides are reactive toward air and water—those of Rb, Cs and Ba ignite spontaneously in moist air. Reactivity increases from LiH to CsH and from CaH_2 to BaH_2. CaH_2 is less reactive than LiH. They all react instantly and completely with any substance capable of providing the minutest trace of H^+ ion (water, ammonia, alcohol).

$$H^+ + H^- \longrightarrow H_2 \qquad \Delta H = -1850 \text{ kJ mol}^{-1}.$$

$$LiH + H_2O = LiOH + H_2; \; KH + NH_3 = KNH_2 + H_2.$$

The standard reduction potential of the H_2/H^- couple is −2.25V, making the H^- ion a very strong reducing agent. A few examples are:

$$SO_2 \longrightarrow S + S_2O_3^{2-}; \; SO_4^{2} \longrightarrow S^{2-};$$

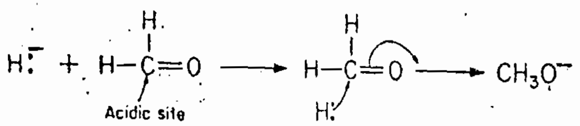
$$Al_2O_3 \longrightarrow Al; \; CO \longrightarrow CH_4; \; CO_2 \longrightarrow HCOO^-$$

Typical equations are:

$$CaH_2 + MO = CaO + M + H_2$$

$$CaH_2 + 2NaCl = 2Na + CaCl_2 + H_2.$$

The hydride ion also acts as a strong Lewis base:

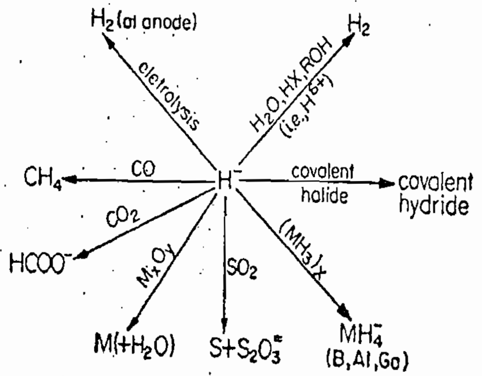


A very important reaction is

$$4LiH + AlCl_3 = LiAlH_4 + 3LiCl.$$

The chemistry of the complex hydride anions, (hydrido complexes) is discussed separately.

Important reactions of the hydride ion are schematically shown below:



Structure The alkali metal hydrides have NaCl type structure (FCC). The alkaline earth metal hydrides have slightly distorted hexagonal close packed structure (HCP). MgH_2 has a rutile structure. The effective radius of the free hydride ion has been calculated (Pauling) to be 2.08A°—more than twice that for He. This is due to (i) strong interelectron repulsion and (ii) mutual screening from the single positive charge of the nucleus. However, the apparent radius of the H^- ion in the hydrides is much smaller: subtraction of the metal ion radii from measured M − H distances in crystals gives radius of the H^- ion ranging from 1.36A° in LiH to 1.52A° in CsH. This may be ascribed to the high compressibility of the rather "fluffy" electron cloud of the hydride ion—the greater the charge density of the metal ion, the smaller is the hydride ion.

Uses

LiH is used in organic synthesis and in preparing $LiAlH_4$. NaH is used similarly in the preparation of $NaBH_4$ and in other organic synthesis. Calcium hydride (hydrolith) is used as a ready source of hydrogen (one liter per g) and as a drying agent for organic solvents and gases. MgH_2 has some possibility of being used for storage of hydrogen (see use.).

Complex Hydride Anions: These have the representative formula MXH_4 where M is an alkali metal and X = B, Al, Ga. In these, and in Li_2BeH_4, the anion is tetrahedral. Na_3AlH_6 with octahedral AlH_6^{3-} ion is also known.

Sodium tetrahydroborate is prepared by reacting sodium hydride with methyl borate at elevated temperatures:

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3.$$

Sodium hydroborate is stable in alkaline solutions in water. It decomposes rapidly in acidic solutions:

$$BH_4^- + H^+ + 3H_2O \rightarrow 4H_2 + H_3BO_3.$$

An ether solution of $NaBH_4$ reacts with diborane at 100°C to form sodium octahydrotriborate:

$$B_2H_6 + NaBH_4 \rightarrow NaB_3H_8 + H_2.$$

Other anions of the general formula $B_nH_n^{2-}$ (n = 6 – 12) may be similary prepared by varying the reaction conditions and solvent. These ions have a remarkably stable boron skeleton (see boron hydrides).

Lithium hydroaluminate (Lithium aluminium hydride) is prepared in ether solution from LiH : $4LiH + AlCl_3 = LiAlH_4 + 3LiCl$. This (and the Na, K-salt) may also be prepared by direct reaction at high pressure:

$$Li + Al + 2H_2 \xrightarrow[100\,-\,300\text{ atm.}]{\text{ether}/120\,-\,150°C} LiAlH_4.$$

Less electropositive elements also form borohydrides or aluminohydrides. However, they are more closely related to the parent hydrides of boron and aluminium, which are electron-deficient covalent compounds.

The complex hydrides, specially $LiAlH_4$ and $NaBH_4$ are extremely useful reducing agents in organic chemistry. Their chemistry will be dealt with in Group III.

17.3.3 The Covalent Hydrides

Such hydrides are generally characterized by normal two-center two-electron bonds, though the electron-deficient hydrides of boron and aluminium may also be included in this category. Similarly, the metal hydrides BeH_2, MgH_2 and ZnH_2 possess a greater degree of covalence. All other covalent hydrides are derived from the typical elements in the p-block. These will be discussed in connection with the individual group chemistry. Only a brief survey is done here.

Preparation

Some of the more important preparative methods may be represented by the typical equations as follows:

(i) Reduction of a covalent chloride:

$$SiCl_4 + 4LiAlH_4 \xrightarrow{\text{ether}} SiH_4 + 4LiCl + 4AlH_3$$

(ii) Pyrolysis or reduction of metal alkyls:

$$M(CH_3)_2 \xrightarrow{\text{heat}} MH_2 + C_2H_4 \ (M = Zn, Mg)$$

$$Zn(CH_3)_2 \xrightarrow{H_2} ZnH_2 + 2CH_4.$$

(iii) Hydrolysis of magnesium compounds or alloy : (*Stock's reaction*) :

$$Mg_3X_2 + 6HCl \longrightarrow 3MgCl_2 + 2XH_3 \ (X = N, P, As \text{ etc.}).$$

(iv) Hydrolysis of suitable compounds, e.g. polysulphides giving polysulphanes:

$$(NH_4)_2S_x + 2HCl \dashrightarrow 2NH_4Cl + H_2S_x$$

$$Mg_2Si + 4NH_4Br \xrightarrow{\text{liq } NH_3} SiH_4 + 2MgBr_2 + 4NH_3.$$

(v) Cathodic reduction (e.g. SnH_4 and PbH_4), reduction by BH_4^-, pyrolysis, electric discharge etc. are also used. Some typical examples are

$$3BH_4^- + 4H_3AsO_3 + 3H^+ \xrightarrow[\text{solution}]{\text{aqueous}} 4AsH_3 + 3H_3BO_3 + 3H_2O$$

$$B_2H_6 \xrightarrow{\Delta} H_2 + B_4H_{10} + B_5H_{11} + \ldots;$$

$$GeH_4 + PH_3 \xrightarrow[\text{discharge}]{\text{electric}} GeH_3PH_2 + Ge_2H_6 + P_2H_4 + \ldots$$

$$KSiH_3 + SiH_3Br \longrightarrow KBr + Si_2H_6.$$

Properties

The covalent hydrides are usually volatile with low melting and boiling points but hydrogen-bonding or other types of association may result in higher boiling and melting points, water being a ready example.

In any group, thermal stability of the hydrides decreases downward. (CH_4 vs. PbH_4; NH_3 vs BiH_3). As we proceed downward along any group, sizes of the elements increase and disparity in orbital size gives poor overlap with the small 1*s* orbital of the hydrogen atom. This makes the bonds weaker. Catenation among the elements is also affected to a varying degree, as is observed in Gr. IV in particular. Other than carbon, the longest chain hydrides characterized are

$$Si_{10}H_{22},\ Ge_{10}H_{22},\ Sn_2H_6,\ HN_3,\ P_3H_5,\ As_3H_5,\ Sb_2H_4,\ H_2O_3 \text{ and } H_2S_6.$$

In Group II, BeH_2 is believed to have a polymeric structure similar to the boranes. In Group III, boron and aluminium form electrondeficient hydrides of complicated structures which are described in the group study. Gallium probably forms an unstable (– 15°C) liquid GaH_3. Hydrides of In and Tl are not well characterized.

In Group IV, carbon is unique in forming a very large number of saturated and unsaturated hydrogen compounds of a variety of structure. There appears to be a unique combination of size and charge so that the C – H bond is sufficiently stable in comparison to other C – X bonds, including C – O bonds (see Group IV). This advantage disappears for silicon, which cannot also form stable Si – Si pi-bonds due to poorer overlap and hence silicon analogues of C_2H_4 and C_2H_2 are not known. In Group V, NH_3 is noted for its basic nature while both NH_3 and PH_3 and their derivatives have remarkable reducing properties and coordinating ability. Thanks to the role of extensive hydrogen bonding, with it H_2O has made its own place not only among the Group VI hydrides, but also in our entire chemistry and life as a whole. H_2S is important as a reagent and as a reducing agent. The hydrides of group VII, rather the hydrogen halides, are all distinguished acids.

Thus, the hydrides become gradually more acidic as one moves from left to right horizontally in the periodic table. After the salt-like hydrides, we find some residual "hydridic" character in the hydride of the relatively electropositive nonmetal boron: B_2H_6 reacts with water to form hydrogen ($B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$). The elements of Group IV have intermediate electronegativity and accordingly their hydrides display both hydridic or protonic character depending on the reagent, as exemplified by the reactions of GeH_4:

Hydridic character: $GeH_4 + HBr \rightarrow GeH_3Br + H_2$

Protonic character: $GeH_4 + NaNH_2 \rightarrow NaGeH_3 + NH_3$

The hydrides of more electronegative elements, e.g. those in groups VI and VII have marked protonic character. Thermodynamic aspects of such periodic trend in acidity have already been discussed.

The effective covalent radius of the hydrogen decreases gradually as the effective nuclear charge of the other element increases (Table 17.9) and is always less than half the H – H distance in H_2. This contraction, in absence of any scope for π-bonding (as in SiF_4, say), may be, at least partly, attributed to the absence of an inner electron core.

TABLE 17.9

Effective covalent radius of Hydrogen.

Molecule	Covalent radius (pm.)	Molecule	Covalent radius (pm.)
H_2	37	NH_3	28
CH_4	32	H_2O	22
SiH_4	30	HF	21

Uses

AlH_3 is a useful reducing agent in organic chemistry—it reduces nitriles to amines. It reduces alkyl halides more slowly than does $LiAlH_4$ and hence carboxyl or ester groups can be reduced preferentially in presence of alkyl halides. Many other covalent hydrides have specific synthetic, analytical and technical uses—those of the boranes, ammonia, hydrazine and hydrogen sulfide being well known.

17.3.4 Hydrides of the Transition Elements

Hydrogen reacts with many transition elements, both of the d- and f-block, to form a number of "compounds" lacking stoichiometry. Their nature is complicated as they often contain more than one phase. They often exhibit many of the physical characteristics of metals like high thermal and electrical conductivity, hardness and lustre. But they are usually more brittle than the corresponding metals. Their composition varies with temperature and the pressure of the hydrogen in the gaseous phase. They are less dense than the parent metals owing to expansion of the metal lattice after absorption of hydrogen. Sometimes a total rearrangement of the original metal structure is also observed.

Model structures

Nevertheless, such "compounds" cannot be considered mere solid solutions, hydrogen occupying interstices in the metal lattice. Many of them have heats of formation of about 170 kJ per mol of H_2, a value comparable to those for the saline hydrides. The structural change in the metal lattice also indicates stronger interaction than merely the formation of a solid solution. No uniform bonding scheme is adequate to cover such compounds. Models based on either H^- or H^+ ions, or on covalent character of the hydrogen have been suggested. For example, one may consider some of the electrons in the crystal lattice of the metal to be donated to the hydrogen atoms giving H^- ions; the remaining electrons will still occupy the energy bands in the metal. Thus, a metal hydride MH_x may be supposed to contain M^{n+} ions, x H^- ions and $(n - x)$ electrons delocalized over the metallic band. The structure of the hydride will be determined by the relative size and charge of the ions; the metallic properties may be attributed to the delocalized electrons. As an example, TiH_2 may be regarded as consisting of Ti^{4+}, two H^- and two delocalized electrons per formula unit. However, recent investigations show that the properties of such compounds can be best explained from elaborate band structure calculations. The more important hydrides in this category are mentioned below:

The principal metallic hydirdes with their limiting formula are shown in Table 17.10. Separate discussions for *d*- and *f*-block elements follow.

TABLE 17.10

Limiting formula of metallic hydrides and structures.

(f : fluorite; h : hexagonal; c : cubic; w : wurtzite.)

ScH_2(f)	TiH_2(f)	VH (bcc) $VH_{1.6}$(fl)	CrH........ (anti NiAS)	NiH(fcc)[1]	CuH(w)
YH_2(f)	ZrH_2(f)	NbH(bcc)?	....	$PdH_{0.7}$(fcc)	
YH_3(h)		NbH_2(fl)?			
LaH_2(f)	HfH_2(f)	TaH(bcc)	....		
LaH_3(c)					

Lanthanides: MH_2(f) : Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu[2].
MH_3(c) : Ce, Pr, Nd, Yb.
MH_3(h) : Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu.

Actinides : MH_2(f) : Th, Np, Pu, Am.
MH_3(g) : Np, Pu, Am
MH_3(c?): Pa, U.

1. Exists only under very high hydrogen pressure (10^4 atm.)
2. EuH_2 and YbH_2 are orthorhombic, similar to CaH_2 (ionic).

Hydrides of d-block metals. The elements in the d-block of the periodic table show little affinity for hydrogen—a fact which gave rise to the phrase "hydrogen gap". Only Pd, Ti, Zr, Hf and to a negligible extent V, Nb, Ta, Cr and Cu form weak compounds with hydrogen.

Ti, Zr and Hf absorb hydrogen exothermically to give nonstoichiometric hydrides with compositions varying from $MH_{1.6}$ to $MH_{1.8}$. These have the fluorite structure in which certain of the hydrogen lattice sites are vacant. With absorption of more hydrogen, the structure changes to face-centered tetragonal structure with compositions $MH_{1.8}$ to $MH_{1.98}$. The limiting phases are thus MH_2. These and similar hydrides of V, Nb and Ta are greyish-black solids stable in air. But they react when heated with air or acidic reagents.

Chromium does not combine directly with hydrogen, but a hydride CrH can be prepared electrolytically. Reduction of Cu^{2+} solutions by hypophosphorus acid produces red insoluble CuH : $2CuSO_4 + 3H_3PO_2 + 3H_2O = 2CuH + 3H_3PO_3 + 2H_2SO_4$.

Palladium, on being cooled from red heat, can absorb upto 935 times its own volume of H_2. As hydrogen is absorbed, the electrical conductivity of the metal falls and ultimately it shows semiconductor behaviour (corresponding to the composition $PdH_{0.5}$). Pressure-temperature-composition curves indicate the presence of palladium hydride phases. The precise nature of the metal-hydrogen interaction is still uncertain. It is interesting to note in this connection that palladium is highly permeable only to H_2 (and D_2) but it is impervious to other gases, even He. This fact is utilized in the industrial separation of hydrogen from mixtures of gases. The permeability is increased by alloying with about 20% Ag.

Titanium and zirconium hydrides are used as reducing agents in metallurgy and in other processes. The iron-titanium-hydrogen ternary system ($FeTiH_{1.96}$) has immense potentiality in hydrogen storage (See use).

Hydrides of Lanthanoids. Most of the lanthanoid elements combine with H_2 to give non-stoichiometric compounds. Phase studies indicate two limiting compositions—MH_2 and MH_3. Europium and ytterbium normally give only the MH_2 phase (isostructural with CaH_2). Under pressure YbH_2 absorbs further hydrogen to about $YbH_{2\cdot55}$.

The hydrides are black solids—brittle and pyrophoric, reacting vigorously with water. Their properties are often described satisfactorily on an ionic model. The metal seems to be predominantly in + 3 state—even in the MH_2 phase. The odd valence electron is then probably located in a metallic conduction band. Eu(II) and Yb(II) are, however, most likely to be present in EuH_2 and YbH_2, corresponding to the stable electron configurations (Eu^{II}: $4f^7$; Yb^{II}: $4f^{14}$). $YbH_{2\cdot55}$ probably contains both Yb^{II} and Yb^{III}. The structures of the MH_3 type hydrides are rather complex and varies with the size of the metal ion. The third hydrogen is often found to be less strongly bound than the other two.

Hydrides of the Actinoids. Like the lanthanoids, most of the actinoids form hydrides with the limiting compositions MH_2 and MH_3. Their properties are also similar.

Uranium hydride, UH_3, is technically important. It is prepared by reacting uranium metal with hydrogen at 250° – 300°C.

$$2U + 3H_2 = 2UH_3 \qquad \Delta H^\circ = -129 \text{ kJ mol}^{-1}.$$

It is a black pyrophoric powder which decomposes at higher temperatures to give the finely divided metal. This makes UH_3 a suitable starting material for the preparation of uranium compounds:

$$UH_3 + \begin{cases} \xrightarrow{Cl,\ 200^\circ} UCl_4 \\ \xrightarrow{H_2O,\ 350^\circ} UO_2 \\ \xrightarrow{H_2S,\ 450^\circ} US_2 \\ \xrightarrow{HF,\ 400^\circ} UF_4 \\ \xrightarrow{HCl,\ 300^\circ} UCl_3. \end{cases}$$

Uranium hydride is widely used in preference to the metal itself in the preparation of uranium compounds. It is also used in the purification of hydrogen and deuterium gas.

17.3.5 Hydrogen Bridge Bonds

The most familiar example of a hydrogen bridge bond, i.e. an atom of hydrogen acting as a bridge between two atoms, is provided by the boron hydrides. Let us first consider the simplest boron hydride, diborane, B_2H_6. Twelve valence electrons are insufficient to account for normal two-center, two-electron covalent bonds between all the atoms. An approximate description of the bonding is obtained by assuming that both boron atoms are sp^3 hybridized. Each boron forms two normal σ-bonds with two terminal hydrogen atoms on each side. Each boron now participates in two BHB hydrogen bridge bonds. Each bridge bond is formed by (i) one 1s a.o. of the hydrogen and (ii) two sp^3-hybrid orbital from the boron atoms, one from each. The three atomic orbitals give rise to three molecular orbitals, one bonding, one nonbonding and one antibonding. For each bridge-bond, there are two electrons, one from the hydrogen and one from either of the boron atoms. These two electrons enter the lowest energy bonding m.o. (Fig. 17.8).

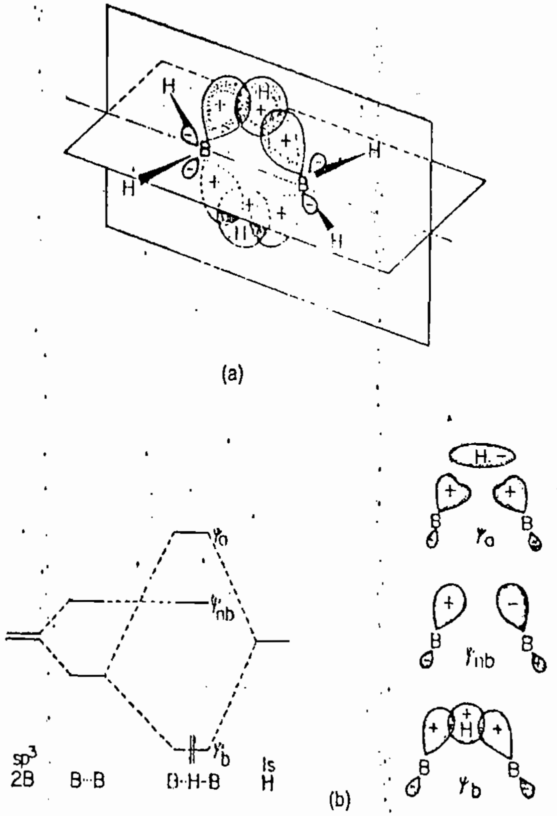
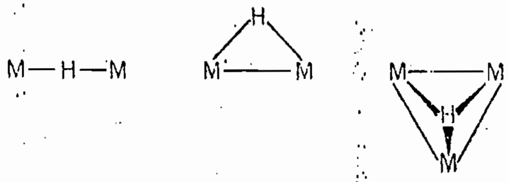


Fig. 17.8. (a) The hydrogen bridge bond in B_2H_6. **(b)** The corresponding M.O. diagram for one B–H–B system.

The higher boron hydrides contain similar B – H – B bridges together with other multicenter bonds (see Gr III).

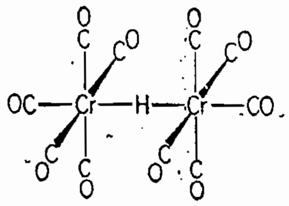
Bridging hydrogen atoms have also been well established in bi- and polynuclear carbonyl hydrides by direct and accurate neutron diffraction studies. Even triply-bridging hydrogen atoms have also been characterised in some cases.

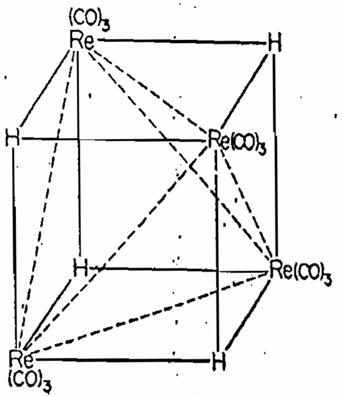
The following representative forms of hydrogen bridge bond have been established:



The existence of a strictly linear and symmetrical M – H – M bridge is doubtful.

Examples of some of the other bridge types are given below:





The last example of a triply bridging hydrogen is a metal cluster. Similar other examples are also known (a few more examples in p. 103).

The exact mode of bonding and structural role of the hydrogen atom in such bridge bonds are not fully understood. In many cases such bridgebonds may be looked upon as "protonated metal-metal bonds" and may be treated in the same manner as the 3c-2e B – H – B bond.

17.3.6 The Hydrogen Bond

The hydrogen bond (see chapter 7) is generally represented as A – H .. B where A is a sufficiently electronegative element to cause acidic nature on the hydrogen and B has sufficient electron density to act as a base to this hydrogen. Such interaction is strongest when both A and B belong to the first row of the periodic table. F, N and O form prominent H-bonds as both A and B; weaker H-bonds are formed when A is carbon or a second row element (P, S, Cl, or even Br, I). Carbon never acts as B (other than in certain π-electron system). Cl, Br or I are less efficient in the role of B unless negatively charged. S and P also participate weakly in the role of B. Enhancement of the electronegativity of atom A by other substituents will also give stronger H-bonds. Thus bond strength increases from aliphatic alcohols to phenols, from NH_4^+ to substituted ammonium ions (not quaternery) and from methyl chloride to methylene chloride to chloroform. The effect of size is also important, as pointed out for HCl vs. NH_3 (p. 169).

Evidence

As already mentioned (p. 170, Ch.-7), information regarding the existence of H-bond is obtained from IR and Raman spectroscopy, proton nmr spectroscopy and neutron or X-ray diffraction. In vibrational spectroscopy, an A–H..B hydrogen bond is marked primarily by a significant drop in the A–H stretching frequency (See Exercise, Q. 10). Changes are also observed in the breadth and intensity of the lines, A–H bending mode etc.

Effects

The effects of hydrogen bonding on different physical properties of substances are already well-known: they range from melting and boiling points, viscosity, solubility, miscibility to the existence of azeotropes, or even sensitivity of chromatographic separation. The influence of H-bonding on the electrical properties of some solids and liquids is also noteworthy. The high electrical conductance of H^+ and OH^- ions in aqueous solutions is associated with rapid formation and rupture of H-bonds between neighbouring water molecules. The dielectric constants of H-bonded liquids are also unusually large owing to the orienting effect of the H-bonds—the molecular dipoles reinforce one another rather than cancelling each other due to random thermal motion. A permanent electric polarization arising from ordered H-bonds is found to operate in some ferroelectric crystals*.

Ferro-electrics

Thus, in crystalline KH_2PO_4, each tetrahedral $[O_2P(OH)_2]^-$ unit is joined to four other $[O_2P(OH)_2]^-$ units by hydrogen bonds. Two short O – H bonds and two long O .. H bonds are present around each PO_4 group. Below 121K, all the short O – H bonds are on the same side of the PO_4 groups. By appropriate application of an electric field, the polarization of the hydrogen bonds can be reversed (Fig. 17.9). This spontaneous and reversible electric polarization gives rise to the ferroelectric behaviour. Above 121K, thermal agitation breaks down the ordering due to H-bonds and the crystal is said to become para-electric.

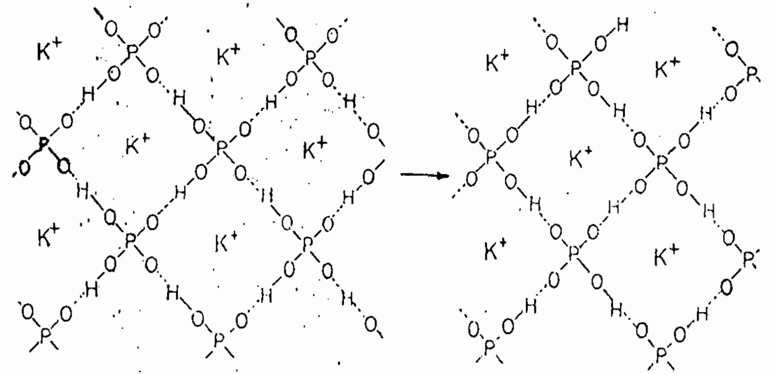


Fig. 17.9. Change in the environment of H-bonds in crystalline KH_2PO_4.

Ferroelectrics have many practical applications in electronic industry, e.g. as miniature ceramic capacitors and in modulating and deflecting laser beams. Ferroelectrics are also piezoelectrics (acquire or alter an electric polarization under external mechanical stress and vice versa) and hence can convert mechanical pulses into electrical ones and vice versa. Hence their use in ultrasonic generators, microphones, frequency controllers and in computer technology.

In recent years, experimental values of ΔG, ΔH and ΔS for hydrogen bond formation have been obtained. These have been supplemented by quantum-mechanical calculations. The values obtained are, however, susceptible to large uncertainties. Some typical bond dissociation enthalpies are given in Table 17.11.

The strength of H-bonds is greatly increased in cases of ion-molecule associations. Besides the $F - H .. F^-$ mentioned above, some values are (kJ mol^{-1}) $Cl - H .. Cl^-(g)$ 100; $HOH .. F^-(g)$ 96; $H_3OH^+ .. OH_2(g)$ 151; $HOH .. Cl^-(g)$ 55. In general, H bonds of energy less than 25 kJ mol^{-1} are classified as weak; those in the range 25-35 kJ mol^{-1} as medium and those above are called strong. The $[F - H - F]^-$ ion and the $[HCO_2H .. F]^-$ systems exceed any other known system in H-bond energy: HF_2^- calculated 220; $HCO_2H .. F^-$ calculated 250 kJ mol^{-1}. The weakly hydrogen bonded $[HCl_2]^-$ ion forms unstable salts with large cations (e.g. Cs^+).

Much theoretical work is being carried out on the nature of the hydrogen bond. It appears that electrostatic contributions predominate, among others,

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* A ferroelectric crystal has an electric dipole moment even in the absence of an external electric field. The centers of positive and negative charges in such crystals do not coincide and the dipole moment can be very high due to presence of a stable permanent electric polarization. Such polarization may arise from (a) ordering by H-bonding, as in KH_2PO_4 and KH_2AsO_4 or (b) a displacement of one sublattice with respect to another, as in barium titanate $BaTiO_3$ and potassium niobate $KNbO_3$.

TABLE 17.11

Energies of some common hydrogen bond
($-\Delta H$, kJ mol^{-1}).

Type of bond	System	$-\Delta H$, kJ mol^{-1}
F – H .. F	HF (g)	29
	KHF_2	150
F – H .. O	HF + CH_3COCH_3	46
O – H .. O	$(HCOOH)_2$	30
	H_2O(g)	22
	H_2O (s)	21
N – H .. O	$CH_3CONHCH_3$ (in CCl_4)	16
N – H .. N	NH_3 (g)	17
C – H .. O	$CHCl_3$ + CH_3COCH_3	4
C – H .. N	HCN(g)	16
S – H .. S	H_2S(g)	7

particularly for weak bonds; but as the bond becomes stronger, effects of covalency become gradually important. The formation of a 3-center 4-electron m.o. for the symmetrical F – H – F$^-$ ion is probably an extreme.

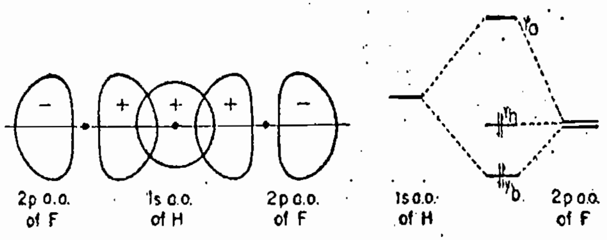


Fig. 17.10. M.O. description of symmetrical H-bond in HF_2^- ion.

This may be rationalized and extended by the HOMO – LUMO interaction principle (......). In a typical A – H .. B bond, the HOMO of the donor (B) is often occupied by an sp^n hybridized lone pair (or the π electron density, in $>C=O$ for example). The LUMO must be the AH σ^* m.o. The donor HOMO overlaps with both the bonding and antibonding mo's on AH. This stabilizes the lowest energy orbital but destabilizes the highest energy orbital. If the two effects were equal, no net bonding would result. But the presence of the σ^* m.o. of the A – H gives a net stabilization of the donor electron pair. Greater the electronegativity of A, the closer is σ_{AH} to A, and less is its overlap with the donor orbital; conversely, this leads to a better overlap between σ^*_{AH} and the donor HOMO, and hence, better stabilization of the donor electron pair. Also higher electronegativity on A makes both σ_{AH} and σ^*_{AH} lower in energy, ultimately increasing the "gap" between the donor HOMO and σ_{AH} while the separation with the σ^*_{AH} is effectively reduced. Thus the increase in H-bond strength with increasing electronegativity of A is readily explained. This also explains why *self-association among alcohols decrease as the electronegativity of the alkyl group increases*. Here the donor atom is the oxygen atom of a neighbouring alcohol molecule in which the oxygen is directly bound to the substituent. As the substituent becomes more electronegative, the oxygen lone pairs are stabilized i.e. the HOMO is lowered in energy. This leads to poorer overlap with σ^*_{AH}, where A – H is another alcohol molecule.

Self-association among alcohols

A fairly satisfactory value of the dissociation enthalpy of H-bonds may be calculated from the following considerations (Allen, L. C., 1975). The energy of a hydrogen bond A – H .. B depends on (1) the bond dipole moment, μ_{A-H}. This is an indication of the effectiveness of the screening of the proton. (2) The ability of the donor B to donate electrons. This may be related to ΔI, the difference between the ionization energy of B and the noble gas atom in its row. (3) The internuclear separation R between A and B. This is related to the extension of the hydrogen-bonding lone pair. The energy E required to break the H-bond A – H .. B is then given by

$$E = K \cdot \mu_{A-H}\, \Delta I/R$$

where K is an energy scale factor. The values are in good agreement with those obtained theoretically.

Note: The hydrogen bond differs from the hydrogen-bridge bond in that it is not electron-deficient and the nature of interaction is mainly ion-dipole type.

It is not difficult to understand **why other atoms cannot replace hydrogen in the hydrogen bond.** For greatest electrostatic interaction, the participants should approach as close together as possible. Hydrogen has two favourable points in this respect: (i) its small size and (ii) absence of inner electron shells. This is why in a hydrogen bond A – H....B, A and B can approach very close to each other without involving large repulsion. If we attempt to replace H by a larger electropositive atom, say Na, the presence of an inner L shell would cause enough repulsion to offset the net binding.

17.3.7. Ice, Water, Hydrates and Clathrates

The physical and chemical properties of water will be described in connection with oxygen compounds (Group VI-B). Here we give a brief survey of the structural features of ice, water and the hydrates as they essentially involve H-bonds.

Structure of Ice

The structures of both ice and water are complex and undecided in many respect. At least nine structural forms of ice have been established, each stable over a certain range of temperature and pressure. The ordinary form of ice obtained on freezing water, at 0°C and 1 atm pressure (I_h) consists of puckered hexagons, and is structurally similar to Wurtzite. Thus, ice is miscible in all proportions with NH_4F which also has a wurtzite structure. Each H_2O unit is surrounded tetrahedrally by the oxygen atoms of four other H_2O molecules—unsymmetrical hydrogen bonds extend over the entire structure. The O – H .. O distances are: O – H : 1.01A°, H .. O : 1.74A°. This O – H distance is slightly greater than that in water vapour (0.96A°). Each oxygen has two near and two distant neighbours (recall Fig. 7.43, p. 169). Theoretical consideration of the probable arrangements at absolute zero lead to an estimated zero point entropy of 3.4 J mol^{-1} deg^{-1}, which is in excellent agreement with experiment. This rather open structure accounts for the low density (0.92) of ice and its anomalous expansion. At very low temperatures (– 120°) a cubic form, I_c has been observed. Both I_c and I_h forms can exist upto about 2000 atm pressure at – 50°C. Above this pressure, the density of ice increases and different structural forms are attained. Four structural forms are observed between 2000 ÷ 6000 atm. pressure below 0°C (density ~ 1.2 g. cm^{-3}). The sixth form of ice ranges from ~6000 to ~18000 atm pressure and its stability extends to about 80°C. (density 1.3 g cm^{-3}). At still higher pressures, three forms are known, (density ~ 1.5 g cm^{-3}). One form is vitreous at – 160°C or below.

Structure of liquid water.

The structure of liquid water is still controversial inspite of extensive studies, both theoretical and experimental, for over the last fifty years. In a small region, the structure is no doubt ordered due to extensive hydrogen bonds. But the overall structure has the usual disorder of a liquid. An easy-to-grasp model describes the structure as being closely similar to that of ordinary ice (I_h); but the short range ordered regions are supposed to undergo continuous destruction and reformation—quite appropriately described as "flickering clusters". The higher density of water in comparison to ice is explained by assuming the presence of interstitial water molecules, enough to more than offset the expansion of the network of ice I_h.

Crystalline solids containing water molecules are called hydrates. They are usually formed by metal ions, but hydrates of organic substances are also known.

Hydrates

Anion-water in $CuSO_4, 5H_2O$

Some of these water molecules may establish extensive ion-dipole interaction by coordination from the oxygen to the cation, in complexes like $[Be(OH_2)_4]^{2+}$, $[Mg(OH_2)_6]^{2+}$ and others. In addition, these water molecules almost always undergo extensive hydrogen bonding to the anion or other water molecules. The lattice of $CuSO_4$, $5H_2O$ contain a water molecule that links two SO_4^{2-} ions by H-bonds—it is sometimes referred to as *anion water*. In Fig. 17.10, we find that four water molecules are coordinated to each Cu^{2+} ion; the remaining two octahedral sites of the Cu^{2+} ion are occupied by O-atoms from SO_4^{2-}. The fifth water molecule (shown in bold) is not bound to Cu. It connects two SO_4 groups on neighbouring Cu-ions by H-bonds. At the same time, the oxygen of this water molecule forms two more H-bonds with two cis-H_2O molecules on one of the Cu^{2+} ions. This fifth water molecule thus links the structural units into a continuous lattice, and is held much more firmly than the others. Application of heat first results in the loss of (i) two co-ordinated water molecules not linked to the anion water, and then (ii) the rest two of the co-ordinated water molecules. The last water molecule (anion water) can only be removed by heating above 350°C (or 250°C in vacuo). The first four water molecules can also be removed over phosphorus pentoxide. $NiSO_4$, $7H_2O$ and $ZnSO_4$, $7H_2O$ probably also contain a single mole of anion water.

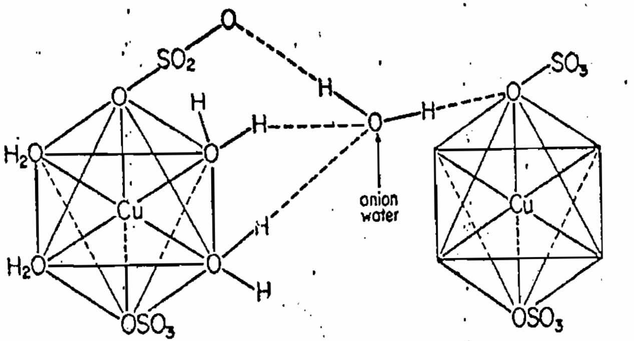


Fig. 17.11. Structure of Copper Sulfate pentahydrate.

Sometimes water molecules fill the voids in lattices formed by ions of disproportionate size. In $FeSiF_6$, $6H_2O$; Na_4XeO_6, $8H_2O$; and $H_3[PW_{12}O_{40}]$, $29H_2O$, the water molecules probably help in minimizing repulsion between the large, highly charged anions. The role of hydration in matching the sizes of the packing units of a crystal lattice is nicely demonstrated by the alkali metal halides:

Anhydrous	**Hydrates**
LiF, NaF	KF, $2H_2O$; RbF, 3/2 H_2O; CsF, 3/2 H_2O or 2/3 H_2O.
KCl, RbCl, CsCl	LiCl, nH_2O (n = 1, 2, 3, 5); NaCl, $2H_2O$.

Clathrates

Water also forms a number of enclosure compounds or "*clathrates*". In clathrates, one component (host) crystallizes with a very open structure containing cavities; these act as trap for other atoms or molecules (guest). Crystallization of solutions of *p*-quinol, $C_6H_4(OH)_2$, in presence of Xe, Ar or Kr at 10 – 40 atm pressure produce long crystals in which the noble gases are entrapped. The crystals are stable at room temperature. Quinol can also form clathrates with N_2, O_2, CO, CH_4, SO_2, HCl, H_2S and many other molecules.

Gas hydrates

The clathrate compounds formed by water (as host) are called "*gas hydrates*". Polyhedral frameworks, ith more than one size of cavities, are formed by unit cells containing (i) 12 (ii) 46 or (iii) 136 molecules of water.

(i) There is a cubic array of 24-cornered cavities. Each H_2O is common to two adjacent cavities. HPF_6, $6H_2O$ is an example of this type.

(ii) 46 molecules of water form six medium-size and two smaller cavities. If all holes are filled, 46/8 H_2O are available per guest molecules, as in high-pressure clathrates with Ar, Kr, CH_4, SO_2 etc. as guests. Filling of the larger cavities alone gives ~ 46/6 H_2O per guest molecule, e.g. in Cl_2, 7.3 H_2O.

(iii) With 136 water molecules, there are eight large and sixteen smaller cavities. Only the former are filled in $CHCl_3$, $17H_2O$ (136/8) and CHI_3. $7H_2O$. These are also called liquid hydrates as they are formed in the presence of larger molecules of liquids like $CHCl_3$, C_2H_5Cl etc. The anesthetic action of chloroform is believed to take place via similar clathrate formation in brain tissue.

When tetraalkyl ammonium or sulfonium salts crystallize from aqueous solutions, a large number of water molecules are present in the crystals, e.g. $[(n\text{-}C_4H_9)_3S]F$, $20H_2O$. or $[N(i\text{-}C_5H_{11})_4]F$, $38H_2O$. The structure of these crystals (*Salt-hydrates*) are similar to the gas or liquid hydrates but here the framework contains, in addition to H_2O, other species which can be H-bonded to the network; as for example the F^- ion or the O-atoms of benzoate ion etc.

17.3.8. Cluster and encapsulated hydrides

We have already encountered some examples of cluster polyhydrido compounds in connection with hydrogen bridge bonds. Certain cluster compounds also contain, in addition to normal and bridging bonds, hydrogen atoms encapsulated in a sufficiently large metal polyhedron of 10 – 20 atoms. The rhodium cluster anion, $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 2, 3) is an example. The size of the holes in the cluster is less than the atomic radius of H (0.37 A°) and hence it must be protonic in nature.

17.3.9. Co-ordination Compounds of Hydrogen

Both atomic and molecular hydrogen form several interesting complexes with transition metals. The first compounds of this category were prepared in 1930 (Hieber and Blanchard)—the carbonyl hydrides or hydrido carbonyls $HCo(CO)_4$ and $H_2Fe(CO)_4$. Since the late 1950s, a large number of such compounds have been prepared. The nature of the metal-hydrogen bond has been explored only recently, mainly by IR and proton magnetic resonance studies. The M—H stretching frequency usually lies in the range 1600—2250 cm^{-1}.

These complexes are usually formed in presence of other ligands having both σ-donor and π-acceptor properties like CO, PR_3, cyclopentadiene etc. Some cyano and nitrosyl containing complexes are also known. Typical examples of simple hydride complexes are $K_3[CoH(CN)_5]$, $PtHCl(PEt_3)_2$, $HMn(CO)_5$ etc. $[RhH(NH_3)_5]^{2+}$ is a rare example of a stable hydride complex with a non-π-bonding ligand. Complexes with hydrogen bridges are also known: $[Cr_2(CO)_{10}H]^-$, linear and $[W_2(CO)_9HNO]$, bent. $Mo_2(H)_2(\mu\text{—}H)_2\text{—}(PMe_3)_6$ has both bridging (μ–) and non-bridging hydrogen. Besides, there are a number of polyhydridic complexes containing 3 to 9 H-atoms; Cp_2TaH_3 (C_p=cyclopentadienyl), $RuH_6(PR_3)_2$ etc. Homoleptic polyhydride anions like ReH_9^{2-} and FeH_6^{4-} have also been well characterized.

Several stable complex compounds of molecular H_2 have also been reported, e.g., in $Ru^{II}(H)_2(H_2)(PPh_3)_3$ both the H-atoms in the H_2 molecule are engaged in bouding to the metal (η^2—H_2 complex). These have been discussed in chapter 32.

The transition metal hydride complexes are generally prepared by the reduction of transition metal compounds in the presence of π-bonding ligands. $NaBH_4$, $LiAlH_4$, N_2H_4 and H_3PO_2 are typical reducing agents for the purpose.

$$C_5H_5Fe(CO)_2Cl \xrightarrow{NaBH_4} C_5H_5Fe(CO)_2H \qquad \text{in tetrahydrofuran}$$

$$trans\text{-}Pt(PR_3)_2Cl_2 \xrightarrow{LiAlH_4} trans\text{-}Pt(PR_3)_2(H)Cl \qquad ,,$$

The transition metal-hydrogen complexes are important as catalysts in hydrogenation and cracking processes. Thus, $K_3[CoH(CN)_5]$ is a homogeneous hydrogenation catalyst for the conversion of alkenes to alkynes. Several other examples will be found in connection with the chemistry of the transition metals (carbonyls, catalysts).

17.3.10 Agostic interactions (M···H—C and others)

A coordinatively unsaturated metal (usually having fewer than 18 valence shell electrons) may sometimes interact with a nearby C—H bond to partly compensate for its unsaturation. Such C—H···M interactions have been termed *agostic* (Greek "to clasp"). In such interaction the C—H bond practically "supplies" electrons to the metal and raises the formal electroncount of the latter. The agostic interaction thus differs from a classical hydrogen bond of the $\overset{\delta-}{X}—\overset{\delta+}{H}\cdots\overset{\delta-}{Y}$ type where the X—H part "seeks" electrons from the electronegative atom Y. Such H-bonds were described by 3*c*—4*e* bonding; an agostic interaction, on the other hand, is best interpreted as a 3*c*—2*e* bonding. Several *d*-block and some *f*-block elements are known to exhibit such interactions. Other X—H···M agostic interactions are also known where X may be Si, Sn, B, P or S. Usually such interactions are marked by appreciable distortion of ligand geometry to place the hydrogen close to the metal.

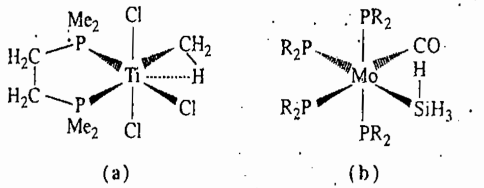


Fig. 17.12 (a) C—H···Ti and (b) Si—H···Mo agostic interactions. The latter is indicative of an η^2–SiH_4 coordination.

Though these agostic interactions are mostly weak and dynamic at room temperature, some are slow enough to be observable on an NMR time scale.

SUMMARY

Introduction. Hydrogen is the most abundant element in the universe and the third most abundant on the earth's surface. Terrestrial hydrogen contains ~0.0156% of deuterium (^2_1H) and trace (1 in 10^{17}) tritium (^3_1H). The last isotope is formed in the upper atmosphere by nuclear reactions induced by cosmic rays; it is β-active, $t_{1/2}$ = 12.4y.

Among the various ionized forms of hydrogen, H^+ (proton), H^- (hydride ion) H_2^+ (hydrogen molecule ion) and H_3^+ (tri-hydrogen cation) are well characterized. Due to high energy requirement in its formation and its extremely small size, the bare proton exists only in gas discharge tubes. Solvated protons exist in solution and in crystals. Hydride ions are present in the salt-like hydrides. H_2^+ and H_3^+ have transient existence in discharge tubes.

Properties and Bonding: Ordinarily hydrogen is not very reactive due to its high bond dissociation energy. It can form a wide variety of compounds by (i) loss of the valence electron to form a proton, H^+, which is stabilized by solvation, (ii) gain of an electron to form the hydride ion (H^-)—present in the hydrides of alkali and alkaline earth metals, (iii) formation of an electron pair bond, (iv) formaion of hydrogen bridge bonds involving 3-center 2-electron molecular orbitals. Hydrogen bonding and formation of different non-stoichiometric hydrides and coordination compounds also present important aspects of hydrogen chemistry.

All the protons in water are undergoing rapid migration from one oxygen atom to another. Acid-base neutralization processes in water involve the diffusion of a proton to a base (both solvated) followed by rapid transfer of the proton. The rates of such diffusion controlled reactions are very high, with k ≈ 10^{-11}.

In nonaqueous media, and in concentrated aqueous solutions (e.g., those not covered by the pH scale 0–14, an acidity function H_0, the Hammett acidity function has been defined to express the protonation equilibrium of an indicator base : $B + H^+ \rightleftharpoons BH$; By definition, $H_0 = pK_{BH+} - \log\,[BH^+]/[B]$.

In dilute aqueous solution of a protonic acid, H_0 becomes synonymous with pH. The more negative the value of H_0, the greater the strength of the acid that transfers its proton to the base B.

Acid media with $-H_0$ values greater than ~ 6 are often referred to as superacids. $H_2S_2O_7$ and HSO_3F ($-H_0 \simeq 15$ for both) are examples of superacids. The addition of a Lewis acid like SbF_5, BF_3, NbF_5 etc. to HF and HSO_3F remarkably raises the $-H_0$ values to 21 or higher by equilibria of the type: $2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^-$. Such superacid systems provide opportunity for the study of many cations which are unstable in less acidic solutions, e.g. $(CH_3)_3C^+$, I_2^+, S_{16}^{2+}, Se_8^{2+} etc.

The Saline hydrides are formed by the reaction of hydrogen on the metals (alkali and alkaline earth) at 200 – 700°, better in dispersion in an inert solvent like tetrahydrofuran. They are white crystalline solids containing the H^- ion. $r_{H^-} \simeq r_{F^-}$, but the H^- ion undergoes easy distortion owing to its loosely held charge cloud. The hydrides combine readily with protonic substances (H_2O, NH_3) to form H_2. They have uses in synthetic organic chemistry.

Binary hydrogen compounds of predominant covalent character are broadly classed as covalent hydrides, irrespective of the polarity of the hydrogen. The hydrides become more acidic as one proceeds from left to right in the periodic table. Stability decreases down any group owing to bond weakening.

The transition metals form a large number of mainly nonstoichiometric hydrides which are not products of mere absorption. The hydrides of Ti, Zr, Hf, the lanthanides and of U are important.

Hydrogen bridge bonds are formed when an atom of hydrogen acts a bridge between two (or more) atoms. The structure of electrondeficient B_2H_6 and other boranes was explained with the help of BHB bridge bonds, justified by a 3 center 2 electron m.o. description. The same scheme may he extended to numerous hydrogen bridge bonds in transition metal complexes.

The hydrogen bond is represented as A – H . . B where A is a sufficiently electronegative element to cause acidic nature on the hydrogen, and B has sufficient electron density to act as a base to this hydrogen. Such interaction is strongest when both A and B belong to the first row of the periodic table. The structure of ice and water involve extensive hydrogen bonding.

Crystalline hydrates of many compounds contain water molecules coordinated to the cation by strong ion-dipole interaction. In addition, these water molecules are hydrogen bonded to the anion or other water molecules. $CuSO_4$, $5H_2O$ contains one water molecule strongly hydrogen bonded to a SO_4^{2-} ion (anion water).

EXERCISE

1. *What are the peculiarities in the chemistry of hydrogen?*
2. *Mention two important factors which may be held responsible for the variety of chemical combinations undergone by hydrogen.*
3. *Justify the chemical resemblances of hydrogen with the elements of group I, IV and VII.*
4. *Discuss the potentiality of liquid hydrogen as an alternative energy source.*
5. *What are the principles used in the large scale production of (i) H_2 (ii) D_2O?*
6. *How would you prepare HD? HDO?*
7. *What are ortho- and para-hydrogen? How does their relative stability vary with temperature? Explain why the ortho-para stability sequence is reversed in the case of D_2.*
8. *What are the uses of D_2O and T_2?*
9. *Starting from D_2O and ordinary chemicals, how would you prepare (i) C_2D_2, (ii) CD_4, (iii) D_3PO_4, (iv) ND_3, and (v) PD_3?*
10. *Explain:*
    - (*a*) *The O – H stretching frequency in ice is lower than that in water vapour* (3250 cm^{-1} *vs.* 3750 cm^{-1}).
    - (*b*) *The IR spectrum of a* 0.01*M solution of tert-butanol in* CCl_4 *has a sharp peak at* 3610 cm^{-1}; *the spectrum of a similar* 1.0*M solution shows a broad peak centered around* 3325 cm^{-1}.
    - (*c*) *Hydrogen does not occur in the atmosphere of the earth, but it occurs in the atmosphere of heavier planets like the Jupiter.*
    - (*d*) *Caesium chloride, but not lithium chloride, absorbs HCl at low temperatures.* [See p. 99].
    - (*e*) *Boiling point of* C_2H_5OH *is* 78°C, *while that of* C_2H_5SH *is* 37°C.
    - (*f*) *Solid* NH_4F *is miscible with ice in all proportions.*

(g) ZnH_2 *decomposes slowly at room temperature.* CdH_2 *decomposes rapidly at* 0°C. HgH_2 *decomposes at* -125°C.

(h) *Certain electropositive metals do not liberate* H_2 *from water.*

(i) *The gas phase acidity sequence of* CF_3COOH *and* CCl_3COOH *is opposite to that in aqueous solution.*

(j) *LiF and NaF crystallize as the anhydrous salt from their aqueous solutions but LiCl and NaCl separate as* $LiCl, 2H_2O$ *or* $NaCl, 2H_2O$. *The converse is true for KF and KCl.*

(k) *Chlorine forms a crystalline hydrate of composition* Cl_2, $7.3H_2O$.

(l) $CuSO_4$, $5H_2O$ *can be completely dehydrated only above* 250°C.

(m) *The thermal stability of the hydrides is generally less than the corresponding fluorides.*

(n) *The radius of the* H^- *ion is* 1.36A° *in LiH and* 1.52 A° *in CsH.*

(o) *The covalent radius of hydrogen decreases in the order* $H_2 > CH_4 > SiH_4 > NH_3 > H_2O$.

11. *What happens when*
    (i) *Calcium hydride is reacted with aqueous sodium carbonate solution?*
    (ii) *Atomic hydrogen reacts with oxygen?*
    (iii) *Powdered silicon is boiled with aqueous caustic soda solution?*
    (iv) *A mixture of methane and steam is passed over a heated Ni-catalyst?*
    (v) *Calcium hydride is heated with sodium chloride?*
    (vi) *Lithium hydride is reacted with anhydrous aluminium chloride?*
    (vii) *Silicon tetrachloride is reduced with lithium tetrahydroaluminate?*

12. *Why is it that bonds similar to the hydrogen bond are not formed by other electropositive elements?*

13. *Which will be the strongest protonic acid in each horizontal group? The major factor involved is given in parenthesis.*

(a) SnH_4, SbH_3, H_2Te	*(change in EA of central atom)*
(b) NH_3, PH_3, SbH_3	*(X – H bond energy)*
(c) H_5IO_6, H_6TeO_6, HIO	*(Pauling's rule)*
(d) $Fe(H_2O)_6^{3+}, Fe(H_2O)_6^{2+}, H_2O$	*(charge on central atom).*
(e) $Na(H_2O)_x^+, K(H_2O)_x^+$	*(size and polarizing power of cation)*

14. *Give the approximate* pK_a *values for the following acids:*
    (o) H_3PO_3, (b) HNO_3, (c) $HClO_4$, (d) H_5IO_6.

15. *The heat of neutralization of* $H^+(aq)$ *and* $OH^-(aq)$ *in dilute aqueous solution is* ~ 56.5 *kJ mol*$^{-1}$ *as* $\mu \to 0$. *In concentrated NaCl solution, this is appreciably higher, e.g.* ~ 85.5 *kJ mol*$^{-1}$ *at* $\mu = 16$. *Explain.* (μ = *ionic strength*)

    [*Hint: In concentrated salt solutions, the ions are strongly hydrated by water molecules. Hence the average number of water molecules bound to the proton is smaller—less energy is required for the release of a proton from* $H^+(H_2O)_x$. *Same reasoning for* $OH^-(H_2O)_x$.]

16. *How do you expect the hydrogen bond strength to vary, at constant temperature, among* $H_2O(l)$, $D_2O(l)$ and $T_2O(l)$?

    [**Hint:** *Think Allen's empirical relation for hydrogen-bond energy. R increases from H → D → T.*

CHAPTER EIGHTEEN

THE ALKALI METALS

Li, Na, K, Rb, Cs

OBJECTIVES

1. General Considerations.
    - Abundance & Occurrence [18.1.1]
    - General Trend in Properties [18.1.2]
    - Solutions in Liquid Ammonia [18.1.3]
2. Isolation and Use.
    - Isolation [18.2.1—18.2.3]
    - Use [18.2.4]
3. Principal Compounds.
    - Oxides [18.3.1]
    - Halides [18.3.2]
    - Hydrides, Nitrides and Sulphides [18.3.3]
    - Salts of oxoacids [18.3.4]
    - Organometallic Compounds [18.3.5]
    - Coordination Compounds [18.3.6]
    - The "alkalide" ions [18.3.7]

18

18.1 GENERAL CONSIDERATIONS

Consistent with their ns^1 outer electron configuration, the alkali metals occupy group IA in the periodic table. They provide an important area of systematic study in inorganic chemistry—their physical and chemical properties can be readily understood in terms of their simple outer electron configuration. Some of these elements, specially sodium and potassium, are extensively involved in our life processes. Many of their compounds have been used from the early days of human civilization. Lithium, sodium and potassium have wide industrial applications in the present-day world.

In this section we shall discuss (i) the abundance and occurrence of the elements, and (ii) their general properties and periodic trends.

18.1.1 Abundance and Occurrence

Lithium: Total abundance: 65 ppm. In crustal rocks: 18 ppm (comparable to Ga, 18 ppm and Nb, 20 ppm). ^{6}Li:~7 per cent; ^{7}Li:~93 per cent.

The very low terrestrial as well as cosmic abundance of lithium compared to oher alkali metals may be attributed to its small nuclear charge and consequent low potential barrier for proton or alpha-capture reactions. This might have facilitated thermonuclear reactions to produce heavier elements (also true for Be and B).

Li occurs in aluminosilicate minerals: Spodumene $LiAl(SiO_3)_2$ (2.5—3% Li) and Lepidolite LiF, LiOH, $Al_2(SiO_3)_3$ (3.8—5.6% Li). Large deposits of spodumene occur in the USA, Canada, Brazil, Argentina, Soviet Union, Spain and the Congo.

Li also occurs in many springs and some readioactive minerals (carnotite). Ashes of plants, particularly tobacco; milk and blood are also known to contain lithium.

Why Li does not occur with Na or K?

Lithium forms independent minerals because Li^+ is too small to replace the more abundant Na^+ or K^+ in their minerals. Rather it occurs in the alumino silicate minerals along with magnesium. These minerals are expected to separate in the very late stage of crystallization of a magma—i.e., they belong to the pegmatites. (see p. 43).

The nearly dry and alkaline (pH=9.5) Searles lake in California (Mohave Desert) is also an important source of lithium.

Sodium: Total abundance: 28,300 ppm; 22,700 ppm in the earth's crust. Fifth most abundant metal, after Al, Fe, Ca and Mg. It has only one natural isotope, ^{23}Na.

It occurs principally as rock-salt, NaCl, and also as carbonate (trona), nitrate (salt peter), borate (borax) etc. It is likely that the metal (with potassium) has been leached out from silicate rocks by weathering. The vast deposits of rock-salt probably resulted from evaporation of ancient seas. The Cheshire salt-field in UK occupies an area of 60 km×24 km and is nearly 400 m thick (>10^{11} tonnes!) Similar deposits are present in Saskachewan, Canada and Carlsbad, New Mexico. Besides rock-salt, natural brines and oceanic waters contain large amount of sodium chloride. The origin of the nitrates is also interesting (p. 128).

Plant and animal organisms contain sodium compounds—in animals it is mainly present as sodium chloride. Na^+ ions constitute about 0.3 per cent of human blood, 0.6 per cent of bone and 0.6 to 1.5 per cent of our body muscles.

Potassium: Total abundance 25,900 ppm; in crustal rocks—18,400 ppm. Of the three natural isotopes ^{39}K, ^{40}K and ^{41}K, ^{40}K (0.01 per cent) is radioactive (β^-; $t_{1/2}=1.3\times10^9$y).

The important minerals are: Sylvite KCl; Sylvinite KCl, NaCl; Carnallite, KCl, $MgCl_2$, $6H_2O$. Like Na, potassium salts are also leached out from silicate minerals by the action of weather. Soluble minerals of potassium are generally (incorrectly though) referred to as potash. Massive deposits of potash resulting from evaporation of ancient seas have been found in many places like Stassfurt (Germany), North Yorkshire (UK), Canada and the USSR. Natural brines are also important sources of potassium (e.g., the Dead Sea, Jordan)

Note: Although the abundances of Na and K in the earth's crust are comparable, sodium is nearly 30 times as abundant as potassium in the oceans. We recall that these metals were leached from the alumino silicate rocks by weathering. The K-salts of large anions are less soluble than the Na-salts. Moreover, potassium is also preferentially absorbed by plants. *Abundance: Na vs K*

Potassium present in the ashes of plants and sea-weeds may be recovered to prepare potassium compounds.

Rubidium: Total abundance 310 ppm; crustal rocks 78 ppm (comparable to Ni, Cu, Zn). But there is no single Rb-containing mineral. Lepidolite contains 0—3.5% Rb_2O from which the metal is obtained as a by-product of lithium industry. ^{87}Rb (~28 per cent of natural rubidium) is β-active ($t_{1/2}$ 5.7×10^{10}y).

Cesium: Total abundance 7 ppm; crust 2.6 ppm. (similar to Br, U). One mineral is known—pollucite, $CsAl_2(SiO_3)_2.xH_2O$. But the metal is mainly obtained from lepidolite as a by-product.

Francium occurs in minute traces - its terrestrial abundance is estimated at 2×10^{-18} ppm. It results from the branched decay (1%) of ^{227}Ac. ^{223}Fr is β-active with $t_{1/2}=21.8$ min.

18.1.2 General Trend in Properties

The principal properties of the alkali metals are collected in Table 18.1. The nature of variation of some important properties along the group may be appreciated from Figs. 18.1(*a*, *b* and *c*).

TABLE 18.1: Major Properties of the Alkali Metals

		$_3$Li	$_{11}$Na	$_{19}$K	$_{37}$Rb	$_{55}$Cs
Density (g. cm^{-3})		0.53	0.97	0.87	1.53	1.87
Melting point (°C)		180.5	97.8	63.7	38.9	28.6
Boiling point (°C)		1325	883	756	688	690
Ionization Energy	1st	520.1	495.7	418.6	402.9	375.6
(kJ mol^{-1})	2nd	7296	4563	3069	2640	2260
Metallic radius (pm)		152	186	227	248	265
Ionic radius (pm) (Octahedral)		76	102	138	152	167
Hydrated radii (pm)		340	276	232	228	228
Heat of hydration of M^+(g); kJ mol^{-1}; —ve.		519	406	322	293	264
E° for $M^+(aq)+e \rightleftharpoons M(s)$		−3.02	−2.71	−2.92	−2.99	−3.02

The tables and graphs indicate that the changes in certain properties between lithium and sodium are relatively large. This is reflected in the general chemistry of the elements.

Elemental forms

The alkali metals are soft, low-melting, silvery-white metals—only cesium is golden yellow. They normally adopt a body-centered cubic structure. At low temperatures, lithium forms a hexagonal close-packed arrangement. Only the outer *ns* electrons of the metal atoms take part in metallic bonding—rendering the metals soft and low melting. Repulsive interactions due to non-bonding inner shell electrons increase from Li to Cs. This results in lower degree of cohesion from Li to Cs. Hence the decrease in hardness and melting point.

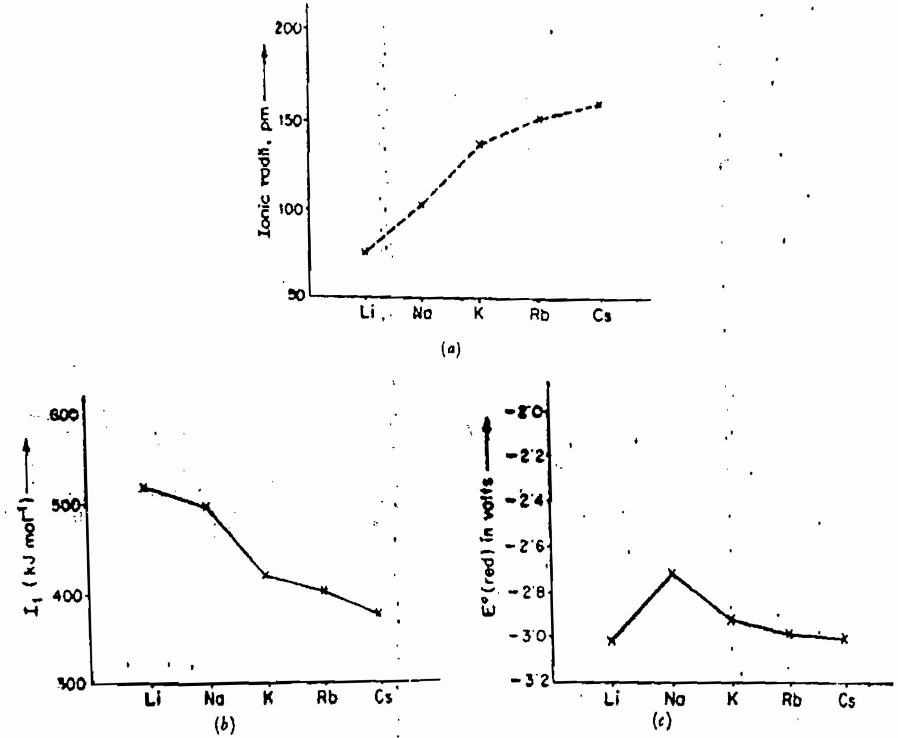


Fig. 18.1. The trend of variation of some physical properties of the alkali metals: (a) ionic radius (b) first ionization energy (c) E° (red).

Flame colorations

All the alkali metals give characteristic flame colorations due to easy excitation of outermost electrons: Li—crimson, Na—yellow, K—violet, Rb—red-violet, Cs—blue. This fact has led to the development of analytical methods for the precise estimation of these metals by flame photometry and atomic absorption spectroscopy.

Standard redox potential

The metals are highly electropositive, Li having the lowest $E°$(red) value. This is apparently "anomalous" as Li has the highest ionization energy among the alkali metals. As already explained earlier (9.2.7), the ionization energy is only one of the several factors contributing to the standard EMF of an element. Lithium owes its most electropositive character to its small size and very large hydration energy of the free gaseous Li^+ ion. The entropy change for the half-cell reaction of lithium is also much larger as the Li^+ ion disrupts the ordered arrangement of water molecules, and at the same time forms an well-ordered sheath of water molecules around it. The trend of electrode potential set by the alkali metals results from a delicate balance between the enthalpy and entropy effects.

Chemical reactivity

The large difference between the first and second ionization energy of the elements suggests that the preferred oxidation state of the alkali metals will be +1.

The first ionization energy of the metals is more than compensated by the lattice energy term for most ionic compounds, and hence the elements have their major chemistry in the form of M^+ ions. The presence of such ions in the solid compounds has been confirmed by X-ray studies (6.1). In solution also, the M^+ ions are largely stabilised by high solvation energies, as exemplified by the energies of hydration in aqueous solution (Table 18.1). The possibility of the formation of ionic compounds like $NaCl_2$ appears highly unlikely from the very high second ionization potentials (section 6.6.2).

Water

The reactivity of the alkali metals increases from lithium to cesium, except toward N_2. Thus, by water at 25°C lithium is attacked only slowly; sodium reacts vigorously, potassium inflames. Rubidium and cesium react with explosion. However, the slow reactivity of lithium is probably due to kinetic factors (p. 114).

Air

When burnt in air/oxygen, lithium forms Li_2O (+trace Li_2O_2), sodium gives principally Na_2O_2 while others give mainly the superoxides, MO_2.

Lithium reacts uniquely with N_2, slowly at room temperature and rapidly at 400°C, to give ruby-red crystalline Li_3N (see p. 126).

Lithium and sodium react with carbon on heating to form the acetylides Li_2C_2 and Na_2C_2. The other alkali metals give non-stoichiometric interstitial compounds.

The poor chemical reactivity of lithium is further illustrated by the fact that Li cannot replace the weakly acidic hydrogen in phenyl acetylene, $C_6H_5C \equiv CH$; the other alkali metals liberate hydrogen. Li and Na also react very feebly with liquid bromine, but the others do so violently.

The principal reaction-types may be summarised as in Table 18.2.

TABLE 18.2

Reaction	Note
1. $2M + X_2 = 2MX$	X=halogen
2. $2M + Y = M_2Y$	Y=O, S, Se, Te. Higher oxides and polysulfides are formed with heavier metals.
3. $6Li + N_2 = 2Li_3N$ (ruby-red)	Slowly at room temp. but rapidly at 400°C.
4. $3M + Z = M_3Z$	Z=P, As, Sb, Bi. Polyanions like $(Bi_9)^{4-}$ or $(Sb_5)^{3-}$ are formed by solutions of metals in liq.NH_3.
5. $2M + 2C = M_2C_2$	Particularly Li, Na. K, Rb and Cs form colored non-stoichiometric interstitial carbides with graphite (see graphitic compound)
5. $2M + H_2 = 2MH$	Ease decreasing from Li → Cs.
6. $M + H_2O = MOH + \frac{1}{2}H_2$	Violence increasing from Li → Cs.
7. $M + NH_3 = MNH_2 + \frac{1}{2}H_2$	NH_3(g) at high temp. or NH_3(l) plus catalyst.

The alkali metals form stable series of salts with different anions. They are usually high melting crystalline solids soluble in water—they conduct electricity in the molten state and in solution in polar solvents. Except lithium salts, they crystallize from aqueous solutions in the anhydrous state—the hydration energy is not sufficint to overcome the loss in lattice energy due to inclusion of the larger hydrated ions. Li^+, with its smallest size and highest ion-dipole interaction (hence hydration energy), form series of trihydrates $LiX.3H_2O$, X=Cl, Br, I, ClO_3, ClO_4, MnO_4, NO_3, BF_4. In most cases, the Li^+ ion is surrounded octahedrally by six water molecules—the octahedra share faces, forming chains (Fig. 18.2)

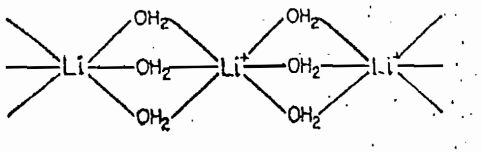


Fig 18.2. Hydration of Li^+ ion.

In alums, $M_2^I SO_4$, $M_2^{III}(SO_4)_3$, $24H_2O$ (M^I=alkali metal, M^{III}=a trivalent metal), each alkali metal is coordinated to six separate water molecules: $[M(H_2O)_6]^{3+}[Al(H_2O)_6]^{3+}(SO_4^{2-})_2$. Lithium does not form alums, probably because the small $Li(H_2O)_6^+$ is too small to form a stable lattice required for alum formation.

The alkali metal salts are mostly soluble in water owing to comparable lattice and hydration energies (see, however, halides and oxo-salts, section 18.3). The salts are completely ionized in solution. Li^+ is most strongly hydrated, extent of hydration decreasing to Cs^+. This is revealed in their ionic mobility: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. Hydrolysis does not occur in solution as the charges on the metal are low. The hydroxides behave as strong bases.

Some of the least soluble salts of the alkali metals are:

Sodium Zinc (or Magnesium) uranyl acetate,	$NaZn(UO_2)(Ac)_9.6H_2O$	qualitative and quantitative analysis
potassium (or rubidium/cesium) tetraphenyl borate	$K[B(C_6H_5)_4]$	quantitative analysis
potassium cobaltinitrite	$K_3[Co(NO_2)_6]$	qualitative analysis

Sodium bismuthate, and perchlorates and hexachloroplatinates ($PtCl_6^{2-}$) of K, Rb, Cs are also insoluble. The low solubilities result from poor hydration energies (bulky anion). Li and Na salts like ML_3Cl, L=4, 4′-diaminodiphenylmethane may be precipitated by methanolic solutions of the ligand.

Ionic compounds of the alkali metals are colourless except when caused by the anions, e.g., $CrO_4^{=}$, MnO_4^- etc. The peroxides, superoxides (and suboxides) are also coloured. Colour may also result from lattice defects. The absence of colour is related to the high energy required to excite electrons in the stable metal ions to the lowest available empty orbital—the energy lies far above the visible region. Thus in Cs^+, the transition $5p^6 \rightarrow 5p^5 6s$ occurs at ~ 1000 A°.

The structure and stabilities of the ionic salts are determined by the lattice energy and radius ratio effects (see halides, oxides, and salts of oxo-acids).

A very interesting and important class of nonaqueous solvents are provided by the molten salts or their eutectic mixtures like $LiNO_3$–KNO_3 (m.p. 132°C); $LiNO_3$–$NaNO_3$–KNO_3 (m.p. 120°C); LiCl–KCl (m.p. 350°C) etc. Such melts dissolve many metals which exist in zero or low oxidation state like Al^+, Ca^+, Be^+ etc. The solutions are intensely coloured and reducing in nature. They are important for many metallurgical processes and chemical synthesis. Reactions in molten salt system are being greatly explored.

Covalent compounds:

Ion-clusters

However, not all compounds of the alkali metals are ionic. The alkali metal halides vaporize on strong heating in vacuum. The resulting MX "molecules" are actually ion-clusters held mainly by coulombic forces, as also are the higher aggregates M_2X_2, M_3X_3 and M_4X_4. High dipole moment and nuclear quadrupole coupling measurement show that there is very little covalence between the metal and halogen—at best 4 per cent in NaCl. The alkali metal hydroxides also vaporize to give ion clusters.

Organo-metallics

Alkali metals also form a number of organometallic compounds—those of lithium being particularly important. Lithium alkyls are readily obtained by reacting lithium metal with alkyl or aryl halides (usually chloride) in benzene or petroleum.

$$RX + 2Li = RLi + LiX$$

Lithium alkyls and aryls are widely used in organic chemical industries. These organolithium compounds have properties of typical covalent substances; they are usually liquids or low-melting solids which are highly volatile and soluble in hydrocarbons or other nonpolar solvents. In their reactions they generally resemble Grignard reagents. The organosodium and potassium compounds are fairly ionic—they do not dissolve in hydrocarbons to any appreciable extent and are very reactive towards air and water. At low temperatures, sodium or potassium react with aromatic hydrocarbons in tetrahydrofuran to form highly coloured *radical anions* in which the negative charge is delocalized over an aromatic system. Species such as benzenide ($C_6H_6^-$), naphthalenide or anthracenide ions have been characterized. They have potentialities for large scale use as powerful reducing agents, e.g., sodium naphthalenide, $Na^+(C_{10}H_8)^-$ in N_2-fixation using Ti-catalysts.

The alkali metals also form a series of interesting coordination compounds with cyclic polyethers (*crown* ethers) and cryptates (p. 129) in which the metal ions are encapsulated in the cavity of the ligands. Such compounds may serve as models to understand the transport mechanism of the metals in our body.

Study of such complex compounds has also led to the characterization of the alkalide ion, M^{-1}, in which the metal ion is present in the otherwise unfavourable −1 oxidation state.

Solutions of the alkali metals in liquid ammonia provide an interesting field of study. The electron-rich solutions serve as a good medium for many difficult reduction reactions.

"Exceptions" of Lithium

The properties of lithium and its compounds differ significantly from those of the remaining alkali metals. In fact, lithium resembles magnesium more closely in its behaviour which emphasizes the diagonal relationship in the periodic table. However, this behaviour is not unexpected and cannot be called anomalous when we remember the small size of the Li^+ ion and its consequences—polarizing power, lattice energy, hydration energy etc.

The major differences of lithium from the other alkali metals may be summarised as follows:

(i) It is immiscible with molten K, Rb and Cs and miscible with Na only above 380°C. All other pairs of alkali metals are freely miscible with each other. The metal decomposes water only slowly and shows very poor chemical reactivity.

(ii) The solubility of many lithium compounds in water is very low, comparable to the magnesium salts: the fluoride, hydroxide, phosphate and carbonates of Li (and Mg) are much less soluble than the corresponding Na and K compounds. On the other hand, lithium salts of large nonpolarizable anions, like $LiClO_4$, are more soluble than those of the other alkali metals (18.3.4).

(iii) Li_2CO_3 and $LiNO_3$ decompose readily on heating to the oxide, like the Mg-salts (see salts of oxoacids).

(iv) (Like magnesium) Lithium combines directly with nitrogen to form a nitride. No other alkali metal forms nitrides. Similarly, with oxygen, Li forms only Li_2O, while others form peroxides and superoxides.

(v) Many simple lithium salts are normally hydrated and the anhydrous salts are extremely hygroscopic (e.g., LiCl and LiBr; see halides). The structures of $LiClO_4$, $3H_2O$ and $Mg(ClO_4)_2$. $6H_2O$ are similar; both contain octahedral $M(H_2O)_6$ groups. Lithium sulfate does not form an alum, other alkali metals do.

(vi) The lithium alkyls are in many ways similar to those of magnesium.

As already mentioned, these expected "anomalies" of lithium originate from its very small size and high polarizing power of the cation. The size of Li^+ (76 pm) is closer to that of Mg^{2+} (78 pm) than to Na^+ (102 pm). The lower solubility of many lithium compounds results from their high lattice energy. On the other hand, salts of large nonpolarizable anions (e.g., perchlorate) have much lower lattice energy due to anion-anion repulsion; they are more soluble than those of other alkali metals. Formation of hydrates, and inability to form alums are similarly related to ionic size (p. 112). The same reason plays behind the formation of oxides and nitrides: the larger peroxide and superoxide ions do not pack effectively with the small Li^+ ion (p. 121). As regards nitrides, very high lattice energy is required to overcome the high bond energy of nitrogen plus its negative electron affinity. This seems to be attained only in Li_3N (structure: p. 126). The strong polarizing power of the Li^+ ion explains the thermal instability of Li_2CO_3 (p. 127).

In most of the reactions entered by the alkali metals, reactivity increases from lithium to cesium. The high sublimation and ionization energies of lithium, the key energy terms in the initial steps of a reaction, may be partly responsible for this. But ultimately the reactions of lithium are thermodynamically more favourable in certain cases owing to the highest lattice and hydration energies of the reaction products. Hence the order of reactivity arises due mainly to kinetic effects.

Differences from Group IB

The elements of Group IB also contain a single s-electron in their outermost shell. But they have a filled (n−1)d shell which is similar in energy to the ns shell. These d-electrons participate in metallic bonding and impart much higher melting point to the IB metals. The chemistry of these elements is also greatly influenced by the presence of the filled d-shell. Lack of penetration and poor mutual shielding of the filled d-orbitals result in high first ionization energy and very small size of the M^+ ions. A comparison of copper with sodium and potassium is shown in Table 18.3.

TABLE 18.3

		M.P. (°C)	r_+ (*pm*)	I_1	I_2	I_3 (*kJ mol*$^{-1}$)
Na	K.L. $3s^1$	98	102	496	4564	6911
K	K.L. $3s^2 3p^6 4s^1$	63.5	138	419	2932	4602
Cu	K.L. $3s^2 3p^6 3d^{10} 4s^1$	1083	77	745	1957	3577

We further observe that though the first ionization energy of copper is much higher than those of the alkali metals, the second and third ionization energies of copper are considerably lower. This is not unusual since they involve removal of the d-electrons; however, the d-orbitals do not penetrate close to the nucleus and so the d-electrons are lost rather easily. As a consequence, the IB elements also exhibit oxidation states other than +1, while the high second ionization potential restricts the alkali metals to do so. In fact, Cu(1) is highly unstable in aqueous solution and readily disproportionates to Cu° and Cu(II), aided by the higher hydration energy of Cu(II). Similarly, involvement of the d-electrons influences the chemistry of the group IB elements significantly to justify their discussion with the transitional elements.

Ions formally similar to the alkali metal cations

Monopositive ions with radii comparable to those of the alkali metal ions are likely to have parallel chemical properties. Some prospective examples are:

1. Ammonium and substituted ammonium ions. Many NH_4^+ salts have crystal structures resembling those of K^+. Their solubilities are often similar.

2. The thallous ion, Tl^+, with an ionic radius similar to that of Rb^+ (154 pm).

3. The spherical complex ion $(\eta^5-C_5H_5)_2Co^+$ is formally similar to the alkali metal ions as it forms numerous stable salts (~400°C) and a stable strong base which absorbs CO_2 from air.

18.1.3 Solutions in Liquid Ammonia

The alkali metals dissolve in pure liquid ammonia without the evolution of H_2; the metals can be recovered from such solutions by evaporation. The saturation solubilities are quite high, e.g., at −33°C,

	Li	Na	K
Solubility (g/kg NH_3)	108	250	463

Similar solutions are formed by Ca, Sr, Ba as well as the divalent lanthanoids europium and ytterbium. Solubility is favoured by low metal lattice energy, low ionization energy and high solvation energy of the cation. The electropositive metals having *aqueous* reduction potential more negative than −2.5V fall in this category.

The colour, electrical property and magnetic susceptibility of these solutions are interesting:

Properties

1. Colour: The solutions are all blue when dilute. At higher concentrations (>3M approx.) they become bronze-coloured and a metallic luster appears.

2. Conductance: The solutions are extremely good conductors of electricity: they have higher conductivity than that of completely ionized salts in any known solvent. But the equivalent conductance *decreases* as the solutions become more concentrated and reaches a minimum around 0.05M. Beyond this concentration the conductivity *increases* dramatically sharply and the saturated solutions practically conduct electricity like liquid metals: specific conductivity of $Hg \simeq 10^4$ ohm^{-1}; Na in liq. $NH_3 \simeq 0.5 \times 10^4$ ohm^{-1}.

3. Density: The solutions, particularly the dilute ones, have much lower density than the pure solvent.

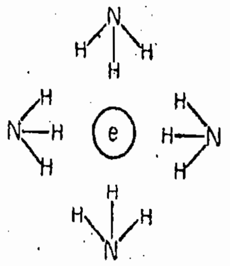
4. Magnetic property: The dilute solutions are paramagnetic with a susceptibility corresponding to one free electron per metal atom. But the paramagnetic susceptibility *decreases* with increasing concentration—around the region of minimum conductivity the solutions become diamagnetic. At still higher concentrations, the solutions again become weakly paramagnetic.

Explanation

It is now generally agreed that these properties arise due to the presence of ammoniated metal cations and ammoniated electrons to various extent. At low concentrations, the equilibrium predominant is

$$M_{am} \rightleftharpoons M^+_{am} + e^-_{am} \; ; \; K \simeq 10^{-2}$$

The strongly polarizing electron orients ammonia molecules around it with the protons pointed inwards. The formation of such cavities explains the lower density of the solution. The blue colour appears due to light absorption by the solvated electrons around 1,500 nm. The high conductivity arises from the quasi-free electrons—with mobility 280 times that of the cation. The electrons also account for the paramagnetic susceptibility.



An electron surrounded by ammonia molecules. Estimated diameter of the cavity ≃3–3·4A°.

As the concentration is raised, the ammoniated cations and ammoniated electrons are involved in various types of aggregations like

$$M^+_{am} + e^-_{am} \rightleftharpoons M_{am}$$
$$M_{am} + e^-_{am} \rightleftharpoons M^-_{am}$$
$$2M^+_{am} + 2e^-_{am} \rightleftharpoons (M^+_{am})_2(e^-_{am})_2$$

These processes remove the conducting cations and electrons and account for the decrease in equivalent conductance. The formation of the dimers with appreciable spin-pairing causes the drop in paramagnetism. But in very concentrated solutions, ($>1M$), there are not enough ammonia to adequately solvate the electrons. The solution then conforms to the description $(M^+_{am})e$ and behaves like a molten expanded metal.

The solutions of alkali metals in liquid ammonia are not very stable; they readily form amides:

$$M + NH_3 \rightarrow MNH_2 + \tfrac{1}{2}H_2$$

But in absence of catalytic impurities (transition metal ions) and under strictly anhydrous condition, such solutions are fairly stable. They are potential reducing agents—their reactions are virtually reactions of the ammoniated electron. Various types of reductions have been carried out, without or with bond cleavege;

Without bond cleavage

$$O_2 + e^-_{am} \rightarrow O_2^-$$
$$MnO_4^- + e^-_{am} \rightarrow MnO_4^{2-}$$
$$[Ni^{II}(CN)_4]^{2-} + 2e^-_{am} \rightarrow [Ni^{\circ}(CN)_4]^{4-}$$

With bond cleavage: One or two electrons may be involved initially. Subsequent ammonolysis may occur in the latter case.

$$NH_3 + e^-_{am} \rightarrow NH_2^- + \tfrac{1}{2}H_2$$
$$NH_4^+ + e^-_{am} \rightarrow NH_3 + \tfrac{1}{2}H_2$$
$$EtOH + e^-_{am} \rightarrow EtO^- + \tfrac{1}{2}H_2$$
$$S_8 + 2e^-_{am} \rightarrow S_8^{2-}$$
$$Mn_2(CO)_{10} + 2e^-_{am} \rightarrow 2[Mn^{-1}(CO)_5]^-$$
$$C_6H_5NHNH_2 + 2e^-_{am} \rightarrow C_6H_5NH^- + NH_2^-$$

$$N_2O + 2e^-_{am} \rightarrow N_2 + O^{2-} \xrightarrow{NH_3} N_2 + OH^- + \underset{(ammonolysis)}{NH_2^-}$$

$$NCO^- + 2e^-_{am} \rightarrow CN^- + O^{2-} \xrightarrow{NH_3} CN^- + OH^- + \underset{(ammonolysis)}{NH_2^-}$$

$$RBr + 2e^-_{am} \rightarrow Br^- + R^- \xrightarrow{NH_3} Br^- + RH + \underset{(ammonolysis)}{NH_2^-}$$

These reactions are very useful in many organic synthesis. For example, alkynes are stereo-specifically reduced to *trans-alkenes* while the conventional Pd/H_2 reduction would give only *cis* alkenes.

Alkali metals also dissolve in aliphatic amines, tetrahydrofuran, ethylene glycol dimethyl ether etc. solvents to form reducing solutions.

18.2 ISOLATION AND USE OF THE ELEMENTS

Discovery

Sodium and potassium were first isolated (Humphrey Davy; 1807) by electrolysis of molten alkalis. Lithium was discovered by Arfvedson (1817) in the laboratory of Berzelius from the mineral petalite—the name was chosen (Greek *lithios*=stone) to signify its mineral origin (sodium and potassium could be obtained from plant ashes). Rubidium (Bunsen, 1861) and Cesium (Kirchoff, 1861) were discovered spectroscopically and named after the colour of the most prominent lines in their spectra (Latin *rubidus*=deep red; *casius*=sky blue).

As the alkali metals are highly electropositive and react promptly with water, they cannot be obtained by electrolysis of aqueous salt solutions. Electrolysis of fused chlorides or hydroxides is used for lithium and sodium. K, Rb and Cs are obtained by reducing respective halide melts with sodium or calcium. As the metals are reactive toward air, they (and their alloys) must be handled in an inert atmosphere.

18.2.1 Extraction of lithium

(A) Lithium is usually extracted from spodumene which contains 1–3% Li. The following steps are usually involved in the extraction procedure:

Process	**Change**
1. Oil-floatation	Concentration (4–6%)
2. Heating to ~1100°C	Conversion of the α-form of the ore to less-dense and more friable β-form.
3. (a) Digestion (conc. H_2SO_4, 250°C); evaporation.	Silica rendered insoluble.
(b) Leaching (water)	Solution of Li_2SO_4
4. Na_2CO_3	Precipitation of Li_2CO_3
5. HCl	Conversion to LiCl
6. Electrolysis of fused mixture: 55% LiCl + 45% KCl, ~450°C; graphite anode, iron cathode.	Lithium metal liberated at cathode.

(B) Alternatively, lithium chloride may be separated from the other metals by extraction with absolute alcohol and ether: the chlorides may be obtained as follows:

1. (a) Fusion of ore with $BaCO_3$, $BaSO_4$ and K_2SO_4:	Formation of Li, K, Na, Ba—sulphates (melt).
(b) Layer separation	Top layer: Li, Na, K-sulphates. Bottom layer: Ba-sulfates+silicate (rejected)
(c) Leaching (top layer) with water	Li, Na, K-sulfates
2. (a) $BaCl_2$ added, filtered	$BaCl_2 + Li_2SO_4 = 2LiCl + BaSO_4\downarrow$
(b) Filtrate evaporated.	LiCl, KCl, NaCl as residue
3. (a) Extraction with absolute alcohol and ether	LiCl separated (in solution)
(b) Extract evaporated	LiCl
4. Electrolysis (as in A)	Li-metal

About 1000 tonnes of the metal are extracted annually throughout the world. Besides, several thousand tonnes of lithium salts are produced for various purposes (see use).

18.2.2 Sodium and Potassium

Sodium

Sodium is extracted by electrolysis of fused sodium chloride-calcium chloride (upto 65%) eutectic, m.p. 505°C. This temperature is considerably lower than the m.p. of pure NaCl (803°C) and so difficulties from volatility of sodium (b.p. 887°C) are largely eliminated. Under this condition the discharge potential for the Na^+ ion is lower than that of the Ca^{+2} ion. Sodium is preferentially deposited, with 1–2% calcium, at a cylindrical steel cathode. The calcium solidify at a cool collecting pipe and fall back into the melt. Chlorine liberated at the central graphite anode is collected through a nickel dome.

Potassium

Electrolysis of fused potassium chloride alone (m.p. 790°C) is also complicated by the problem of vaporization of the metal (b.p. 760°C). Attempts to use a lower temperature by adding metal salts have also failed: (1) potassium ions have a higher discharge potential than the metal added and (2) potassium is very soluble in the molten chloride and does not float on the top of the electrolyte melt.

Potassium is isolated by reducing molten potassium chloride in a packed fractionating tower by rising sodium vapour on a counter current principle: The reaction

$$KCl + Na = NaCl + K$$

is normally contrary to the usual reactivity trend (K > Na). But higher volatility of potassium in the temperature range 850°–880°C shifts the equilibrium towards right:

$$KCl(l) + Na(g) \rightleftharpoons NaCl(l) + K(g)$$

Fractionation may be carried out to obtain potassium of 99.5% purity; but usually a Na–K alloy (15—55% Na) liquid at room temperature is prepared for easy transport.

Several kilotonnes of sodium metal are annually prepared over the world. Potassium, however, is prepared on a much lower quantity (see use).

18.2.3 Rubidium and Cesium

These metals are practically obtained as by products from the extraction of lithium from lepidolite. They are obtained by reducing the fused chlorides with calcium metal at 750°C under reduced pressure. As the two elements occur together in very small quantities in minerals like lepidolite and carnallite, their separation from other alkali metals is a tideous job—lower solubility of their alums is generally used for the purpose. Separation of rubidium from cesium is also achieved by fractional crystallization. Differences in solubilities of the chloroplatinates and silicomolybdates of the two metals may also be used—the rubidium compound being more soluble in all cases. The metals are purified by fractional distillation.

Production of these elements is limited by their consumption—only about 5 tonnes per year for each.

18.2.4 Uses

Lithium 1. It is a good alloying metal and forms high strength low density aluminium alloys for aircraft construction. Extremely tough low density alloys are formed with Mg and Al which are used in armour plates and aerospace components e.g., LA 141 contains 14% Li, 1% Al and 85% Mg, and has a density 1.35 g cm^{-3}.

2. Lithium stearate (LiOH+tallow) is used as a thickener and gelling agent to transform oils into lubricating greases. The greases are highly water resistant and withstand large temperature range (−20°C–150°C).

3. Lithium carbonate is now being used extensively in cells for the extraction of aluminium—it permits larger current flow, reduces fluorine emission, lowers melting point and reduces production cost. It is also used as a flux in making porcelain and enamel and in the production of special toughened glass.

Medicinal

4. Small daily doses of Li_2CO_3 is effective in the treatment of manic-depressive psychoses.

Minor uses

5. Lithium hydroxide is used for absorption of CO_2 in space capsules and submarines. Lithium hydride is used to generate hydrogen for military or meterological requirements. Lithium aluminium hydride and several organolithium compounds are widely used in organic synthesis. Lithium tantalate, $LiTaO_3$ is a ferroelectric used to modulate laser beams. Lithium fluoride is used in X-ray dosimetry due to its thermoluminescence.

Future prospects

6. Storage cells with Li–Si (or Li–Al) alloy as anode and FeS_x cathode in molten LiCl/KCl eutectic (470°C) are under trial. Another promising combination consists of liquid sodium anode and sulfur cathode in β-alumina (300°C).

7. Lithium may be used to prepare tritium:

$${}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + {}^{4}_{2}He.$$

Tritium is a promising fuel for thermonuclear power generation by fusion:

$${}^{3}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6\text{MeV}$$

Sodium 1. More than half of the sodium produced every year is used as Na/Pb alloy in the manufacture of lead tetraethyl (see lead)—an antiknock compound. However, the production and use of lead tetraethyl is likely to fall in the near future due to lead-poisoning of the environment through exhaust gases.

2. The second important use of sodium is as a reducing agent in the extraction of Ti, Zr etc. metals.

3. A considerable amount of sodium is consumed in the production of sodium hydride, sodium peroxide and other sodium compounds, including a large number of organosodium compounds of widespread synthetic interest. Dispersions of sodium in various media (e.g., Kieselguhr, carbon, K_2CO_3) are used as catalysts for various reactions of alkenes in the production of artificial rubbers and elastomers.

4. Low melting point, low viscosity and low neutron absorption cross-section together with high heat-capacity and thermal conductivity make sodium (or Na–K alloy) the most favoured material for heat exchange in fast breeder nuclear reactors.

Uses of "salt" (NaCl)

5. The use of sodium salts in industry is simply numerous—millions of tonnes of the chloride, carbonate, sulfate, nitrite, chlorate, perchlorate, phosphate etc., salts as well as the hydroxide are consumed annually. Of these, sodium chloride alone accounts for more than 150 million tonnes—it is the starting material for any sodium compound—NaOH, Na_2CO_3, Na_2SO_4 etc., as well as H_2, Cl_2, HCl. About 50% of the total annual consumption goes toward the manufacture of NaOH and Na (plus Cl_2+H_2); about 10% is used for making Na_2CO_3. Another 8–10% goes toward food (including animal feeds) and food preservatives. In certain countries, a fairly large quantity of salt is required to clear the snow on highways in the winter. Paper, Rubber, and textile industries, water softening plants and tanning industries are other chief consumers of salt.

Sodium hydroxide is largely used in the manufacture of different chemicals like phenol, resorcinol, sodium hypochlorite, phosphate etc. A substantial amount is used in the paper and pulp industries, in rayon industries and in the extraction of aluminium.

Sodium carbonate is largely used in the glass industry as well as in the manufacture of other chemicals. In many cases, it can replace sodium hydroxide (e.g., paper).

Sodium sulphate is largely used in paper industry for making brown wrapping papers and corrugated boxes.

The use of certain other compounds are mentioned in respective context.

Potassium. 1. Potassium, in the form of Na – K alloy, is used as heat-exchanger in breeder reactors.

2. It is used to make KO_2 by direct burning in air; KO_2 is used to supplement oxygen in submarines, space capsules etc., by absorbing CO_2 (see KO_2).

3. Potassium amalgam and different potassium compounds have wide uses:

KCl : an important fertilizer (muriate of potash, MOP).
KOH : rubber processing, preparation of potassium phosphate (for liquid detergents) and other chemicals.
K_2CO_3 : Decorative glass, colour T.V. tube, textile, dye and pigment industry.
KNO_3 : (oxidizing agent) – gun-powder.
$KClO_3$: explosives, matches.
KBr : photography.
$KMnO_4$: oxidizing and bleaching agent, manufacture of saccharin.

Rubidium and Cesium: Extensive uses of these metals are yet to be explored. They are used in photoelectric cells and to remove last traces of gas in vacuum tubes. RbI has some medicinal use.

18.3 COMPOUNDS OF THE ALKALI METALS

18.3.1 Oxygen compounds

The alkali metals form variety of oxides: the normal oxide (M_2O), the peroxide (M_2O_2), the superoxide (MO_2), the sesqui oxide (M_2O_3 or M_4O_6), ozonide (MO_3) and a considerable number of suboxides. As already mentioned, the principal products from burning the metals in a free supply of air are different (p. 111). The larger anions pack most effectively with large cations – the resulting high lattice energy is the main factor for the stability of these compounds.

The monoxide

M_2O

Some representative methods of preparation are:

$$2Li_2O_2 \xrightarrow{450°C} 2Li_2O + O_2$$
$$Na_2O_2 + 2Na \longrightarrow 2Na_2O$$
$$NaOH + Na \longrightarrow Na_2O + \tfrac{1}{2}H_2$$
$$NaNO_2 + 3Na \longrightarrow 2Na_2O + \tfrac{1}{2}N_2$$

All the oxides are stable towards heat (upto about 500°C). Their colours become intense from Li_2O to Cs_2O:

Li_2O	**Na_2O**	**K_2O**	**Rb_2O**	**Cs_2O**
white	white	cold-white hot-yellow	pale yellow	orange

The colours are most probably due to lattice defects. Li_2O–Rb_2O have structures similar to CaF_2 with metals in the positions of F^- and oxygen in the positions of Ca^{2+} ions – the antifluorite structure. Cs_2O has anti-$CdCl_2$ structure. All the oxides are strongly basic and hygroscopic – they dissolve exothermically in water forming hydroxides:

$$M_2O + H_2O \rightarrow 2MOH$$

The peroxides

M_2O_2

The preparative methods are somewhat varied.

$$LiOH.H_2O + H_2O_2 \longrightarrow \underset{\text{lithium hydroperoxide}}{LiOOH.H_2O} + H_2O$$

$$2LiOOH.H_2O \xrightarrow[\text{reduced pressure}]{\text{gentle heat}} Li_2O_2 + H_2O + 2H_2O$$

$$2Na + \tfrac{1}{2}O_2 \xrightarrow[\text{limited air}]{\text{heat}} Na_2O \xrightarrow{O_2} Na_2O_2$$

K_2O_2, Rb_2O_2 and Cs_2O_2 formed in this manner are oxidized further to the superoxides. They are best prepared by quantitative oxidation of the metals in liquid ammonia by oxygen.

Li_2O_2, a white crystalline solid, decomposes to Li_2O above 195°C. Others are thermally stable to ~600°C. Colours also deepen down the group – Li_2O_2 is white; Na_2O_2 : pale yellow, K_2O_2 : orange, Rb_2O_2 : dark brown ; Cs_2O_2 is yellow but black when fused. Defective lattice and small amounts of superoxides may be responsible for this colour.

The peroxides contain the peroxide ion, O_2^{2-} and liberate H_2O_2 with water or dilute acids. They are strongly basic as well as oxidizing.

$$M_2O_2 + 2H_2O \rightarrow 2MOH + H_2O$$

Sodium peroxide combines explosively with charcoal and aluminium and ignites many organic liquids. It also combines with sulfur with incandescence. Carbon monoxide and carbon dioxide form sodium carbonate – the latter giving also oxygen:

$$Na_2O_2 + CO \rightarrow Na_2CO_3$$
$$Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + \tfrac{1}{2}O_2$$

As such, it is used to restore oxygen in submarines and breathing apparatus for divers. The lighter Li_2O_2 is used in space capsules. Na_2O_2 is also used as an oxidizing agent in industry and in analysis [e.g., Cr(III) to Cr(VI)]. It is also used as a bleaching agent for paper, pulp, wood and fabrics.

Superoxides

MO_2

K, Rb and Cs directly form the superoxide when burnt in air. It appears that the large O_2^- ion is stabilized only with the large cations. However, LiO_2 has been prepared (?) at 15K; NaO_2 has been prepared by reacting O_2 with Na at high temperature and pressure (450 – 500°C, 150 – 300 atm), or Na dissolved in liquid NH_3.

NaO_2 is yellow, KO_2 is orange, RbO_2 is dark brown and CsO_2 is orange. Their increasing stability is reflected in their increasing melting points – 380°C, 412°C and 432°C respectively. They adopt the CaC_2 structure (distorted NaCl). NaO_2 is cubic owing to disordered array of O_2^- ions.

Lithium does not form a superoxide as it has a very small ion with strong polarizing power. Instead of forming a stable lattice with the large superoxide ion, Li^+ destabilizes it by deforming the electron cloud.

The superoxides are also powerful oxidizing agents. They react vigorously with water:

$$2MO_2 + 2H_2O = 2MOH + H_2O_2 + O_2$$

Their reaction with CO_2 is used to regenerate oxygen in closed systems like submarines (also Na_2O_2).

$$4MO_2 + 2CO_2 = 2M_2CO_3 + 3O_2$$

The paramagnetic O_2^- ion contains one unpaired electron in one of the π^*_{2g} m.o. (Ch. 7). The peroxide ion has both the π^*_{2g} m.o.-s filled. The change $O_2 \rightarrow O_2^- \rightarrow O_2^{2-}$ involves successive addition of an electron in the anti-bonding m.o.; this results in gradual decrease in bond order and increase in bond length: 121, 126 and 149 pm respectively.

M_2O_3 Sesquioxides

(i) Thermal decomposition of MO_2 (K, Rb, Cs), (ii) controlled oxidation of the peroxides or (iii) oxidation of metals in liquid ammonia solution give dark coloured paramagnetic powders of stoichiometry M_2O_3. There are reasons to consider them as peroxide disuperoxides: $M_2O_2, 2MO_2$

MO_3 Ozonides

O_3 acts on powdered anhydrous MOH (Na—Cs), or KO_2/RbO_2 at low temperature to form red MO_3:

$$3MOH(s) + 2O_3(g) \rightarrow 2MO_3(s) + MOH.H_2O(s) + \tfrac{1}{2}O_2(g)$$

MO_3 may be extracted by liquid NH_3. LiOH gives $[Li(NH_3)_4]O_3$; it decomposes if the ammonia is removed (small size of Li^+).

The ozonides decompose to MO_2 and O_2 on standing. Hydrolysis gives the hydroxides.

$$MO_3 \rightarrow MO_2 + \tfrac{1}{2}O_2;\ 2MO_3 + H_2O \rightarrow 2MOH + .5/2O_2$$

Suboxides

The formal oxidation states of the metals in these oxides are less than 1. Their structure and properties have not been fully established.

Rb_6O: Partial oxidation of Rb at low temperature; decomposes above −7.3°C to Rb_9O_2 and Rb. Structure contains alternating layers of Rb_9O_2 and close-packed metal atoms. Unit cell has 4 formula units.

Rb_9O_2: $2Rb_6O_2 \rightarrow Rb_9O_2 + 3Rb$.

Rb_9O_2

Copper coloured. Inflames with H_2O. Melts at 40°C to $Rb_2O + Rb$. Structure consists of two ORb_6 octahedra sharing a common face. Rb—Rb distance is much less than in metallic Rb; Rb—O distance is also much less than $r_+ + r_-$.

Cs_7O, bronze-coloured, m.p. 4.3°C; **Cs_4O,** red-violet, decomposes above 10.5°C; **$Cs_{11}O_3$,** violet, m.p. 52.5°C; non-stoichiometric $Cs_{3+x}O = (x \text{ upto } 1)$, decomposes at 166°C. Three octahedral OCs_6 groups share 2 adjacent faces to form $Cs_{11}O_3$—the main structural unit. The Cs—Cs distance within this group is lower than that in the metal.

Hydroxides: The alkali metal hydroxides, MOH, are all very strong bases. They are white crystalline solids soluble in water and alcohol. Their melting points decrease gradually: LiOH 471°; NaOH 318°; KOH 360°; CsOH 272°. They can also be sublimed unchanged (350−400°C). The vapour mostly consists of dimers. The anhydrous solids possess oriented OH groups with weak zig-zag hydrogen bonding in KOH and RbOH. They are strongly deliquescent in nature.

Evaporation of aqueous solutions of the hydroxides yield LiOH, H_2O and several hydrates for the others. These may be dehydrated by heating in an inert atmosphere or under reduced pressure.

Measurements of the proton affinities of MOH in the gas phase show that base strength increases from LiOH to CsOH (chapter 17). The aqueous solutions appear nearly equally strong due to levelling effect of the solvent. Being strong bases, they react with acids (and acidic oxides, e.g., CO_2) to form salts and with alcohols to form alkoxides.

NaOH has wide industrial use, seconded by LiOH (see use).

LiOH: It is prepared by the following reactions:

(a) $2Li + 2H_2O = 2LiOH + H_2$

(b) $Li_2SO_4 + Ba(OH)_2 = 2LiOH + BaSO_4\downarrow$

The filtered solution is concentrated by evaporation. It is much less soluble in water than NaOH or KOH (about one-fifth).

NaOH: It is produced mostly by electrolysis of brine using graphite anode and mercury cathode. But the method presents severe pollution hazard by contamination of soil and water by mercury via sewage (see under mercury). Causticising of sodium carbonate provides an alternative method:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

The reversible equilibrium is determined by the solubility of both $Ca(OH)_2$ and $CaCO_3$. In fact, efficiency of causticising increases when dilute (normal) solution of sodium carbonate is used. The liquor of NaOH is concentrated in vacuum evaporators where the unchanged sodium carbonate separates.

KOH: It is also made by electrolysis of KCl solution or by the reactions

$$2K\ (\text{amalgam}) + 2H_2O = 2KOH + H_2$$

$$K_2SO_4 + Ba(OH)_2 = 2KOH + BaSO_4$$

18.3.2 Halides (MX)

All alkali metal halides are colourless*, crystalline solids with high melting and boiling points (Table 18.4 and Fig. 18.3). They are highly soluble in water. They all may be prepared by reacting MOH or M_2CO_3 with appropriate HX.

Fluorides differ from other halides

The lattice energies and standard heats of formation of these halides are given in Table 18.5 and plotted in Fig. 18.4. We observe that the lattice energies decrease regularly from Li—Cs and from F^-—I^-. (In Fig. 18.4, $-U$ values are plotted. Hence the plots have an upward slope). But the values of ΔH°_f show two different trends. For flourides, ΔH°_f becomes less negative from Li—Cs, but the trend is reversed with the other three halides. For a given metal, ΔH°_f becomes less negative from the fluoride to the iodide.

The Born-Haber cycle (Ch. 6) may be recalled to explain these observations. With the same anion, ΔH°_f of MX depends on $S_M + I_M - U$ (sublimation,

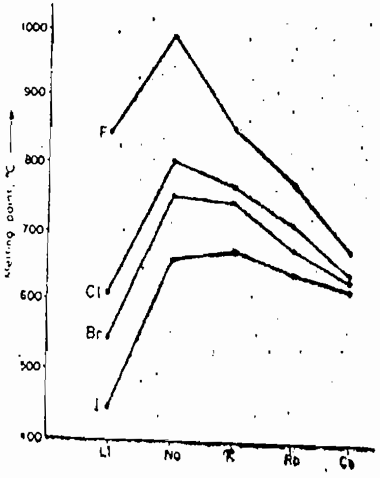


Fig. 18.3. Trend of variation of melting points of the alkali metal halides.

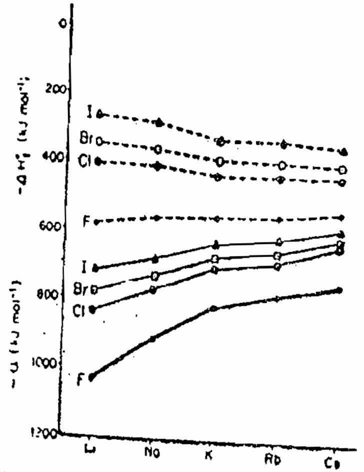


Fig. 18.4. Variation of lattice energy and hydration energy among the alkali metal halides.

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*A defective crystal lattice may give rise to colour. If a small amount of sodium metal is doped into a sodium chloride crystal, the sodium ionizes: Na−e = Na^+. The electron occupies a site that would normally contain a chloride ion. It is thus a Schottky defect (Ch. 6) with the vacant site occupied by an electron. This trapped electron can absorb light in the visible region and cause colour. Such imperfections are called *F* centers (F=German *Farbe*, colour).

ionisation and lattice energy respectively). The variation of $S+I$ from Li to Cs is shown below:

	Li	Na	K	Rb	Cs
$S+I$ (kJ mol^{-1})	682	606	509	491	464

TABLE 18.4

Melting and Boiling Points (°C) of alkali metal halides (MX)

M	Fluoride		Chloride		Bromide		Iodide	
	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.	M.P.	B.P.
Li	845	1681	610	1382	547	1265	446	1190
Na	995	1704	808	1465	755	1390	661	1300
K	856	1502	772	1407	748	1380	677	1325
Rb	775	1408	717	1381	682	1340	642	1300
Cs	682	—	645	1300	636	—	621	1280

TABLE 18.5

Lattice Energy ($-U_0$; from B—H cycle) and Enthalpy of formation ($-\Delta H°$) of the alkali metal halides (MX); kJ mol^{-1}

M	Fluoride		Chloride		Bromide		Iodide	
	$-U°$	$-\Delta H°$	$-U°$	$-\Delta H°$	$-U°$	$-\Delta H°$	$-U°$	$-\Delta H°$
Li	1034	612	840	409	781	350	718	271
Na	914	569	770	411	728	360	681	288
K	812	563	701	436	671	392	632	328
Rb	780	549	682	430	654	389	616	329
Cs	744	531	629	433	612	395	584	337

Explanation

Referring to table 18.5, we find that the lattice energies of the fluorides vary *more rapidly* (from Li to Cs) than does the sum $S+I$. Lattice energy depends inversely on $(r_+ + r_-)$ and so the variation in lattice energy is greatest with smallest r_- (i.e., the F$^-$ ion) and least when r^- is largest (I$^-$ ion). For chlorides to iodides, the sum $S+I$ decreases *more rapidly* than do the lattice energies. Thus in the fluorides, the lattice energy term predominates over others; this leads to a decreasing trend in the enthalpies of formation from LiF to CsF. For the larger halides, the lattice energies become smaller and less dominant. Greater ease of sublimation and ionization of the heavier alkali metals (i.e., lower values of S and I) drives $\Delta H°_f$ to larger numerical values.

M.P. and B.P. trend: *Deviation for LiX*

The trends in melting and boiling points of the halides are also very interesting (Fig. 18.3). The general trend of F$^-$>Cl$^-$>Br$^-$>I$^-$ can be readily understood. But for any particular halide ion (X$^-$), NaX has the highest melting and boiling point, *not* LiX. This can be largely rationalized in terms of the very small size of the Li$^+$ ion—a fact that leads to appreciable anion-anion repulsion. As a consequence, the actual Li—X distance in the lithium salts is always considerably larger than expected from the sum of ionic radii. This results in appreciable lowering of the energy of the crystal, which, in turn, leads to lower melting and boiling points for the lithium halides.

Pauling made some corrections for the anion-anion repulsion and showed that the corrected melting and boiling points follow the expected regular trend. According to him, the equilibrium distance (R_0) between two ions in a crystal is given by

$$R_0 = (r_+ + r_-)\,F(\rho)$$

Radius-ratio correction for anion-anion repulsion

in which $F(\rho)$ is a function of the radius ratio $\rho = r_+/r_-$. It was shown that $F(\rho)$ becomes unity when $\rho = 0.75$. Pauling then corrected the lattice energy of the crystals for the radius-ratio effect. It was found that the corrected crystal energies are much higher for the lithium halides: about 33 kJ mol^{-1} for LiF, increasing to 63 kJ mol^{-1} in LiI. The corresponding corrections in melting and boiling points are also appreciable: the m.p. of LiF should be higher by about 264 °C, the difference increasing to ~504 °C in LiI. The values of sodium halides show that they are only slightly affected by this radius-ratio effect, e.g., lattice energy of NaI changes by only 23 kJ mol^{-1}, with a melting point correction by 180 °C. For other halides, this influence is still smaller. The corrected melting points show a regular trend.

Solubility trend: *Fluorides vs Iodides*

The solubility of these halides in water depends on the relative magnitudes of lattice energy and the total hydration energy. The first factor opposes solubility, while the second one favours it. Now both these energy terms increase with increasing charge and decreasing size of the ions involved. But their exact nature of dependence on the size is different. Lattice energy (Born-Lande eqn.) varies inversely with the sum $(r_+ + r_-)$. The hydration energy depends on the inverse of each *individual* radius, and so the total hydration energy varies with $(1/r_+ + 1/r_-)$. When either r_+ or r_- are very large, the sum $(r_+ + r_-)$ increases, decreasing lattice energy. But the total hydration energy may not decrease to the same extent—the hydration energy of the smaller ion may partly compensate for the loss in hydration energy of its larger counterion. The effect is nicely illustrated by the solubilities of the two extreme halides—the fluorides and the iodides. *Among the fluorides, the lattice energy decreases more rapidly* from LiF to CsF than does the hydration energy (Table 18.6). For LiF and NaF, the lattice energy is actually higher than the hydration energy. It begins to fall below the hydration energy from KF. Consequently, solubility increases greatly from LiF (2.7 g dm^{-3}) to CsF (3670 g dm^{-3}). *For the iodides, the hydration energy decreases more rapidly* than does the lattice energy (Table 18.6). The hydration energy of LiI is *more* than its lattice energy, while the hydration energy of CsI is *less* than its lattice energy. As a result, LiI is the most soluble iodide among the series.

TABLE 18.6

Hydration Energy and Lattice Energy of alkali metal Fluorides and iodides (kJ mol^{-1})

	Fluorides (ΔH_{hyd} for F$^-$ $=-515$)		**Iodides** (ΔH_{hyd} for I$^-$ $=-305$)	
	Total ΔH_{hyd}	U_0	Total ΔH_{hyd}	U_0
Li	−1034	−1034	−824	−718
Na	−921	−914	−711	−681
K	−837	−812	−627	−632
Rb	−808	−780	−598	−616
Cs	−780	−744	−569	−584

Crystal structure

Only CsCl, CsBr and CsI adopt body centered cubic arrangement with co-ordination number eight. All other alkali metal halides crystallize in a face-centered cubic arrangement (NaCl-type). Many of these structures do not agree with the radius-ratio rule ($r_+/r_- = 0.41-0.73$); e.g., LiCl, LiBr, LiI ($r_+/r_- \simeq 0.3$), KF (0.98), RbF (1.1), RbCl, RbBr, CsF (~0.8). In fact, the radius-ratio rule is a crude approximation. The ions are not hard spheres, nor are their radii known accurately. Actually, the radii change with coordination number: a change from C.N. six to eight results in an increase in ionic radius by about 3%; a change to C.N. four causes a decrease by ~ 6%. Summarily, the structures adopted are most stable and favourable from energy considerations. RbCl, RbBr and RbI have nearly equal energies in C.N. six and eight—the lattice energies differ by only about 3 per cent. When crystallized at high pressure and temperature, they adopt C.N. eight and change from face-centered cubic to body-centered cubic arrangement. The Madelung constants and the radii for these two coordination numbers (r_8 and r_6, say) are not very different: $r_8/r_6=1.032$.

LiCl, LiBr and LiI form trihydrates **LiX, 3H$_2$O**. Other alkali metal halides form anhydrous crystals. The loss of lattice energy in expanding the lattice through hydration is not compensated for by the hydration energy.

On strong heating in vacuum, the halides vaporize to highly polar ion pairs $M^+—X^-$ with little covalence. Higher aggregates like M_2X_2, M_3X_3 and M_4X_4 are also known.

The alkali metal halides may form polyhalides (see halogens):

$$KI \;+\; Cl_2 \;\rightarrow\; KICl_2;\quad KCl \;+\; ICl \;\rightarrow\; KICl_2$$

Rb^+ and Cs^+ are particularly effective in stabilizing large polyhalide ions.

18.3.3 Hydrides, Nitrides and Sulphides

Hydrides The alkali metals react directly with hydrogen when heated to give ionic hydrides containing H^- ions. They have been discussed in connection with the hydrides (p. 90).

Nitrides Only lithium combines with nitrogen to form a nitride; the reaction is slow at ordinary temperature but rapid at 450°C.

$$6Li \;+\; N_2 \;=\; 2Li_3N$$

Li_3N is a ruby red crystalline solid which melts at 548°C with decomposition. It reacts with water to give NH_3 (similar to Mg_3N_2):

$$Li_3N \;+\; 3H_2O \;=\; 3LiOH \;+\; NH_3$$

It appears that Li_3N owes its stability to very high lattice energy—other singly charged larger alkali metal ions cannot compensate for the high bond dissociation energy of N_2 and the electron attachment energy to form the N^{3-} ion. Probably steric reasons are also an important factor. Born-Haber calculations, however, suggest that Na_3N should exist, but none has been detected upto 800°C in a mixture of sodium and nitrogen. An impure form of it is reportedly obtained by treating sodium with active nitrogen.

The structure of Li_3N is complicated. On the basis of size, Li should be tetrahedrally coordinated by nitrogen but this cannot be fitted with the stoichiometry of the compound. Li_3N is said to have a unique structure—each nitrogen is surrounded by two lithium at 194 pm and six others at 211 pm; one-third of the lithium atoms have two nitrogen atoms at 194 pm and the others have three nitrogen atoms at 211 pm.

Sulphides The alkali metals combine with sulphur to give a range of sulphides M_2S_x, $x=1-6$. The higher sulphides are best prepared in liquid ammonia. The sulphides M_2S_2 and M_2S_4 have been found to be most stable for Li and Na, while M_2S_5 is stable for K, Rb and Cs. The sulphides undergo hydrolysis in aqueous solution and react alkaline. The extent of hydrolysis decreases as the sulphur chain increases.

The sulphur chains in the polysulphide ions are zigzag. The exact mode of bonding is complex. In Cs_2S_6, the S—S—S angle is about 109° and the S—S bond lengths vary alternately: the terminal and central bonds are about 2A°, while the others are 2.1A° each. Weak interaction among the chains is also suggested.

Sodium sulphide, Na_2S, is prepared commercially by heating salt cake (Na_2SO_4) with carbon at 1000°C: $Na_2SO_4 \;+\; 4C \;\rightarrow\; Na_2S \;+\; 4CO$. It is used in textile industries, in the extraction of silver, in making sulphur dyes and in tanning (hair remover).

18.3.4 Salts of oxoacids

As already mentioned, the alkali metals form salts with almost all anions. They will be mentioned in respective sections. A few representative compounds are mentioned here. The general trend of hydration of the metal ions and the formation of trihydrates by lithium alone have already been mentioned (p. 111). The trend of solubility can be understood in the light of the discussion made for the halides (p. 125): lithium salts of large nonpolarizable anions like ClO_4^- (or in other words, salts of strong acids) are more soluble than those of the other alkali metals. The lattice energy is overcome by the high solvation energy of Li^+.

Carbonates: The alkali metals form a wide variety of hydrated carbonates and hydrogen-carbonates (bicarbonates). The solubility of these salts in water increases from lithium to cesium. Li_2CO_3 has the highest lattice energy due to the small cation and doubly charged anion—it is insoluble in water ($MgCO_3$). The carbonates are thermally stable to high temperatures and melt before they decompose above 1000°C. The dissociation pressure (mm Hg) of CO_2 at 1000°C are: Li_2CO_3, 90; Na_2CO_3, 19; K_2CO_3, 8. This shows that stability decreases as the cation becomes smaller. The relative gain in lattice energy in forming the oxide rather than the carbonate becomes the controlling factor. The high polarizing power of the smaller cations, specially Li^+, may be an additional advantage.

Lithium does not form a solid bicarbonate, which is again a reflection of the strong polarizing power of Li^+ on the soft HCO_3^- ion. The other bicarbonates decompose to carbonates on heating:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\ (Na > K > Rb > Cs).$$

Higher lattice energy of the product seems to be the key factor. This reactio forms the basis for the use of $NaHCO_3$ in baking powder.

The bicarbonates are much less soluble than the corresponding carbonates—solubility again increasing from sodium to cesium. The solid bicarbonates are H-bonded: $NaHCO_3$ has an infinite chain of unsymmetrical H-bonds; $KHCO_3$ is dimeric. The lower solubility of $NaHCO_3$ is probably due to its H-bonded structure. This forms the basis of the Solvay process of manufacturing Na_2CO_3.

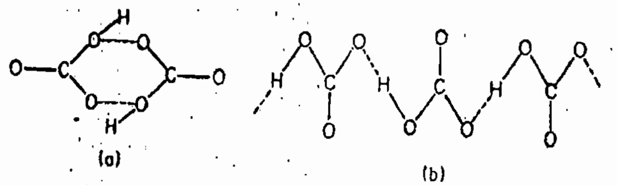


Fig. 18.5. Hydrogen bonding in (a) $KHCO_3$ (b) $NaHCO_3$; metal ions not shown.

There are large deposits of sodium carbonate in nature—in USA alone the reserve in Green river, Wyoming, has a deposit of 10^{10} tonnes over an area of 2300 km². Interest in such natural deposits is increasing in view of the hazards of environment pollution by the alkali and chlorine industries.

Nitrates: The alkali metal nitrates are highly soluble in water. $LiNO_3$ and $NaNO_3$ are deliquescent. The nitrates have low melting points and form the nitrite on heating (except Li), giving off oxygen. On stronger heating (~800°C)

$$2NaNO_3 \;\overset{\sim 500°C}{\rightleftharpoons}\; 2NaNO_2 \;+\; O_2$$

the nitrite will decompose to give the oxide ($+N_2+O_2$). $LiNO_3$ decomposes directly to the oxide Li_2O, the high lattice energy being the probable driving force. Thermal stability of the nitrates increases with increasing atomic number, as expected (like the carbonates). All nitrates can be prepared by reacting the hydroxide or carbonate with dilute nitric acid.

Large deposits of $NaNO_3$ are present in Chile. These were probably formed by decay of small marine organisms by bacteria. This produced ammonia, which was subsequently oxidized to nitrous and nitric acid. The acid then reacted with NaCl. The nitrates are largely used as oxidizing agents and as molten salt media.

Nitrites. The alkali metal nitrites may be prepared by heating the nitrates or by other reactions:

$$2RbNO_3 + C \rightarrow 2RbNO_2 + CO_2$$

$$6NO + 4KOH \rightarrow 4KNO_2 + N_2 + 2H_2O$$

$NaNO_2$ is prepared on a large scale as follows:

$$Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$$

All the nitrites are colourless crystalline hygroscopic solids highly soluble in water. They disproportionate on heating in absence of air.

$$5NaNO_2 \rightarrow 3NaNO_3 + Na_2O + N_2$$

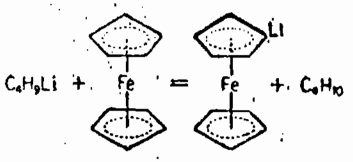
The driving force obviously lies in the lattice energy difference of the solids and the high bond energy of N_2.

$NaNO_2$ is largely used in the manufacture of azo dyes and other nitrogenous organic compounds and as a corrosion inhibitor.

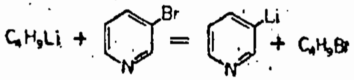
18.3.5 Organometallic compounds

The organometallic compounds of the alkali metals, particularly of Li, are very important. An introductory discussion has already been made earlier (p. 113). Some other methods of preparation are:

metal-hydrogen exchange (metalation)



metal-halogen exchange



metal-metal exchange $2Li + R_2Hg = 2RLi + Hg$

metal-addition to alkenes $2Na + 3C_2H_4 \rightleftharpoons 2C_2H_3^-Na^+ + C_2H_6$

and alkynes $RC \equiv CH + Na = RC \equiv C^-Na^+ + \frac{1}{2}H_2$

The first three reactions are usually carried out in petrol or benzene while the last two reactions are best performed using sodium dispersed in tetrahydrofuran (THF), dimethylformamide (DMF) etc.

The organolithium compounds are generally liquids or low melting solids which are extremely sensitive to oxygen and water. They dissolve in hydrocarbons and other nonpolar liquids. They are mostly thermally unstable and decompose to LiH on standing at room temperature. LiMe, LiBu^t and LiBu^n are comparatively stable. Thus LiMe is a colorless crystalline solid which decomposes above 200°C. It has a tetrameric structure involving covalent multi-center bonds between Li and C. Four Li atoms are arranged in the form of a tetrahedron; the four methyl groups are placed symmetrically above the midpoint of each tetrahedral face. Each Li atom may be considered to be sp^3 hybridized; the three Li atoms in each tetrahedral face combine with an sp^3 hybrid orbital of carbon forming a 4-center 2-electron molecular orbital for each Li_3C unit. Only four electron pairs are thus required to hold the tetramer together.

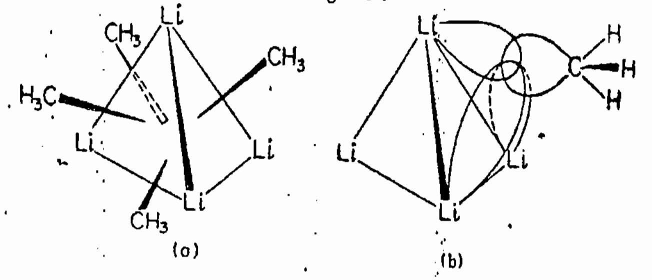
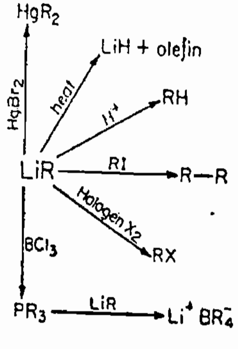


Fig. 18.6. (a) Structural unit of $(CH_3Li)_4$ (b) Mode of attachment of the methyl group (only one face shown).

Such type of molecular association is an important feature of the alkyls in both crystal and in solution. The extent of aggregation in solution depends on the solvent and the size of the organic group. The reactivities of the Li-alkyls depend on the nature of such aggregations. Thus benzyllithium (monomeric in THF) reacts about 10^4 times faster as a benzylating agent than methyllithium (tetrameric) does act as a methylating agent.



The lithium alkyls generally behave as carbanionic in its reaction. Some typical reactions are shown on the right. Besides, alkylation (arylation) by LiR may give rise to lithium alkylate (arylate) anions:

$$MgPh_2 + 2PhLi \xrightarrow{THF} Li_2[MgPh_4]$$

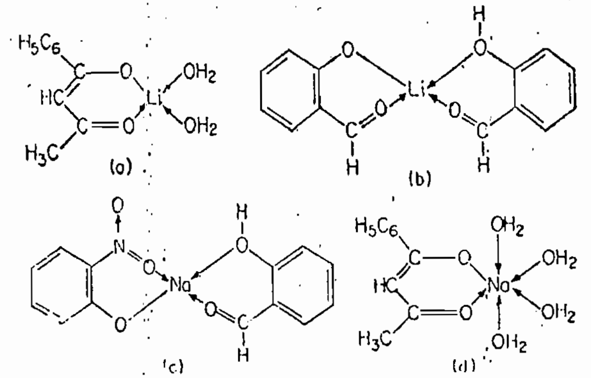
$$WMe_6 + 2MgLi \longrightarrow Li_2[WMe_8]$$

The lithium alkyls are valuable synthetic reagents in both laboratory and industry. More than 1000 tonnes of LiBu^n alone are consumed annually. They are mostly used as alkylating agent and catalyst in polymerization of alkenes—often stereospecific.

The organometallic compounds of other alkali metals are essentially ionic (p. 113). They are also used in different synthesis.

18.3.6 Coordination Compounds

Prior to 1967, few coordination compounds of alkali metals were known—the relatively large size and low charge density of the M+ ions were held responsible for this. Some tetrahedral complexes of lithium were known—e.g., the tetrahedral $[Li(OPPh_3)_4]^+$ in $LiX.4Ph_3PO$, X=I, NO_3, ClO_4 etc.; large anions. The compounds are stable to air and water, having melting points in the range of 200—300°C. Chelates with β-diketones, nitrophenols, salicylaldehyde etc., have also been prepared; the stability of these complexes decreases as Li>Na>K. The reaction of NaI with $NH_3(l)$ at low temperature gives the unstable ammine complex $[Na(NH_3)_4]^+$.



Some typical coordinations compounds of the alkali metals: **(a)** lithium—benzoylacetone (tetrahedral); **(b)** lithium—salicylaldehyde (tetrahedral); **(c)** sodium—nitrophenol (tetrahedral); **(d)** sodium—benzoylacetone (octahedral).

In 1967, several macrocyclic polyethers were shown to form very stable complexes with the alkali metals (Pedersen, C.J.)*. Because of their crownlike coordination, the polyethers are commonly called *crown ethers*, two typical structures being shown below. Their routine names would be very much complicated e.g., dibenzo-18-crown-6 would have the name 2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16 -hexaoxacyclooctadeca-2, 11-diene! Their short names indicate the (i) number of total atoms in the ring (e.g., 15 or 18) as suffix and (ii) the number of O-atoms (e.g., 5 or 6) as prefix (see figure). The alkali metal simply has to fit into the cavity of the ligand and obviously the larger alkali metals require larger "crown"s:

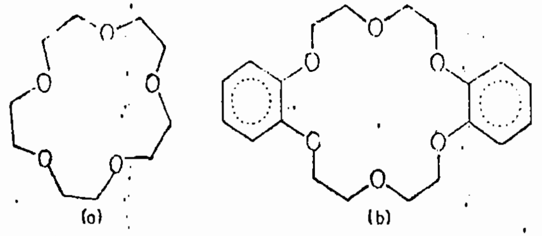


Fig. 18.7. Skeleton representation of (a) 15—crown—5 and (b) dibenzo—18—crown—6.

Cation	**(r^+, pm)**	**"Crown" specification**	**"Hole" size** r, pm
Li^+	76	14—crown—4	~ 75
Na^+	102	15—crown—5	~110
K^+	138	18—crown—6	~160
Rb^+	152	21—crown—7	~215

***Unexpectedly,** though! In an attempt to prepare an alkyl phenolic ether, a complex of Na^+ with dibenzo—18—C—6 was obtained due to contaminating catechol.

$$C_6H_4(OH)_2 + (ClCH_2CH_2)_2O \xrightarrow[2.\ H^+]{1.\ NaOH\ in\ butanol} \text{Dibenzo-18-crown-6.}$$

Alkali metals are insoluble in ethers and similar organic solvents. But they dissolve in such solvents in presence of crown ligands. The solubility depends on how well the metal fits into the "hole" of the ligand.

$$K + \text{crown-6} \xrightarrow{Et_2O \text{ or } THF} [K\ (\text{crown-6})]^+ + e\ (\text{solvent})^-.$$

The bonding in these "complexes" is largely electrostatic.

Even more interesting than the crown ethers are the "*cryptates*" (from Greek *hidden*), which are polycyclic species containing both nitrogen and oxygen in the heterocyclic ring (also S- or even P) a typical graphic representation being shown below: the numbers indicate the numbers of O-atoms in each ring. They can encapsulate a metal ion in a cage-like structure and hence the term **clathro chelate** is also sometimes used for such complexes. The complexes are so stable that they can effectively stabilize **an alkali metal anion,** e.g., the sodide ion, Na^-. The addition of a cryptand (e.g., the 2, 2, 2-crypt, abbreviated as C) to ethylamine solution of Na or K greatly increases the solubility of the alkali metal by the process.

$$2M(s) + C \rightleftharpoons MC^+ + M^-$$

Actual crystals of $[NaC]^+Na^-$, stable at −10°C, have been isolated by cooling such solutions. They are yellow and diamagnetic. The crystal structure consists of alternate layers of NaC^+ and Na^- ions in hexagonal arrangement. The corresponding potassium analogue is less stable.

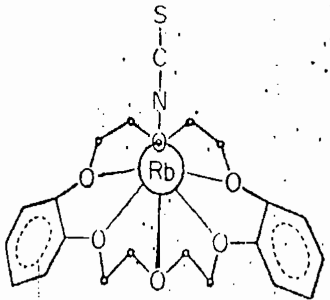


Fig. 18.8. Skeleton representation of the Rb-complex of dibenzo—18—C—6.

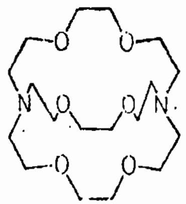


Fig. 18.9. Skeleton representation of a 2,2,2-cryptate.

Complexes of the alkali metal ions are not limited to the macrocyclic ligands. Benzene derivatives with 2 to 6 pendant mercaptopolyether groups, $C_6H_{6-n}R_n$ ($R = -SC_2H_4OC_2H_4OMe$; $-S(C_2H_4O)_3Bu$ etc.,) have enough conformational flexibility and coordinating ability to form stable complexes with the alkali metal cations. They are referred to as "octopus" ligands and are sometimes more effective than crowns. An *inorganic cryptate* completely surrounding a sodium atom is present in the hetero polytungstate $(NH_4)_{17}Na[NaW_{21}Sb_9O_{86}]$.

Studies on crown and cryptate ligands and their alkali metal complexes provide scope for biochemical modelling as they are similar to the naturally occurring cyclic polypeptides like valinomycin and nonactin. Such studies may throw some light on the transport mechanism of these metals across membranes in living systems. Certain cryptate complexes are finding increasing use in solvent extraction, phase-transfer catalysis, stabilization of uncommon oxidation states (e.g., −1 for Na) etc. The "inorganic cryptate" heteropoly tungstate mentioned above has strong antiviral activity.

18.3.7 The alkalide ions

The reaction

$$2Na(g) = Na^+(g) + Na^-(g)$$

is endothermic by 438 kJ mol^{-1}. So we can readily understand the nonexistence of a -1 oxidation state for the alkali metals. Yet such states are made feasible in unusual conditions—as we have just come across in the coordination compounds with cryptates. The endothermic sodide ion seems to derive its stablization from the energy of complex formation and lattice energy. A closely related series of compounds are the *electrides*, M$^+$(crown)e_-. These black, paramagnetic substances have the same structure as the alkalides.

Solutions of sodium in ethylenediamine or methylamine show electrical conductance of normal 1 : 1 electrolytes—presumably due to the presence of Na$^+$ and Na$^-$. Dilute solutions of cesium in these solvents have very high conductance—indicating the presence of Cs$^+$ and solvated electrons (e_{solv}); at higher concentrations the conductivity approaches that of Cs$^+$ and Cs$^-$. Alkali metals also dissolve in certain ethers, tetrahydrofuran and other solvents forming relatively unstable solutions. The optical spectra of such solutions clearly indicate two distinct absorption bands—one for the solvated electron and another which can reasonably be assigned to the species M$^-$, the alkalide ion. Several evidences support their existence:

(i) The solutions are diamagnetic, as expected for spin-paired M$^-$ ions in the ground state.

(ii) The molar conductivity of solutions containing sodium decrease slowly as the concentration is raised: this is consistent with the formation of ion-pairs Na$^+$Na$^-$.

(iii) Certain aspects of the absorption band lends support to the existence of such ions.

The M$^-$ species may have utility as two-electron reducing agents in synthesis.

SUMMARY

The alkali metals Li, Na, K, Rb and Cs occur extensively in the earth's crust, Li as aluminosilicates (Lepidolite, Spodumene); Na and K as halides; Rb and Cs: dispersed in lepidolite. Francium is radioactive (highest $t_{1/2}$=23 min.) and hence not available.

The physical and chemical properties of these elements reflect their ns^1 electron configuration. Poor participation in metallic bond makes the metals soft and low melting; m.p. and b.p. decreases down the group due to increased repulsion from nonbonding electrons.

Li has the highest ionization potential, and at the same time Li$^+$ ion has the highest hydration energy. This makes Li the most electropositive in the group.

The metals react readily with water, air and most nonmetals—the vigour usually increasing from Li to Cs. The reason should be kinetic. In air, Li burns to Li_2O, Na to Na_2O_2 while others burn to the superoxides, MO_2. Only Li react with N_2 (400°C) to give a red crystalline nitride Li_3N.

Except Li-salts, the salts are not hydrated; Li-salts form trihydrates. The salts are mostly soluble in water. For salts of strong acids, the hydration energy of Li$^+$ readily overcomes the lattice energy, (the anions are large and nonpolarizable, hence low lattice energy)—the Li-salts are most soluble, e.g., $LiClO_4$. In other cases, salts with high lattice energy, e.g., LiF, are the least soluble in a series. The lithium halides have lower m.p. than the sodium halides due to anion-anion repulsion.

Lithium exhibits certain apparent exceptions owing to its very small size and high polarizing power. LiOH and Li_2CO_3 are insoluble in water.

The salts of the alkali metals are all colorless, except due to lattice defect.

In the gaseous states, alkali metal halides form ion-clusters. Organometallic compounds of lithium are very important in laboratory and industrial synthesis—they act as stereospecific catalysts in many polymerization reactions of alkanes. The compounds are volatile and soluble in nonpolar organic solvents with various degree of aggregation. CH_3Li forms a tetrameric crystal and is stable to ~200°C.

Coordination chemistry of the alkali metals have reached a new horizon with the discovery of cyclic polyethers and other macrocyclic ligands—the "crown" ethers and cryptates. They virtually encapsulate a metal atom and can even stabilize an alkalide ion, M$^-$, in a formally -1 oxidation state.

The alkali metals dissolve in liquid ammonia giving highly conducting blue solutions rich in electrons—such solutions provide good reducing medium for many otherwise difficult reactions. The electrons in such solutions are enclosed in "cavities" surrounded by NH_3 molecules, leading to an expansion in volume. At concentrations >0.05 M, the solutions show metallic conductance characteristic of "free" electrons.

The metals are extracted by electrolysis of molten halides. Li is extracted from lepidolite via roasting and digestion with H_2SO_4 to give Li_2SO_4: from this Li_2CO_3 is precipitated and dissolved in HCl and the LiCl is electrolysed in fused state (+45% KCl, ~450°C). Sodium is extracted by electrolysis of molten NaCl–$CaCl_2$ eutectic (505°C). It is difficult to obtain potassium in this procedure. It is prepared by reduction of molten KCl with rising sodium vapour on a counter-current principle. Rb and Cs are usually separated from residues of Li-extraction by fractional crystallization.

EXERCISE

1. *Suggest reasonable explanations for the following*:
   - (i) *Lithium does not occur in the same type of minerals as the other alkali metals.*
   - (ii) *Sodium chloride is about 30 times more abundant in sea water than potassium chloride.*
   - (iii) *Melting point of the alkali metals decrease down the group while in many other family of elements it actually increases with increasing atomic number.*
   - (iv) *Li has the highest I.P. and the lowest aqueous E° (red), among the alkali metals.*
   - (v) *Li is the only alkali metal to form a stable nitride.*
   - (vi) *Only lithium salts form hydrated crystals from aqueous solutions.*
   - (vii) *Both potassium and copper have a 4s outer electron configuration. But the two metals differ widely in their physical and chemical properties.*
   - (viii) *Concentrated solutions of alkali metals in liquid ammonia show high electrical conductance.*
   - (ix) *Potassium cannot be extracted by electrolysis of fused potassium chloride.*
   - (x) *When heated, potassium nitrate forms the nitrite; but lithium and sodium nitrates give the oxides.*
   - (xi) *The reactions*

     $$M_2O_2(s) \longrightarrow M_2O(s) + \tfrac{1}{2}O_2(g) \qquad M_2CO_3(s) \longrightarrow M_2O(s) + CO_2(g)$$

     occur most readily when M=Li and the ease of the reactions decreases from Li to Cs.
   - (xii) *CsOH is a stronger base that LiOH.*
   - (xiii) *For a given halide ion X$^-$, NaX has the highest melting point among all the alkali metal halides.*
   - (xiv) *The observed trend of solubility in water are*:

     $$LiF < NaF < KF < CsF \quad \text{but,} \quad LiI > NaI < KI < CsI.$$
   - (xv) *Lithium does not form a solid bicarbonate.*
   - (xvi) *In water, Potassium bicarbonate is less soluble than potassium carbonate, but it is more soluble than sodium bicarbonate.*
2. *Mention some of the important differences of lithium from the remaining alkali metals. How can you explain these differences?*
3. *Explain the trend of variation, with concentration, of the electrical conductance and magnetic properties of solutions of alkali metals in liquid ammonia.*
4. *The reaction* $4MO_2(s) + 2CO_2(g) \longrightarrow 2M_2CO_3(s) + 3O_2$ *is to be used to regenerate oxygen in a space-craft. Discuss the choice of M among the alkali metals.*
5. *Write a brief account of the coordination compounds of the alkali metals.*
6. *Explain the following observations*:

   (a) $2\,LiOH \xrightarrow{\text{red heat}} Li_2O + H_2O$ but $2\,NaOH \xrightarrow{\text{red heat}}$ *no reaction*

   (b) $LiH \xrightarrow{\text{heat}}$ *no reaction* but $2\,NaH \xrightarrow{\text{heat}} Na_2 + H_2$

[**Hint**: The Li$^+$ ion has great polarizing power .... the highly polarizable H$^-$ ion is bound more strongly by a covalent bond in LiH].

CHAPTER NINETEEN

THE ALKALINE EARTH METALS

Be, Mg, Ca, Sr, Ba (Ra)

OBJECTIVES

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    Carbides and Nitrides [19.3.3]
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19

19.1 INTRODUCTION

The elements of Gr II A follow the typical *s*-group chemistry exemplified by the alkali metals. The difference in chemistry between the two groups lies only in the extent, not in the very nature. In most cases, this may be explained in terms of the smaller size of M^{2+} cations of Gr IIA in comparison to M^+ cations of Gr IA. The first member, beryllium, is again out of line from the others owing to its very small size and high effective nuclear charge. The "diagonal relationship" (shown by lithium with magnesium) is also observed in the chemistry of beryllium and aluminium. The elements also show little resemblance to the elements of group IIB (Zn, Cd, Hg). The presence of the inner *d*-shell, and consequent high effective nuclear charge is agian the main cause. However, magnesium shows certain similaritites with zinc.

The elements Mg—Ba are called the alkaline earth metals. All substances that remained unchanged by fire were called "earth" by the ancient chemists. Lime, magnesia, strontia and baryta were among such "earths"—they were called alkaline earths for their alkaline reaction.

19.1.1 Abundance and Occurrence of the elements

Beryllium is of very low abundance, 2—6 ppm in the earth's crust. The reason for this is similar to that for lithium and boron: low nuclear charge—low potential to proton or alpha capture reactions, easy transmutation to other heavier nuclides.

However, the element is readily accessible through its surface deposits in the form of silicates: *Beryl*, $Be_3Al_2Si_6O_{18}$ ($3BeO, Al_2O_3, 6SiO_2$) and *Phenacite*, Be_2SiO_4.

Beryllium occurs in pegmatite rocks—the last portions of crystallization of igneous rocks. As such, they form beautiful large crystals which are often used as gems. Emerald (green) is beryl coloured by a small amount of Cr (III); aquamarine (bluish green) also belongs to the same category.

Due to its small size, beryllium can replace Si in SiO_4 units. The balance of charge between Be (II) and Si (IV) is maintained by incorporation of other cations. This may be one of the several reasons for the late crystallization of beryllium minerals. [In contrast, the magnesuim minerals are considered to have crystallized very early from the magma].

Magnesium is highly abundant, at least 2.1% in the earth's crust (20,000 —1,00,000 ppm). It occurs principally as sedimentary rocks—dolomite, $MgCO_3$ ($+CaCO_3$) and other evaporated forms like carnalite ($KCl, MgCl_2, 6H_2O$). Besides, there are a large number of silicates: soapstone (talc), asbestos and the micas. It is likely that the magnesium minerals separated in the early stages of the crystallization of magma and thereafter it has accumulated into the sedimentary rocks. The huge quantity of magnesium (0.13%) in sea water resulted from the leaching of these rocks. The major supply of magnesium now comes from the sea water.

Large amounts of magnesium are also believed to be present in the mantle of the earth (olivine). The chlorophylls in plants contain magnesium.

Calcium is the fifth most abundant element (3.63%) in the earth's crust. It is concentrated in minerals which probably separated during the main stage of crystallization of magma. About two-thirds of the crust is formed by feldspars. Weathering and leaching led to the formation of $CaCO_3$ (limestones, dolomites). The very low solubility of $CaCO_3$ is the most probable reason for the absence of significant amount of Ca^{2+} ions in sea-water. Gypsum ($CaSO_4, 2H_2O$), fluorspar

(CaF_2) and apatite $[3Ca_3(PO_4)_2, CaF_2]$ etc. are some of the other important minerals of calcium.

Strontium (380 ppm) occurs principally as celestite ($SrSO_4$) and strontianite ($SrCO_3$). It has three natural isotopes: ^{86}Sr (9.7%), ^{87}Sr (7.0%) and ^{88}Sr (82.6%). Beta-decay of ^{87}Rb gives rise to pure ^{87}Sr in some minerals:

$$^{87}_{37}Rb \rightarrow ^{87}_{38}Sr + \beta^-.$$

Barium (390 ppm) occurs mainly as barytes, $BaSO_4$.

Radium: All four isotopes of the element are radioactive (longest $t_{\frac{1}{2}}=1600$ y); hence it does not occur naturally in significant amounts. It occurs in small amounts (~1 g in 7 tonnes) in pitchblende as a decay product of uranium.

19.1.2. General Trend

The elements are all characterized by two valence electrons in an *s*-shell outside an inert gas core. These two electrons are always involved together—giving rise to uniform bivalency of the elements. The principal features of these elements also show a uniform variation, as evident from Table 19.1.

TABLE 19.1: Some Properties of Gr. IIA Elements

	Be	Mg	Ca	Sr	Ba	Ra
M.P. (°C)	1,287	650	839	770	727	700
Density, g cm^{-3}	1.8	1.7	1.5	2.6	3.6	5.5
I.P., kJ mol^{-1}						
I_1	900	737	590	549	503	509
I_2	1,757	1,450	1,145	1,064	965	975
I_3	14,840	7,731	4,942	—	—	—
Radius of M^{2+} (pm)*	27	72	100	118	135	140
E° (V) for $M^{2+}(aq)/M(s)$	−1.85	−2.37	−2.87	−2.89	−2.91	−2.92
− **ΔH** hydration of $M^{2+}(g)$ (kJ mol^{-1})	2,385	1,940	1,600	1,460	1,320	—

* 6-coordinated except Be (4-coord.).

Properties of the metals

The metals are all silvery white, lustrous and relatively soft. However, they are much harder than the alkali metals as two electrons (per atom) are now available for bonding. The melting points are also considerably higher for the same reason. The anomalous variation is due to differences in the crystal structures: Be, Mg—hexagonal close-packing; Ca, Sr—face centered cube; Ba, Ra—body centered cube. All the metals tarnish in moist air due to the formation of oxide films. Reactions of the metals with air, water etc., are given in Table 19.2.

The ionization energies are also higher than with the alkali metals—again a reflection of higher nuclear charge and smaller size. The abruptly high values of third ionization energy is quite expected from the closed shell configuration of M^{2+} ions. This explains the upper limit of +2 oxidation state for the elements.

The radii of M^{2+} ions increase gradually as expected. The value for beryllium is notional as no compounds containing an uncoordinated Be with a +2 charge are known; the Be^{2+} ion is strongly polarizing, its compounds are largely covalent. Parallel to the increase in radius, the hydration energy decreases down the group. The values are again much higher than for the alkali metal cations and are large enough to largely compensate the second ionization potential of the Group IIA elements. This, together with the higher lattice energy provided by the +2 ions in crystals, explains the non-existence of the +1 oxidation state in solution or in crystals.

Why univalent ions are not formed

We have already seen (section 6.6.2, Part I) that ionic compounds of the type CaF would be unstable towards disproportionation:

$$2CaF \rightarrow Ca + CaF_2$$

The much higher lattice energy for the divalent compound provides the principal driving force for the change. In fact, the lattice energy of CaF_2 would be nearly three times as large as that of the hypothetical CaF (assumed NaCl structure) for three main reasons: (i) the charge on the metal is double, (ii) the size of the Ca^{2+} ion is smaller and (iii) the Madelung constant has a higher value of 2.52 (instead of 1.75 for CaF). Similarly, it has been estimated that in solution the free energy of solvation of the Ca^{+2} ion would be more than four times that of the Ca^+ ion.

Suspected univalence

The large difference between the first and second ionization energies, specially for Be, suggests that a +1 state might be possible. But no compound has been isolated in spite of some evidence for Be(I) in fused chloride melts and in studies on the dissolution of Be from anodes. Transitory Mg^+ ions have been similarly detected in anodic dissolution of magnesium in pyridine and in aqueous solutions. A compound claimed as CaCl has been shown to be actually CaHCl.

The aqueous reduction potential of Be is much less, showing its lower electropositive character. The reduction potentials of Ca, Sr, Ba and Ra are nearly the same as with the heavier alkali metals. Magnesium occupies an intermediate position. This is reflected in the trend of chemical reactivity of the elements. (Table 19.2)

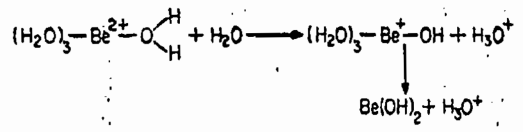
TABLE 19.2: Chemical Properties of the Alkaline Earth Metals

	Be	Mg	Ca—Ba(Ra)
1. Air	No reaction below 600°C with massive metal, Powdered Be burns (BeO + Be_3N_2)	Brilliantly burns (MgO + Mg_3N_2)	MO + M_3N_2 Ca → chiefly nitride Ba → chiefly oxide
2. (a) Water cold/hot	No reaction	No reaction (amalgam reacts, H_2)	$M(OH)_2 + H_2$ (Vigour increases from Ca — Ba.
(b) Steam	No reaction	$MgO + H_2$	$M(OH)_2 + H_2$ (vigorous)
3. H_2	No reaction (Atomic hydrogen gives BeH_2)	570°C, 200 atm (in pr. of MgI_2)	MH_2 on gentle heating Ca reacts more readily than Ba
4. N_2	1000°C, Be_3N_2	800-850°C Mg_3N_2	M_3N_2 on gentle heating
5. Cl_2, Br_2, I_2	No reaction in cold. Burns: $BeCl_2$ etc.	Burns: $MgCl_2$ etc.	Readily gives MCl_2 etc.
6. C	1700°C; Be_2C	MgC_2 at red heat	MC_2 at red heat. Lower stability than Be_2C, MgC_2

Special features of Be

We observe that beryllium is much less reactive than the other elements in the group. In fact, beryllium differs from the rest to a greater extent than lithium does from the other alkali metals. This is mainly because the sizes of Be and Mg (or of Be^{2+} and Mg^{2+}) differ to a greater extent than in the case of Li and Na. As a consequence, analogous salts of Be and Mg do not crystallize in the same structure (but Li and Na salts do). Beryllium dissolves in aqueous mineral acids (HCl, HNO$_3$, H$_2$SO$_4$) evolving H$_2$, though concentrated HNO$_3$ renders it passive. But Be also dissolves in aqueous caustic alkali, liberating H$_2$. The hydrides, halides and alkyls of beryllium have bridged structure (see p. 146). The bare Be^{2+} ion appears to be too strongly polarizing to exist in salts as such. All anhydrous beryllium compounds are therefore covalent. Stable ionic salts may be formed by the tetrahedral [Be(H$_2$O)$_4$]$^{2+}$ ion.

In this hydrated ion, the water molecules are extensively polarized—ultimately leading to weakening of O—H bonds. Hydrolysis takes place, making the solution distinctly acidic:



19-1.

Alkaline solutions facilitate the proton transfer. The other Gr II metal ions interact poorly with the water molecules and hydrolysis becomes insignificant.

Beryllium also shows many resemblance with the diagonally related element aluminium in Gr IIIA (see later) and zinc in Gr IIB.

Magnesium reacts more readily with most of the non-metals. It also reacts with ammonia at high temperatures to give Mg$_3$N$_2$; ammonia activated with I$_2$ at 350—400°C gives Mg(NH$_2$)$_2$. Methanol (200°C) and ethanol (room temperature, activated by a trace of I$_2$) react to give Mg(OCH$_3$)$_2$ and Mg(OEt)$_2$ respectively. Grignard reagents (RMgX) are formed by alkyl and aryl halides in dry ether. In general, the chemistry of magnesium is also marked by the small size and consequent strong polarizing power of the Mg^{2+} ion (compare Li$^+$) and is appreciably different from the heavier members, Ca—Ra.

Trend in properties

There is a systematic and gradual change in the properties of Ca, Sr, Ba, Ra and their compounds. Electropositive character and ionic radius increases to Ra and results in a systematic group trend:

(a) larger cations stabilize larger anions—Ca, Sr and Ba form peroxides and superoxides. BaO$_2$ forms readily in air at 500°C, while SrO$_2$ can be synthesized only at high pressure of oxygen.

(b) Thermal stabilities of carbonates, nitrates, sulphates etc. also increase. Those of magnesium decompose most readily.

Solubility: unusual behaviour of fluorides

(c) The solubility of salts with large anions like sulphates and nitrates decrease with increasing atomic number of the metal. The halides also follow the same trend, except the fluorides. The hydration energy decreases more rapidly than the lattice energies. Thus the magnesium salts are highly soluble due to the high solvation energy of the Mg^{2+} ion; in fact, the hydrated Mg(H$_2$O)$_6$$^{2+}$ is present in many crystalline salts. The solubility of the fluorides follow the reverse trend: Mg$<$Ca$<$Sr$<$Ba. As the F$^-$ ion is very small, the larger cations touch each other before they can make contact with the small anion. The lattice energies decrease very rapidly with increase in size of M^{2+} ions.

Structure of gaseous halides

The halides of elements Mg—Ra are all ionic, but they can be sublimed as monomers. The halides of small cations with large anions are linear in the vapour—CaCl$_2$, CaBr$_2$, SrBr$_2$ and SrI$_2$. But others, like CaF$_2$ or SrCl$_2$ are nonlinear, and hence polar. If the monomers were simple ion-clusters, they would have been linear (minimum anion-anion repulsion). So, the non-linear species are most likely to be covalently bonded. It has been estimated that *sp* hybridization is important only in linear molecules like BeCl$_2$. For the heavier metals, *s* → *d* promotion is energetically more favourable. The polarizing power of the smaller halide

ions may enhance the contraction of d-orbitals necessary for such hybridization. The bent structure is thus explained.

Solution in liquid NH$_3$: why Mg differs

Be and Mg also differ from other members of the group in their behaviour toward liquid ammonia. Like alkali metals, Ca, Sr and Ba dissolve in liquid ammonia; the deep blue-black solutions give bronze-coloured ammoniates, M(NH$_3$)$_6$, on evaporation. But beryllium and magnesium do not readily dissolve in liquid ammonia. On prolonged boiling with liquid ammonia, magnesium evolves hydrogen. However, a blue solution of magnesium is formed only in presence of a strong base: NaOCH$_3$ or KNH$_2$. The high charge-density of Mg^{2+} ion offers an explanation for this behaviour. The Mg^{2+} ion, ammoniated, is expected to cause ammonolysis:

$$[\mathrm{Mg(NH_3)}_x]^{2+} + \mathrm{NH_3} \rightleftharpoons [\mathrm{Mg(NH_3)}_{x-1}]^{2+}(\mathrm{NH_2}^-) + \mathrm{NH_4}^+$$
$$\mathrm{NH_4}^+ + e(\mathrm{NH_3})_x \rightarrow (x+1)\mathrm{NH_3} + \tfrac{1}{2}\mathrm{H_2}$$

The presence of a strong base reduces the concentration of NH$_4^+$ appreciably, so that the second step does not occur; the ammoniated electron imparts the blue colour. Similar arguments should apply to beryllium.

The elements form numerous complex compounds, tendency decreasing with decreasing ion-dipole interaction

$$\mathrm{Be} > \mathrm{Mg} > \mathrm{Ca} > \mathrm{Sr} > \mathrm{Ba}.$$

Coordination compounds

Be forms very stable [Be(H$_2$O]$_4$]$^{2+}$, while the other metal ions tend to achieve 6-coordination, e.g., [Ca(H$_2$O)$_6$]$^{2+}$. Various oxygen donors like ethers, alcohols, carboxylic acids, phenols, as well as nitrogen donors like NH$_3$ form stable complexes like [Be(NH$_3$)$_4$]$^{2+}$, [Mg(NH$_3$)$_6$]$^{2+}$ etc. The acetate and nitrate complexes of beryllium involve bridging acetate and nitrate groups. (p. 152). Complexation of Ca^{2+} by EDTA and polyphosphates plays an important role in the removal of the metal in water softening. Though most complexes of nitrogen donor ligands are weak and exist only in the solid state, magnesium complexes of the tetrapyrrole system—porphine (p. 155) are extremely important to the living world. Such complexes are present in the chlorophylls—vitally important in photosynthesis in plants.

Similarities between beryllium and aluminium

The charge by radius ratio for Be^{2+} is indeed very high ($Z^+/r \simeq 6.5$, r in A°)—greater than any other cation except H$^+$ and B^{3+}. The closest value is found with Al^{3+} ($\sim$6·0). This suggests that Be and Al should have similar properties. This is really observed in practice—Be resembles Al more closely than it does Mg. For example:

(i) Both metals dissolve in aqueous alkali evolving hydrogen:

$$\mathrm{Be(OH)_2} + 2\mathrm{NaOH} = \mathrm{Na_2BeO_2} + 2\mathrm{H_2O}$$
$$\mathrm{Al(OH)_3} + \mathrm{NaOH} = \mathrm{NaAlO_2} + 2\mathrm{H_2O}$$

(ii) The standard electrode potentials of the two metals are equal (−1.7V).

(iii) Both are rendered passive by concentrated nitric acid.

(iv) The oxides and hydroxides are amphoteric.

(v) The anhydrous halides of both are dimeric with metal-halogen-metal bridges. They are useful catalysts in Friedel-Crafts reactions.

(vi) The carbides of both yield methane with water; their lattices contain approximately C^{4-} ion.

(vii) Both metals form a protective oxide layer on surface.

(viii) The alkyls contain M—C—M bridges held by three-center bonds.

(ix) Thermal stability of the anhydrous sulfates is nearly the same.

But BeS is insoluble in water, while Al$_2$S$_3$ (also CaS etc.) is rapidly hydrolyzed.

19.2 ISOLATION, USE, DETECTION AND ESTIMATION

Beryls and emeralds were known from antiquity. Beryllium was discovered from Beryl in 1798 (Vanquelin), but its atomic weight was finalised much later by Mendeleev (see Periodic Table). The metal was prepared independently by Wohler and Bussy in 1828, by the reduction of $BeCl_2$ with K.

Calcium and magnesium compounds were also known from ancient times. A soft white stone (talc) available in the Magnesia district of Thessaly was named Magnesian stone. Calx/Calcis, meaning lime, obtained by heating limestone, was used as mortar by the ancient Romans. Ca, Mg, Sr and Ba were isolated by Davy in 1808 by electrolysis.

Radium was discovered by P. and M. Curie in 1898 from Pitchblende. The metal was isolated by M. Curie and Debierne in 1910 electrolytically.

19.2.1 Beryllium

Beryllium is extracted from Beryl, $Be_3Al_2Si_6O_{18}$ ($\equiv 3BeO, Al_2O_3, 6SiO_2$)

(i) Beryl is roasted with NaF and Na_2SiF_6 (700°—750°).	Insoluble Na_3AlF_6 and soluble Na_2BeF_4 are formed. ($+SiO_2$ $+SiF_4$).
(ii) The roasted mass is leached with boiling water.	Na_2BeF_4 (sodium fluoberyllate) solution is obtained.
(iii) Extract+NaOH (pH 12)	Precipitate of $Be(OH)_2$.
(iv) $Be(OH)_2+NH_4HF_2$	$(NH_4)_2BeF_4$ Ammonium fluoberyllate.
(v) $(NH_4)_2BeF_4$ is heated at 900°C.	BeF_2 is formed.
(vi) BeF_2 reduced by Mg/1300°C	Be-metal.

Reactions:

(i) $3BeO. Al_2O_3, 6SiO_2 + 6Na_2SiF_6 = 3Na_2BeF_4 + 2Na_3AlF_6 + 3SiF_4 + 9SiO_2$

(iii) $Na_2BeF_4 + 2NaOH = Be(OH)_2 + 4NaF$

(iv) $Be(OH)_2 + 2NH_4HF_2 = (NH_4)_2BeF_4 + H_2O$

(v) $(NH_4)_2BeF_4 = BeF_2 + 2NH_3 + 2HF$

(vi) $BeF_2 + Mg = Be + MgF_2$.

The last reaction proceeds rapidly at 900°C. But the temperature is raised to 1300°C —above the m.p. of Be (1278°C) and MgF_2. This makes separation of the products easier.

Alternatively, steps (iv) to (vi) may be replaced as

(iv)—(a) $Be(OH)_2$ dissolved in HF. Solution evaporated and heated to 900°C.	$2BeO, BeF_2$ Basic beryllium fluoride.
(iv)—(b) The basic fluoride is fused—mixed with BaF_2 and NaF—electrolyzed (1400°C). Graphite crucible (anode) and water-cooled iron cathode.	Be

Extraction via BeO

(i) Beryl is fused in an electric furnace at 1500—1600°C and quenched by water. A vitrefied (glassy) mass is obtained.

(ii) The mass is crushed and digested with concentrated H_2SO_4. $BeSO_4$ and $Al_2(SO_4)_3$ are formed in solution, insoluble silica is filtered out.

(iii) Ammonium sulphate is added. Sparingly soluble $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$ is separated by filtration.

(iv) *Excess* ammonium carbonate solution is added. Beryllium remains in solution as $(NH_4)_2[Be(CO_3)_2]$. Precipitated $Fe(OH)_3$ and $Al(OH)_3$ are separated.

(v) The solution is diluted and boiled. Basic beryllium carbonate is precipitated.

(vi) The basic carbonate is ignited (600°) to BeO.

(vii) BeO is heated (600-800°) with carbon in a stream of chlorine to obtain anhydrous $BeCl_2$:

$$BeO + C + Cl_2 \rightleftharpoons BeCl_2 + CO.$$

(viii) A mixture of fused $BeCl_2+NaCl$ is electrolysed (800°C) to obtain beryllium.

Alternatively, Beryllium may be obtained by electrothermal reduction of BeO (+coke) in carbon crucible in an A.C. electric arc furnace with carbon electrodes.

19.2.2. Magnesium

Magnesium is produced either by electrolysis or silicothermal reduction.

In the electrolytic method, fused anhydrous magnesium chloride ($+CaCl_2$ $+NaCl$) is electrolysed at 750°C using iron cathode and graphite anode in an inert atmosphere. The least electropositive metal magnesium deposits alone.

In the silicothermal process, (Pidgeon process), magnesium oxide or calcined dolomite (CaO, MgO) is heated with ferrosilicon at about 1150°C in alloy steel retorts; high vacuum is maintained to distill out the magnesium formed

$$2(CaO. MgO) + FeSi = 2Mg + Fe + CaO. CaSiO_3$$

Magnesium in seawater may be enriched by ion-exchange through calcined dolomite (CaO, MgO). $Mg(OH)_2$ is less soluble than $Ca(OH)_2$—this leads to the replacement of calcium by magnesium:

$$Ca(OH)_2.Mg(OH)_2 + Mg^{2+} \rightarrow 2Mg(OH)_2 + Ca^{2+}.$$

The magnesium hydroxide may be heated to give MgO.

Carbon reduction of MgO (2000°C) also gives magnesium: $MgO+C \rightleftharpoons Mg+CO$. The metal is deposited by rapidly cooling the product to ~200°C by dilution with hydrogen or natural gas. Some magnesium oxide is still formed. The metal is purified by redistillation in vacuum.

Magnesium may be prepared as a highly reactive black powder by (i) reducing $MgCl_2$ with molten Na or K or (ii) decomposition of MgH_2 at low pressure and 250°C. This may be used to prepare many Grignard reagents which were previously unknown. Reaction of magnesium metal with anthracene and methyl iodide in tetrahydrofuran gives an orange adduct which is also very useful in synthesis.

19.2.3. Ca, Sr, Ba and Ra

Calcium is produced by electrolysis of fused calcium chloride (plus fluorspar, to lower the m.p. from 774° to 664°) using graphite anode and water-cooled iron rod cathodes.

Strontium and barium may also be obtained by electrolysis of the fused chlorides. The metals are however best prepared by reducing their oxides with aluminium in an evacuated retort (~1400°). Silicon is also used to reduce BaO (1200°C).

$$2Al + 3BaO = 3Ba + Al_2O_3; \quad Si + 3BaO = 2Ba + BaSiO_3$$

Radium is recovered in small quantities from uranium minerals—less than 100g a year over the world. Nearly 10 tonnes of ore have to be processed for 1 mg Ra. With minor modifications, the method remains the same as that used by Mme Curie:

Extraction of Radium

(i) Pitchblende is finely ground and roasted (~500°C).

(b) It is digested with 1 : 1 H_2SO_4 for ~6 hours. U (with Mn, Fe, Cu etc.) goes into solution. Ra remains as insoluble sulfate with $BaSO_4$, $PbSO_4$, silica etc. Sometimes barium chloride is added during the process to form sufficient $BaSO_4$.

(c) The residue is leached with sodium thiosulfate solution (to remove silver) and digested with 10% NaOH solution (to remove some lead and silica).

(d) The sulfates are then converted to carbonates by digestion with Na_2CO_3. The carbonate is dissolved in HCl to give chlorides. The two processes are repeated several times.

(e) The carbonate is finally dissolved in HBr. Residual lead and iron are removed as sulfide. $RaBr_2$ (less soluble) is then separated from $BaBr_2$ by fractional crystallization.

25 to 200 crystallizations may be necessary to obtain sufficiently pure $RaBr_2$. The finished product is ignited at 600° and powdered and sealed in glass capillaries. It is usually supplied in this form. Metallic radium may be obtained by electrolysis of $RaBr_2$ or $RaCl_2$ solutions.

19.2.4 Uses of the metals

Beryllium

Beryllium is largely used to improve the properties of Cu and Ni-alloys. About 2% Be increases the strength of Cu six fold. The alloys are non-magnetic, corrosion resistant and possess high strength and good electrical conductivity. They find extensive applications in critical moving parts of aero-engines, and in many precision instruments and electronic industries. Beryllium is also used in nuclear reactors as a moderator and as window material in X-ray tubes (it transmits X-rays 17 times better than Al).

Magnesium

Magnesium is largely used as a light weight construction metal. For equal strength, the best magnesium alloy weighs one-fourth as much as steel. Alloying is usually made with 2—9% Al, 1—3% Zn and 0·2—1% Mn. Rare-earth elements (Pr, Nd) and Th improve retention of strength upto 450°C and make them suitable for use in automobile engines and aeroplanes. More than 3,00,000 tonnes of magnesium are produced annually over the world.

Calcium

Calcium is also used as an alloying agent to improve the strength of aluminium bearings. It is an important reducing agent in the production of Cr, Zr, Th and U. It is also used to remove N_2 from argon, as a scavenger in steel industry (to remove O, S, P) and in the manufacture of hydrolith (CaH_2). About 1,000 tonnes of the metal are produced annually in the whole world.

The uses of Sr and Ba are limited. A Ni-Ba alloy has high emissive power and is used for spark-plug wire.

Radium is chiefly used as a radioactive source. Its use in the treatment of cancer has declined due to the availability of other synthetic radioactive isotopes.

19.2.5. Detection and Estimation

Detection of beryllium: Beryllium is divalent in its salts and closely resembles aluminium in chemical reactions. It may be detected in solution by the following reactions:

(*a*) *Sodium hydroxide solution*: White, gelatinous precipitate of $Be(OH)_2$; dissolves in excess NaOH solution forming $Na_2[BeO_2]$ (Sodium beryllate). On dilution and boiling, $Be(OH)_2$ is reprecipitated [$Al(OH)_3$ does not]. $Be(OH)_2$ is also soluble in 10% $NaHCO_3$ solution [$Al(OH)_3$ is not].

$$Be(OH)_2 + 2NaOH = Na_2[BeO_2] + 2H_2O$$

(*b*) *Formation of basic acetate*: When a solution of $Be(OH)_2$ in glacial acetic acid is evaporated to dryness, the basic acetate $BeO, 3BeAc_2$ ($Ac{=}CH_3COO$) is produced. This dissolves readily in chloroform. Basic aluminium acetate is insoluble in chloroform.

(*c*) *Quinalizarin* : (1 : 2 : 5 : 8—Tetrahydroxy-anthraquinone, 0·05% solution in 0·1N NaOH). A characteristic corn-flower blue precipitate or colour is obtained in presence of dilute NaOH (aluminium to be kept as aluminate).

Magnesium produces a similar colour but this is completely destroyed by bromine water. A blank test is recommended (blue-violet colour). Cu, Ni, Co and Fe interfere.

In general group separation of cations, beryllium is precipitated in Gr IIIA and remains in solution as sodium beryllate with sodium aluminate. The quinalizarin test may be applied to this solution or $Be(OH)_2$ may be precipitated by dilution and boiling.

Separation from aluminium

Beryllium is most satisfactorily separated by means of "oxine" (8-hydroxyquinoline). Aluminium (also Fe) is precipitated as $Al(C_9H_6ON)_3$ in ammonium acetate-acetic acid buffer medium. The precipitating solution consists of a 2% solution of oxine in 2N acetic acid; a permanent precipitate obtained by adding ammonia solution is redissolved by dilute HCl. The filtrate after separation of aluminium oxinate is heated nearly to boiling and a slight excess of ammonia solution is added to precipitate $Be(OH)_2$. It is ignited to BeO (1000°C) and weighed. In presence of other metals forming an insoluble hydroxide, EDTA may be used to precipitate beryllium selectively.

Be may also be estimated as $Be_2P_2O_7$ obtained by igniting the insoluble ammonium beryllium phosphate.

Beryllium may be determined spectrophotometrically with 4-nitrobenzene-azo-orcinol in presence of 0·2*M* NaOH solution. The transmittance of the reddish brown colour is measured at 520 nm. Interference of small amounts of Cu, Ni, Fe and Ca may be prevented by EDTA and triethanolamine.

The acetylacetone complex of beryllium may be extracted with chloroform; the excess of acetylacetone removed by rapid washing with 0·1 *M* NaOH solution and the absorbance may be measured at 295 nm.

Magnesium is detected in solution by

(*a*) *Disodium hydrogen phosphate solution*: A white crystalline precipitate of $Mg(NH_4)PO_4, 6H_2O$ is formed in ammoniacal medium in presence of ammonium chloride (to prevent the precipitation of $Mg(OH)_2$).

$$MgSO_4 + Na_2HPO_4 + NH_3 = Mg(NH_4)PO_4 + Na_2SO_4$$

The precipitate has a tendency to form supersaturated solutions—rubbing with a glass-rod aids precipitation. It is soluble in acetic acid and mineral acids. In neutral solutions, a white precipitate of $MgHPO_4$ is formed.

(*b*) *Quinalizarin*: A 0·05% solution of the reagent in 0·1N NaOH gives a corn-flower blue colour or precipitate in presence of 2N NaOH solution. The colour disappears on adding a little bromine water (difference from Be).

The cations of Gr I to Gr IIIB should be absent. Phosphates and ammonium salts decrease the sensitivity of the test.

Estimation

Magnesium may be estimated by igniting the precipitate of $Mg(NH_4)PO_4$ and weighing as $Mg_2P_2O_7$: $2Mg(NH_4)PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$.

Alternatively, the precipitate may be dissolved in known excess of a standard acid; back-titration of the excess acid gives an estimate of Mg.

8-hydroxyquinoline or oxine (2% solution in 2N acetic acid) gives a yellow precipitate of magnesium oxinate in an ammoniacal solution in presence of ammonium chloride. The precipitate may be weighed in a sintered glass crucible after drying at 100—110°; the composition is taken as $Mg(C_9H_6NO)_2, 2H_2O$.

The precipitate may also be dissolved in dilute HCl. The liberated oxine is titrated by $KBrO_3$ in presence of KBr.

$$Mg(C_9H_6NO)_2 + 2HCl = 2HC_9H_6NO + MgCl_2$$

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 2H_2O$$

$$HC_9H_6NO + 2Br_2 = HC_9H_4Br_2NO + 2HBr$$

$$1{,}000\ cm^3\ of\ 1N\ KBrO_3 \equiv 3{\cdot}04\ g\ Mg.$$

The method permits estimation of magnesium in presence of Al(III) and Fe (III) which may be arrested as tartrate complex in presence of NaOH. Separation from calcium is also possible as calcium oxinate fairly readily dissolves in hot ammonia solution. Reprecipitation is recommended.

Problem 19.1 A precipitate of magnesium oxinate was dissolved in 2N HCl. 1g KBr was added, followed by 2—3 drops of methyl orange (or methyl red). The solution was then titrated with standard 0·106N $KBrO_3$ solution until it became colourless. Addition of $KBrO_3$ was continued till the solution attained a yellow colour due to free bromine. The burette reading was 27·5 cm³. KI was then added and the liberated iodine required 8·0 cm³ of 0.023N $Na_2S_2O_3$. Calculate the quantity of magnesium in the precipitate.

Solution:

$KBrO_3$ consumed by oxine ≡ Total $KBrO_3$ added — $KBrO_3$ used in liberating extra Br_2.

The last quantity is obtained from the equivalent of I_2 liberated, which, in turn, is equal to the equivalents of thio.

$\therefore$ $KBrO_3$ consumed by oxine ≡ (27·5×0·106−8·0×0·023) milliequivalent

=2·731 m-eq.

$\therefore$ magnesium present = 2·731×3·04 milligram [See equations above]

Magnesium may be estimated colorimetrically by measuring the absorbance (520 nm) of the red colour produced by Solochrome Black at pH 10·1. Minute quantities of magnesium in drinking water is measured by flame spectrometry.

Magnesium may also be determined by titration with EDTA solution at pH 10 (aq. NH_3, NH_4Cl) using Solochrome Black indicator; the colour changes from red to blue at the end point. If the sample contains both calcium and magnesium, as in hard water or in dolomite, the titre value corresponds to the total Ca+Mg. Interference by other metals like Co, Ni, Cu, Zn, Hg and Mn may be avoided by adding a little hydroxylamine hydrochloride and NaCN. The calcium may be next titrated selectively using Patton and Reeder's indicator (red to blue). Magnesium is found by difference.

Magnesium may also be determined in admixture with zinc and manganese by EDTA titration using NaF and NaCN as demasking agent.

Calcium salts in solution form a white precipitate of CaC_2O_4, H_2O with ammonium oxalate solution (better in presence of a little ammonia). The precipitate is insoluble in water (S.P.$=10^{-9}$) and acetic acid but soluble in mineral acids.

With dilute H_2SO_4, calcium salts also produce a white precipitate of $CaSO_4$, $2H_2O$ from concentrated solutions. This is slightly soluble in water (~2g per liter at 25°) and is more soluble in acids than $BaSO_4$ or $SrSO_4$. $CaSO_4$ dissolves in hot concentrated ammonium sulphate solution: $CaSO_4+(NH_4)_2SO_4=(NH_4)_2[Ca(SO_4)_2]$. Addition of a little sodium thiosulfate increases the solubility of $CaSO_4$.

Estimation

Calcium may be estimated quantitatively via its oxalate. To enable easy filtration, precipitation is carried out from homogeneous solution, thereby forming coarser grains. The ammonium oxalate solution is added to a warm acid (HCl) solution of the Ca^{2+} ion. Ammonia solution is now slowly added to raise the pH to ~4 (methyl orange). The concentration of $C_2O_4^{2-}$ ion rises very slowly and gradually and precipitation proceeds all the time from a solution that is very slightly supersaturated with CaC_2O_4. This facilitates the formation of larger crystals.

The precipitate of calcium oxalate is first washed with 0·1% solution of ammonium oxalate and then with small portions of cold water. It is dissolved in hot dil (4N) H_2SO_4 and the liberated oxalic acid is titrated by standard $KMnO_4$ solution.

Calcium may be titrated with standard EDTA solution using Solochrome Black only in presence of magnesium; calcium alone does not give a sharp end-point. If magnesium ions are not present in the solution, a small amount of magnesium chloride is added to the EDTA solution before standardisation. A buffer solution of ammonia-ammonium chloride is used to maintain the pH at 10. Interference from Co, Ni, etc. may be overcome by hydroxylamine hydrochloride and sodium cyanide.

Calcium alone may be determined by titration with EDTA using Patton and Reeder's indicator in presence of ~ 1 *M* KOH. At the high pH, magnesium is present as $Mg(OH)_2$ which does not react with EDTA until all the free calcium and the calcium-indicator complex is complexed by the EDTA. The colour changes from red to blue.

However, the above method is not satisfactory when the solution contains magnesium more than 10 per cent of the calcium present ($Ca(OH)_2$ may be coprecipitated). So titration of small amounts of calcium is better carried out with EGTA (ethylene glycolbis (2-aminoethyl ether) N, N, N′, N′-tetra-acetic acid; zincon is used as an indicator (blue to orange-red).

Strontium salts in solution are identified by

(*a*) *dilute sulphuric acid*, which forms a sparingly soluble (~0·14 g/L) white precipitate; it is slightly soluble in boiling HCl, but insoluble in boiling $(NH_4)_2SO_4$ solution (difference from Ca).

Ba^{2+} also forms an insoluble white precipitate ($BaSO_4$) with dil. H_2SO_4. But $BaSO_4$ is also precipitated by a saturated solution of calcium sulphate while $SrSO_4$ is not (difference from Ba).

Potassium chromate solution does not precipitate $SrCrO_4$ in presence of dilute acetic acid (see barium).

(*b*) *Flame colouration*: Volatile strontium compounds, particularly the chloride, gives a persistent crimson red colour to a non-luminous flame. $SrSO_4$ may be reduced with carbon to SrS and the latter dissolved in HCl to perform this test.

Strontium is estimated by weighing as $SrSO_4$ which is precipitated from a medium containing excess sulphuric acid and ethyl alcohol. Calcium, barium and lead must be absent.

Strontium may also be precipitated as $SrHPO_4$ by a solution of KH_2PO_4 around pH 6. It may be weighed as such after drying at 120°C or may be ignited to $Sr_2P_2O_7$. Metals forming insoluble phosphates should be absent.

Barium is detected in solution by

(*a*) *Dilute H_2SO_4*: $BaSO_4$ is highly insoluble in water (~2·5 mg per liter, S.P.$\simeq10^{-10}$) and dilute acids and ammonium sulphate solutions.

Ba may be distinguished from Sr or Ca by the precipitation of $BaSO_4$ by a saturated solution of $CaSO_4$ (or $SrSO_4$).

(*b*) *Potassium chromate solution*: Yellow $BaCrO_4$ is sparingly soluble in water (S.P.$\simeq10^{-10}$). It is also insoluble in dilute acetic acid but readily soluble in dilute mineral acids.

(*c*) *Flame colouration*: Volatile barium compounds impart a persistent apple-green colour to a non-luminous flame. This test may be performed with $BaSO_4$ after reduction to BaS.

Barium may be estimated gravimetrically by precipitation as $BaSO_4$ by dilute H_2SO_4 from boiling solution. Dimethyl sulphate or sulphamic acid are also used to effect precipitation from homogeneous solution; on boiling, these slowly give sulphate ions and form crystalline precipitates.

Volumetrically barium is estimated by precipitation as barium chromate from dilute acetic acid—ammonium acetate buffer. Strontium, when present in large excess, may be precipitated above pH 5·7. Below this pH, separation from Ca and Sr is quite satisfactory. A double precipitation is more effective. The precipitate is then dissolved in cold dilute HCl and the liberated chromium (VI) is titrated iodometrically or by adding a known excess of standard ammonium iron (II) sulphate solution.

$BaCrO_4+2HCl=BaCl_2+H_2CrO_4$; $CrO_4^{=}+8H^++3I^-=Cr^{3+}+4H_2O+3/2I_2$.

1000 cm³ of 1N $Na_2S_2O_3$ ≡ 137·34/3 g Ba ≡ 52/3 g Cr.

Barium may be estimated by titration with EDTA using Methyl Thymol Blue indicator at pH 12. Colour change: blue to grey.

19.3 COMPOUNDS OF THE ALKALINE EARTH METALS

The general trend in the properties of the alkaline earth elements and their compounds has been discussed in section 19.1.2. Summarily we noted that

(i) The elements show uniform divalence.

(ii) The compounds of beryllium are largely covalent due to extensive polarisation. This falls appreciably to Mg(II), where it is still significant, but practically loses importance among the remaining elements. The effect is reflected in low thermal stability of the salts of oxoacids.

(iii) The coordination number of beryllium is limited to 4; it is 6 for others.

(iv) Be and Mg form several interesting organometallic and coordination compounds.

The important compound types of these elements are briefly covered below.

19.3.1. Hydrides

As noted in section 19.2, beryllium does not form any hydride directly. But BeH_2 may be obtained by reducing $BeCl_2$ with LiH or $BeMe_2$ with $LiAlH_4$. A better method involves pyrolysis of di-*tert*-butylberyllium:

$$[(CH_3)_3C]_2Be \xrightarrow{210°} 2(CH_3)_2C=CH_2 + BeH_2$$

$$[(CH_3)_3CMgBr + BeCl_2 \xrightarrow{\text{ether}} [(CH_3)_3C]_2Be].$$

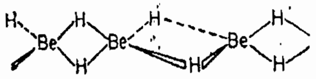
BeH_2 is an amorphous white solid. It decomposes above 250°C giving H_2. It is also moderately stable in air or water, but undergoes rapid hydrolysis by acids (evolving H_2).

BeH_2 is a polymeric compound—the beryllium atoms are linked by 3-center 2-electron hydrogen bridge bonds similar to those in boron hydrides (19—II).

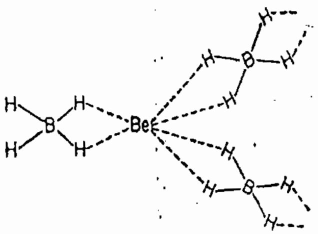
BeH_2 reacts with diborane to form the volatile boro-hydride, $Be(BH_4)_2$. It is also obtained by reacting $BeCl_2$ with $LiBH_4$ in a sealed tube (120°C).

$$BeCl_2 + 2LiBH_4 \longrightarrow BeB_2H_8 + 2HCl$$

The compound inflames in air and reacts vigorously with water.



19-II. A likely structure for BeH_2. Several other structures may be possible. In the gas phase, all the H- atoms appear equivalent (nmr), indicating fluxional behaviour.



19-III. A section of the helical arrangement in $Be(BH_4)_2$. The Be is apparently 6-coordinated from a large distance (distorted trigonal prism). The H-atoms are much closer to B.

The structure of solid BeB_2H_8 has been confirmed by single crystal X-ray studies. It consists of helical polymers of BH_4Be units linked by bridging BH_4 units. (19-III). The bonding involves 3-center 2-electron Be—H—B bridges:

AlH_3 forms similar borohydride.

Other hydrides of the group II elements are ionic in nature; their properties follow from those discussed in connection with the hydride ion.

19.3.2 Oxides and hydroxides

The alkaline earth metals form their monoxides (MO) when heated in oxygen. They also result from thermal decomposition of the respective carbonates, nitrates and hydroxides.

As expected, the oxides are strongly basic in nature. The high charge of the metal cause strong polarization on the oxide ion. BeO is covalent, it has the wurtzite* structure. Others have the NaCl structure. Radius ratio for SrO (0.81) and BaO (0.96) suggest that eight oxide ions may be accommodated around the metal ions. In spite of this these oxides prefer the NaCl structure for more favourable lattice energy. High charges on both the cation and anion give rise to high lattice energy—as reflected in their high melting points (°C):

BeO	MgO	CaO	SrO	BaO
2530	2826	2600	2400	1900

Peroxides, superoxides and ozonides of the alkaline earth metals are also known, specially for the larger ones. High polarizing power of the smaller cations makes the peroxide and superoxide ions unstable to heat. So these compounds are not formed readily by direct reaction of the metals with oxygen. However, stability increases with electro-positive character and size of the metal. Thus SrO_2 can be obtained by heating the metal in O_2 at high pressure; BaO_2 may be obtained by heating the metal in air at 500°. Hydrated peroxides of Mg, Ca, Sr and Ba may be obtained by adding H_2O_2 into aqueous solutions of these metal salts or hydroxides.

$$Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2 \cdot 8H_2O.$$

Except with magnesium, the hydrates give the anhydrous peroxide on gentle heating (~130°C). Anhydrous MgO_2 can only be made in liquid ammonia solution.

Dilute aqueous acids liberate H_2O_2 from the peroxides and $H_2O_2 + O_2$ from the superoxides. The compounds thus act as oxidizing and bleaching agents.

$$BaO_2(s) + H_2SO_4 \longrightarrow BaSO_4(s) + H_2O_2$$

$$Ba(O_2)_2(s) + H_2SO_4 \longrightarrow BaSO_4(s) + H_2O_2 + O_2$$

The hydroxides of all the Gr IIA metals can be obtained by treating their monoxides with water or by adding alkali to an aqueous solution of the salts. Their properties vary smoothly down the group with increasing size and decreasing polarizing power of the metal ion. Thus solubility in water and basic character increases from $Be(OH)_2$ to $Ba(OH)_2$. $Be(OH)_2$ is amphoteric in nature and $Mg(OH)_2$ is a mild base. Base strength increases to $Ba(OH)_2$ which is comparable in strength to the alkali metal hydroxides. Solubility ($g\ l^{-1}$) in water at 20°C and Kb_2 are approximately as follows:

	$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
Solubility	3×10^{-4}	3×10^{-2}	1·3	8	38
Kb_2	—	$2{\cdot}5\times10^{-3}$	4×10^{-2}	$1{\cdot}5\times10^{-1}$	$2{\cdot}3\times10^{-1}$

The increase in base strength from $Ca(OH)_2$ to $Ba(OH)_2$ is also reflected in the $\Delta G°$ values of the reaction $M(OH)_2(s) + CO_2(g) = MCO_3(s) + H_2O$.

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
$\Delta G_0°$, kJ mol^{-1}	30	−38	−75	−110	−112

Similarly, decrease in polarizing power of the M^{2+} ion and lower lattice energy from BeO to BaO result in increasing thermal stability of the hydroxides:

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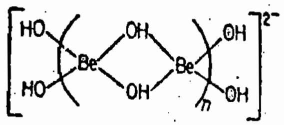
*Wurtzite is a mineral variety of ZnS. The crystal structure consists of two interpenetrating hexagonal close-packed lattices of Zn and S atoms, both having coordination number 4. (See p. 463.)

Being amphoteric in nature, $Be(OH)_2$ dissolves in excess alkali. The initial solution is believed to consist of a polymeric chain:



19-IV.

Further addition of alkali depolymerizes the chain—the mononuclear beryllate anion $[Be(OH)_4]^{2-}$ is ultimately formed.

19.3.3. Carbides and Nitrides

The group IIA metals form several carbides of the representative formula M_2C, MC_2 and M_2C_3.

A carbide corresponding to the formula M_2C is formed only by Be. Be_2C is formed by direct reaction at 1900°C. Other metals of this group cannot be accomodated in the small space available between the carbon atoms in the antifluorite structure adopted by this type of carbides (See carbides, Gr IV B). Be_2C (brown) slowly liberates methane on hydrolysis (methanide).

Carbides of formula MC_2 are formed by all the elements in the group. BeC_2 and MgC_2 are obtained by heating the metals in acetylene around 400°C. Ca, Sr and Ba react directly with carbon at 2000°C (electric arc furnace). CaC_2 can also be obtained by heating $CaCO_3$ with carbon. It readily liberates acetylene with water (acetylide) at ordinary temperatures and is largely used where oxy-acetylene flames are required. At red heat CaC_2 absorbs nitrogen from air forming the important nitrogenous fertilizer calcium cyanamide, Ca (N=C=N). The cyanamide ion is linear like CO_2 and isoelectronic with it. $CaCN_2$ slowly liberates ammonia on hydrolysis. Its fertilizer action in the soil is thus prolonged.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

The MC_2 carbides have sodium chloride type structure in which M^{2+} ions replace Na^+ ions and C_2^{2-} (acetylide) ions replace Cl^- ions.

Only magnesium forms Mg_2C_3 when heated in acetylene at 600°C. On hydrolysis it gives propyne (allylene or methyl acetylene), $CH_3C\equiv CH$. It is thus called an allylide with the probable ionic structure $(Mg^{2+})_2(C_3^{4-})$.

The alkaline earth elements burn in nitrogen to form nitrides M_3N_2. Be_3N_2 is formed by the action of NH_3 or N_2 on the metal at 900—1000°C, while Mg_3N_2 is formed from Mg and N_2 at 300°C. They are all colourless crystalline solids. The high energy requirement for the formation of the N^{3-} (nitride) ion from $N\equiv N$ is more than compensated by the lattice energy provided by the doubly charged M^{2+} ions. Among the alkali metals, only lithium is small enough to meet this requirement. All these nitrides react with water to give ammonia and the respective hydroxide.

The elements from Ca to Ba are also known to form nitrides with other stoichiometries. Ca_2N has a lustrous, graphitic appearance.

19.3.4 Halides

All the metals of Gr IIA combine with halogens at suitable temperatures to form the dihalides. These are also obtained by reacting the halogen hydracid with the metal, its oxide, or carbonate. However, anhydrous beryllium and magnesium halides cannot be obtained by simply heating the aqueous solutions owing to hydrolysis (see p. 151). Reaction of the halogen on a mixture of the metal oxide and carbon provides a better method. Some representative equations are

$$(NH_4)_2BeF_4 = BeF_2 + 2NH_3 + 2HF$$

$$BeO + C + Cl_2 = BeCl_2 + CO \ (600—800°C)$$

$$MgO + C + Cl_2 = MgCl_2 + CO \ (\text{red heat})$$

$$MgCl_2, NH_4Cl, 6H_2O = MgCl_2 + NH_4Cl + 6H_2O.$$

$BeCl_2$ is also prepared by heating BeO in CCl_4 vapour at 800°C.

The beryllium halides are covalent and polymeric. They sublime readily on heating and do not conduct electricity in the molten state. But conductance increases considerably on adding an alkali halide even in small quantities—complex anions like $BeCl_4^{2-}$ are formed. Except BeF_2, the halides dissolve in polar organic solvents with the formation of complex compounds. Thus $BeCl_2$ dissolves in pyridine to give the monomeric tetrahedral complex $Cl_2Be(py)_2$. The anhydrous halides also absorb water to give $Be(H_2O)_4X_2$, but BeI_2 vigorously hydrolyses to HI:

$$BeI_2 + 2H_2O = Be(OH)_2 + 2HI.$$

Being ionic in nature, the compounds $Be(H_2O)_4X_2$ are insoluble in organic solvents. The chloroberyllate ion $[BeCl_4]^{2-}$ does not exist in aqueous solutions, but may be formed in melts with alkali metals.

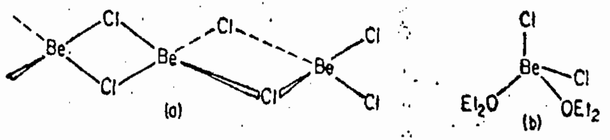
BeF_2 is a glassy solid containing randomly oriented chains like $..F_2BeF_2Be...$ Each F-bridged Be-atom is 4-coordinated—the structure is similar to that of vitreous silica. Above 270°C, BeF_2 spontaneously adopts a crystalline structure analogous to that of quarz (Gr IVB). Structural analogues of other forms of silica, e.g., crystobalite and tridymite, have also been prepared. BeF_2 melts at 555°C to a viscous liquid having low electrical conductivity. In the gaseous phase, it is monomeric.

BeF_2 acts as a Lewis acid and readily forms the tetrafluoberyllate (II) anion, BeF_4^{2-}. Stability increases from $CaBeF_4$—$SrBeF_4$—$BaBeF_4$ as basic character increases in the order CaF_2—SrF_2—BaF_2. The decreasing lattice energy of the heavier fluorides also contribute and we find that the reaction

$$MBeF_4(s) = MF_2(s) + BeF_2(s)$$

requires increasingly higher temperature from M=Ca to M=Ba. $CaBeF_4$ decomposes at 890°C while $BaBeF_4$ melts without decomposition at 1080°C.

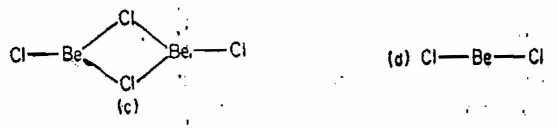
Anhydrous $BeCl_2$ (m.p. 405°C) is polymeric in the solid state. The Be atoms are approximatly sp^3 hybridized with bridging chlorine atoms [19-V (a)].



19-V (a) and (b)

The ClBeCl angle is considerably less than 109°—this increases the Be—Be distance (263 pm) and minimises the repulsion between neighbouring Be atoms. Addition of weak ligands break the polymer giving 4-coordinate molecular complexes like $[BeCl_2(Et_2O)_2]$ [19-V(b)]. Stronger donor ligands may form ionic complexes like $[Be(NH_3)_4]^{2+}Cl_2$.

In the vapour state, $BeCl_2$ forms a mixture of dimer 19-V(c) and monomers [19-V(d)]. In the dimer, Be is approximately sp^3 hybridized, while it is sp hybridized in the monomer. Dissociation to the monomer is not complete below 900°C.



19-V (c) and (d).

$BeBr_2$ (m.p. 490°C) and BeI_2 (m.p. ~500°C) are similar to the chloride but with lower stability (see p. 149 for hydrolysis of BeI_2).

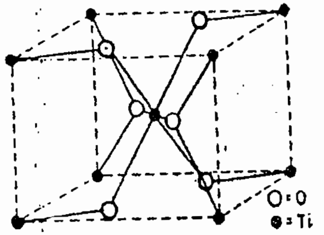


Fig. 19.1. The rutile structure. Rutile is the most common form of TiO_2; it is based on a slightly distorted hexagonal close packing of oxygen atoms. Ti atoms occupy half the octahedral interstices of the O-atoms. This structure is commonly adopted by ionic dioxides and difluorides having r_+/r_- ratio between 0.73 to 0.41.

The halides of the heavier alkaline earth metals are typical ionic solids. MgF_2 has the rutile structure (TiO_2 Fig. 19.1); other fluorides have the fluorite structure characteristic of CaF_2 (Fig. 19.2).

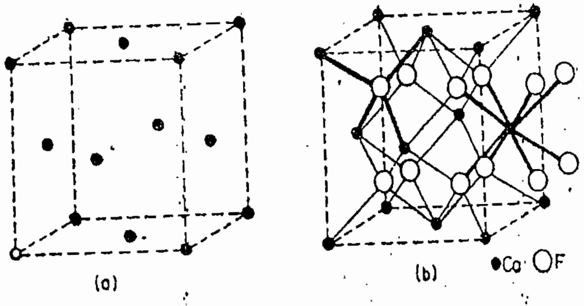


Fig. 19.2. The fluorite structure. The structure can be thought of as an fcc array of Ca, (shown separately in a) with the tetrahedral interstices occupied by F. Each Ca is surrounded by eight F in a cubic arrangement while each F is surrounded tetrahedrally by 4 Ca (shown in bold lines in b).

The other halides have different layer-lattice structures-$CdCl_2$, CdI_2, etc. SrI_2 is unique in having a sevenfold coordination around the Sr atom.

CaF_2 is a high melting solid (1418°C) with very low solubility in water. Present in nature as fluorspar, it is the only source of fluorine. The fluorides of other metals are also high melting and very little soluble in water (see below). In contrast, the chlorides (Mg, Ca) readily form hydrates and are deliquescent.

The effect of increasing cation size (and decreasing charge density) is again reflected in the gradual change in properties from Mg to Ra:

1. Magnesium and calcium halides readily absorb water while others are normally anhydrous. Hydration energies decrease more rapidly than the lattice energies as the size of M^{2+} ion increases.

2. The anhydrous halides may be usually made by dehydration of the hydrated salts. But $MgCl_2$ undergoes slight hydrolysis in solution. $MgCl_2, 6H_2O$ undergoes rapid hydrolysis on being heated in air (~200°C), evolving steam and HCl. Magnesium oxychloride, Mg(OH)Cl is formed which decomposes at 600°C to MgO:

$$MgCl_2 + H_2O = Mg(OH)Cl + HCl \;;\; Mg(OH)Cl = MgO + HCl.$$

The anhydrous salt may be prepared by heating the hydrate *in vacuum* (175°) or in a current of HCl.

3. Anhydrous magnesium halides dissolve in certain organic solvents like alcohols, ethers and ketones. Solid complexes like $MgCl_2, 6C_2H_5OH$ may be isolated from such solutions.

4. The solubility of the halides in water decrease from Mg—Ra, but the fluorides show the reverse trend. The F^- ion is unusually small in comparison to the M^{2+} ions. The large cations touch one another without at the same time making contact with the F^- ion. As a result lattice energies decrease unusually rapidly. For other halides, the decrease of hydration energy becomes dominant.

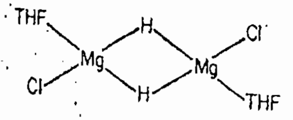
Though typically ionic in the solid state, the halides may be vaporized as single molecules. The molecules are not all linear; hence they are not simple $X^-—M^{2+}—X^-$ ion clusters. The bent structure may be explained by assuming d-orbital participation by the metal (p. 138).

Salts MHX have been prepared for M = Ca, Sr, Ba and X = Cl, Br or I. The usual method is to fuse the halide MX_2 with the hydride MH_2. Heating the metal with MX_2 in an atmosphere of H_2 (~900°C) also leads to MHX. Specially activated MgH_2 and MgX_2 (X=Cl, Br) react in tetrahydrofuran (THF) to give the solvated dimer of MgXH.

$$MgR_2 + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2R_2$$

$$MgH_2 + MgX_2 \xrightarrow{THF} [MgXH(THF)]_2$$

The chloride can be crystallized; the bromide disproportionates. IR studies and molecular weight suggests the hydrogen-bridged structure



19-VI.

19.3.5 Salts of Oxoacids

The effect of increasing cation size and the consequent decrease in polarizing power is nicely demonstrated by the salts of oxoacids of the Gr II metals. The tendency to form hydrates decrease from Be to Ba, while the thermal stability of carbonates, sulfates and nitrates increase. In fact, the strong polarizing power of the Be^{2+} ion make $BeCO_3$ so unstable that it can only be precipitated from solution under an atmosphere of carbondioxide. The temperature at which the various carbonates decompose to give 1 atmosphere pressure of CO_2 increases sharply:

$BeCO_3, 4H_2O$	$MgCO_3$	$CaCO_3$	$BaCO_3$
25°C	420°C	810°C	1280°C

The solid bicarbonates of all are unknown for the same reason. But they are formed in solution:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

The solubility of the sulphates in water decreases in the order Be>Mg>>Ca>Sr>Ba, the sulphates from calcium onward being practically insoluble. Tendency to form hydrates decreases with increaing cation size—$SrSO_4$, $BaSO_4$ and $RaSO_4$ are anhydrous. Several factors contribute to the high solubility of $BeSO_4$ and $MgSO_4$; of them, two appear to be most important: (i) high solvation energy of small Be^{2+} or Mg^{2+}; (ii) loose packing with the relatively larger sulfate ion. The temperatures of decomposition of the sulphates (giving SO_3) also increase with decrease in polarizing power of the cation:

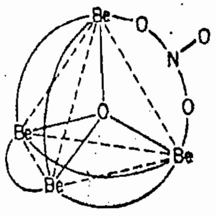
$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
580°C	895°C	1149°C	1374°C

Nitrates of the Gr II metals can be obtained by treating the oxides, hydroxides or carbonates with nitric acid; crystallization of the solution gives the hydrated salts. On heating, these hydrated salts decompose to the oxides. Anhydrous beryllium nitrate may be prepared by dissolving $BeCl_2$ in liquid dinitrogen tetroxide:

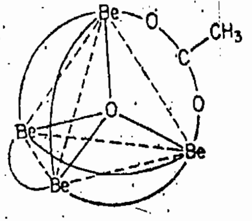
$$BeCl_2 + N_2O_4 \longrightarrow Be(NO_3)_2, 2N_2O_4 \xrightarrow[\text{vacuum}]{50°C} Be(NO_3)_2.$$

When heated to 125°C, $Be(NO_3)_2$ decomposes to N_2O_4 and a basic nitrate, $[Be_4O(NO_3)_6]$. Its structrue (19–VII) consists of a regular tetrahedral arrangement of 4 Be atoms around a central oxygen with six bridging nitrate groups (acting as a bidentate ligand). The structure is similar to that of basic beryllium acetate (19–VIII).

Beryllium forms a series of stable basic carboxylates of the general formula $[OBe_4(RCOO)_6]$, R=H, Me, Et, Pr, Ph etc. The basic acetate (R=Me) is typical among such compounds. These are readily obtained by refluxing the oxide (or hydroxide) with the carboxylic acid. They are white crystalline molecular solids—volatile and soluble in organic solvents but insoluble in water or the lower alcohols. The acetate melts at 285°C and boils at 330°. Stable towards heat, it undergoes slow hydrolysis with hot water. Mineral acids decompose it into the beryllium salt.



19–VII.



19–VIII.

The structure of basic beryllium acetate (19–VIII) is similar to that of the nitrate. A central O is surrounded by 4 Be atoms tetrahedrally (X-ray). The six edges of the tetrahedron are now bridged by the six acetate groups; each Be is tetrahedrally coordinated by four oxygen atoms.

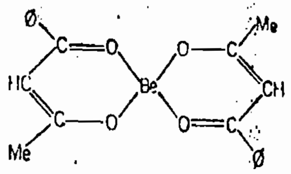
Many oxoacid salts of this group are important to our daily life. Calcium and magnesium bicarbonates make water hard ("temporary"; removable by boiling only); their sulfates and other soluble salts make water "permanent" hard. Calcium carbonate has widespread industrial use—particularly in the extraction of metals and in making glass. It is also an important raw material for cement. Gypsum ($CaSO_4$, $2H_2O$) is largely used in making plaster of paris, $CaSO_4$, 1/2 H_2O. Calcium phosphate is an important fertilizer.

19.3.6 Co-ordination compounds

The tendency for complex formation by the alkaline-earth metals generally falls as Be>Mg>Ca>Sr>Ba. As the cation size increases, ion-dipole interaction decreases. But with macrocyclic ligands (p. 130), matching of size becomes more important and the simple order may be reversed (see later).

Beryllium forms a large number of stable tetrahedral complexes with various oxygen donor ligands. We have already come across the $[Be(H_2O)_4]^{2+}$ ion in acidic aqueous solutions. The ion forms crystalline salts with many anions. The water molecules in such salts cannot be treated as mere water of crystallization—they indicate stronger binding. Thus $[Be(H_2O)_4]Cl_2$ loses no water over P_4O_{10}. With gradual addition of alkali to an aqueous solution, several polymeric hydroxo species are formed. In concentrated alkaline medium, the main species is $[Be(OH)_4]^{2-}$.

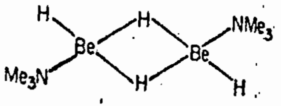
The adducts of beryllium halides or alkyls with ethers and ketones are also remarkably stable. For example, $[BeCl_2(OEt_2)_2]$ (Fig. 19–Vb) has a dipole moment of ~6.7D in benzene solution at various concentrations; this shows that no dissociation of ligands from the tetra-coordinated beryllium takes place. Neutral complexes with various β-diketones are also known. Bis(benzoylacetonato) beryllium (II) (19—IX) is optically active.



19–IX.

The basic carboxylates and nitrate of beryllium have been mentioned earlier.

The only stable halogen complexes of beryllium are the tetrafluoroberyllates, containing the anion $[BeF_4]^{2-}$. It is obtained by dissolving BeO or $Be(OH)_2$ in concentrated solution (or melt) of an acid fluoride, e.g., NH_4HF_2. $BaSO_4$ is isomorphous with $BaBeF_4$. The interaction of Cl^- with $[Be(H_2O)_4]^{2+}$ is very weak in nature.

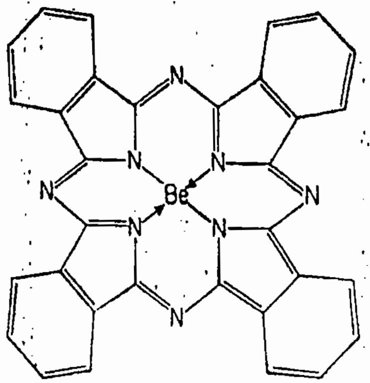


19–X.

Complexes of beryllium with nitrogen donor ligands (ammonia, amines, nitrites etc.) are comparatively fewer and less stable. Thus $[Be(NH_3)_4]Cl_2$ undergoes rapid hydrolysis by water. Beryllium hydride and beryllium alkyls form several complexes with nitrogen donor ligands, e.g., $[Me_3N BeH_2]_2$ (19—X), $[bipy Be(C_2H_5)_2]$ etc.

Beryllium also forms complexes with cyclopentadiene, e.g., C_5H_5BeX (X=Cl, Br, $-CH_3$ etc), or $(C_5H_5)_2Be$. The last compound is highly air-sensitive. Its structure is not fully understood.

An unusual example of **planar 4-coordinate** Be is provided by the blue phthalocyanine complex (19—XI). It is obtained by reacting beryllium metal with phthalonitrile, $1,2\text{—}C_6H_4(CN)_2$.



19-XI.

Among the remaining Gr II metals, only magnesium and calcium show any appreciable tendency to complex formation, particularly with oxygen donor ligands. However, the order of stability of such complex compounds depends very much on the nature of the ligand and is somewhat anomalous:

(a) For anions of small size and high charge, stability decreases with increasing size of the metal ion, i.e., Mg>Ca>Sr>Ba.

(b) For somewhat larger oxoanions, like NO_3^-, $SO_4^=$, IO_4^- etc. the order of stability is reversed, i.e., Mg<Ca<Sr<Ba. This is consistent with the hydrated radii of the metal ions.

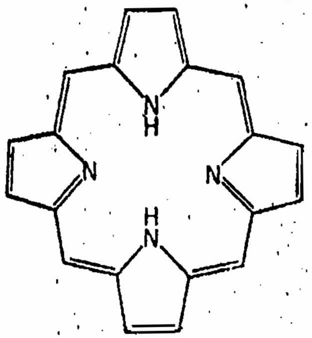
(c) For ligands derived from carboxylic acids, e.g., hydroxy-carboxylic, polycarboxylic and polyamino-carboxylic acids, the order is Mg<Ca>Sr>Ba. The stability constants for the EDTA complexes at 20°C are illustrative:

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K	8.7	10.7	8.6	7.8

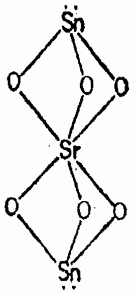
(d) For crown ethers and cryptates, size factors are more important than electrostatic considerations. Thus dicyclohexyl-18-crown-6 forms stronger complexes with Sr and Ba than with Ca. Cryptates also follow the stability sequence Mg<Ca<Sr<Ba.

Among the oxygen chelate compounds, the complexes formed by ethylenediaminetetraacetate (EDTA) and the polyphosphates are important in industry and analysis. They provide effective methods of removing magnesium and calcium from hard water and also for their volumetric estimation.

The alkaline earth metals form fewer complexes with nitrogen donor ligands like ammonia and amines. Non-stoichiometric adducts like MCl_2, $n NH_3$ are, however known. In presence of anthracene, barium forms an anionic complex in liquid ammonia: $[Ba(NH_3)_2\ (anthracene)_2]^-$. But magnesium forms a very important complex with tetrapyrroles, the basic structural unit of which is the porphine (19—XII).



19-XII.



19-XIII.

The chlorophylls and related compounds contain such magnesium chelates and these are of crucial importance in photosynthesis in plants. In such complexes, the conjugated heterocyclic system provides a rigid planar environment for the metal ions. The metal is formally 4-coordinate, but further interaction with water or other solvent molecules is also indicated in many cases. In presence of light, chlorophyll forms radicals; the electrons are then involved in the photosynthetic reduction of CO_2 by water.

Some "Sandwich" type complexes of Sr and Ba have been prepared recently:

$$Ba(O\text{-}t\text{-}Bu)_2 + [Sn(O\text{-}t\text{-}Bu)_2]_2 \longrightarrow BaSn_2(O\text{-}t\text{-}Bu)_6$$

These have high thermal stability and are soluble in petroleum. The Sr or Ba atom appears to be sandwiched between two trigonal planar arrangement of oxygen atoms (19—XIII).

The calcium atom seems to be too small to form a stable compound of this type.

19.3.7 Organometallic Compounds

Beryllium alkyls are best made by reactions like

$$HgMe_2 + Be \xrightarrow{110°C} Hg + BeMe_2$$

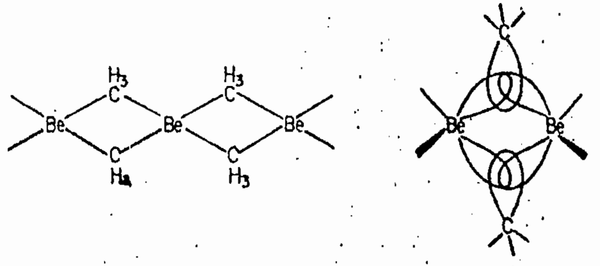
The alkyl can be sublimed or distilled in vacuum.

Beryllium aryls are made by reacting a lithium aryl (in a hydrocarbon) with $BeCl_2$ in ether; LiCl is precipitated.

$$2LiC_6H_5 + BeCl_2 \longrightarrow 2LiCl\downarrow + Be(C_6H_5)_2$$

These compounds are viscous liquids or solids which are spontaneously flammable in air. They are also rapidly hydrolysed by water. $BeMe_2$ (like $MgMe_2$) has a polymeric structure with bridging methyl groups (19—XIV). Each carbon has a coordination number of 5 and each bridge bond is best described by tetrahedral Be (sp^3 hybridized) and 3-center-2-electron bonds. (unlike $BeCl_2$, which has two 2—c—2e bridge bonds).

When strong donors like Et_2O or Me_3N are added, the polymeric structure breaks down in favour of adduct formation.



19-XIV (a) 19-XIV (b)

19-XIV. (a) Polymeric structure of $Be(CH_3)_2$. (b) Schematic representation of orbital overlap in the bridging part.

The higher alkyls are progressively less polymerized. Di-*tert*-butylberyllium is linear and monomeric; steric crowding appears to be mostly responsible for the adoption of this structure (sp hybridized Be).

Beryllium forms a series of *cyclopentadienyl complexes*, $[Be(\eta^5—C_5H_5)X]$, X=H, Cl, Br, —C≡CH or BH_4. The compounds possess the expected C_{5v} symmetry, with the ring attached to the metal in a symmetrical manner. But the structure of bis(cyclopentadienyl)beryllium, $(C_5H_5)_2Be$ is not clear. One C_5H_5 ring is symmetrical and pentahapto (η^5), while the bonding of the second C_5H_5 ring has found different interpretations. A sandwich structure like that of ferrocene (see text) is not expected in view of the small size of the Be atom. The crystalline compound (at −120°C) has the second cyclopentadiene ring coordinating through only one carbon, i.e., the compound is formulated as $[Be(\eta^5—C_5H_5)(\eta^1—C_5H_5)]$.

Magnesium dialkyls and diaryls may be made similar to the beryllium compounds (HgR_2+Mg). These may also be made by the reaction of LiR/LiAr on Grignard reagent or by the following type of reaction (industrial scale)

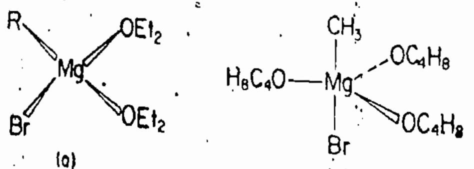
$$Mg + H_2 + 2C_2H_4 \xrightarrow{pr/100°C} MgEt_2$$

$MgMe_2$ is a white polymeric solid with structure similar to that of $BeMe_2$. It decomposes at about 250°C. $MgEt_2$ and higher homologues are similar but they decompose at a lower temperature (<200°C) to MgH_2 and the relevant alkene.

$(C_5H_5)_2Mg$ can be prepared by the action of cyclopentadiene vapour on hot magnesium. Similarly, C_5H_6 reacts with EtMgBr in ether to give C_5H_5MgBr.

Grignard reagents (**MgRX**) are the most widely used organometallic compounds. They are usually made by the slow addition of an alkyl or aryl halide RX to a stirred suspension of magnesium metal in an ether or other solvent. Perfect elimination of air and moisture is vital to the reaction. The reaction requires an induction period and is slow at the beginning. A small crystal of iodine is often used as an initiator—this penetrates the protective oxide layer on the metal surface. Alkyl halides are more reactive than aryl halides; reactivity decreases with the halogen as I>Br>Cl. RMgF can be prepared by exchange reactions of MgR_2 with mild fluorinating agents like $BF_3.OEt_2$, SiF_4 or Bu_3SnF. A very reactive form of magnesium (p. 141) enables the preparation of many Grignard reagents which were so far unknown.

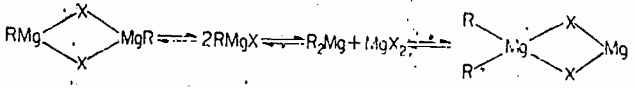
The structure of crystalline Grignard reagents show that the basic structure is RMgX.*n*(solvent). The Mg atom is essentially tetrahedral as in structure 19—XV-a. A five-coordinate species like 19.XVb may also occur in some cases.



(a) (b)

19-XV(a) and (b). (OC_4H_8 = tetrahydrofuran.)

In solutions in diethyl ether at concentrations greater than 0.1 *M*, association is believed to occur through halogen bridges (bridging by CH_3 groups may occur when $R=CH_3$). Several species may be present in a series of mobile equilibria (Schlenk equilibria) like:



19-XVI.

All the above species are solvated which has not been shown for clarity. These equilibria, are, however largely influenced by temperature, concentration, solvent and the nature of R and X. Spectral studies, molecular weight determination, radioisotopic exchange (^{28}Mg), electrical conductivity etc., may be used to study such equilibria. The monomeric species normally predominates in dilute solutions and in more strongly donor solvents.

Grignard reagents find wide applications in synthetic organic chemistry. They are also invaluable in the synthesis of a wide variety of organo-compounds of elements other than carbon, e.g.,

$$RMgX + \begin{cases} \xrightarrow{BCl_3} BR_3 \\ \xrightarrow{SnCl_4} SnR_4 \\ \xrightarrow{BeCl_2} BeR_2 \end{cases}$$

A number of organometallic compounds of Ca, Sr and Ba have now been prepared but they are of little general utility and less extensively studied. Cyclopentadienyl compounds of these metals are also known.

$$Ca\ (or\ Sr) + Hg(C_5H_5)_2 \longrightarrow Ca(C_5H_5)_2$$

$$CaC_2 + C_5H_6 \xrightarrow{liq.\ NH_3} Ca(C_5H_5)_2 + C_2H_2$$

$$BaH_2 + C_5H_6 \longrightarrow Ba(C_5H_5)_2$$

The structure of $Ca(C_5H_5)_2$ is interesting. Four planar cyclopentadienyl rings surround each Ca—the metal appears to be bridged by a complex sharing of the Cp-rings. Bond-distances suggest that two of the Cp-rings are η^5, one ring is η^3 and the other ring is η^1. The matter is further complicated by different bonding modes of the same bridging Cp ring to two different Ca atoms—e.g., η^5 to one Ca and η^1 to another.

SUMMARY

The elements of Gr IIA (Be, Mg, Ca, Sr, Ba and Ra) follow the typical *s*-group chemistry exemplified by the alkali metals. The difference from the alkali metals may be generally inferred from the smaller size and higher charge of the M^{2+} ions. The first member, beryllium, is again somewhat different from the remaining elements in the group; the differences may again be understood from size-charge effects. It shows many similarities with the diagonally related element aluminium.

Be occurs in the form of silicate minerals. Magnesium occurs principally as dolomite, $MgCO_3$; it also occurs in the sea-water. Ca occurs mainly as $CaCO_3$ in limestone and dolomite. Sr occurs as $SrCO_3$ and $SrSO_4$ while Ba is found mainly as $BaSO_4$.

The alkaline earth metals are all silvery white, lustrous and relatively soft metal, though much harder and high melting than the alkali metals. Like alkali metals, these metals also (except Be, Mg) dissolve in liquid ammonia forming deep blue solutions. Mg dissolves in liquid NH_3 in presence of a strong base like KNH_2 or $NaOCH_3$. The base prevents ammonolysis of the solvent by the ammoniated Mg^{2+} ion.

The metals burn in air to form the oxide and nitride. The heavier metals readily form peroxides and superoxides. Except Be, the metals decompose boiling water/steam with increasing vigour. They also burn in the halogens to form the dihalides. The following general observations are useful:

(i) The elements show uniform divalence.

(ii) Be(II) compounds are mostly covalent. High charge density of the small Be^{2+} ion gives rise to extensive polarization in its compounds. The $[Be(H_2O)_4]^{2+}$ ion forms many crystalline compounds. Its aqueous solution is acidic due to hydrolysis.

Polarisation is also important in the compounds of Mg^{2+}, though to a smaller extent. The effect of polarisation is reflected in the low thermal stabilities of the salts of oxoacids; stability increases from Mg—Ba.

(iii) The coordination number of beryllium is limited to 4; it is 6 for others.

(iv) Be and Mg form several interesting organometallic and coordination compounds.

Be is extracted from Beryl via soluble Na_2BeF_4 and insoluble $Be(OH)_2$. This may be dissolved in HF; the solution gives the basic fluoride on evaporation. This may be electrolysed in the molten state. Alternatively, $Be(OH_2)$ may be converted to BeF_2 by the action of NH_4HF_2 followed by heating. Reduction of BeF_2 by Mg gives Be.

Magnesium is produced by the electrolysis of fused anhydrous $MgCl_2$ or by the reduction of its oxide with ferrosilicon. Calcium is also obtained by the electrolysis of its fused chloride.

Beryllium is largely used to improve the strength of Cu and Ni. The alloys are non-magnetic and corrosion resistant. Be is also used as a moderator in nuclear reactors and as a window material in X-ray tubes. Magnesium alloys are widely used for their lightness and durability. Calcium is used as a reducing agent in the production of Cr, Zr, Th and U and also as an alloying agent.

BeH_2 may be obtained by reducing $BeCl_2$ with LiH. It is a polymeric white solid in which Be-atoms are linked by 3 center-2 electron hydrogen bridge bonds. Other hydrides of this group are typical saline hydrides.

Monoxides, MO, are formed by heating the metals in oxygen. Peroxides, superoxides and ozonides are also known, specially with the larger metal ions. Thus BaO_2 may be obtained by simply heating the metal in air at 500°C. Hydrated peroxides are obtained by adding H_2O_2 to solutions containing the metal ions. The monoxides react with water to form the respective hydroxides. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a mild base; base strength increases to $Ba(OH)_2$ which is comparable in strength to the alkali metal hydroxides.

Be reacts with C at 1900°C to form Be_2C which gives methane on hydrolysis. Carbides of formula MC_2 are formed by Be and Mg on heating in acetylene and by the others on direct reaction at 2000°C. They give acetylene on hydrolysis.

The Gr II A metals combine with halogens to form their dihalides. The beryllium halides are covalent and polymeric with halogen bridges. The halides of the remaining metals in this group are typical ionic solids. The effect of increasing cation size is again reflected in the properties of the halides. The fluorides are anhydrous; the chlorides of magnesium and calcium readily form hydrates, while others are normally anhydrous. The solubility of the halides in water decrease from Mg to Ra, but the fluorides show the reverse trend.

The salts of oxoacids become increasingly stable from Be to Ra. The strong polarizing power of Be^{2+} ion make $BeCO_3$ unstable in air. The bircarbonates of all are unknown in the solid state for the same reason. Solubility of the sulphates in water decrease from Be to Ba owing to increasing match of packing of the large SO_4^{2-} ion with the M^{2+} cation.

When heated to 125°C, $Be(NO_3)_2$ decomposes to N_2O_4 and a basic nitrate, $[Be_4O(NO_3)_6]$. It consists of 4 Be atoms arranged tetrahedrally around a central oxygen atom with bridging nitrate groups. A similar basic acetate (carboxytate) is also known.

The tendency of complex formation decreases from Be to Ba, parallel to the increase in size of the cation and decrease in ion-dipole interaction. However, macrocyclic ligands form stable complexes when the size of the metal ion matches best with that of the ligand.

The complexes of Be are mostly tetrahedral: $[Be(H_2O)_4]^{2+}$, $[BeCl_2(OEt_2)_2]$, $[Be(acac)_2]$, $[BeF_4]^{2-}$ are some of the examples. Complexes with nitrogen donor ligands are comparatively fewer. Only magnesium and calcium show any appreciable tendency to complex formation. The complexes of Ca and Mg with EDTA are technically important in removing hardness of water. Though complexes with nitrogen donor ligands are much less common, the complex of magnesium with tetrapyrroles is very important to plant life. Such complexes constitute the chlorophylls in green plants which are essential for photosynthesis.

Be and Mg form a large number of organometallic compounds; a few examples are also known for the remaining elements in the group. $Be(CH_3)_2$ and $Mg(CH_3)_2$ have polymeric structures with bridging methyl groups. Cyclopentadienyl compounds are also known for these metals. Alkyl magnesium halides, also known as Grignard reagents, are widely used in organic synthesis.

EXERCISE

1. *Explain:*

(i) *The abundance of beryllium in the universe is very low.*

(ii) *Magnesium occurs in nature largely as* $MgCO_3$ *but beryllium does never occur as* $BeCO_3$.

(iii) *An ionic solid of the formula MgCl does not exist though it has an estimated negative* ΔH°_f.

(iv) *An aqueous solution of* $Be(NO_3)_2$ *is strongly acidic in nature.*

(v) *Magnesium forms a blue solution in liquid* NH_3 *only in presence of bases like* KNH_2 *or* $NaOCH_3$.

(vi) *Basic character increases in the order* $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2$.

(vii) *The reaction* $MBeF_4(s) = MF_2(s) + BeF_2(s)$ *requires increasingly higher temperature as M varies from Ca to Ba.*

(viii) *The observed trends of solubility in water are:*

$$MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2 \text{ but } MgF_2 < CaF_2 < SrF_2 < BaF_2.$$

(ix) $MgSO_4$ *is more soluble in water than* $SrSO_4$ *and decomposes at a much lower temperature* ($MgSO_4$: 895°C; $SrSO_4$: 1374°C).

(x) *Beryllium chloride hydrate loses no water over* P_4O_{10}.

(xi) *The stability of crown-6 complexes increase as* $Ca < Sr < Ba$.

(xii) *Linear X–Be–X molecules exist only in the gas phase.*

2. *"The chemistry of the s-block elements is dominated by their tendency to lose the outer s-electrons."—Comment.*

Which parameters reflect this tendency?

Explain, with examples, why all the s-block elements do not form all types of compounds?

Mention some cases where the s-block elements form compounds without losing their s-electrons.

3. *Compare the chemistry of*

(i) *Li and Mg.*

(ii) *Be and Al.*

4. *Discuss the chemistry of beryllium with reference to its hydride, halides, oxide and complex compounds.*

5. *How do the physical properties like melting point, boiling point and density of the alkaline earth metals differ from those of the alkali metals?*

6. *How do the solubilities (in water) of (a) hydroxides, (b) chlorides and (c) sulfates of the alkaline earth metals vary from one element to the other?*

7. *Discuss the likely structures for (a) basic beryllium acetate, (b) beryllium chloride solid, (c) dimethylberyllium and (d) Grignard reagent.*

CHEMISTRY OF THE ELEMENTS

SECTION—II : THE p-BLOCK ELEMENTS

CHAPTER TWENTY

ELEMENTS OF GROUP 13(IIIA)

B, Al, Ga, In, Tl

OBJECTIVES

- **20.1** General Discussion on *p*-block Elements
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  - Isolation of the Elements [20.1.2]
  - Use [20.1.3]
- **20.2** General Trend in Properties
  - Physical Properties [20.2.1]
  - Valence and Oxidation States [20.2.2]
  - Properties of individual elements [20.2.3]
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  - Hydrides and hydrido complexes [20.3.2—20.3.3]
  - Higher boranes and carboranes [20.3.4]
  - Halides [20.3.5]
  - Oxygen compounds [20.3.6]
  - Salts of oxo-acids; Aqueous solution chemistry [20.3.7]
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  - Sulphides [20.3.9]
  - Complex compounds [20.3.10]
  - Organometallic compounds [20.3.11]
- **20.4** Detection and Estimation

20

ELEMENTS OF GROUP 13(IIIA)

20.1 INTRODUCTION : p-BLOCK ELEMENTS

The main groups of the periodic table headed by B, C, N, O, F and He contain elements whose last electrons occupy a p orbital (except He itself). The maximum oxidation state shown by these p-block elements is the sum of the s and p electrons; this is the Mendeleev group number of the elements. In addition, these elements form compounds in other oxidation states : they usually differ by steps of two; but π bonding or element-element bonds ($H_2N–NH_2$ for example) may give rise to intermediate oxidation states as well. As usual, positive oxidation states are more common in groups headed by B, C and N; the heavier members of these groups show the "inert pair effect." Negative oxidation states become more important in the oxygen and fluorine groups. Fluorine is the most electronegative element and exists always in the —I state. Oxygen also assumes negative oxidation states except in its fluorides and the compounds of dioxygenyl cation, O_2^+. Sulphur has a stable group oxidation state VI, but is also known in several other oxidation states. The stability of the VI state decreases in the heavier elements. In the halogen group, the group oxidation state VII is shown in oxyanions. Oxidation states I, III and V (in addition to the most common —I state) are also known. In the helium group, radon and krypton are known to form only difluorides while xenon exhibits a number of stable oxidation states (II, IV, VI and VIII).

The p-block elements form oxides, sulfides and all four halides in their stable oxidation states. When a higher oxidation state becomes unstable for an element, the element shows oxidizing property in that state and will not form compounds with a readily oxidizable anion like $S^{=}$, Br^-, I^- etc. The group oxidation states of Tl, Pb and Bi readily confirm this generalization. Thus, Tl(III) and Pb (IV) do not form iodides. On the other hand, unstable low oxidation states are reducing in nature and should be stable with sulfides or iodides, but not with oxides or fluorides, e.g. Ga(I).

The chemistry of the p-block elements in any group may be conveniently classified into three main divisions

(i) the first element
(ii) the three middle elements
(iii) the last element.

(i) The first element in a p-group

The first element in any group has the smallest size and highest electronegativity. These facts control their properties to a great extent. Also, the valence shell of these elements is restricted to the small compact $2p$ orbitals. So they can form strong σ–bond as well as strong p-p π–bonds (Section 16.4). After their $2s^22p^n$ valence shell configuration, the next available orbital is the $3s$ orbital. But this is separated from the $2p$ level by a considerable energy gap and cannot be used in bonding. Owing to this lack of low-lying vacant orbitals the maximum coordination number of these elements is restricted to four only.

(ii) The three middle elements

The greatest relative size change takes place between the first and second members of a group. At the same time, the second members show a tendency to exhibit higher covalence and coordination number under favourable conditions. The strength of σ–bonds with other elements decreases in comparison to the first member while p-p π-bonding is practically excluded (see section 16.4 for d-orbital participation and π-bond formation). Thus there occurs a sharp discontinuity from the first member to the second. This is most marked in groups IV and V. The chemistry of the three middle elements follows a graded transition, though not a smooth one. The middle element of the group ($4s^24p^n$ configuration) is often out of line from the others owing to the presence of a filled $3d$ orbital just below the valence shell (section 16.4). We also notice that the stability of the highest oxidation state begins to fall from this element; the oxidation state lower by two units gradually gains importance. The elements also become distinctly metallic. The general tendency to show higher coordination number is somewhat offset by bond weakening.

(iii) The last element

The last element is the largest in size and the most metallic in character. It preferentially exists in an oxidation state two units less than the group oxidation state. This has already been discussed in connection with the "inert pair effect" (16.4).

Theoretical calculations show that *relativistic effects* (chapter 29) are also involved in these elements : an electron close to a nucleus of high charge possesses velocities comparable to that of light. This causes an increase in both mass and binding energy of the electron and a corresponding decrease in the orbital radius. Such effects contribute nearly 15% toward lanthanide contraction and even greater for the later elements. The relativistic effects on orbitals of a given n depend upon how close the orbital penetrates the inner electron core and hence follows the order $s > p > d > f$. Hence the effect is most prominent on the s electrons.

With these points in mind, we shall discuss the chemistry of the p-block elements groupwise. The present chapter covers the Group III elements.

20.1.1 Abundance and occurrence of Gr 13(IIIA) elements

Boron

The abundance of boron in the universe is very low (section 16.3.1). Its abundance in crustal rocks (9 ppm) is even less than that of lithium (18 ppm) or lead (13.1 ppm). It occurs as borate minerals or borosilicates—vast deposits are found in regions of former volcanic activities and in waters from hot springs—California, Turkey, Russia and Argentina. The principal minerals are : *colemanite*, $Ca_2\left[B_3O_4(OH)_3\right]_2 . 2H_2O$; *kernite*, $Na_2\left[B_4O_5(OH)_4\right] . 2H_2O$; *borax*, $Na_2\left[B_4O_5(OH)_4\right] . 8H_2O$. In India, borax occurs as a precipitate from the hot springs of the Puga valley in Ladakh. Borax also occurs in Tibet and Sri Lanka.

Natural boron consists of two isotopes, ^{10}B (19.6%) and ^{11}B (80.4%).

Aluminium

Aluminium is the most abundant metal in the earth's crust (8% by weight). Its abundance among the elements is after O (45.5%) and Si (25.7%). It is a major constituent of various silicate minerals as well as clay : mica, feldspar, kaolinite etc. The only fluoride mineral is cryolite, Na_3AlF_6, found in Greenland. The most important minerals of aluminium are the oxides, anhydrous as well as various hydrated forms. Corundum (Al_2O_3) is remarkable for its hardness and is used as an abrasive. Gems like ruby, sapphire etc. also contain aluminium oxide coloured with traces of Fe, Co, Mn etc. (see oxides).

The chief commercial source of the metal is the oxide hydroxide (hydroxo oxide), $Al_2O_3 \cdot xH_2O$ generally known as bauxite. Vast deposits of bauxite are found in tropical and subtropical regions, usually formed by leaching out of silica and other metals from aluminosilicates. A workable sample contains Al_2O_3, 40-60%; combined water 12-30%; SiO_2 1–15%; Fe_2O_3 7–30% and TiO_2 3–4%. Rich deposits of bauxite are found in Australia, Brazil, Guinea, Jamaica, several African countries as well as France, USA and Russia.

Indian scenario

India is rich in aluminium minerals. Corundum occurs in Madhya Pradesh (Morena and Sidhi district); Karnataka (Sringeri Jagir, Hassan Chitaldurg, Tumkur and Kolar districts); Tamilnadu (Salem, Coimbatore districts), Bihar, Assam and Andhrapradesh. India has vast deposits of bauxite. The annual production in 1990 was 4.6 million tonnes (world production 100 million tonnes). The principal centres of occurrence of bauxite (mainly districts) are shown below for each State. The percentage figure refers to contribution to India's total annual production of bauxite in 1989-90.

TABLE 20.1

Occurrence of bauxite in India

Bihar ~ 30%	Ranchi; Palamau; Santhal Parganas	High grade (50-58% Al_2O_3)
*Madhya Pradesh** ~ 27%	Jabalpur, Balaghat, Bilaspur, Shahdol, Sarguja, Jashpur.	High grade
Gujrat ~ 19%	Jamnagar, Khera, Bhrauch, coasts of Bhavnagar, Junagar.	Medium — high grade
Maharastra ~ 18%	Kolhapur; Thana, Puna, Ratnagiri, Satara.	Low grade but large deposit.
Tamil Nadu ~ 2%	Peaks of Shevaroyan and Sholaradn in the Shevaroy hills; Nilgiri hills.	~ 6-7 million tonnes total reserve.
Karnataka ~ 1.7%	Bokanur Navige ridge; Karle Hill; Bailpur; Jamboti; Mogulgarh; Kasarawada.	High grade.
Orissa < 1%	Kalahandi, Sambalpur	Mostly inaccessible.
*Andhra Pradesh*** < 1%	Eastern Ghats of Visakhapatnam, East Godavadi and West Godavadi.	High grade
Jammu and Kashmir	Jammu and Punch (extensive surface deposits)	Millions of tonnes of very high grade (60-80% Al_2O_3) but highly refractory type; not amenable to usual methods of extraction.

* A reserve of about 35 million tonnes is being explored in the Banda and adjoining regions.

** A huge reserve of estimated 400 million tonnes of high grade bauxite is under consideration in the Chintapalli sapria area of Visakhapatnam district.

Without taking into account the new explorations, the estimated total reserve amounted to about 254 million tonnes of all grade; among this, ~ 28 million tonnes are of high grade. Hence aluminium industry has high prospect in India though the extraction of aluminium depends critically on the availability of cheap electricity.

Ga, In, Tl

Gallium (19 ppm), Indium (0.2 ppm) and Thallium (0.7 ppm) are all much less abundant than aluminium. Ga is found associated with Al in bauxite (0.003-0.01%); in coal and in sulphide minerals containing Zn and Ge. Previously it was obtained from flew dusts emitted during burning of coal or roasting of sulphide ores. Now it is mostly recovered as a bye-product in aluminium industry.

Indium and thallium are definitely chalcophiles and occur exclusively in sulphide minerals. In is usually associated with ZnS and Tl is found associated with galena (PbS). Similarity in atomic and ionic sizes may be responsible for such association. Tl(I) also occurs with similarly sized Rb(I) in feldspars and micas.

20.1.2 History and Isolation of the Elements

History

In India, Egypt and other ancient civilizations, borax was used as a flux and to prepare glazes and hard glasses. The element itself was isolated in the nineteenth century by Davy, Gay-Lussac and Thenard (1808); B_2O_3 + K; electrolysis of moist boric acid). Moissan prepared rather pure specimens (~ 95%) by heating B_2O_3 with Mg (1892). The name boron was proposed by Davy to illustrate its source and its similarity to carbon (*bor ax + carbon*).

Alum was also used in ancient India (Susruta) and in Rome as medicine (*Latin alumen* = bitter salt). Davy failed to isolate the metal but suggested it the names alumium/aluminum. Oersted (Denmark) first isolated the metal by reducing $AlCl_3$ with K-amalgam. Commercial production started in 1854 (St. C. Deville, Na on $AlCl_3$; also Bunsen, electrolysis of $NaAlCl_4$).

In 1870, Mendeleev made wonderful predictions about gallium (eka-aluminium). In 1875, P. Lecoq de Boisbaudran (France) isolated the element from crude zinc blende. The naming was done in honour of France (Latin *gallia*).

Indium and Thallium were discovered and named from their flame colours. Indium (1863; Reich and Richter) gives a brilliant indigo blue line in its spectrum (Latin *indicum*). Thallium (1861; Crookes, Lamy) gives a bright green flame (Greek *thallos* = a young shoot).

Isolation

Boron

(i) *Crystalline boron* of high purity (> 99.9%) is now obtained by reduction of volatile boron compounds (BCl_3 or better, BBr_3) with H_2 on a heated tantalum wire. However, the method can be operated only in kilogram scales. Below 1000°C, amorphous boron is obtained; α and β-rhombohedral B is obtained between 1000-1200°C, while above 1200°C, tetragonal crystals are formed.

BF_3 would require temperatures above 2000°C (high B-F bond energy) for similar reaction and hence is unsuitable. BI_3 would decompose readily, but it is very difficult to purify it.

(ii) *Amorphous boron* in large quantities is obtained by reducing B_2O_3 with Mg (or other electropositive elements) at high temperatures. The reaction is exothermic : $B_2O_3 + 3\,Mg = 2B + 3\,MgO$. $\Delta G°$ (298 K) = –515 kJ. The unreacted substances and MgO can be removed by washing with dilute HCl and dilute NaOH solutions. The boron so obtained is usually 95-98% pure.

(iii) *Powdered boron* (95% pure) may be cheaply obtained by electrolytic reduction of KBF_4 in molten KCl/KF at 800°C.

(iv) Thermal decomposition of boron hydrides (900°C) gives amorphous B. Decomposition of BI_3 on Ta at 800–1000° gives α-rhombohedral boron exclusively.

Aluminium

Aluminium is extracted electrolytically from bauxite. Purified bauxite* (mp 2050°C) is dissolved in cryolite and electrolysed at 950°C in carbon-lined steel cells (cathode). A typical electrolyte composition is : cryolite 80-85%, CaF_2 5-7%, AlF_3 5-7%, Al_2O_3 2-8%. Li_2CO_3 is also used to (i) lower the m.p. of the electrolyte, (ii) permit larger current flow and (iii) reduce fluorine emission. Hard carbon rods are used as anode.

The details of the electrolytic process is not fully understood; the main sequences may be represented as

$$Al_2O_3 = 2Al^{3+} + 3O^{=}$$

$$\textit{Cathode}: 2Al^{3+} + 6e = 2Al; \qquad \textit{Anode}: 3O^{=} = 3O + 6e.$$

The alumina is intermittently recharged when exhausted (resistance increases, voltage jumps). The molten aluminium sinks to the bottom of the cell and is drained out. The surface of the electrolyte is covered with a layer of coke; this is oxidized by the evolving oxygen and the valuable anodes are saved.

Synthetic cryolite

Cryolite is an essential flux in the process — it lowers the melting point of alumina which is aided by the presence of CaF_2. At the same time, it is electrochemically more stable than alumina itself. Natural cryolite occurs only in Greenland but the supply is inadequate. Synthetic cryolite is made by the reaction.

$$Al(OH)_3 + 6HF + 3NaOH = Na_3AlF_6 + 6H_2O.$$

*Purification of bauxite involves two main steps (Bayer's process) :

(i) Dissolution of bauxite in aqueous NaOH by digestion. Bauxites approximating to the composition $Al(OH)_3$ may be treated at 120-140°C with dilute (~3*M*) NaOH solution. Bauxites with higher oxide content ("AlOOH") are treated at higher temperatures and pressures (200-250°C, 35 atm) with 5-7 *M* NaOH solution.

(ii) The insoluble impurities (red mud) are separated by filtration. $Al(OH)_3$ is precipitated by carbon dioxide and ignited to ~ 1200° C to obtain Al_2O_3.

$$2\,NaAlO_2 + 3H_2O + CO_2 = Na_2CO_3 + 2Al(OH)_3$$

Gallium

Gallium was previously extracted from ashes of certain coals; heating with HCl formed both $GeCl_4$ and $GaCl_3$. The germanium chloride was first distilled out; $GaCl_3$ was then extracted from the residue with isopropyl ether. This was reduced with H_2 (quartz tube) to obtain the metal. Ga was also obtained by electrolysing an alkaline solution of its salt.

At present, gallium is obtained as a by-product of aluminium extraction. $Ga(OH)_3$ is a stronger acid than $Al(OH)_3$ (greater polarizing power of Ga^{3+}). Enriched sodium gallate solutions (Na_3GaO_3) are obtained during the purification of bauxite by Bayer's process. The solution is then electrolysed to obtain the metal (feasible because of high overvoltage for hydrogen evolution). Very pure Ga for semiconductor use is made by further chemical treatment followed by zone refining (section 21.1.2).

Indium

Indium is recovered from the purification of zinc obtained from zinc blende. The metal remains associated with lead from which it is separated as sulphate and finally electrodeposited from aqueous solution.

Thallium

Thallium is extracted from the flue dust from roasting of sulphide minerals containing the element in traces. The flue dust is leached with sulphuric acid; lead, tin etc. are separated by H_2S; thallium is then precipitated as insoluble TlCl. It is purified by recrystallization as Tl_2SO_4 and electrodeposited from an aqueous solution (dil H_2SO_4, Pt electrodes). The metal may be purified by melting at 350°-400° C under an atmosphere of H_2.

20.1.3 Uses

Boron

Boron and its compounds find extensive use in the modern age. Boron filaments and boron fibre composites are used as reinforcement materials in space shuttles and aircrafts. These are formed by reducing BCl_3 with H_2 on carbon yarn (1600-1900°C). Boron carbide is also used as abrasive for polishing or grinding.

Boron carbides and metal borides are extensively used as neutron shields and control rods in nuclear reactors. ^{10}B has high absorption cross-section for thermal neutrons—even for high-energy neutrons ($10^4 - 10^6$ eV) it is more effective than any other nuclide. The accompanying (n, α) reaction produces Li and He which are nonradioactive and harmless. This fact has recently been used in *B-10 neutron capture therapy* of brain tumours.

Metal borides

Metal borides (e.g., TiB_2, ZrB_2) have recently found many technical applications. They are extremely hard and high melting refractory solids (e.g., TiB_2 : m.p. 2980° C) which are also chemically very inert (resistant to attack by molten metals, slags and salts). As such, they are used as coatings on turbine blades, rocket nozzles and high temperature reaction vessels. They also possess high electrial conductance (e.g., TiB_2 : 5 times greater than Ti itself).

Boric acid, B_2O_3 and borax are used in medicine, in making borosilicate glasses and enamels and as fire retardant.

Sodium perborate is used in detergents.

Aluminium

The extensive use of *aluminium* in our everyday life can be realised without the slightest effort. In recent years it has acquired a high position among the metals due to several exclusive properties : it is cheap, easily malleable, light, non-toxic and fairly corrosion resistant in dry condition (due to a protective oxide layer); in addition, it has high thermal and electrical conductivity. Its mechanical strength can be significantly increased by alloying with other metals (Table 20.2).

TABLE 20.2
Types of aluminium alloys

Type	Main features	Typical Use
Commercially pure Al. (<1% other elements)	Limited mechanical strength.	Chemical equipment, refle-ctors, heat exchangers.
Cu-alloys (~5%)	Good strength and machi-nability.	Panels of trucks and trailers and structural parts of aircrafts.
Mn-alloys (~ 1.2%)	Moderate strength, high work ability.	Cooking utensils, storage tanks, furniture, roofing.
Si-alloys (<12%)	Low m.p., low coefficient of expansion.	Castings, filler in brazing and welding.
Mg-alloys (0.3-5%)	Good strength. Can be easily welded. Excellent corrosion resistant in marine environments.	Ships, boats, cryogenic vessels, street lighting.
Zn-alloys (3-8%; with some Mg).	Very high strength when heat treated.	Air-craft structure.
Mg/Si alloys	High corrosion resistance.	Buildings, bridges, railings.

Foundry or casting alloys are expressed in abbreviation with GAL, followed by the principal alloying element with percentage and also the symbols of other elements present : GAL Si12·7FeCu is a casting alloy containing 12·7% Si together with some iron and copper.

Plastically used alloys (for construction) are prefixed by PAL, followed by the principal alloying element with percentage. Thus "*duralumin*", an alloy containing 4·5% Cu, 1% Mg, 0·8% Si and 0·75% Mn is expressed as PAL Cu 4·5MgSiMn.

The principal uses of aluminium and its alloys may be summarised as follows :

(i) *Construction work* : The metal and its alloys are now extensively used in making windows, doors, building panels, mobile homes etc.

(ii) *Transportation* : Aircrafts, truck-trailer- and car frames are now being made from aluminium alloys.

(iii) *Containers and Packaging* materials utilise aluminium sheets and foils on a large scale.

(iv) *Electrical Power lines* are the next consumer of aluminium in order of quantity. The electrical conductivity of pure Al is ~ 63% of the conductivity of same volume of Cu. But owing to its lower density, Al has more than double conductivity of an equal mass of Cu. Corrosion resistance and lower cost are additional advantages.

Alloys of the Aldrey type (Si 0·5%; Mg 0·5%; Fe 0·2%) has a slightly lower electrical conductivity than that of pure aluminium but have improved mechanical properties and are used in high voltage electrical transmission lines.

(v) Machinery, utensils and other house-hold items, including furniture, are also made from aluminium.

(vi) Powdered aluminium is used in paints and as an ingredient in solid fuels in rockets (with an oxidizer like NH_4ClO_4).

Aluminium compounds like the oxide, bauxite (as such), alum and organo-compounds are also widely used. These have been mentioned in connection with each compound type.

Gallium

The use of *gallium* has sharply increased in recent years due to development of semiconductor technology. GaAs is largely used in light-emitting diodes (LED); it can directly convert electricity into coherent light (laser diodes); such LEDs are familiar in pocket calculators and similar output displays of many instruments. They are also used in infra-red emitting diodes, infrared detectors and photomultiplier tubes. The ternary $GaAs_{1-x}P_x$ system now virturally dominates the LED market.

Gallium is also used as high temperature liquid seals, low-temperature solders, manometric fluid and heat-transfer media.

Indium

Indium metal is now used in making low melting alloys with Bi, Cd, Pb and Sn (mp 50-100°C); these are widely used in heat regulators and certain type of safety devices against excess heating. In-rich solders are used in high vacuum apparatus in sealing metal-nonmetal joints. It is also used in semiconductors (InAs, InSb, InP) and in control rods of some nuclear reactors (high neutron capture cross-section).

Thallium

There is no large scale industrial use of *thallium*. It is used in making highly refractive optical glass. Thallium(III) sulfate is a rat poison. Tl_2CO_3 prevents the growth of mildews on textiles. Some thallium compounds have antiknock properties. TlBr and TlI may find use in photosensitive diodes and infra-red detectors. Aqueous solutions of the formate and malonate salts of thallium have very high densities (4.3 g cm^{-3} at 20°C for saturated solution); these may be diluted to desired range and used in the small scale separation of different precious minerals.

20.2 GENERAL TREND IN PROPERTIES

The general trend in properties of the Gr III elements may be largely understood in terms of the discussion made in section 16.4 and the introduction to *p*-block elements in section 20.1.

20.2.1 Physical Properties

Some important physical properties and related facts about the Group 13(IIIA) elements have been given in Table 20.3; the trend in variation of certain properties may be appreciated from figures 20.1 and 20.2. The general features of the *p*-block elements are reflected in these trends.

Thus, the ionization energies do not decrease smoothly as in groups I and II. The effect of poor screening by $3d^{10}$ and $4f^{14}$ core is clearly reflected in the higher values for Ga and Tl. This effect of filled inner d^{10} configurations (Ga, In) and $f^{14}d^{10}$ configurations (Tl) is also reflected in the variation of size and electronegativity. The influence of these factors on the chemistry of these elements will be discussed in due context.

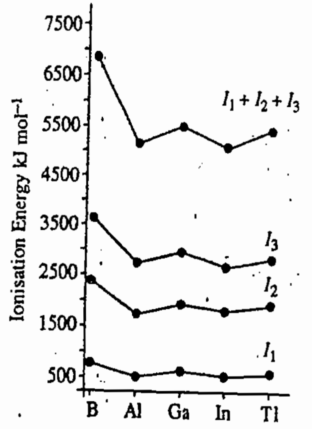
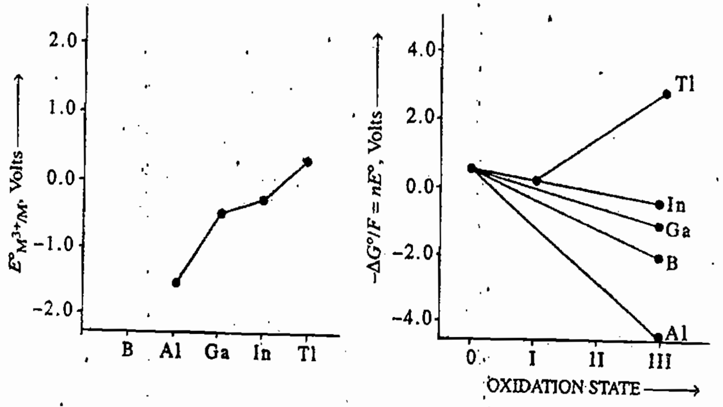


Fig. 20.1

Variation of Ionization Energy.



(a) (b)

Fig. 20.2

Variation of $E°$.

TABLE 20.3

Some important physical properties of the elements of Gr 13(III)

	B	Al	Ga	In	Tl
Electron Configuration	$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10}4s^2 4p^1$	$[Kr]4d^{10}5s^2 5p^1$	$[Xe]4f^{14}5d^{10}6s^2 6p^1$
M.P. (°C)	2180 (2250)	660	29.8	157	303
B.P. (°C)	3650	~ 2400	~ 2250	2070	1550 (1475)
$\Delta H^\circ_{atomisation}$; **kJ mol^{-1}**	565	324	272	244	180
I.E (kJ mol^{-1})					
I_1	800	577	579	558	589
I_2	2426	1816	1970	1811	1959
I_3	3660	2741	2962	2689	2863
I_4	25,000	11,563	6,150	5571	4868
$(I_1 + I_2 + I_3)$	6886	5134	5511	5058	5411
Ionic Radius$^{(a)}$ (pm)					
M^{3+}	27	53	62	80	88.5
M^+	—	—	120	140	150
E° (V) :					
$M^{3+} + 3e = M(s)$	$-0.89^{(b)}$	-1.66	-0.56	-0.34	$+1.26$
$M^+ + e = M(s)$	—	0.55	-0.79 (acid) -1.39 (alkali)	-0.13	-0.34
Electronegativity (Pauling values re-calculated)	2.04	1.61	1.81	1.78	2.04

20.2.2 Oxidation State and Valence

The type of valence and oxidation states of the elements may be appreciated from the ionization energies and allied factors. Ionic compounds containing M^+ ions (M = B, Al) are not likely to be energetically favourable in view of the high ionization energy involved against the poor gain of lattice energy by univalent ions. However, the tendency to form M^+ ions increases down the group and only thallium has a significant chemistry of the Tl^+ ion in salts like TlF, Tl_2SO_4 etc. The remaining halides of Tl(I) are largely covalent owing to the expected strong polarizing effect of the Tl^+ ion (high effective nuclear charge; comparable with silver halides). As already pointed out ("inert pair effect"), this marked tendency of thallium to attain +I oxidation state is in contrast to other members of the group which are dominantly covalent in the +3 oxidation state. This can be attributed to the decrease of M^{III}—X covalent bond energy down the group; this fails to compensate for the energy terms involved in reaching the tricovalent state — heat of atomisation, s-p promotion, hybridization etc. The decrease in free energy in formation of M^+X^- salts becomes gradually larger than that for forming $M^{III}X_3$ type covalent compounds.

[Sec. 20.2.2 *Oxidation States etc.*]

The +I state is also not common among covalent compounds of the other elements. Energy required to raise the elements to the oxidation state III (promotion, hybridization etc.) is more than compensated by the energy released in the formation of two additional bonds. Hence the compounds are dominantly tricovalent. But at high temperatures in the gaseous state, diatomic monohalides M^IX are formed.

$$2B + BF_3 \xrightarrow{2000°C} 3BF ; \quad 2Al + AlCl_3 \xrightarrow{800-1000°C} 3AlCl.$$

At such high temperatures, the $T\Delta S$ terms (ΔS is highly positive) supersedes the ΔH term. With the exception of Tl(I) fluoride, all the gaseous monohalides are covalent.

Oxidation State II

Formation of compounds containing M(II) is suggested from the fairly large difference (~ 1000 kJ) between I_2 and I_3. A few compounds apparently correspond to this stoichiometry, for example GaX_2 and InX_2 (Ga+ GaX_3, heat; X = halogen). But they do not seem to contain the paramagnetic Ga^{2+} ion (one unpaired e); these are actually mixed valence salts $Ga^I[Ga^{III}X_4]$. GaS, GaSe and GaTe (direct synthesis at high temp) contain $[Ga^{II}-Ga^{II}]^{4+}$ units arranged in a layer lattice (X-ray diffraction). The presence of Ga–Ga coupling explains the diamagnetism of the compounds (see halides).

Oxidation State III

Boron

Formation of the B^{3+} ion appears unlikely for two main reasons : (a) the ionization energy required would be very large and (b) the small ion would be highly polarizing — even water of hydration would be appreciably deformed by this. Hence the B^{3+} (aq) ion is not known in aqueous solution. In a very few cases the effective size of the B^{3+} ion may be increased by complexing a number of suitable donor molecules around it. This reduces the polarizing power of the cation and the ionization energy is partly compensated by the strong ion-dipole interaction. The resulting large cation may now give rise to stable salts, as in the reaction of pyridine with trimethylamine-boron tribromide adduct :

$$Me_3N—BBr_3 + \underset{(py)}{4C_5H_5N} \longrightarrow \left[\begin{smallmatrix} py & & py \\ & B & \\ py & & py \end{smallmatrix}\right]^{3+} + 3Br^- + Me_3N$$

The resulting solution conducts electricity corresponding to the presence of four ions. (Other examples of cationic boron species are given later).

Aluminium (Ga, In, Tl)

Decrease of lattice energy with increasing cation size suggests that Al should be the most likely element to form M^{3+} ion. For others, the large ionization energy is not likely to be compensated by the weak lattice energy. These elements more commonly show a marked tendency to attain an oxidation state III by covalent bond formation (via $s \rightarrow p$ promotion etc). Even aluminium shows a delicate balance between ionic and covalent bonding. Solid aluminium trifluoride and trichloride are ionic, but aluminium tribromide forms a molecular crystal consisting of Al_2Br_6 dimers. Replacement of the chloride ions by larger bromide ions causes loss of lattice energy which is sufficient to offset the mode of bonding. For similar reasons trihalides of Ga, In and Tl except the trifluorides are all covalent.

(a) 6-co-ordinated except B;

(b) For the reaction $H_3BO_3 + 3H^+ + 3e = B(s) + 3H_2O$.

Though solid aluminium chloride forms an ionic lattice, on melting it changes to covalent Al_2Cl_6 dimers—the forces in the liquid are no longer sufficient to meet the high ionization energy required to form Al^{+3}. The coordination number of aluminium drops from six (in the crystal) to four and the density of the liquid is nearly 45 per cent lower than that of the solid at the melting point. The switchover from ionic to covalent bonding is also reflected in the electrical conductivity of the compound : in the solid state it increases rapidly as the melting point is approached, but at the melting point the conductivity suddenly falls to zero.

The tripositive M^{3+} ions (Al—Tl) may be stabilized in aqueous solution through strong hydration, usually six molecules of water being held strongly by the ions. These water molecules are often retained as water of crystallization in hydrated crystals. As expected, the high cationic charge facilitates proton release from a coordinated water molecule (hydrolysis) :

$$[M(H_2O)_6]^{3+} \rightleftharpoons [(OH)M(H_2O)_5]^{2+} + H^+(aq) \rightleftharpoons \ldots\ldots \rightleftharpoons M(OH)_3 + H^+(aq).$$

In strongly acid medium, anionic complexes may result, specially with halogen hydracids :

$$Ga^{3+}(aq) + 4X^- \rightleftharpoons [GaX_4]^- \quad (X = Cl, Br, I).$$

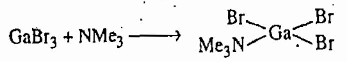
Electron deficiency

The foregoing discussion makes it clear that with a few exceptions, the elemens of Group 13(IIIA) will show covalence in the oxidation state + III involving $ns \rightarrow np$ promotion and sp^2 hybridization. Of course, formation of only three covalent bonds will render the valence shell of the central atom electron-deficient. This can be overcome in a number of ways; for example,

(i) Formation of pi-bonds using the vacant *p*-orbital excluded from hybridization with filled orbitals on the atoms bonded through sigma bonds, as in the boron trihalides (see halides; section 20.3.5).

(ii) Formation of 3-center 2-electron "bridge-bonds" as in boron hydrides or in Al_2Cl_6 vapour (see hydrides and halides).

(iii) Formation of adduct with electron-pair donors (Lewis bases), e.g.,



$$GaBr_3 + NMe_3 \longrightarrow Me_3N{-}GaBr_3$$

Aluminium, gallium, indium and thallium have *nd* orbitals available for bonding; it is likely that the elements use these *d* orbitals in bonding (Fig. 20.3).

$AlCl_3(NMe_3)_2$ $[InCl_5]^{2-}$ $[AlF_6]^{3-}$

Fig. 20.3

Distribution of valence orbitals around M (= Al, Ga, In, Tl).

(a) trigonal bipyramid; (b) square pyramid and (c) octahedral.

The formal hybridizations at M are (a) $d_{z^2} - sp^3$ (b) $d_{x^2-y^2} - sp^3$ or, d^4s (c) sp^3d^2 in adducts like $MX_3 \cdot B_2$ (B = base) or complex ions like MX_5^{2-} or, MX_6^{3-}.

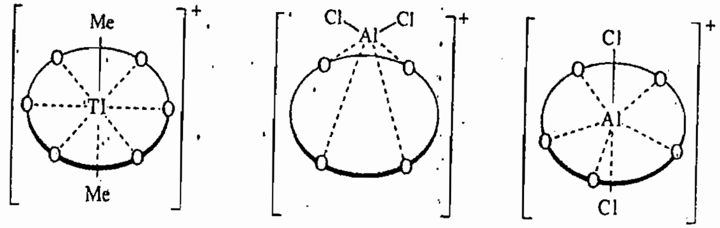
The stereochemistry of the elements in different oxidation states are summarized in Table 20.4.

TABLE 20.4

Sterochemistry of Gr 13(III) elements in different oxidation states

Oxidation State	Co-ordination number	Geometry	Examples
+ 1	6	Distorted octahedral	TlF
+ 2	4	Tetrahedral	$Ga_2Cl_6^{2-}$
+ 3	3	Planar	BX_3 (X = Halogen) In $[Co(CO)_4]_3$
	4	Tetrahedral	BX_4^- (X = H, F), $AlCl_4^-$
	5	Trigonal bipyramid	$AlCl_3(NMe_3)_2$
		Square pyramid	$[InCl_5]^{2-}$
	6	Octahedral	$[Al(H_2O)_6]^{3+}$, $[AlF_6]^{3-}$

Crown ether complexes of $AlCl_2^+$ and $TlMe_2^+$ are also known, e.g.,



With dibenzo—18-C-6, as 2, 4, 6-trinitrophenolate

With 12-C-4 and $(EtAlCl_3)^-$

With benzo 15-C-5 and $(EtAlCl_3)^-$

Fig. 20.4

Skeleton of crown-ether complexes of Tl and Al.

18 – C – 6 = dibenzo-18-crown-6; 12-C-4 = 12-crown-4 and so on (Ch. 18).

20.2.3 Properties of the Individual Elements

Boron is a high melting solid which be either crystalline (black) or amorphous (brown). It is a diamagnetic substance with semiconductor properties, ΔE = 1.55 eV. Crystalline boron exists in several allotropic modifications. These are structurally very complex. All of them are built up of B_{12} icosa hedra (Fig 20.5). Different ways of

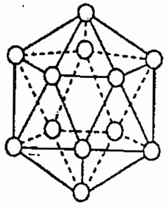


Fig. 20.5

The icosahedron, a solid figure with twelve vertices bound by twenty equilateral triangles.

Each B-atom forms the apex of a pentagonal pyramid and has 5 neighbours at the base at 1.77 A°—a C_5 axis of symmetry passes through each. Six of the 12 B-atoms have a sixth neighbour (on the C^5 axis) at 1.71 A° from adjacent B_{12} icosahedron. The other 65-atoms have two neighbour B-atoms at 2.03 A° from two different icosahedron.

packing these icosahedra in the unit cell give rise to different structural forms. The simplest form is α-rhombohedral boron : nearly regular B_{12} icosahedra in approximately cubic close packing. The bonding involves $2c$ - $2e$ as well as $3c$ -$2e$ bonds.

> **Q. 20.1** *A boron atom in the icosahedron has five other B atoms bonded to it, while a carbon atom in diamond has only four nearest neighbours.—Comment.*
>
> **Hints :** C, with 1 electron in each of its 4 valence orbitals, can form four 2 center-2-electron bonds.
>
> B, with 3 electrons and 4 valence orbitals, forms 3-center-2-electron bonds to engage all its valence orbitals. The formation of 3-center bond places a fifth B-atom within bonding distances.

The remaining elements of this group are all low-melting, soft metals. The low melting and boiling points may be related to the inert pair effect. The unusually low melting point of gallium has no simple explanation. This might be a manifestation of the first appearance of a filled d^{10} core. But the boiling point of Ga is not lower by the same extent from the boiling point of Al. Thus gallium has the longest liquid range for any element. Gallium contracts on melting, similar to Ge, Sb and Bi. Liquid gallium is liable to supercooling.

Al, In and Tl adopt typical metallic structures : Al – fcc; In – face-centered tetragonal and Tl — hcp. Gallium has a complex orthorhombic structure : each Ga has 1 very close neighbour and 6 farther neighbours. The X-ray diffraction pattern of liquid gallium is also different from that of a simple liquid like mercury. It is likely that some diatomic species are present in this state.

Appearance

Al, Ga, In and Tl are all silvery white lustrous metals. Unlike other lustrous metals, indium reflects light of all wavelengths uniformly; hence its use in making mirrors. In air, Al, Ga and In get a thin coating of an adherent oxide film (~ 0.00001 mm). The oxide film on aluminium articles may be thickened by anodic oxidation or by suitable oxidizing agents. The film can retain pigments to impart a coloured finish to the metal.

Reactivity :

Crystalline elemental boron is chemically very inert; it is not affected by acids or oxidizing agents. Fused sodium hydroxide attacks it above 500°C giving $NaBO_2$ and H_2. The amorphous variety is more reactive.

Air/Water

Amorphous boron, Al, Ga and In burn in air to give their trioxides and nitrides. Thallium forms Tl_2O. Aluminium burns in nitrogen to form AlN.

Boron reduces steam at red heat ($B_2O_3 + H_2$). Al, Ga and In are not attacked by water owing to the protective oxide coating. If the film is removed, for example by amalgamation, water is decomposed [$M(OH)_3 + H_2$]. Thallium has no protective oxide coating and is oxidized in moist air to TlOH. It decomposes steam at red heat ($TlOH + H_2$). Aluminium corrodes rapidly in saline water.

Acid

Boron dissolves in oxidizing acids like HNO_3 or H_2SO_4 (conc), but is unattacked by HCl.

$$2B + 3H_2SO_4 = 2H_3BO_3 + 3SO_2$$

Al, Ga and In dissolve in aqueous HCl giving M^{3+} (aq) ions but Tl does not due to the insolubility of TlCl. Al, Ga and In are scarcely attacked by dilute H_2SO_4 but conc. H_2SO_4 is reduced to SO_2. Tl dissolves in dilute acids forming Tl^+ ions. Dilute and concentrated HNO_3 render Al (Ga, In) passive by forming a protective oxide layer.

Boron reacts with fused alkali to form a borate and liberates H_2.

$$2B + 2NaOH + 2H_2O = 2NaBO_2 + 3H_2.$$

Al and Ga dissolve in hot aqueous alkali to form the $[M(OH)_4]^-(aq)$ ion.

Except Tl, all the elements in the group burn in halogens to form trivalent halides MX_3. Tl forms TlX.

Only B and Al combine directly with nitrogen when heated to form BN and AlN. GaN and InN may be obtained indirectly by heating the metals with NH_3.

Some of the main properties of the elements are summarised in Table 20.5.

TABLE 20 5

Some important reactions of the elements of the boron group Gr 13(III)

	B	Al, Ga, In	Tl
1. **Air/O_2**	*Crystalline* : No action. *Amorphous* : B_2O_3 + BN	*Heat* : M_2O_3 (MN)	*Heat* : Tl_2O
2. **H_2O**	*Steam* : $B_2O_3 + 3H_2$	*Amalgam* : $M(OH)_3 + H_2$	*Steam at red heat* : $TlOH + H_2$
3. **N_2**	*Heat* : BN	*Heat, only Al* gives AlN	
4. **Alkali**	*Fused alkali* $2NaBO_2 + 3H_2$	*Hot aqueous solution* $[M(OH)_4]^-(aq) + H_2$ M = Al, Ga	—
5. **Acids**	No action by non-oxidizing acid, e.g., HCl. Oxidizing acids give boric acid.	*Dil. HCl* : gives M^{3+} HNO_3 renders passive	*Dil acids* : gives Tl^+ (except HCl; TlCl is insoluble).
6. **Halogens**	*Heat* : BX_3	MX_3	TlX

20.2.4 General Compound Types

[Sec. 20.2.4 Compound Types]

The basic features in the chemistry of these elements may now be summarized as follows. This summary will be helpful in understanding their principal compound types as outlined in the following sections.

The first element

The chemistry of the first member in the group, boron, is naturally influenced by its small size and high ionization energy. (i) As explained, the compounds will be essentially covalent in the oxidation state III. We expect an extensive chemistry involving small elements of similar electronegativity, e.g., C and H. (ii) The presence of only three valence electrons suggests electron deficiency around the boron (three conventional bond pairs of electrons in four orbitals in the valence shell) – we expect it to function as a Lewis acid by accepting electron pairs from Lewis base donors. We shall also find multicenter bonding as a wayout from electron deficiency. (iii) The high affinity of boron for oxygen gives rise to an extensive chemistry involving boron-oxygen link, e.g., the borates. (iv) Due to its small size, the boron atom can readily form stable lattice with metal atoms giving rise to many interstitial alloy type metal borides. An extensive range of compounds result from the tendency of boron atoms to form chains, planes and three-dimensional networks.

Depending upon their individualistic structure and chemical systematics, the principal boron compounds may be classified into the following broad headings :

(i) Boron hydrides and their derivatives – these include the carbaboranes and polyhedral borane metal complexes (sections 20.3.2—20.3.4).

(ii) Boron halides, their adducts and derivatives (section 20.3.5).

(iii) Oxo-compounds including polyborates, borosilicates etc. (sections 20.3.6 and 20.3.7).

(iv) Metal borides (section 20.3.1).

(v) Boron-nitrogen and organoboron compounds (section 20.3.8 and 20.3.11).

Resemblance of B to Si and difference from Al

In general, the chemistry of boron is out of line from those of its group members—Al, Ga, In and Tl. Rather, boron resembles silicon in several aspects. Some points of resemblance to silicon and difference from aluminium are illustrative :

1. The hydrides of B and Si are spontaneously flammable volatile compounds; these are readily hydrolyzed by water. The only binary hydride of aluminium is a solid at room temperature with a three-dimensional lattice.

The boron hydrides are of course unique in structure and bonding as they are "electron-deficient" from the conventional 2-electron view for a localized chemical bond.

2. The common halides of boron and silicon are mostly gases or liquids — they do not dimerize in the vapour state. The trifluorides of Al, Ga and In are all high melting solids, while other halides of these elements have much lower melting points. These latter halides exist as dimers in their vapours. However, despite this dimerization, the halides (and also the aluminium alkyls) behave as Lewis acids similar to the boron halides and form adducts.

3. Oxides of boron and silicon are dominantly acidic in nature — they readily form borates and silicates on fusion with metal oxides. Aluminium oxide is more basic in nature and is classed as an amphoteric oxide.

Similarly, $B(OH)_3$ and "$Si(OH)_4$" are weakly but definitely acidic (boric acid and silicic acid) whereas $Al(OH)_3$ is mainly basic with some amphoteric character.

Certain borates and silicates have similar structures, with linear $(BO_2)x$ and $(SiO_3)x$ units in metaborates and pyroxene silicates.

However, aluminium forms volatile alkoxides, e.g. $Al(OC_2H_5)_3$ corresponding to the borate esters, $B(OR)_3$.

The middle elements : Al, Ga, In

The middle elements of the group differ remarkably from the first member boron : (i) they exhibit greater chemical reactivity at moderate temperatures (ii) they have distinct cationic chemistry in aqueous solutions (ii) they form no series of volatile hydrides and cluster compounds analogous to the boranes and carboranes. Aluminium shows many similarities with beryllium which is diagonally placed with it in the Mendeleev periodic table (see section 19.1.2). It also combines with most nonmetallic elements like N, S, halogens and also forms intermetallic compounds with a large number of metals. As is well known, hydrated aluminium oxide is amphoteric in character; however, Ga_2O_3 is somewhat *more acidic* than Al_2O_3. pK_a for the equilibrium (all species are aquated) :

$$[M(H_2O)_6]^{3+} \rightleftharpoons [M(H_2O)_5OH]^{2+} + H^+$$

is 4.95 when M = Al and 2.60 for M = Ga. Consequently we expect solutions of gallates to be more stable than aluminates. In_2O_3 is again more basic in character than Ga_2O_3. The metal also does not dissolve in aqueous alkali (diff. from Al and Ga). This variation in basicity and similar properties in Ga is associated with poor shielding by the $3d^{10}$ core, as explained earlier.

The last element : Tl

The same effect, in a more intense form, is reflected in the chemistry of thallium. The element has its principal chemistry in the +1 state and readily forms TlOH with steam or moisture. TlOH is very soluble and is a strong base. This and many other compounds of Tl(I) resemble those of the alkali metals. Some compounds of Tl(I) e.g., the halides except fluoride, chromate, sulfide etc. resemble those formed by Ag(I) in their colour and insolubility. This may be readily attributed to the storng polarizing power of both the ions.

20.3 PRINCIPAL COMPOUNDS

20.3.1 Borides

Introduction

Binary compounds of boron with elements having electronegativity lower than boron itself (e.g., metals) are called borides. However, compounds of boron with some metalloid elements (e.g., As) and less metallic elements (e.g., P) are often included in this category. The compositions range from metal-rich borides (like M_4B, M_3B etc.) to boron-rich borides (e.g., MB_{12}, MB_6, MB_4,......). Clearly, these do not conform to usual concepts of valence and stoichiometry. They result from various modes of packing of boron units (atoms, chains, sheets etc) with metal atoms (see structure) and to some extent resemble the interstitial carbides and nitrides.

Preparation

Borides are usually prepared by direct combination of the metal (or its oxide) with elemental boron at high temperature in electric arc furnace : $Mg + 2B = MgB_2$. Industrially, $(B_2O_3 + C)$ or B_4C may be reacted with the metal or its oxide or boron halides may be reduced with the metal, sometimes assisted by H_2. Electrodeposition from a molten salt bath containing the metal oxide and B_2O_3 is also used, particularly for the borides of Mo, W, Fe, Co, Ni and MB_6 type borides of alkaline earth metals and rare earths (700 – 1000°C; graphite anode; graphite or steel cathode).

Some typical preparative reactions are :

(i) $Sc_2O_3 + 7B = 2\,ScB_2 + 3BO$ (1800°C).

(ii) $V_2O_5 + B_2O_3 + 8C = 2VB + 8CO$ (1500°C).

(iii) $7Ti + B_2O_3 + 3B_4C = 7TiB_2 + 3CO$ (2000°C).

(iv) $Eu_2O_3 + 3B_4C = 2EuB_6 + 3CO$ (1600°C).

(v) $2TiCl_4 + 4BCl_3 + 10H_2 = 2TiB_2 + 20\,HCl$ (1300°C).

(vi) $2BCl_3 + 2W + H_2 = 2WB + 2Cl_2 + 2\,HCl$ (1200°C).

Precise stoichiometry is difficult to achieve. The compounds are normally prepared as powders but can be fabricated by standard techniques.

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Properties

Most borides of *d* and *f* elements are generally extremely hard, involatile, refractory materials; their melting points and electrical conductivities are often much higher than those of the metals present. Thus TiB_2 (m. p. 2980°C) has a conductivity ~ 10 times greater than that of Ti metal (also other MB_2 : M = Zr, Hf, Nb, Ta).

Chemically, the borides are very inert and resistant to attack by even molten metals, slags and salts. Borides of *s*-block elements are chemically active and are decomposed, for example, by acids to produce a mixture of boron hydrides (see section 20.3.2).

Uses

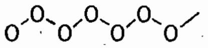
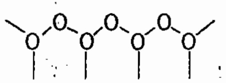
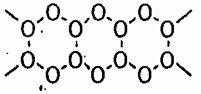
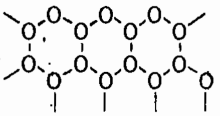
Borides and boride coated metals find application as turbine blades, rocket nozzles, liners in combustion chambers and high temperature reaction vessels. They may also find application as electrodes.

Structural types

Structural types : Borides may be classified according to the boron units present - from single B-atoms to complex three dimensional arrangements.

TABLE 20.6.

Some structural types of metal borides

Boron-atom arrangement		Formula type	Examples (M =)
(a) Isolated atoms	O OO O	M_2B M_3B M_4B	Be, Cr, Fe, Co, Ni. Ni, Pd Mn
(b) Isolated pairs	O—O O—O	M_3B_2 M_5B_3	V, Nb, Ta. Cr.
(c) Zigzag chain of B-atoms		MB	Ti, Hf, Cr, Mo, Fe, Co.
(d) Branched chains of B-atoms		$M_{11}B_8$	Ru
(e) Double chains		M_3B_4	V, Nb, Ta, Cr, Mn.
(f) Two dimensional		MB_2	Mg, Al, Cr, Ti, Zr.
(g) Three-dimensional network.	B_6 octahedron	MB_4	La
		MB_6	La
	B_{12} cubooctahedron	MB_{12}	Y
	B_{12} icosahedron	MB_{15}	Na
	B_{12} (B_{12}) B_{12} giant icosahedron	MB_{66}	Y

Among the metal-rich borides, the B atoms are often at the centres of trigonal prism arrangement of metal atoms. The structures with isolated B atoms may have widely different inter-boron separations (210-330 pm); in other structures, the B-B distances lie in the same range (170-185 pm) irrespective of the size of the metal atom. This indicates appreciable bonding between the B-atoms. The boron-rich borides have structures made up of three dimesional networks of B atoms and clusters in which voids act as hosts to metal atoms. Thus the structure of MB_6 compounds may be looked upon as a central M atom surrounded by eight B_6-octahedron at the corners of a cube (similar to the Cl^- ions in CsCl structure).

In the borides ZrB_{12} and UB_{12}, the structure resembles that of NaCl to some extent, based on metal and B_{12} units. The diborides MB_2 have structures made up of hexagonal layers of boron atoms placed alternately with triangular layers of the much larger metal atoms.

[Sec. 20.3.2 *Hydrides*]

20.3.2 Hydrides

A. *Compound types*

MH_3, the representative simple monomeric hydrides of the group (expected from usual valency considerations) do not exist under normal conditions. Such molecules would contain only six electrons in the valence shells of the central atom, leaving a *p*-orbital completely vacant. So the molecules readily dimerize or polymerize or form adduct with suitable donor species.

$$BH_3\,(g) + BH_3\,(g) = B_2H_6\,(g); \qquad \Delta G^\circ_{298} = -127 \text{ kJ}.$$

For boron, the simplest hydride is diborane, B_2H_6; a large number of higher boranes are also established. All of them are beyond the scope of conventional two center two electron (2*c*-2*e*) bonds and present interesting bonding features (see later). ΔG°_f for all are much greater than zero, so that they are obtained indirectly.

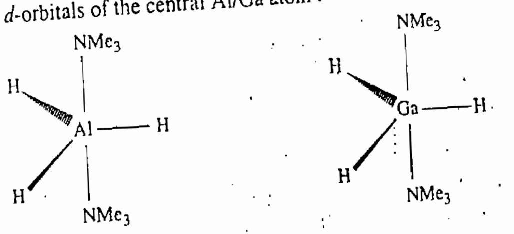
AlH_3 is revealed by mass spectral analysis when the metal is *slowly* vaporized off a tungsten filament in a current of hydrogen gas; on quick volatilization, Al_2H_6 is also observed. Solid aluminium hydride is polymeric in nature with hydrogen bridges between the aluminium atoms—each Al atom is surrounded by six hydrogen atoms octahedrally.

GaH_3 and InH_3 may be detected similar to AlH_3 but they are thermally less stable; there is also no indication of Ga_2H_6 or In_2H_6. GaH_3 is a viscous liquid (m.p. ~ 15°C) which decomposes completely to the free elements at room temperature. InH_3 and TlH_3 are too unstable to exist uncoordinated.

As expected, the hydrides form stable adducts with suitable donors like the amines, CO as well as the H^- ion. The 1 : 1 adducts are tetrahedral, corresponding to sp^3 hybridization of the central atom. Thermal stability of the tetrahydro complexes decreases as follows (decomposition temperatures in °C given).

$$LiBH_4\,(380°) > LiAlH_4\,(100°) > LiGaH_4\,(50°) > LiInH_4\,(0°) \approx LiTlH_4\,(0°)$$

1 : 2 adducts are known for Al and Ga; their trigonal bipyramidal structure (20-I) suggests use of *d*-orbitals of the central Al/Ga atom :



20-1

Complexes of the type [$GaH_2X(NMe_3)$] and [$GaH X_2(NMe_3)$] are also known with X = Cl, Br, I (see preparation).

B. *Boron Hydrides (Boranes)*

Introduction

The 1976 Nobel Prize for Chemistry was awarded to W.N.Lipscomb (Harvard) for his "studies of boranes which have illuminated problems of chemical bonding". Boranes thus provide an interesting area of study for principles of chemical bonding (and structure) and also open a versatile and extensive reaction chemistry. Historically, the study was initiated by Alfred Stock during the years 1912-1936 who prepared and characterized several boron hydrides : B_2H_6, B_4H_{10}, B_5H_9, B_6H_{10} and $B_{10}H_{14}$. B_2H_6 was prepared by pyrolysis of the higher boranes; these, in turn, were obtained as a mixture by the action of acid (10% HCl at 60°C or 8*N* H_3PO_4 at 70°C) on magnesium boride, MgB_2.

$$Mg + B_2O_3 \xrightarrow{\text{heat}} MgB_2 \xrightarrow{\text{acid}} \text{Boranes} + H_2 \xrightarrow{\text{liq. air}}$$

$$\text{Liq. Boranes} \xrightarrow[\text{red. pressure}]{\text{fractionation}} B_4H_{10} \text{ etc.}$$

Many of these compounds were sensitive to air and moisture; so Stock had to develop vacuum technique for their study. Superior preparative methods have now been developed for all boranes. Only B_6H_{10} is still prepared by Stock's method.

For convenience, we shall first discuss the chemistry and structure of diborane, B_2H_6. Higher boranes will be treated in a separate section later on (section 20.3.4).

Diborane, B_2H_6

The study of diborane is interesting for several reasons — e.g. (i) all higher boranes can be prepared from it directly or indirectly (ii) its reactions have a very wide range of synthetic applications (iii) its structure adds a new dimension to our concepts of chemical bonding.

Preparation

Points to remember

The preparation of diborane requires considerable laboratory technique. Like all other boron hydrides, it has a small positive enthalpy of formation ($\Delta H = 36$ kJ mol^{-1}). The gas (b.p. –93°C) is highly toxic and gets rapidly decomposed by water ($H_3BO_3 + H_2$); its mixtures with air or oxygen are inflammable and explosive. Further, diborane (and other boron hydrides) reacts with stopcock grease. Hence, it has to be prepared using all glass vacuum apparatus using vacuum line techniques.

Reactions

(i) Action of I_2 on $NaBH_4$ in diglyme (dimethyl ether of diethylene glycol, $(MeOCH_2CH_2)_2O$. $2NaBH_4 + I_2 = B_2H_6 + 2NaI + H_2$ (~ 98% yield).

(ii) Reaction of $NaBH_4$ with 85% phosphoric acid or, anhydrous sulphuric acid.

$$2NaBH_4 + 2H_3PO_4 = B_2H_6 + 2NaH_2PO_4 + 2H_2 \text{ (~ 70\% yield).}$$

(iii) Addition of BF_3 ether adduct to $NaBH_4$ in diglyme at room temperature (25°C).

$$3NaBH_4 + 4Et_2O.BF_3 = 2B_2H_6 + 3NaBF_4 + 4Et_2O.$$

The method is particularly useful when B_2H_6 is required as a reaction intermediate without the need of isolation or purification.

The gas can be readily isolated from H_2 by condensation at liquid air temperature.

Industrial methods

(iv) Industrially, BF_3 gas can be directly reduced with solid sodium hydride at 180°C.

$$2BF_3\,(g) + 6NaH\,(s) = B_2H_6\,(g) + 6NaF\,(s).$$

To prevent pyrolysis, B_2H_6 is to be trapped out as soon as it is formed.

(v) Another method of potential industrial importance involves direct reduction of B_2O_3 with aluminium and H_2 (750 atm, 150°C) in presence of aluminium chloride as catalyst :

$$B_2O_3 + 2\,Al + 3\,H_2 = B_2H_6 + Al_2O_3.$$

Borane adducts

Borane adducts may be readily obtained by reacting B_2H_6 with Lewis bases e.g.

$$B_2H_6 + 2\,Me_3N = 2\,H_3BNMe_3$$

$$B_2H_6 + 2\,CO = 2\,H_3BCO \text{ (200°C; 20 atm).}$$

Preparation of higher boranes and "borohydrides" (tetrahydroborates) is given later.

Properties

(i) **Oxidation :** Diborane is a colorless, diamagnetic gas (bp –93°C; mp –165°C). It reacts spontaneously and vigorously with air (explosively with O_2); the heat of combustion is very high :

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3\,H_2O;\ \Delta H = -2105 \text{ kJ mol}^{-1}$$

[Except H_2, BeH_2 and Be $(BH_4)_2$, this value, per unit weight of fuel, is higher than any other substance].

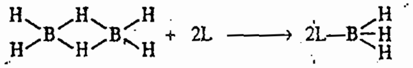
Thermal decomposition of diborane (in sealed vessles, > 100°C) yields a variety of higher boranes by a series of complex steps, involving mainly the BH_3 intermediate. The nature of product (B_4H_{10}, B_5H_9, B_5H_{11},........) depends upon the condition (see higher boranes; 20.3.5).

Diborane is readily hydrolyzed by water which coordinates as a Lewis base

$$B_2H_6 + 6H_2O \longrightarrow 2B\,(OH)_3 + 6H_2.$$

Symmetric cleavage

(ii) **Lewis acidity :** The hydrolysis of B_2H_6 illustrates its Lewis acid character— a molecule of water acts as a Lewis base and splits B_2H_6 into two symmetrical fragments (BH_3). This is called symmetric or homolytic cleavage. In general for any Lewis base L, we may write



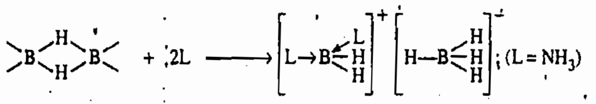
$$B_2H_6 + 2L \longrightarrow 2L{-}BH_3$$

For various L, stability of the adduct $L.BH_3$ follows the sequence :

$$PF_3 < CO < Et_2O < Me_2O < Et_2S < Me_2S < py < Me_2N < H^-$$

Unsymmetrical cleavage

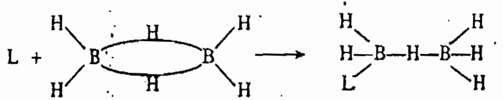
Unsysmmetrical cleavage of B_2H_6 is also known, forming ionic products :



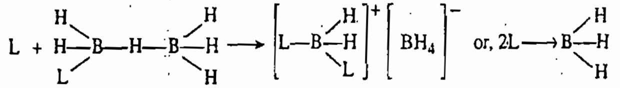
Unsymmetrical cleavage of this kind is generally observed when diborane reacts at low temperatures with strong bases having no steric crowding (e.g., NH_3 and $MeNH_2$).

Cleavage of diborane is presumed to occur by a two step mechanism :

Step I :

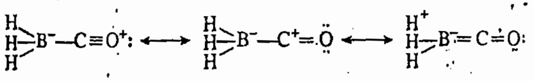


Step II :

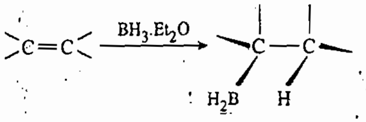


In step II, the final product depends upon the choice of L for the two B-atoms. Since most donor atoms are sufficiently electronegative, (more than the H^- ion), the B-atom containing L develops greater partial positive charge and favours the attack by the second L. This leads to unsymmetrical cleavage. However, if such attack causes steric congestion, the second L is expected to attack the other B-atom, when symmetrical cleavage would occur. However, it is also possible that an unsymmetrical product formed initially undergoes rapid hydride ion transfer to give the symmetrical end product. It has been possible to isolate $[BH_2(H_2O)_2]^+[BH_4]^-$ at –130°C.

For $B_2H_6 \longrightarrow 2BH_3$, $\Delta H \simeq 150$ kJ mol^{-1}. With this value in mind, it is possible to compare the strength of BH_3 as a Lewis acid with the strengths of the boron alkyls and boron trihalides. As expected from electronegativity considerations, the acceptor properties of BH_3 towards simple bases (e.g., Me_3N) are intermediate between boron trihalides and boron trimethyl. However, BH_3 alone forms stable complexes with CO and PF_3. These ligands are good σ-donors (using lone pair electrons on C or P) as well as good acceptors via π-bond (π-acid) using empty *p* or *d* orbitals on C and P respectively. In its adducts with these ligands. BH_3 probably acts as an electron donor through "hyperconjugation"; one may write the following canonical forms for the $BH_3.CO$ adduct (V.B. description) :



(iii) **Hydroboration :** The hydroboration reactions cover the addition of diborane in ether solvents (diethyl ether, tetrahydrofuran, polyether etc) to alkenes and alkynes at room temperatures in N_2 atmosphere — H and BH_2 groups are added anti-Markownikov and cis (syn).



$$H_3C—CH_2—CH=CH_2 \longrightarrow \underset{\longleftarrow R \longrightarrow}{H_3C.CH_2.CH_2.CH_2}.BH_2 \longrightarrow R_2BH \longrightarrow R_3B$$

The RBH_2 may react further to form R_3B when the alkene is unhindered. Trisubstituted and some disubstituted alkenes (e.g. cyclohexene) proceed upto R_2BH stage while tetrasubstituted alkenes give RBH_2.

Usually, these alkyl or aryl boranes are not isolated; rather, they are converted in situ into a wide variety of organic compounds with stereospecificity and without complications arising from rearrangement. A few examples are given :

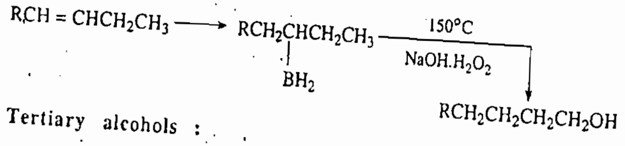
(a) **Alkanes :** Protonolysis by refluxing with an anhydrous carboxylic acid,

$$B(CH_2\,CH_2R)_3 \longrightarrow 3RCH_2\,CH_3.$$

(b) **Primary alcohols :** Oxidative hydrolysis with alkaline hydrogen peroxide ($NaOH, H_2O_2$) :

$$B(CH_2\,CH_2R)_3 \longrightarrow 3RCH_2\,CH_2\,OH.$$

With internal alkenes, the BH_2 group migrates to a terminal position by reversible addition-dissociation, (the double-bond "walks") : this gives a primary alcohol as an end product :



$$RCH=CHCH_2CH_3 \longrightarrow \underset{BH_2}{RCH_2CHCH_2CH_3} \xrightarrow[NaOH.H_2O_2]{150°C} RCH_2CH_2CH_2CH_2OH$$

(c) **Tertiary alcohols :**

$$R_3B + CO \xrightarrow[110°]{diglyme} R_3CBO \xrightarrow[H_2O_2]{NaOH} R_3COH$$

(d) **Miscellaneous compounds :**

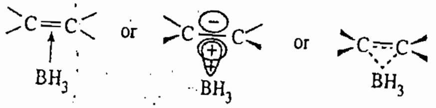
(i) $B(CH_2R)_3 \xrightarrow[\text{Chromic acid}]{[O]} R\,COOH$

(ii) $BR_3 \xrightarrow{AgNO_3/alkali} R\text{-}R$

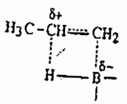
(iii) $BR_3 \xrightarrow[\text{Sulphamic acid}]{NH_2Cl \text{ or}} RNH_2$

(iv) $BR_3 \xrightarrow{Br_2 \text{ or } I_2/OH^-} RBr \text{ or } RI$

Though hydroboration proceeds quickly in other solvents, it is very slow in the gas phase or when the reactants are allowed to combine directly. We know that gas phase dissociation of B_2H_6 to BH_3 is negligible while in ether solvents the BH_3-ether adduct is the dominant species. This shows that the addition to double bond takes place via the electron-deficient species BH_3. The acidic (electron-deficient) B-atom attaches to the π-electron cloud in such a way that the carbon atom "losing" the π-electrons is best able to accomodate the positive charge developed on it. The attack of BH_3 on the π-cloud may be represented in a number of equivalent ways, for example,



The reaction does not proceed to the extent of producing a carbocation or carbonium ion (formerly called). Instead, this electron-deficient carbon now begins to attach itself to a hydrogen of BH_3, leading to a transition state (20-II) in which B and H are attached to two carbon atoms across the multiple bond in a concerted 1, 2-addition. The loss of a hydrogen by the boron, with the bonding electron pairs, is equivalent to the addition of an H^- ion to a carbon atom. This explains the difference from pro-Markownikov electrophilic addition with HX where the hydrogen adds without electrons, i.e., as H^+, an acid.



20-II

Hydroboration reactions were discovered by H.C. Brown and B.C. Subba Rao in 1956. Subsequent development of these reactions in outstanding synthetic utility in organic chemistry has led to the 1979 Nobel award in Chemistry to Prof. Brown (Purdue University). It may be worthwhile to mention that though Prof. Brown is now recognised as a renowned organic chemist, he was originally trained as an inorganic chemist at the University of Chicago in the laboratory of H.I. Schlessinger. Lithium aluminium hydride and sodium borohydride were first prepared and studied here (1942) during a search for volatile uranium compounds like $U(BH_4)_4$.

Reducing Character:

(iv) **Reducing Character : We understand that diborane is an electrophilic reagent or reducing agent; it will preferentially attack a molecule at a position of high electron density as we have found in hydroboration reactions.** Naturally, in a heteropolar double bond, the BH_2 group should normally add to the more electronegative (electron-rich) atom, i.e., O in $\rangle C=O$ and N in $C\equiv N$ or, $C=N$. Subsequent protonolysis yields alcohols or amines.

Some reactions of diborane are summarised below :

$$B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 6H_2$$

$$+ 4MeOH \longrightarrow 2BH(OMe)_2 + 4H_2.$$

$$B_2H_6 + BMe_3 \longrightarrow Me_n\,B_2H_{6-n}\ (n = 1-4).$$

$$B_2H_6 + BCl_3 \longrightarrow B_2H_5Cl + BHCl_2 \text{ (also with } BBr_3)$$

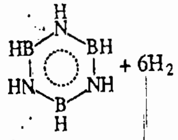
$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2.$$

$$B_2H_6 + 3\,Cl_2 \longrightarrow 2BCl_3 + 6\,HCl \text{ (low temp } -25°C\text{; also with } F_2)$$

$$B_2H_6 + Me_3N \longrightarrow H_3\bar{B} - \overset{+}{N}Me_3.$$

$$B_2H_6 + Me_2NH \xrightarrow{-42°} H_3\bar{B} - \overset{+}{N}HMe_2 \xrightarrow{\text{heat}} Me_2NBH_2$$

$$B_2H_6 + 2NH_3 \xrightarrow{-120°} [H_2B(NH_3)_2]^+\,[BH_4]^- \xrightarrow{90°C}$$



(Borazine, see later)

$$B_2H_6 + H_2 \longrightarrow \text{higher boranes}$$

$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$

[Also K, Ca or amalgams of the metals. Reaction rapid in presence of ether].

$$B_2H_6 + NaBH_4 \longrightarrow NaB_3H_8 + 2H_2 \text{ [in diglyme/100°]}.$$

$$B_2H_6 + 2LiH \longrightarrow 2LiBH_4$$

$$2B_2H_6 + 3\,LiR \longrightarrow 3LiBH_4 + BR_3$$

Structure of Diborane

[Sec. 20.3.3 *Structure and bonding in B_2H_6*]

Electron-diffraction and other physical studies establish the structure of diborane (Fig. 20.6) — the two B-atoms are joined by two BHB bridges in a plane nearly perpendicular to the plane of terminal B—H bonds. The bridge B—H bonds are somewhat longer (133 pm) than the terminal B-H bonds (119 pm). The terminal B—H distance is similar to that expected for a normal covalent bond involving two electrons shared between two atoms (2*c*—2*e* bond). That the two bridge H-atoms are in a different environment is also confirmed by (i) Raman spectra and (ii) the fact that methylation of diborane proceeds only upto $Me_4B_2H_2$ — further attempt breaks the molecule into BMe_3 fragments.

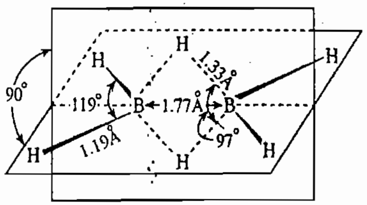


Fig. 20.6
Structure of B_2H_6.

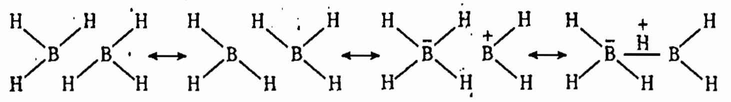
The bridge-structure of diborane is confirmed by nuclear magnetic resonance studies involving B-11.

Bonding in Diborane

With a total of 12 valence electrons from the constituent atoms, B_2H_6 is an "electron deficient compound" when considered by the two-center two-electron localized bond approach. Also, there are no odd electrons in the molecule as evident from its observed diamagnetism.

V.B. description

In valence bond description, B_2H_6 may be represented by resonance among several canonical forms (20-III) :



20-III

The bonding in diborane (as well as higher boron hydrides) has been most satisfactorily explained by the concept of multicenter m.o.'s. Longuet Higgins first put forward (1949) the idea of 3-center-2-electron B—H—B bridge bond to explain the bonding in diborane. He also extended the idea of such multicenter bonding to higher boranes. These were organized and developed by W. N. Lipscomb (Harvard; awarded the 1976 Nobel Prize in Chemistry for his work on bonding in boranes).

M.O. approach

The m.o. description starts with four roughly sp^3 hybrid orbitals on each boron and the 1*s* a.o.-s on the H-atoms. Two orbitals on each boron now overlap with 1*s* atomic orbitals of two hydrogen atoms to give the terminal B—H bonds (conventional 2*c*—2*e* bonds). These correspond to four bonding and four antibonding m.o.'s formed by four hybrid orbitals of two B-atoms and four hydrogen a.o.s. Eight electrons (four from the two B atoms; four from four H-atoms) occupy the bonding m.o.s.

We are now left with two hybrid a.o.-s and one valence electron on each boron atom in the two BH_2 units. If the two BH_2 units are brought close keeping all the B and H atoms in a plane, the unused hybrid orbitals on the two B-atoms will point to each other in an approximately perpendicular plane (Fig. 17.8a; p. 97). Two hydrogen atoms can now overlap suitably with these orbitals forming two sets of BHB bridge bonds.

For each BHB unit, we have three orbitals : two from the B-atoms (one from each BH_2 unit) and one orbital from the H-atom. These three atomic orbitals give rise to three molecular orbitals—one bonding, one nonbonding and one, antibonding (Fig. 17.8). Two electrons, one from either of the B-atoms and one from the H-atom, occupy the lowest energy bonding m.o. Each BHB unit now forms a three center system held by two electrons—this is often referred to as three center two electron, 3*c* -2*e* bond. Since the bonding electron pair operates over three centers, the bond order is 1/2 and the bonds have nearly half the strength of normal 2*c*—2*e* bonds. This is also consistent with longer B—H distances in the bridges.

Figure 17.8 (b) gives the m.o. description for one B—H—B bridge unit. The m.o. description for the whole B_2H_6 molecule is shown below (Fig. 20.7).

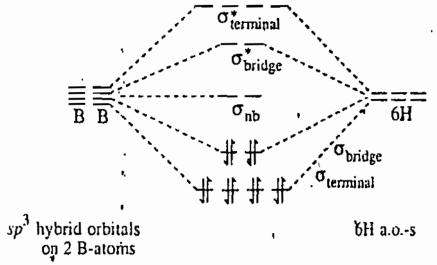


Fig. 20.7
M.O. description of the bonding in diborane.

The bonding in higher boranes may be similarly explained on the basis of BHB as well as BBB three-center m.o.-s, together with B—B bonds (sec. 20.3.4).

C. *Hydrides of Al, Ga, In, Tl*

Aluminium Hydride

Solid polymeric aluminium hydride is prepared via the ether adduct obtained from reduction of aluminium chloride by lithium tetrahydroaluminate in ether solution :

$$3LiAlH_4 + AlCl_3 = 3LiCl + 4AlH_3 \cdot ether.$$

The ether-adduct does not readily give aluminium hydride on evaporation. Hence some $LiBH_4$ is also added.

The LiCl is removed (filtration); the filtrate (containing an excess of $LiAlH_4$ and some $LiBH_4$) is refluxed with a large excess of benzene (70° — 79°C) to obtain colourless, involatile crystals of $(AlH_3)_n$ (called α - AlH_3).

Aluminium hydride is also obtained by reacting $LiAlH_4$ with 100% H_2SO_4 in tetrahydrofuran :

$$2LiAlH_4 + H_2SO_4 = 2AlH_3 + Li_2SO_4 + 2H_2.$$

Properties

The hydride is a colourless involatile solid, thermally unstable above 150-200°C. It is a strong reducing agent and forms adducts with strong Lewis bases, e.g., $AlH_3(NMe_3)_2$ (tbp; see later for preparation).

AlH_3 also reacts vigorously with water and other protic reagents, liberating hydrogen.

At least six crystalline varieties as well as amorphous modifications of the hydride have been reported. The structure of α-AlH_3 (X-ray and neutron diffraction) is similar to that of AlF_3, with each Al surrounded octahedrally by six equidistant H. The structure involves Al—H—Al bridges similar to those in diborane (3*c*—2*e* bonds).

GaH_3 may be prepared as its adduct with trimethylamine (Me_3N) by reacting ethereal solutions of $LiGaH_4$ and $Me_3N.HCl$. GaH_3 may be released from the solid adduct by displacement with a stronger Lewis acid in absence of a solvent below −15°C.

$$GaH_3 : NMe_3\,(s) + BF_3\,(g) \longrightarrow GaH_3\,(l) + BF_3.NMe_3\,(s).$$

Uncoordinated InH_3 and TlH_3 may have only transitory existence in ethereal solutions at low temperatures.

Adducts

Adducts of the hydrides are obtained directly from the tetrahydrido complex in ether solution :

$$LiMH_4 + NMe_3.HCl \xrightarrow{ether} MH_3.NMe_3 + LiCl + H_2\ (M = Al, Ga, In, Tl).$$

As mentioned earlier, AlH_3 and GaH_3 may pick up a further molecule of the base giving adducts of the type $AlH_3.(NMe_3)_2$.

Complexes of the type $GaH_2X.NMe_3$ and $GaHX_2.NMe_3$ (X = Cl, Br) may be obtained by reacting $GaH_3.NMe_3$ with HCl/HBr at low temperature or through double decomposition between $GaX_3.NMe_3$ and $GaH_3.NMe_3$ in inert solvents like benzene. $GaH_3.NMe_3$ is a colourless, crystalline compound (mp 70.5°).

Tetrahydridoaluminates ("aluminohydrides" : $LiAlH_4$ and $NaAlH_4$) are discussed separately.

20.3.3 Hydrido Complexes

Introduction

The boron group elements form tetrahedral tetrahydrido complexes MH_4^- (M = B, Al, Ga, In, Tl) of which the boron and aluminium compounds are very important. These are commonly called borohydride (BH_4^-; tetrahydridoborate or tetrahydroborate) and aluminohydride (AlH_4^-; tetrahydridoaluminate). The decreasing thermal stability of the compounds is shown in the decomposition temperatures of the lithium salt :

$LiBH_4$ (380°C); $LiAlH_4$ (100°C); $LiGaH_4$ (50°C); $LiInH_4$ (0°C); $LiTlH_4$ (0°C).

As expected, theremal as well as chemical stabilities among the MH_4^- species vary according to the ability of MH_3 to function as a Lewis acid towards H^-. Reactivity towards H_2O also increases from BH_4^- to AlH_4^- to GaH_4^- ......, consistent with greater availability of H^- ion and/or more ready nucleophilic attack upon Al or Ga because of their graeater ease of valence shell expansion.

Tetrahydridoborates (Borohydrides)

As pointed out earlier (p. 183), $NaBH_4$ (and $LiAlH_4$) was first prepared and studied in 1942. It has become an industrially important compound since the 1950's.

The borohydrides may be prepared directly from diborane or a boron halide and the metal hydride in a suitable solvent at room temperature, or higher.

$$2LiH + B_2H_6 \xrightarrow{Et_2O} 2LiBH_4$$

$$3LiC_2H_5 + 2B_2H_6 \xrightarrow{Et_2O} 3LiBH_4 + B(C_2H_5)_3$$

$$2NaH + B_2H_6 \xrightarrow{diglyme} 2NaBH_4$$

$$4NaH + BCl_3 \xrightarrow{Al_2Et_6} NaBH_4 + 3NaCl$$

$$4NaH + B(OMe)_3 \xrightarrow{250°\text{-}270°} NaBH_4 + 3NaOMe$$

$$AlCl_3 + 3NaBH_4 \xrightarrow{heat} Al(BH_4)_3 + 3NaCl$$

$$BeCl_2 + 2NaBH_4 \xrightarrow{heat} Be(BH_4)_2 + 2NaCl$$

$$MOCH_3 + NaBH_4 \xrightarrow{MeOH} MBH_4 + NaOCH_3 \ (M = K, Rb, Cs).$$

Industrially, sodium borohydride is prepared on a large scale from borax and hydrogen gas (under moderate pressure) at 450-500°C.

$$Na_2B_4O_7 + 7SiO_2 + 16Na + 8H_2 \longrightarrow 4NaBH_4 + 7Na_2SiO_3.$$

The $NaBH_4$ is extracted with liquid ammonia under pressure and evaporated; pure (98%) $NaBH_4$ is obtained.

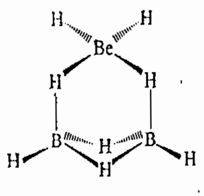
The BH_4^- ion is tetrahedral, as expected from sp^3 hybridization of the central boron atom.

Tetrahydridoborates are known for a number of metals and cations, e.g. :

Li, Na, K, Rb, Cs; Be, Mg, Ca; Zn, Al, Ti, Zr, Hf, Th, U; Me_4N, Et_4N.

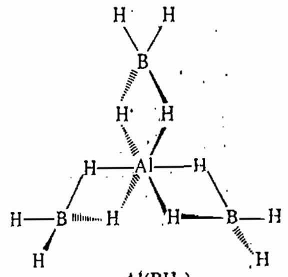
The borohydrides of alkali metals and thorium (as well as nitrogen bases) are nonvolatile crystalline solids with an ionic lattice e.g. $LiBH_4$: orthorhombic, m.p. 275°; $NaBH_4$: NaCl type lattice. The ionic borohydrides are stable in air. Other borohydrides are mostly covalent. Thus $Be(BH_4)_2$ sublimes at 91° while $Al(BH_4)_3$ boils at 44.5°C (covalence increases). BeB_2H_8 may have several structures differing in bridge hydrogen atoms.

The volatile borohydrides of Be, Al, Hf and Zr inflame in air, but volatile $U(BH_4)_4$ is stable in dry air.



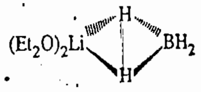
$Be(BH_4)_2$

20-IV



$Al(BH_4)_3$

20-V



$LiBH_4.2Et_2O$

20-VI

The ionic tetrahydridoborates also possess appreciable thermal stability. Thus, $LiBH_4$ is stable upto 380°. The tetrahydridoborates of Na—Cs are stable upto 600°. They are readily soluble in water, tetrahydrofuran, liquid ammonia, pyridine, ethers etc. coordinating solvents. $LiBH_4$ dissolves in diethyl ether forming a coordination compound in which the BH_4^- ion acts as a bidentate ligand. (See later for other examples).

While $LiBH_4$ reacts violently with water, $NaBH_4$ can be crystallized from its solution in cold water with slight decomposition, and KBH_4 is quite stable.

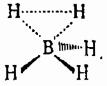
$$LiBH_4 + 3H_2O = LiOH + HBO_2 + 4H_2.$$

$NaBH_4$ is soluble in ethanol while it reacts rapidly with methanol. It is insoluble in nonpolar solvents.

[**Sec. 20.3.3** *Properties of borohydrides*]

In aqueous solution, $NaBH_4$ is kinetically, rather than thermodynamically stable. The BH_4^- ion undergoes slow hydrolysis in aqueous solution; rapidly in presence of acids.

$$BH_4^- \longrightarrow [BH_3OH]^- + H_2 \longrightarrow [BH_2(OH)_2]^{2-} + H_2 \ldots\ldots [B(OH)_4]^- + H_2O.$$



20-VII

The first step seems to determine the overall rate. The rate law contains both an acid-independent term and a term first order in H^+ ion concentration ($K = 2 \times 10^6\ M^{-1}s^{-1}$). A dissociative mechanism (*D* process) aided by the solvent may be responsible for the acid-independent path. The acid-catalyzed path is most likely to proceed through a transient (lifetime 10^{-10} s) five coordinate intermediate BH_5 (20-VII).

Three sp^3 hybrid orbitals of boron form three bonds with hydrogen; the fourth sp^3 hybrid orbital forms a weak 3-center bond with the other two H-atoms. These two H-atoms are subsequently removed by a dissociative mechanism and replaced by OH^-. BH_4^- in D_2O or BD_4^- in H_2O gives mostly HD, supporting the above view. An alternative explanation involves concerted attack from the LUMO of an H^+ on the HOMO of BH_4^-, stripping off a hydrogen atom.

Some hydrogen exchange also takes place, though to a much less extent :

$$BH_4^- + \overset{*}{H}OH = BH_3\overset{*}{H}^- + HOH.$$

Strong acids, protonic or Lewis, react with borohydrides to give diborane.

$$2LiBH_4 + 2HCl = 2LiCl + B_2H_6 + 2H_2$$

$$3LiBH_4 + BF_3 = 3LiF + 2B_2H_6$$

$$3NaBH_4 + 4BF_3 = 3NaBF_4 + 2B_2H_6.$$

The BH_4^- is stable in water in moderately alkaline medium (pH > 9) and is a mild reducing agent. Aqueous solutions of arsenites, antimonites, germanates or stannates are reduced to the respective hydrides : Fe (III) is reduced to Fe (II); Ag (I) is reduced to Ag.

$$3BH_4^- + 4H_3AsO_3 \longrightarrow 3H_2BO_3^- + 4AsH_3 + 3H_2O.$$

The BOROL Process

The nonmetal halides (PCl_3, PCl_5, $SiCl_4$ etc.) are also reduced to their corresponding hydrides. The reduction of SO_2 to dithionite, $S_2O_4^{2-}$, is utilised for the bleaching of wood pulp in situ (BOROL process).

$$NaBH_4 + 8NaOH + 8SO_2 \longrightarrow 4Na_2S_2O_4 + NaBO_2 + 6H_2O.$$

The tetrahydridoborates are nucleophilic reducing agents which attack centres of low electron density (whereas B_2H_6 and its derivatives are electrophilic). $LiBH_4$ is a stronger reducing agent; it reduces aldehydes, ketones as well as esters to alcohols. $NaBH_4$ is a comparatively milder reducing agent and is more selective; it leaves the following functional groups unchanged : olefin, ester, epoxy, nitro and carboxylic acid.

$$C_6H_5CH = CHCHO \longrightarrow C_6H_5CH = CHCH_2OH.$$

Ketones are reduced less rapidly.

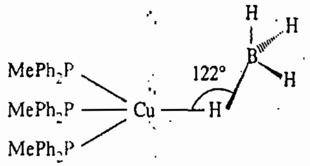
$LiBH_4$ and $NaBH_4$ react with CH_3OH even at very low temperatures (–100°C and –40° C respectively) :

$$LiBH_4 + 4CH_3OH = LiOCH_3 + B(OCH_3)_3 + 4H_2.$$

I_2 in cyclohexane (at room temperature) reacts with borohydrides (MBH_4) to give BI_3, HI and MI. But in diglyme, B_2H_6 is obtained almost quantitatively (see preparation of B_2H_6).

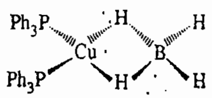
Co-ordination compounds

The BH_4^- ion (and also BH_3Me^-) can coordinate to a metal through M–H–B bridge bonds, donating 2, 4 or 6 electrons and occupying one, two or three coordination sites (unidentate, bidentate or tridentate respectively). This is expressed by adding the prefix η^1–, η^2–, η^3– before the BH_4 group in the formula where η stands for the ***hapticity*** of the ligand (Greek ***haptien*** = to fasten). Monohapto groups are denoted by η^1, dihapto as η^2, etc. The following complexes illustrate η^1 and η^2 coordination by the BH_4 group (20-VIII and 20-IX) :



$[Cu^I(\eta^1-BH_4)(PMePh_2)_3]$

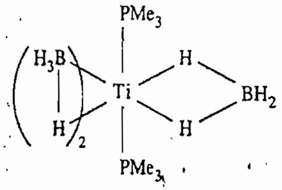
20-VIII



$[Cu^I(\eta^2-BH_4)(PPh_3)_2]$

20-IX

η^3 - type coordination is found in 12-coordinate complexes of the type $M(BH_4)_4$, (M = Ti, Zr, Hf, Np, Pu) for example, $[Zr^{IV}(\eta^3\text{-}BH_4)_4]$. Some polymeric complexes of Th, Pa and U $[M(BH_4)_4$ type$]$ feature 14 - coordinate metal atoms with 2 η^3–BH_4 and 4 bridging η^2 - BH_4 groups. Other bridging modes are also known. An interesting example of side-on bonding is found in the following compound (20-X) :



20-X

The borohydride complexes are non-rigid (fluxional) in solution — the terminal and bridge H-atoms in η^2 and η^3 complexes are found to undergo rapid interchange; all the H-atoms appear same on an nmr time scale. The trisbidentate complex $[Al(\eta^2-BH_4)_3]$ is one of the earliest compounds in which fluxionality was recognized (1955).

$Al(BH_4)_3$ dimerizes at 70° C as :

$$2Al(BH_4)_3 \longrightarrow Al_2B_4H_{18} + B_2H_6.$$

The fluxional binuclear complex has two $Al(\eta^2-BH_4)_2$ units joined by two Al—H—Al bridge bonds.

In the gas phase, $Al(BH_4)_3$ reacts with Al_2Me_6 nearly quantitatively even at room temperature :

$$4Al(BH_4)_3 + Al_2Me_6 \longrightarrow 6[Al(BH_4)_2Me]$$

The product has a square pyramid structure; the η^2 – BH_4 groups lie at the basal plane and the methyl group is at the apex (electron diffraction). $Ga(BH_4)_2H$ ($GaCl_3$ + $LiBH_4$, –45°C) has a similar structure, the H-atom lying at the apex.

[**Sec. 20.3.3** *Alumino hydrides*]

$NaBH_4$ is now produced on a large scale — nearly 2000 tonnes per annum (worldwide). It is largely used as a reducing agent for organic functional groups and bleaching of wood pulp (BOROL process, see above). It is gradually gaining importance in electrodeless plating of metals — for example, deposition of nickel on metal or nonmetallic substances like plastics. Some Ni_3B is deposited with nickel.

Tetrahydridoaluminates (aluminohydrides)

$LiAlH_4$

$LiAlH_4$ is the most important hydrido complex of aluminium. It is prepared as

1. $4\,LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3LiCl$

2. $Na + Al + 2H_2 \xrightarrow[350\text{ atm}]{THF;\,140°} NaAlH_4$ (precipitated by toluene).

$$NaAlH_4 + LiCl \xrightarrow{Et_2O} NaCl\,(s) + LiAlH_4.$$

It is a white crystalline solid (when pure; usually found grey), stable in dry air upto 120°C, above which it decomposes into its elements. It is highly sensitive to moisture, protic solvents and many organic functional groups.

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2.$$

It is largely soluble in ether (~29% at room temperature).

$LiAlH_4$ is a versatile reducing agent in organic and inorganic chemistry. It reduces carboxylic acids to alcohols but usually does not attack double bonds. It is a standard reagent for the reduction of halides to hydrides :

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3.$$

However, the product may vary depending upon the relative stabilities of the tetrahydridoaluminate and the hydride or of the element itself. Thus, $BeCl_2$ gives $Be(AlH_4)_2$, but BCl_3 gives B_2H_6 ·

$$4BCl_3 + 3LiAlH_4 = 2B_2H_6 + 3LiCl + 3AlCl_3$$

HgI_2 gives Hg. Halides of Cu, Ag, Au, Zn, Cd and Hg are reduced to the metals at room temperature but unstable hydrido complexes may result at low temperature.

MX or $MX_2 \longrightarrow M$ (room temperature; M = Cu, Ag, Au, Zn, Cd, Hg)

MX_4 or $MX_5 \longrightarrow MH_4, MH_3$. (M = Si, Ge, Sn, P, As, Sb)

$BiCl_3 \longrightarrow Bi$; $NO \longrightarrow HON = NOH$ (hyponitrous acid).

The AlH_4^- ion is tetrahedral. Substantial covalent character is indicated in the crystal structure of $LiAlH_4$.

$LiAlH_4$ is largely used as a reducing agent in organic chemistry though its use in industry is gradually declining since 1980-s. Several cheaper agents like $Bu^i_2\,AlH$, $Na[AlEt_2H_2]$ and $Na[Al(OCH_2CH_2OMe)_2H_2]$ are gradually taking its place. These are obtained through the following reactions :

$$2Me_2C = CH_2 + Al + H_2 \longrightarrow Bu^i_2\,AlH$$

$$2CH_2 = CH_2 + Al + 2H_2 \longrightarrow \tfrac{1}{2}(Et_2AlH)_2$$

$$2MeOCH_2CH_2OH + Al + Na \xrightarrow[toluene]{H_2} Na[Al(OCH_2CH_2OCH_3)_2H_2].$$

Hydrido complexes of Ga, In, Tl

$LiMH_4$ compounds (M = Ga, In, Tl) may be prepared at low temperatures only through reactions similar to those used for $LiAlH_4$.

$LiGaH_4$ is prepared by reacting $GaCl_3$ with excess LiH in ether.

$$GaCl_3 + 4LiH = LiGaH_4 + 3LiCl.$$

It decomposes slowly even at 25°C (LiH, Ga, H_2) and is completely unstable above 50°C. It reacts with excess $GaCl_3$ in ether to give GaH_3.

$LiInH_4$ and $LiTlH_4$ are unstable above 0°C.

20.3.4 The Higher Boranes and the Carboranes

About 25 neutral boranes and a large number of borane anions are known at present. The neutral boranes mostly belong to either of the two following general classes:

Compound types

Nido*-boranes : B_nH_{n+4}	**Arachno*-Boranes : B_nH_{n+6}**
B_2H_6 diborane (6)	B_4H_{10} tetraborane (10)
B_5H_9 pentaborane (9)	B_5H_{11} pentaborane (11)
B_6H_{10} hexaborane (10)	B_6H_{12} hexaborane (12)

Nido*-boranes : B_nH_{n+4}	**Arachno*-Boranes : B_nH_{n+6}**
B_8H_{12} octaborane (12)	B_8H_{14} octaborane (14)
$B_{10}H_{14}$ decaborane (14)	B_9H_{15} enneaborane (15)

Besides these, a number of boranes (B_nH_m) are known with interconnected borane clusters — these are called conjuncto-boranes (Latin *conjuncto* = join together) e.g., $B_{15}H_{23}$, B_8H_{18}, $B_{16}H_{20}$.

Borane anions are known in all three above structural types as well as in other structural types:

nido-borane anions : $B_nH_{n+3}^-$ (e.g. $B_5H_8^-$, $B_{10}H_{13}^-$);
$B_nH_{n+2}^{2-}$ (e.g. $B_{10}H_{12}^{2-}$, $B_{11}H_{13}^{2-}$).

arachno-borane anions : $B_nH_{n+5}^-$ (e.g. $B_2H_7^-$, $B_3H_8^-$, $B_5H_{10}^-$);
$B_nH_{n+4}^{2-}$ (e.g. $B_{10}H_{14}^{2-}$).

Conjuncto-borane anions : $(B_{10}H_9^{2-})_2$.

Closo-borane anions (Greek closo = cage; these have closed polyhedral clusters of *n* B-atoms) $B_nH_n^{2-}$ (n = 6 – 12).

Boranes with an even more open structure have been classified as ***hypho-boranes*** (Greek *hyphe* = net), though no neutral borane is definitely known. Few borane adducts appear to have this structure.

Nomenclature

In naming neutral boranes, the number of boron atoms in a molecule is indicated with a latin prefix to "borane"; the number of hydrogen atoms in the molecule is shown by a number in parentheses : e.g.,

B_2H_6 : diborane (6); B_5H_9 : pentaborane (9)

$B_{10}H_{14}$: *nido*-decaborane (14); $B_{14}H_{20}$: tetradecaborane (20).

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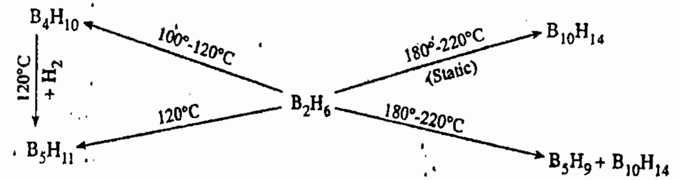
* Nido from Latin *nidus* = nest; they have a non-closed structure like a ployhedron without a vertex.

* Arachno from Greek *arachne* = spider's web; they have a still more open structure — like polyhedra from which two adjacent vertices are missing.

For anions, the name ends in -'ate'; the number of H-atoms is stated in the beginning and the charge is shown at the end; *closo*, *nido* - etc. types are also mentioned :

$B_{10}H_{10}^{2-}$: decahydro - closo - decaborate (2–).

Preparation : The higher boranes are mostly prepared by thermal cracking of diborane under varying conditions. A mixture of boranes is often formed, from which the constituents can be separated by fractional distillation under high vacuum. Thus, heating of diborane under static condition at 180°-220°C produces pure $B_{10}H_{14}$ but passing diborane through a tube heated at this temperature forms mainly B_5H_9 (60%) and $B_{10}H_{14}$ (6%). Lower boranes are formed at 100-120°C :



Controlled pyrolysis of diborane is conveniently carried out in a hot-cold reactor (Fig. 20.8). Diborane is passed through the outer chamber of a double-walled bath. The interior chamber of the bath contains oil which can be heated to any desired temperature by an immersed electrical coil. This double-walled bath is now immersed in a larger cold bath. Diborane passing through the apparatus is thus exposed to one hot surface (inner oil-bath) and one cold surface (outer Dewar). The products of decomposition on the hot surface are rapidly quenched out of the reaction zone by condensation on the cold outer wall. Different boranes may be obtained by maintaining specific temperatures in the hot and cold bath :

Hot bath	*Cold bath*	*Major product*
120°C	–78°C	B_4H_{10}
120°C	–30°C	B_5H_{11}
180°C	–78°C	B_5H_9 (Under a static pressure of B_2H_6 for 2-3 days).

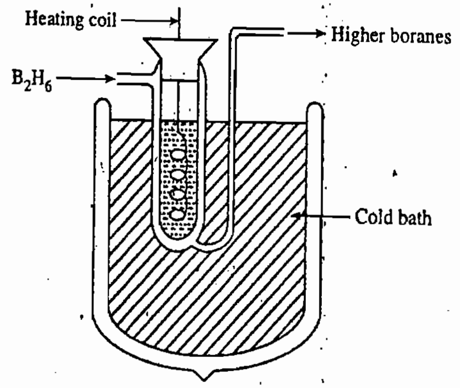


Fig. 20.8
An apparatus for controlled pyrolysis of diborane.

Properties : Both physical and chemical properties of the boranes vary widely. Only B_4H_{10} [decaborane(14)] is a stable solid at room temperature. Important properties of a few boranes are given in Table 20.7.

TABLE 20.7

Properties of boranes

	M.P. °C	B.P. °C	ΔH_f^0 (kJ mol^{-1})	Reactivity to air at 25°C*	Thermal stability*	Reaction with water*
B_4H_{10}	−120	18	58	Not sp. fl. if pure	D (*rapid*) at 25°C	Hy.
B_5H_9	−46.6	48	54	Sp. fl.	D (*slow*) at 150°C	Hy. (*heating*)
B_5H_{11}	−123	63	67 (?)	Sp. fl.	D (*very rapid*) at 25°C	Hy. (*rapid*)
B_6H_{10}	−62.3	108	71	Sp.fl.	D (*slow*) at 25°C	Hy. (*heating*).
B_6H_{16}	−82.3	80-90	111	—	D (*slow*) at 25°C	Hy. (*quantitative*)
$B_{10}H_{14}$	99.7	213	32	Very stable	Stable at 150°C	Hy. (*slow*)

*Sp. fl. = Spontaneously flammable; D = Decomposition; Hy = Hydrolyzed.

The boranes are all endothermic compounds — a reflection of the very strong bonding in elemental boron and H_2 molecule. Typical values of bond energies are (in kJ mol^{-1}) :

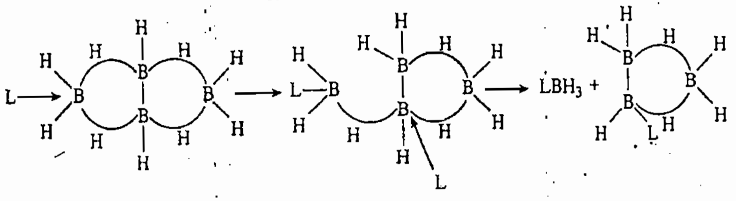
H_2	436	B—H (term)	380	B—B	330
B	555	B—H—B	440	B—B—B	380

As evident from table 20.7, the boranes except $B_{10}H_{14}$ are highly reactive and spontaneously flammable in air. In general, *arachno* - boranes appear to be thermally less stable and more reactive than *nido*-boranes. Reactivity of the boranes diminishes with increasing molecular weight. Reactions of individual boranes are, however, very diverse. As expected from their eletron-deficient nature, they react with Lewis bases under various conditions.

Cleavage

Lewis bases like Me_3N, R_2O, Me_3P or H^- lead to cleavage of the boranes, specially when a BH_2 group is present.

$$B_4H_{10} + 2L \longrightarrow LBH_3 + LB_3H_7$$



NH_3 also leads to unsymmetrical cleavage, yielding ammineboranes which are much more stable than the hydrides.

$$B_4H_{10} + 2NH_3 \longrightarrow [H_2B\,(NH_3)_2]^+\,[B_3H_8]^-$$

$$B_5H_{11} + 2NH_3 \longrightarrow [H_2B\,(NH_3)_2]^+\,[B_4H_9]^-$$

$$B_6H_{12} + 2NH_3 \longrightarrow [H_2B\,(NH_3)_2]^+\,[B_5H_{10}]^-$$

[**Sec. 20.3.4** *Higher boranes*]

Similarly,

$$B_6H_{12} + PMe_3 \longrightarrow [H_3BPMe_3] + B_5H_9$$

$$B_5H_{11} + 2CO \longrightarrow H_3BCO + B_4H_8\,(CO).$$

The BHB bridging portions in the boranes are electron deficient and susceptible to attack by Lewis bases (nucleophiles). Thus,

$$B_{10}H_{14} + 2MeCN \longrightarrow H_2 + B_{10}H_{12}\;2MeCN$$

$$B_5H_9 + NaH \longrightarrow H_2 + Na^+B_5H_8^-$$

$$B_{10}H_{14} + 2PR_3 \longrightarrow H_2 + B_{10}H_{12}\,(PR_3)_2.$$

In general, larger boranes are more acidic than smaller ones. Also, *arachno* boranes are more acidic than *nido* boranes of comparable size.

Bridge proton abstraction

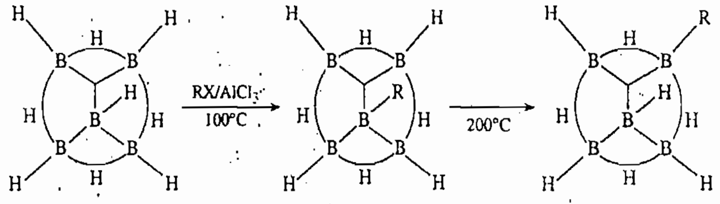
Exchange experiments reveal that $B_{10}H_{14}$ exchanges the four bridge protons in aqueous medium in which it can be titrated as an acid against NaOH solution.

$$B_{10}H_{14} + OH^- \rightleftharpoons B_{10}H_{13}^- + H_2O\;(pK_a = 2.7).$$

The bridge protons may also be abstracted with very strong bases in ethers :

$$B_6H_{10} + KH \longrightarrow K[B_6H_9] + H_2.$$

Electrophilic substitution reactions in boranes are also known. Thus B_5H_9 undergoes Friedel-Crafts alkylation at the apical boron to give the 1-alkyl derivative (20-XI) :



B_5H_9 1-alkyl derivative 2-alkyl derivative

20-XI **20-XII**

M.O. calculations indicate that the apical boron atom has higher electron density than the basal boron atoms. However, alkylation at the apical boron appears to be kinetically controlled; when heated to 200°C, or a Lewis base is added, the alkyl group migrates to the 2-position (20-XII).

Electrophilic substitution by halogens is also known (in presence of a Friedel-Crafts catalyst).

$$B_5H_9 + I_2 \longrightarrow B_5H_8I + HI.$$

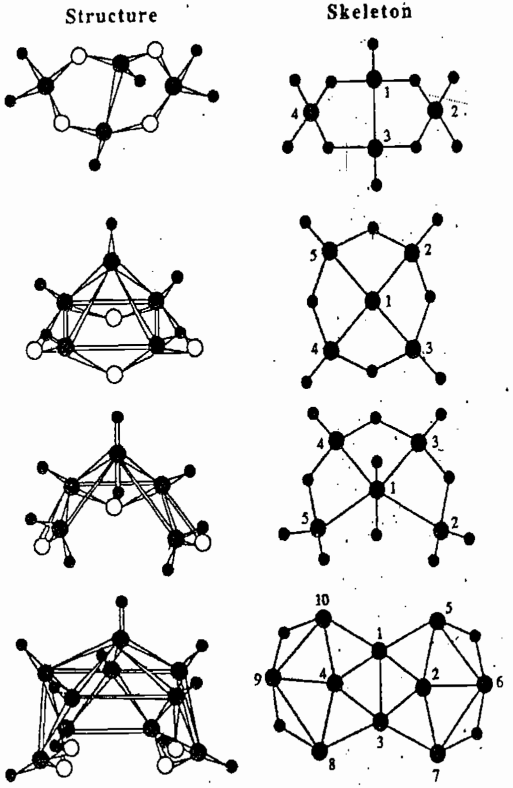
$$B_{10}H_{14} + I_2 \longrightarrow B_{10}H_{12}I_2 + H_2.$$

In the second reaction, only 2,4 or 1,3 disubstituted products are obtained, corresponding to points of higher electron-density (M.O. calculation).

Structure

The three dimensional structures of the higher boranes consist of clusters of B-atoms arranged in the form of incomplete "cages". Some of them are shown in Fig. 20.9.

Fig. 20.9 **Structure of some higher boranes**.
(Figures in bracket represent "styx" numbers which have been explained below.)



B_4H_{10} (4012)
All four boron atoms are tetrahedrally corodinated.

B_5H_9 (4120)
Square-based pyramid of boron atoms.

B_5H_{11} (3203)
Distorted square-based pyramid.

$B_{10}H_{14}$ (4620)
Two pentagonal pyramids "hinged" along the line joining B_1 to B_3.

Bonding

The concept of three center two electron bonds (3*c* -2*e*) developed in connection with B_2H_6 may be extended to obtain valence-structures or a "semi-topological" description of the bonding in most higher boranes (Lipscomb). The bonding scheme rests on the following bonding elements :

(i) Terminal 2*c*-2*e* B-H bond. (ii) 2*c*-2*e* B-B bond. (iii) 3*c*-2*e* BHB hydrogen bridge bonds. (iv) Open 3*c*-2*e* BBB boron bridge bonds. [Fig. 20.10 (a)]. (v) Closed 3*c*-2*e* boron bonds. [Fig. 20.10 (b)]

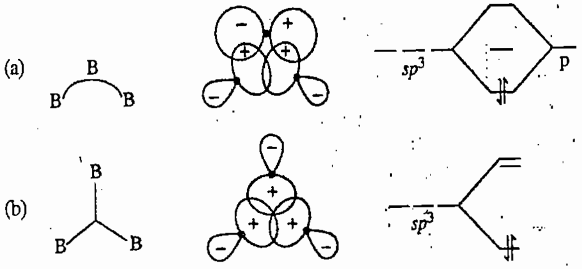


Fig. 20.10 Types of 3c-2e bond overlaps involving B-atoms.

[Sec. 20.3.4 *Higher boranes*]

The open 3*c*—2*e* boron bridge-bond is normally not required for boranes themselves; they become useful in some heterosystems.

Styx Numbers

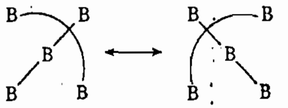
The valence structures of boranes may be conveniently expressed in terms of their *styx* numbers based on the following code system :

s = number of B—H—B bonds
t = number of B—B—B bonds
y = number of B—B bonds
x = number of BH_2 groups.

Thus, diborane (B_2H_6, see Fig. 20.6) has the styx no 2002. The styx numbers for some higher boranes are shown in Fig. 20.9 in parenthesis.

The styx numbers may be arrived at by solving several equations connecting the number of H-atoms, orbitals and valence electrons. However, this does not always lead to a unique styx number and hence an unequivocal structure. The best structure is then selected with other additional criterion.

However, this scheme finds certain limitations when applied to symmetrical close structures and open structures of higher symmetry. In B_5H_9, the four boron atoms in the basal plane are equivalently related to the boron atom in the apex; in terms of localized BBB and B-B bonding elements, this can be depicted in terms of resonance hybrids like



A delocalized m.o. description appears to fit the situation better—there will be a total of seven 5-center molecular orbitals with the lowest three occupied by six electrons (2 × 2 for the two B—B bonds and 2 for the BBB bond). The superiority of such delocalized m.o. approach becomes more prominent with increasing symmetry of the species.

Use : Decaborane (14) is used as a rocket fuel. It is prepared on a large scale by pyrolysis of B_2H_6 at 150°C (dimethyl ether as catalyst).

Borane Anions

Borane anions

Polyhedral borane anions $B_nH_n^{2-}$, $n = 6 - 12$ are well characterized. Many of them result from acid dissociation of boranes. They may also be prepared in other different ways :

(i) $5BH_4^- + 4BF_3.Et_2O \xrightarrow{\text{diglyme}} 2B_3H_8^- + 3BF_4^- + 2H_2 + 4Et_2O$.

Excess BF_3 gives $B_{11}H_{14}^-$.

(ii) Pyrolysis of NaB_3H_8 (200-230°C) in vacuum gives salts of BH_4^-, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.

(iii) $B_{10}H_{14} + 2R_3N \xrightarrow[\text{xylene}]{\text{boiling}} 2R_3NH^+ + B_{10}H_{10}^{2-} + H_2$.

(iv) $5B_2H_6 + 2NaBH_4 \xrightarrow[\text{diglyme}]{180°C} 2Na^+ + B_{12}H_{12}^{2-} + 13H_2$.

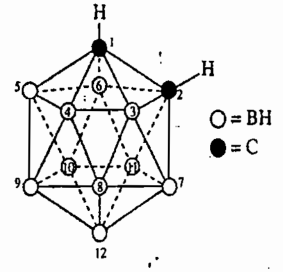
The $B_nH_n^{2-}$ ions have full triangulated *closo* structures. Calculations show that a B_nH_n cage is short of two electrons required to fill the last of $(n + 1)$ bonding m.o.s. This explains the formation of doubly charged anions. They undergo electrophilic substitution reactions by reagents like RCO^+, CO^+, $C_6H_5N_2^+$, Br^+ etc. most readily in strong acid medium.

Carboranes

Carboranes are derived from $B_nH_n^{2-}$ structures by replacing BH^- by iso-electronic and isostructural CH. Replacement of two BH^- by two CH results in neutral *closo* structures having formula type $C_2B_{n-2}H_n$. As an example, $B_{10}H_{14}$ may be heated with diethyl sulfide and acetylene to give 1, 2-$B_{10}C_2H_{12}$ (20-XIII).

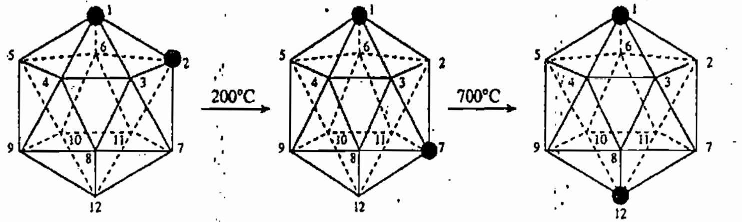
$$B_{10}H_{14} + 2Et_2S = B_{10}H_{12}\,(Et_2S)_2 + H_2.$$

$$B_{10}H_{12}\,(Et_2S)_2 + C_2H_2 = 1,2\text{-}B_{10}C_2H_{12} + 2Et_2S + H_2.$$



20-XIII : 1,2-dicarba-closo-dodecaborane

Depending upon the relative position of the two carbon atoms in the icosahedral framework, three isomers of $B_{10}C_2H_{12}$ are possible. The 1,2 isomer obtained in the above process rearranges to the 1,7 and 1,12 isomers (20-XIV) on heating :



1, 2-carborane

1, 7-carborane

1, 12-carborane (most stable)

20-XIV

The hydrogen atoms attached to the C atoms in $C_2B_{10}H_{12}$ are mildly acidic :

$$C_2B_{10}H_{12} + 2LiC_4H_9 \longrightarrow C_2B_{10}H_{10}\,Li_2 + 2C_4H_{10} \quad \text{(butane).}$$

The dilithiocarborane is a good nucleophile and provides synthetic route to different carborane derivatives.

(a) CO_2, followed by $H_2O \longrightarrow C_2B_{10}H_{10}\,(COOH)_2$;

(b) $NOCl \longrightarrow C_2B_{10}H_{10}\,(NO)_2$;

(c) $I_2 \longrightarrow C_2B_{10}H_{10}I_2$;

(d) $SiMe_3Cl \longrightarrow C_2B_{10}H_{10}\,(SiMe_3)_2$.

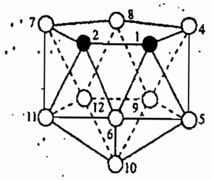
As a consequence of this electron-withdrawing power of the carbon atoms, the boron atoms adjacent to carbon are most electron-deficient (3,6 in 1,2 - $B_{10}C_2H_{12}$; 2,3 in 1,7 - $B_{10}C_2H_{12}$). Such boron atoms suffer nucleophilic attack by strong bases like

OR^-, H^- etc. with the removal of a BH^{2+} unit and formation of *nido*-carborane anion, $B_9C_2H_{12}^-$

$$(1,2 \text{ or } 1,7)\text{-}B_{10}C_2H_{12} + EtO^- + 2EtOH \xrightarrow{\text{heat}} B_9C_2H_{12}^- + B(OEt)_3 + H_2.$$

With NaH, abstraction of one more proton produces another *nido*-carborane anion $B_9C_2H_{11}^{2-}$, which is a strong base and readily acquires H^+ to give back $B_9C_2H_{12}^-$ and $B_9C_2H_{13}$ (a neutral *nido*-carborane).

$$B_9C_2H_{12}^- + NaH \longrightarrow Na^+ + B_9C_2H_{11}^{2-} + H_2$$



1,2 - $B_9C_2H_{11}^{2-}$

20-XV

Both these *nido*-carborane anions may have two isomeric forms — 1,2 or 1,7, according to the nature of the mother *closo* carborane $B_{10}C_2H_{12}$. The structure of the 1, 2 - isomer is shown in which the B-atom at position 3 of the mother closo carborane has been removed. The resulting pot-like structure (20-XV) is the root to the trivial name "*dicarbollide*" for this anion (Spanish *olla* = pot).

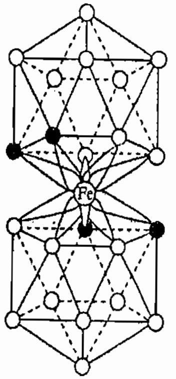
The lost BH^{2+} unit has only 2 valence electrons, and is thus six elctrons short of an inert gas configuration. Two BH^{2+} units from two mother carboranes now require a total of 6 × 2 = 12 electrons to attain an inert gas electron configuration. An Fe^{2+} ion ($3d^6$) also requires 12 electrons to attain the next inert gas configuration of Kr ($3d^6 \rightarrow 3d^{10}4s^24p^6$). Consistent with this electron counting, two $C_2B_9H_{11}^{2-}$ carborane anions form a *metallocarborane* with $FeCl_2$ (20-XVI) :

$$2C_2B_9H_{11}^{2-} + FeCl_2 \xrightarrow[\text{atmosphere}]{N_2} [Fe\,(B_9C_2H_{11})_2]^{2-}.$$

The $C_2B_9H_{11}^{2-}$ anion acts as a six-electron donor ligand like cyclopentadienyl ion, $C_5H_5^-$ (which gives a sandwich complex with Fe(II); (η^5-$C_5H_5)_2$Fe called ferrocene). Both complexes undergo reversible oxidation in air :

$$[(C_5H_5)_2\,Fe^{III}] \underset{-e}{\overset{+e}{\rightleftharpoons}} [(C_5H_5)_2\,Fe^{II}]$$

$$[B_9C_2H_{11})_2\,Fe^{III}] \underset{-e}{\overset{+e}{\rightleftharpoons}} [(B_9C_2H_{11})_2\,Fe^{II}]^{2-}$$



$[Fe^{II}(B_9C_2H_{11})_2]^{2-}$

20-XVI

Co(III), isoelectronic with Fe(II), also forms a similar bis(dicarbollide) metal complex : $[(B_9C_2H_{11})_2\,Co^{III}]^-$.

20.3.5 Halides

All four trihalides ($M^{III}X_3$; X = F, Cl, Br, I) are known for M = B, Al, Ga and In. Tl (III) forms TlF_3, $TlCl_3$, $TlBr_3$ (the chloride and bromide are, however, unstable with respect to TlX and X_2) but the triiodide TlI_3 is actually Tl^IIl_3. Tl (III) is too strongly oxidizing to coexist ordinarily with I^- but may exist as complex $[Tl^{III}I_4]^-$.

General discussion

Simple MX_3 species have only six electrons in the valence shell of M and are formally electron deficient. In spite of this, the trihalides of boron are all monomeric volatile species involving B—X pi-bonding (See p. 205). The remaining elements tend to meet their electron-deficiency by attaining higher coordination number. The trifluorides of elements Al-Tl are all non-volatile solids with dominant ionic character. With larger halides, covalence increases; the trichlorides, tribromides and triiodides of Al, Ga and In are relatively volatile having layer lattices or lattices containing dimeric molecules; solutions of the halides in organic solvents and the vapour consist of halogen-bridged dimeric molecules.

All MX_3 compounds are good Lewis acids; they accept neutral donor molecules or anions forming tetrahedral complexes. The acceptor ability generally decreases as $B > Al > Ga > In$. (The position of Tl is uncertain).

Boron forms a number of electron-deficient subhalides and a series of molecular halides of formula $X_2B - BX_2$. $GaCl_3$ when heated with Ga (180°C) forms a compound of stoichiometry $GaCl_2$ but actually it is $Ga^+[GaCl_4^-]$ (Similarly $InCl_2$). Tl_2Cl_3, Tl_2Br_3 and Tl_3I_4 also contain Tl (I) and Tl (III). Thermal decomposition of the trihalides at high temperature (> 1100°) yields monohalides of Al, Ga and In. As explained earlier in connection with "inert pair effect", decrease in bond energy is primarily responsible for the stabilization of Tl(I) halides under ordinary conditions. The $4f^{14}5d^{10}$ core makes the Tl^+ ion strongly polarizing and the Tl(I) halides resemble those of Ag(I).

Boron Trihalides

Preparation

BF_3 is prepared by heating a mixture of calcium fluoride and boric oxide (or borax) with concentrated sulphuric acid :

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

Excess concentrated H_2SO_4 facilitates removal of water which otherwise would form the adducts BF_3, H_2O or $BF_3, 2H_2O$.

Thermal decomposition of benzene diazonium fluoroborate produces very pure BF_3 :

$$PhN_2BF_4 \longrightarrow PhF + N_2 + BF_3.$$

The gas may be collected over mercury.

BCl_3 and BBr_3 are obtained by heating B_2O_3 with Cl_2 or Br_2 in presence of coke :

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 6CO\ (500°C).$$

BCl_3 (b.p. 12.5°C) condenses in a freezing mixture; BBr_3 (b.p. 91.3°C) condenses at room temperature.

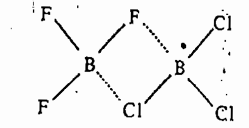
Halogen exchange between BF_3 and Al_2Cl_6/Al_2Br_6 also leads to BCl_3 or BBr_3 (high lattice energy of AlF_3 drives the reaction).

BI_3 may be obtained by reacting I_2 with $LiBH_4$ (or $NaBH_4$).

Both BBr_3 or BI_3 tend to decompose on exposure to light or heat, liberating Br_2 or I_2.

Mixed halides

Mixed boron halides $BFCl_2$, BCl_2F, $BFBr_2$, BF_2Br or even BFClBr have been identified as short-lived transient species in mass-spectrometry, vibrational spectroscopy or nmr spectroscopy (^{11}B or ^{19}F). A 4-centered transition state is probably involved (Fig. 20.XVII).



20-XVII

BF_3 and BCl_3 are gases at room temperature; BBr_3 is a volatile liquid while BI_3 is a solid. Important physical properties of the boron halides are summarized in Table 20.8.

TABLE 20.8

Physical properties of the boron trihalides

	MP (°C)	BP (°C)	ΔH_f^0 (298K) (kJ mol^{-1})	r_{B-X} (Å)	E_{B-X} (kJ mol^{-1})
BF_3	−127.1	−99.9	−1123	1.30	646
BCl_3	−107	12.5	−408	1.75	444
BBr_3	−46	91.3	−208	1.87	368
BI_3	49.9	210	endothermic	2.10	267

BF_3 fumes in moist air and is partially hydrolyzed by water (excess) into fluoroboric acid (see later) and boric acid :

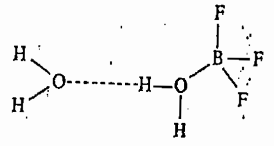
$$4BF_3 + 6H_2O \longrightarrow B(OH)_3 + 3BF_4^- + 3H_3O^+$$

Properties

With small amounts of water at low temperature (below 20°C) BF_3 forms two adducts, $BF_3.H_2O$ (m.p. 10.2°C) and $BF_3.2H_2O$ (m.p. 6.4°C). In the crystalline 1:1 adduct the B-atom is tetrahedrally surrounded by 3 F atoms and an O-atom from the H_2O. In the crystal of the 1 : 2 adduct, a second molecule of H_2O is associated through strong H-bonding (20-XVIII).

On melting, ionization takes place extensively :

$$BF_3.2H_2O \longrightarrow H_3O^+ + [BF_3OH]^-.$$



20-XVIII

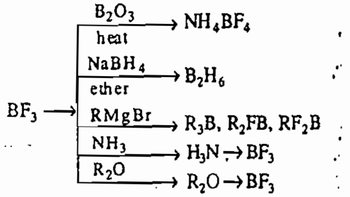
BCl_3 and BBr_3 are rapidly and completely hydrolyzed by water, BI_3 even more vigorously :

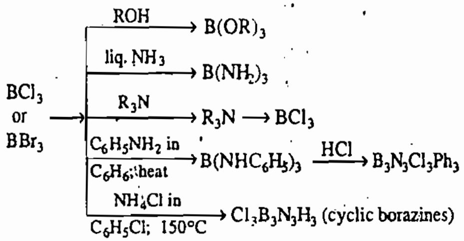
$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl.$$

[BCl_4^-, BBr_4^- and BI_4^- ions are formed only in non-aqueous media and can be isolated as salts of very large cations. See later].

As expected, the boron trihalides are good Lewis acids and they react with Lewis bases like halide ions, ethers, nitriles, amines etc. The 1 : 1 adduct of BF_3 with diethyl ether, $BF_3 . Et_2O$ (b.p. 126°C) is a common source of BF_3 as catalyst in many organic reactions like ester formation, alkyl polymerization and Friedel-Crafts type alkylation or acylation reactions (see later). Similarly, MeOH, EtOH etc (Me = CH_3; Et = C_2H_5) will give stable adducts with BF_3 but with BCl_3, $B(OMe)_3$ and $B(OEt)_3$ will be formed respectively.

Some typical reactions of the boron trihalides are given below :





All BX_3 molecules (unlike BH_3) are classified as hard acids (type-a acceptor; see HSAB) and hence they form stable adducts with N, O and F donor ligands (rather than with P, S and Cl). However, some complexes with transition metal atoms as donors have been characterized, for example $(Ph_3P)_2(CO)ClRh^I \rightarrow BBr_3$.

The order of Lewis acidity among the boron trihalides may be inferred from the stability of the adduct $L \rightarrow BX_3$ for a given ligand L and varying X from F to I. This order appears to be $BF_3 < BCl_3 < BBr_3 < BI_3$ (see box for a set of ΔH° values.) This trend is contrary to our expectation from electronegativity considerations but can be explained when we consider the reorganization at the valence shell of the B-atom; on adduct formation, the B-atom has to change from planar (sp^2 hybridized) to tetrahedral (sp^3 stereo-chemistry). Bond length data (see structure and bonding) indicate that the planar BX_3 molecules involve significant $X \rightarrow B$ π-bonding.

ΔH° (kJ mol^{-1}) for $py + BX_3(g) \longrightarrow pyBX_3(soln)$ in nitrobenzene

$BF_3 : -143$ $BCl_3 : -189$ $BBr_3 : -217$

Lewis acidity order
$BF_3 < BCl_3 < BBr_3$

This is most extensive in BF_3 owing to matching size and energy of the orbitals on F and B atoms and decreases from F to I. Consequently the energy needed for the reorganization of the BX_3 molecule is greatest at BF_3 and decreases as the halogen becomes larger. Summarily, the B-atom in BF_3 may be considered least "electron deficient", and hence the poorest acceptor.

For a given BX_3, stability of a complex depends on several factors like nature of donor atom (mentioned before), steric effects, presence of polar substituents on the ligand etc. Thus pyridine, which is a weaker base towards proton than 2-methylpyridine (or, 2, 2-dimethylpyridine), behaves as a stronger base towards BF_3; the methyl groups in the substituted pyridines prevent close approach of the donor N atom to the acceptor B atom. Stability of the ether adducts of BF_3 also follows the order $Me_2O > Et_2O$.

[Sec. 20.3.5
Boron Halides]

BF_3 is used in a large number of organic reactions, for example,

(i) ethers or alcohols + acids ⟶ esters.

(ii) alcohols + benzene ⟶ alkyl benzenes + H_2O.

(iii) Polymerization of alkenes (with H_2O as a co-catalyst).

(iv) Cracking of hydrocarbons (HF as cocatalyst).

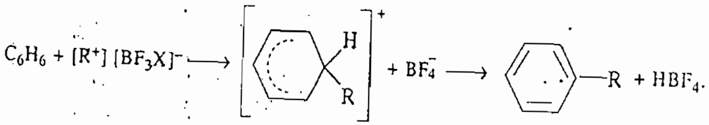
(v) Nitration and sulphonation of aromatic compounds which probably occur via the formation of NO_2^+ (nitryl) and SO_3H^+ (sulphonyl) cations :

$$HONO_2 + BF_3 \rightleftharpoons NO_2^+ + [BF_3(OH)]^-.$$

$$HOSO_3H + BF_3 \rightleftharpoons SO_3H^+ + [BF_3(OH)]^-.$$

(vi) Friedel-Crafts-type alkylations and acylations. The role of BF_3 in such reactions is strictly not of a catalyst since it must be present in essentially equimolar quantities with the reactant. The most likely mechanism involves the ionic intermediate :

$$RX + BF_3 \longrightarrow [\overset{\delta+}{R} \ldots X \ldots \overset{\delta-}{BF_3}] \longrightarrow [R^+][BF_3X]^-$$



Structure and Bonding

All BX_3 molecules are planar with X—B—X bond angles 120°: This is consistent with expected sp^2 hybridization of the B-atom; but the B—X bond lengths are considerably shorter than estimated single bond lengths :

	B-F	B-Cl	B-Br
Estimated single bond length, pm	152	187	199
Observed bond length in BX_3, pm	130	175	187

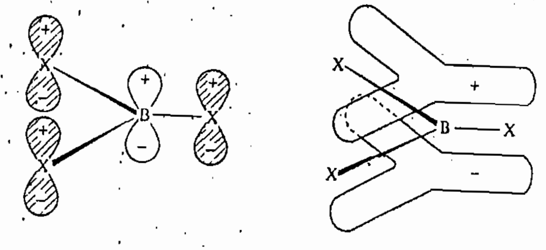


Fig. 20.11
π-overlap (bonding) in BX_3.

This is primarily attributed to appreciable dative p-p π-interaction from a filled p-orbital of matching symmetry on the halogen atom to the vacant p-orbital on B (Fig. 20.11). The interaction is strongest in BF_3 owing to best match of size and energy of the orbitals involved. Two other factors may also contribute to the shortening :

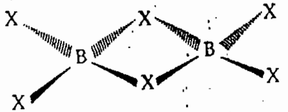
(i) Since the valence shell of boron is incomplete, repulsions between non-bonding electrons is less; this permits the bonded atoms to approach closer. In BF_4^-

(or adducts like $Me_3N \rightarrow BF_3$) steric crowding results in slight increase in the B—F bond length (143 pm).

(ii) Ionic-covalent resonance may also lead to shortening of the bond length. This appears most important for B—F bonds (large eletronegativity difference) and is useful to explain the observed shortening of bonds in BF_4^- or $Me_3N.BF_3$ (where π-bonding is most unlikely).

Why boron trihalides are monomeric

The monomeric nature of the boron trihalides (unlike those of Al etc.) may also be attributed to the stability of the boron-halogen π-bonding which has to be disrupted on forming the halogen-bridged dimer (20-XIX)—the boron atom will have no vacant orbital for π-bonding. This makes the monomer comparatively more stable. It is also likely that the boron atom is too small to form the stable 4-membered ring system in such dimers. $BeCl_2$ may form Be-Cl-Be bridge structures since the Be atom has a larger covalent radius than B (106 pm vs 88 pm).



20-XIX

Halides of Al, Ga, In, Tl

All four trihalides of the elements Al—Tl of the general formula MX_3 are known but TlI_3 is actually thallium(I) tri-iodide. In presence of excess iodide ions, however, Tl(I) may be oxidized by I_2 to $[Tl^{III}I_4]^-$ (see later).

Preparation

All the compounds may be prepared by direct combination of the elements. Other convenient methods are also in use, for example,

(i) $Al_2O_3 + 6HF\,(g) \xrightarrow{700°C} 2AlF_3 + 3H_2O$

(ii) $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} 2AlCl_3 + 3CO$ (also $InCl_3$)

(iii) $(NH_4)_3\,GaF_6 \xrightarrow{300°C} GaF_3$ (also InF_3)

(iv) $Tl_2O_3 + F_2$ (or Cl_2) $\xrightarrow{300°C} TlF_3$ (or $TlCl_3$)

(v) $TlI + I_2 \xrightarrow{\text{conc. aq. HI}} TlI_3$

(vi) Tl (or TlCl or Tl_2CO_3) $\xrightarrow{\text{(i) NOCl (ii) heat}} TlCl_3$

Properties

The properties of the trihalides vary widely. The fluorides are all ionic solids with high melting point; they also enter the gas phase at high temperatures as planar monomers. Covalence increases among all the heavier halides and their melting points are considerably lower. The solid forms consist of octahedrally coordinated metal atoms or dimers, but lower coordination numbers are attained in the liquid and vapour state with dimer-monomer equilibrium. For example in the equilibrium

$$Ga_2Br_6\,(g) \rightleftharpoons 2GaBr_3\,(g)$$

the monomer is present to the extent of about 30% at the boiling point (279° C). The case of aluminium chloride is still more interesting. The crystalline solid has a layer lattice with six-coordinated Al. On melting, it changes to the halogen-bridged dimer (see structure) Al_2Cl_6, in which the coordination number drops to four. This is accompanied by a dramatic increase in volume—the density of the melt is nearly 45% lower than that of the solid at the melting point. The electrical conductivity also approaches zero. The dimers also dominate in the gas phase except at high temperatures when dissociation to monomer occurs reversibly. Al_2Br_6 and Al_2I_6 have dimeric units in the solid, liquid and gaseous states. Such dimers are also present in their solutions in non-polar solvents like benzene.

The halides are mostly colourless to white deliquescent solids (lemon yellow GaI_3 is hygroscopic; InI_3 is yellow; TlI_3 is black). The fluorides have only low solubility in water but the other halides are moderate to highly soluble, yielding acidic solutions. $M(H_2O)_6^{3+}$ and halide ions are present in dilute aqueous solutions. $TlCl_3$ decomposes to TlCl and Cl_2 above 40°C; $TlBr_3$ loses Br_2 at even lower temperatures to give $TlBr_2$ which is actually $Tl^I\,[Tl^{III}Br_4]$. TlI_3, as mentioned before, is $Tl^+I_3^-$, isomorphous with RbI_3. The melting points of the solid halides and their structural types are shown in Table 20.9.

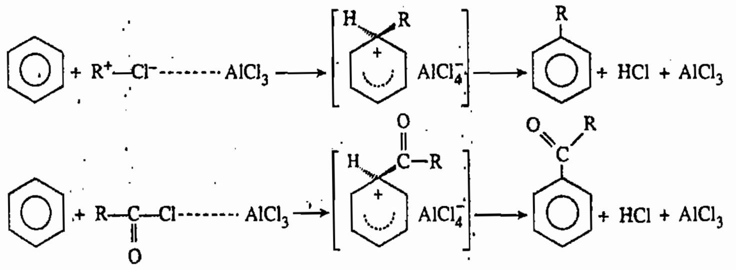
TABLE 20.9

Melting points (°C) of MX_3

(M = Al, Ga, In, Tl; X = F, Cl, Br, I)

	Fluoride	Chloride	Bromide	Iodide
Al	1290 (oct)	192 (oct)	97.8 (dimer)	189.4 (dimer)
Ga	1000 (oct)	78 (dimer)	122 (dimer)	212 (dimer)
In	1170 (oct)	586 (oct)	436 (oct)	210 (dimer)
Tl	550 (oct)	60-70 (oct) (in Cl_2)	–	–

The trihalides except fluorides are strong Lewis acids and readily form adducts with Lewis bases including halide ions. The catalytic behaviour of aluminium chloride in Friedel-Crafts alkylation (or acylation) is attributed to strong polarization of the attacking organic halide to form an intermediate like $R^{\delta+}$——$X^{\delta-}$ ......$AlCl_3$:



With many acyl chlorides and some tertiary alkyl halides extreme polarization may ultimately lead to the formation of an essentially "free" carbocation e.g.

$$Ph_3CCl + AlCl_3 \longrightarrow Ph_3C^+\,AlCl_4^-.$$

Indium and thallium appear to attain coordination numbers higher than four in many adducts. The $InCl_5^{2-}$ ion in $(Et_4N)_2InCl_5$ has a square pyramid geometry (rather than the usual trigonal bipyramid).

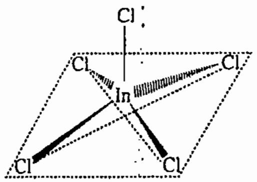


Fig. 20.12

The Geometry of $InCl_5^{2-}$.

[The In-atom is slightly above the basal plane of chlorine atoms].

$(Et_4N)_2TlCl_5$, isomorphous with the indium-analog, is also likely to have the same geometry for the anion. The anions of $K_3[TlCl_6]$ and $Cs_3[Tl_2Cl_9]$ contain six coordinated thallium. In the second anion, two $TlCl_6$ octahedra share three cholorine atoms on a face.

Lewis acidity

While B and Al are classed as class-a or hard acceptor, greater polarizability makes Ga and In class-b or soft. Moreover, the presence of an underlying d^{10} core enables Ga and In to take part, in principle, in *d-d* π-bonding with donors like S, but not with N or O. Combination of these with other factors like bond energy, reorganization of orbitals, steric effect etc. lead to various acceptor sequence. Acceptor-strengths (as measured by gas phase enthalpies of adduct formation) thus vary according to the reference base.

Base

$MeCO_2Et$: $BCl_3 > AlCl_3 > GaCl_3 > InCl_3$

C_5H_5N : $AlX_3 > BX_3 > GaX_3$ $(X = Cl, Br)$

Me_2S : $GaX_3 > AlX_3 > BX_3$ $(X = Cl, Br)$.

Acceptor strengths among a series of halides are similarly found to depend on the nature of both the donor and acceptor atoms :

Base

Et_2O or Et_3N : $MCl_3 > MBr_3 > MI_3$. $(M = Al, Ga, In)$

R_3P : $GaCl_3 > GaBr_3 > GaI_3$

Me_2S or Et_2S : $AlCl_3 > AlBr_3 > AlI_3$ *but,*

$MI_3 > MBr_3 > MCl_3$ $(M = Ga, In)$.

The reversal of sequence with S-donor, which is "softer" than the soft P-donor, may be partly related to (a) higher electronegativity of the S-atom and (b) the possibility of dπ-dπ back-bonding from Ga/In which is not possible with Al (no d^{10} core). This possibility is greatest when the least electronegative I is bonded to the metal.

Uses

Molten aluminium chloride (m.p. 192°C) or a mixture of $AlCl_3$-NaCl (or KCl) has been used as a molten salt medium (m.p. 173°C) for carrying out various electrolytic and other reactions to prepare a variety of unusual cations

$$Hg + HgCl_2-AlCl_3 \xrightarrow{\text{evaporation}} Hg_3(AlCl_4)_2$$

$$Cd + CdCl_2 \xrightarrow{AlCl_3} Cd_2(AlCl_4)_2$$

$$I_2 + Cl_2 \xrightarrow{NaCl\text{-}AlCl_3} I_2^+[AlCl_4]^-$$

$AlCl_3$ may be used to synthesize other aluminium compounds like Al-alkyls :

$$AlCl_3 + 3LiX \longrightarrow AlX_3 + 3LiCl \;......(X = R, NR_2 \text{ etc.}).$$

$$AlCl_3 + 4LiX \longrightarrow LiAlX_4 + 3LiCl \;......(X = R, NR_2, H \text{ etc.}).$$

The high lattice energy of AlF_3 drives many reactions; for example,

$$BF_3 + AlCl_3 \longrightarrow AlF_3 + BCl_3.$$

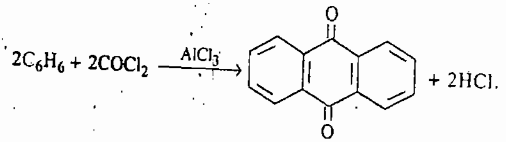
$AlCl_3$ is now widely used as catalyst in Friedel-Crafts type alkylation, acylation as well as various condensation, polymerization etc. reactions. Huge quantities are used in the preparation of (i) ethyl benzene (for styrene) :

$$CH_2 = CH_2 + C_6H_6 \longrightarrow C_6H_5.C_2H_5.$$

(ii) C_2H_5Cl (or Br for preparing lead tetraethyl);

$$CH_2 = CH_2 + HX \longrightarrow C_2H_5X.$$

(iii) anthraquinone for dyestuff



(iv) isomerization of hydrocarbons in petroleum industry.

(v) manufacture of dodecyl benzene for detergents.

Structure

The M_2X_6 dimers have halogen bridged structures similar to that of B_2H_6 : the terminal M-X bonds are shorter than the bridge M—X bonds. It may be assumed that a lone pair of electrons from a halogen atom on one metal is donated to an empty orbital (sp^3) of the other. Alternatively, one can think of M-X-M three-center four-electron ($3c$-$4e$) bonds : the same m.o. description as in BHB $3c$-$2e$ bond in B_2H_6 applies here, but two extra electrons (donated by X) occupy the nonbonding m.o.

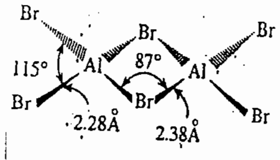


Fig. 20.13

The structure of Al_2Br_6 illustrates the general structure of M_2X_6 dimers.

Fluoroboric acid, Fluoroborates and other Tetrahaloborates

Hydrolysis of BF_3 by excess water or reaction of boric acid with aqueous HF produces fluoroboric acid, HBF_4 in solution. The BF_4^- ion is formed rather slowly (except in strongly acidic solution); the main species appears to be $(BF_3OH)^-$.

$$H_3BO_3 + 3HF \longrightarrow H_3O^+ + [BF_3OH]^- + H_2O \; (\textit{rapid}).$$

$$[BF_3OH^-] + HF \rightleftharpoons BF_4^- + H_2O \; (\textit{slow}).$$

On distillation, a liquid of composition $BF_3.2H_2O$ is obtained. The free acid is not known but solvates have been isolated, e.g., $HBF_4.Et_2O$ and $HBF_4.2MeOH$. Addition of potassium salt to the solution containing BF_4^- precipitates KBF_4. Salts of other alkali metals, ammonium, silver etc. are also known.

NH_4BF_4 is prepared by fusing NH_4HF_2 with B_2O_3. The alkali metal salts MBF_4 are made by reacting the metal fluoride with BF_3 either direct or in nonaqueous media like HF, BrF_3, SO_2 etc. $AgBF_4$ can be similarly prepared by reacting $AgBO_2$ with BrF_3. It is soluble in organic solvents and is used as a valuable reagent in synthesis.

Fluoroborates are also formed in solution when boric acid reacts with bifluorides :

$$H_3BO_3 + 2KHF_2 = KBF_4 + KOH + 2H_2O.$$

The KOH formed makes the solutions alkaline — apparently *two acidic substances (bifluorides are acidic) combine to produce an alkali.*

HBF_4 is a strong acid and remains fully ionized in solution. However, the BF_4^- ion undergoes slow hydrolysis in steps, giving mono and dihydroxy fluoroboric acids as intermediates :

$$BF_4^- \longrightarrow H[BF_3OH] \longrightarrow H[BF_2(OH)_2] \longrightarrow B(OH)_3.$$

The mono and dihydroxy acids may also be obtained by reacting BF_3 and H_2O in the correct molar ratio. They are useful catalysts. The acid strength follows the sequence

$$HBF_4 > H[BF_3OH] > H[BF_2(OH)_2] > B(OH)_3.$$

The crystal structure and solubility of the fluoroborates are similar to those of the corresponding perchlorates — e.g. both KBF_4 and $KClO_4$ are only slightly soluble in water. The alkali metal salts of both ions have two different structures — rhombic at low temperature and cubic at high temperature — they are said to be *isodimorphous*. The fluoroborates of hexaammines of Ni^{2+}, Mn^{2+}, Cd^{2+} and Co^{2+} are very much less soluble in water while the Me_4N, Et_4N, py - and diazonium salts are highly insoluble.

The fluoroborates decompose on heating to give the metal fluoride :

$$MBF_4 \longrightarrow MF + BF_3.$$

The reaction is primarily driven by the gain in lattice energy in forming the compact lattice with the smaller fluoride ion. This gain in lattice energy is comparatively small when the cation M^+ has a larger radius. Hence thermal stability increases with increase in the size of M^+.

The BF_4^- ion is tetrahedral — consistent with sp^3 hybridization of the valence orbitals of boron. As explained earlier, the B-F bond lengths (1.45 A°) are longer than those in BF_3 (130 pm) but are still slightly shorter than the estimated single bond length (152 pm).

The tetrahaloborates of larger halogens, BX_4^-, X = Cl, Br or I have also been prepared in non-aqueous media with large counter-cations like Rb^+, Cs^+, pyridinium, tetraalkylammonium, triphenylcarbonium etc.

$$[Et_4N]^+Cl^- + BCl_3 \xrightarrow{CHCl_3} [Et_4N]^+ BCl_4^-$$

With a given cation, the stability order follows the sequence :

$$MBCl_4 > MBBr_4 > MBI_4.$$

[Sec.20.3.5 *Lower Halides*]

Boron Subhalides

Lower Halides

Monohalides MX are known for all the elements of group 13(IIIA) with all four halogens in the gas phase at high temperatures. Boron alone forms several volatile lower halides which contain catenated boron skeleton or closed cages of boron atoms.

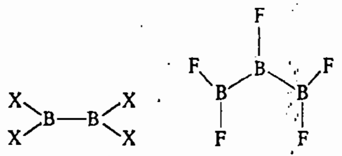


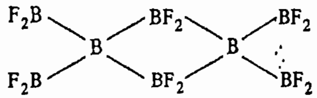
Fig. 20.14

Structures of B_2X_4 and B_3F_5.

BF is obtained by passing BF_3 over crystalline B at 1850° and at a pressure less than 1 mm of Hg. It can be condensed at –196°C. Co-condensation with BF_3 gives B_2F_4 and B_3F_5 (Fig. 20.14). B_3F_5 decomposes at –30°C.

$$4B_3F_5 \longrightarrow 2B_2F_4 + B_8F_{12}.$$

The structure of B_8F_{12} is interesting (20-XX) :



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It undergoes symmetrical cleavage with ligands like CO, PX_3 (X = F, Cl, H), AsH_3 etc. forming adducts like $L.B(BF_2)_3$. These adducts are stable at room temperature in absence of air or moisture.

Boron subhalides of the formula B_2X_4 have been studied most extensively. B_2F_4 (b.p. — 34°C) can be made by the action of SbF_3 on B_2Cl_4. B_2Cl_4 (b.p. 65°C) is prepared by passing BCl_3 vapour at low pressure through an electric discharge between mercury or copper electrodes :

$$2BCl_3 + Hg(Cu) \longrightarrow Hg_2Cl_2(CuCl) + B_2Cl_4.$$

It may also be obtained by co-condensing BCl_3 and copper vapours on a surface cooled with liquid nitrogen. Action of BBr_3 on B_2Cl_4 at –80°C produces B_2Br_4.

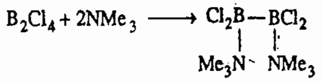
Thermal stability among B_2X_4 compounds follows the same trend as the extent of *p-p* π-bonding :

$$B_2F_4 > B_2Cl_4 > B_2Br_4.$$

The compounds are unstable with respect to decomposition to the trihalide :

$$n\,B_2X_4 \longrightarrow n\,BX_3 + (BX)_n$$

They are also spontaneously flammable in air. With H_2, B_2X_4 gives B_2H_6, BHX_2 and HX. Lewis bases (L) form adducts :



$$B_2Cl_4 + 2NMe_3 \longrightarrow \begin{array}{c}Cl_2B{-}BCl_2\\ |\quad\;\; |\\ Me_3N\;\; NMe_3\end{array}$$

As expected, $B_2Cl_4L_2$ adducts are more stable than $B_2F_4L_2$. BCl_2 groups also add across C-C multiple bonds.

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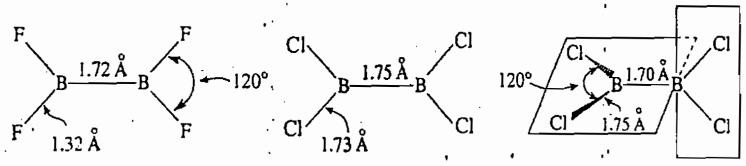
B_2F_4 is planar. But in B_2Cl_4 rotation occurs easily about the B—B bond, leading to a staggered structure in the gaseous and liquid states. In the solid, however, ease of packing into a stable structure makes the molecule planar.



(a) (b) (c)

Fig. 20.15

Structures of (a) B_2F_4 (g); (b) B_2Cl_4 (s) and (c) B_2Cl_4 (g).

A series of crystalline *closo* - halogenoboranes B_nX_n are known with closed cages of boron atoms. For chlorocompounds, $n = 4, 8-12$; for bromo-compounds, $n = 7-10$. These are formed by thermolysis of B_2Cl_4 and B_2Br_4.

$$B_4Cl_4 \xleftarrow[\text{discharge}]{\text{Hg-electrodes}} B_2Cl_4 \xrightarrow[\text{decomposition}]{\text{Thermal}} B_8Cl_8 + B_9Cl_9 + B_nX_n \quad (n = 10, 11, 12).$$

B_4Cl_4 (pale-yellow solid) consists of a tetrahedron of B atoms, each linked to a chlorine atom. B_8Cl_8 (dark purple crystals) has a triangular-faced dodecahedral arrangment of B-atoms. In B_9Cl_9 (yellow-orange), the B-atoms are arranged at the corners of a tricapped trigonal prism. The bromo compounds have identical structures. Chemical reactions of B_nX_n are similar to those of B_2X_4, except that the B—B bonds are not cleaved by alkenes.

Monohalides of Al, Ga, In

All four monohalides MX (M = Al, Ga, In, Tl) can be prepared in the gas phase at elevated temperatures through the entropy-driven reaction.

$$2M + MX_3\ (g) \longrightarrow 3MX\ (g).$$

The application of the reaction for purification of aluminium has been mentioned earlier. In spite of high Al-X bond energy, the aluminium monohalides disproportionate on cooling to the more stable AlX_3 :

$$3AlX\ (s) \longrightarrow 2Al + AlX_3\ (s);\ \Delta H \text{ highly negative.}$$

GaF and InF are also known as unstable gaseous species. Stability increases with larger halide ions, the iodides being most stable. Indium monohalides (Cl, Br, I) may also be prepared directly from the elements. Thallium (I) halides are discussed separately below.

"Dihalides"

Apparent "dihalides" of formula MX_2 (X ≠ F) exist for M = Ga, In and Tl; these solid compounds actually have the ionic composition $M^I\ [M^{III}X_4]$. They may be prepared by (i) reducing the trihalide with equimolar amount of M :

$$MCl_3 + M \longrightarrow M^+\ [MCl_4]^-$$

or (ii) stoichiometric halogenation of the element in presence of mercuric halides :

$$2M + 2HgX_2 \longrightarrow M^+\ [MX_4]^- + 2Hg.$$

In presence of Al, the second reaction gives $M^+\ AlCl_4^-$ (M = Ga, In)

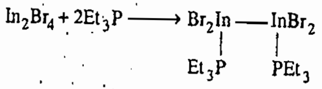
$$Ga + Al + 2HgCl_2 \longrightarrow \overset{+}{Ga}\ AlCl_4^- + 2Hg.$$

Fused Ga_2Cl_4 conducts electricity consistent with the composition $Ga^+[GaCl_4]^-$.

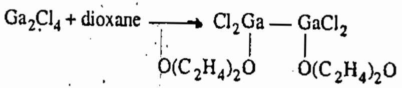
[Sec. 20.3.5

Halides of Tl(I)]

Adducts containing M—M bonds are formed by reacting these "dihalides" with donor ligands; the crystalline dioxan derivative contains Ga(II) in an eclipsed structure (Ga—Ga = 240.6 pm).



$$In_2Br_4 + 2Et_3P \longrightarrow \begin{matrix} Br_2In & — & InBr_2 \\ | & & | \\ Et_3P & & PEt_3 \end{matrix}$$



$$Ga_2Cl_4 + \text{dioxane} \longrightarrow \begin{matrix} Cl_2Ga & — & GaCl_2 \\ | & & | \\ O(C_2H_4)_2O & & O(C_2H_4)_2O \end{matrix}$$

Ga^{II} and In^{II} are also present in the ethane-like anions $[Ga_2X_6]^{2-}$ and $[In_2X_6]^{2-}$:

$$Ga \xrightarrow[\text{6M HCl/0°C}]{\text{anodic dissolution}} \text{solution} \xrightarrow{Me_4NX} (Me_4N)_4\ [Ga_2X_6]$$

$$R_4NX + InX_2 \xrightarrow{\text{xylene}} (R_4N)_2\ [In_2X_6].$$

The Ga-compound is stable; the In-compound disproportionates in nonaqueous solvents to $In^IX_2^-$ and $In^{III}X_4^-$.

Halides of Tl(I)

Thallium(I) is the common oxidation state of the element in its halides. TlF (white) can be prepared by dissolving Tl_2CO_3 in aqueous HF while the other halides are readily precipitated by the respective halide ions from solutions containing Tl^+ (perchlorate, sulfate, nitrate). Melting point, colour and crystal structure of the compounds are summarized in Table 20.10.

TABLE 20.10

Properties of TlX

	TlF	TlCl	TlBr	TlI
M.P. °C	322	431	460	442
Colour	White	White	Pale Yellow	Yellow
Structure	NaCl (dist.)	CsCl	CsCl	dimorphic

TlF is ionic and soluble in water while other halides resemble the silver halides—both Ag^+ and Tl^+ ions have $(n-1)\ d^{10}$ cores and are similar in size (ionic radius of Ag^+ : 127 pm; Tl^+ : 154 pm). Their solubility in water decreases fluoride from to iodide and they darken in light. TlBr and TlI are slightly coloured, consistent with the presence of highly polarized anion. Yellow TlI has a layer structure which transforms at 175° or at high pressure (4.7 kbar) to a metastable red form (CsCl structure).

The black crystals of composition TlI_3 obtained by heating TlI + I_2 in concentrated aqueous HI are isomorphous with CsI_3 and NH_4I_3 and supposed to be $Tl^+I_3^-$ (an alternative suggestion was $[I — Tl^{III} — I]^+I^-$. Redox potential data also suggest that Tl (III) should be completely reduced by I^- in presence of acid :

$$Tl^{3+} + 2e \rightleftharpoons Tl^+ \qquad E° = 1.25\ V;\ E_f^0 \text{ in } 1\ M\ HClO_4 = 1.26\ V$$

$$\tfrac{1}{2} I_2 + e \rightleftharpoons I^- \qquad E° = 0.54\ V.$$

But Tl(III) forms stronger complexes with halide ions than Tl(I) and this effectively lowers the reduction potential of Tl(III) — Tl(I) system; even though the TlX are sparingly soluble. In fact, E° for $[TlCl_4]^-/TlCl$ is only +0.9V and it drops further when I^- is used to complex Tl(III). The effective potential drops below 0.54V so that I_3^- $(I_2 + I^-)$ present in solid $Tl^+I_3^-$ can cause the oxidation of Tl (I)

$$Tl^{I}I_3 + I^- \longrightarrow [Tl^{III}I_4]^-.$$

20.3.6 Oxygen compounds

All the elements in group 13(IIIA) form the normal oxide M_2O_3 when heated in oxygen. Tl_2O_3 begins to lose oxygen at about 100°C to give Tl_2O. Ga_2O_3 also gives a lower oxide when Ga_2O_3 is heated with Ga at 700°C :

$$Ga_2O_3 + 4Ga \rightleftharpoons 3Ga_2O.$$

Glassy polymeric $(BO)_n$ is obtained by heating B_2O_3 with B at 1300°C. It also results frm the dehydration of $B_2(OH)_4$ (i.e., $(OH)_2BB(OH)_2$, obtained by aqueous hydrolysis of $B_2(OEt)_4$ (B_2Cl_4 plus EtOH). Dehydration of $B_2(OH)_4$ in vacuum gives B_2O_2 which presumably contains B-B bond.

The oxides M_2O_3 become gradually more basic as M varies from B to Tl. B_2O_3 is dominantly acidic, though it also shows feeble basic properties (see below). Oxides of the intermediate elements are amphoteric while Tl_2O_3 is basic and dissolves in acids to give thallium (III) salts. A wide range of metal borates is known — these are discussed separately.

B_2O_3 is obtained in a glassy form (i.e., no sharp m.p.) by dehydrating boric acid at red heat :

$$H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{\text{red.heat}} B_2O_3.$$

When HBO_2 is dehydrated under reduced pressure and the temperature very slowly raised to 400°C (over some weeks), a crystalline form (m.p. 450°C) is obtained.

It reacts with water to form metaboric acid, HBO_2 and then orthoboric acid :

$$B_2O_3 + H_2O = 2HBO_2$$

$$HBO_2 + H_2O = H_3BO_3.$$

B_2O_3

B_2O_3 dissolves in alkali to form borates. Fused B_2O_3 dissolves many metal oxides to produce metal borates :

$$CuO + B_2O_3 = Cu\,(BO_2)_2\,;\; CoO + B_2O_3 = Co(BO_2)_2.$$

The colour of the metal meta-borates is used in the borax-bead test for the metals (see under borax).

B_2O_3 is reduced by heated metals like Na, K, Mg (see preparation of B) but it is not reduced by carbon.

Though dominantly acidic, B_2O_3 reacts with acetic anhydride (heat) to form boron acetate $B(CH_3COO)_3$, m.p. 147°. Phosphorus pentoxide gives boron phosphate BPO_4 which can be sublimed unchanged at 1500°C.

$$2B_2O_3 + P_4O_{10} = 4BPO_4.$$

It is insoluble in water and dilute acids. The compound is better considered a mixed oxide rather than a salt of cationic boron. It is an important catalyst for hydration of alkenes and dehydration of amides to nitriles.

[Sec. 20.3.6 *Oxides*].

Al_2O_3

Anhydrous aluminium oxide has two crystalline forms : α - Al_2O_3 (present in the mineral *corundum*) and γ - Al_2O_3. The alpha form is obtained by dehydrating any hydrous oxide above 1000°C. It has a hexgonal close-packed array of oxide ions with aluminium ions distributed symmetrically among the interstices. Extremely hard (9 in Mohs scale) and chemically rather inert, it does not dissolve in acids. The abrasive emery is a granular form of corundum contaminated with iron oxide and silica.

γ-Al_2O_3 can be prepared by dehydrating hydrous aluminium oxide at about 450°C. It can be rehydrated and is soluble in acids. This form is widely used as an absorbent and as a catalyst. It has a defect spinel structure (see later).

Natural corundum (α - Al_2O_3) containing traces of metal ions in the crystal lattice have specific colours and are classified as gem-stones e.g. ruby (Cr^{III}) and blue sapphire (Fe^{II}, Fe^{III}, Ti^{IV}).

Ga_2O_3 etc.

Ga_2O_3 also has a high temperature α and a low temperature γ- form. Yellow In_2O_3 has only one form. Brown black Tl_2O_3 is also obtained by oxidation of aqueous $TlNO_3$ with Cl_2 followed by precipitation. Tl_2O_3 loses oxygen above 100°C to give Tl_2O (black). It is also formed when Tl_2CO_3 is heated in N_2 at 700°C. It gives TlOH with water.

Spinels

Al_2O_3 (and other trivalent ions e.g. Fe(III)) form mixed oxides having the structure of spinel—a mineral of compositon $MgAl_2O_4$. Many other mixed oxide minerals of the general composition $X^{II}Y_2^{III}O_4$ have this structure. X is a "bivalent" metal like Zn, Mg, Cr, Fe, Co, Ni, Cu, Cd, Sn etc. and Y is a "trivalent" metal like Al, Ga, In, Ti, Fe, Cr etc. The unit cell has a cubic close-packed array of oxide ions of which one-eighth of the tetrahedral holes are occupied by the bivalent ions and one-half of the octahedral holes by Y(III) ions. In inverse spinel structure the dipositive ions exchange positions with half of the tripositive ions. Site preference of the ions may be largely understood from crystal field stabilization energies, explained later (Chapter 27).

β-Alumina : Solid Electrolyte

"β-Alumina", which is actually a sodium aluminate, having the approximate formula $Na_{1+x}Al_{11}O_{17}$, has a layer structure based on the spinel lattice. The Na^+ ions are loosely held between layers of Al and O atoms and are quite mobile to make a *solid electrolyte*. The ionic conductance of Na^+ ion at 300°C is approximately equal to that of an aqueous NaCl solution. As such, β-alumina is now being developed as a ceramic ion-conductor useful for high-energy batteries. The sodium-sulfur battery being tried for electric cars operates with molten sodium and sulfur at about 300°C :

$$Na \longrightarrow Na^+ + e;\quad S + 2e \longrightarrow S^{2-}.$$

To prevent direct reaction, the molten sodium and sulfur should be physically separated. This may be achieved by β-alumina acting like a salt-bridge which will transmit only the Na^+ ion, but not the Na atoms.

$B(OH)_3$

$B(OH)_3$ or boric acid is the end product of hydrolysis of boron halides and hydrides. It is commonly prepared by acidifying hot borax solution ($Na_2B_4O_7$). The shining white crystals contain $B(OH)_3$ units linked by H-bonds in infinite layers of nearly hexagonal symmetry. It is moderately soluble in water.

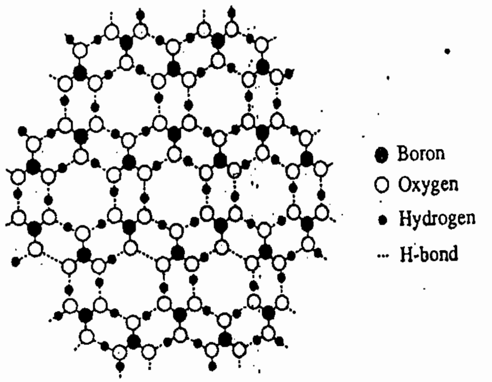
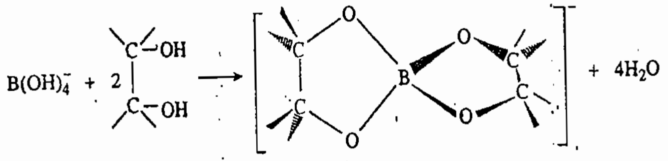


Fig. 20.16
Structure of boric acid.

Boric acid is a weak acid ($pK_a = 9.2$) which acts not as a proton donor but as a Lewis acid—accepting a pair of electrons from a hydroxyl ion. The ionization equilibrium

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+ \quad K = 6 \times 10^{-10}$$

can be shifted largely towards right by forming a stable chelate with *cis* - dihydroxy compounds (e.g. glycerol) :



20-XXI

The proton can now be titrated against strong alkali using phenolphthalein indicator.

Q. 20.2 *The ionization of boric acid is also influenced by the addition of KHF_2, which itself is also acidic. The resulting solution is alkaline. Why ?*

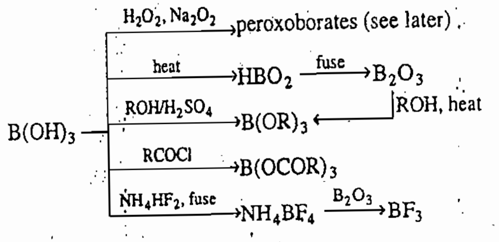
Hint : $BF_4^- + OH^-$. See fluoroborates.

Dilute aqueous solutions of boric acid ($\leq 0.025\ M$) contain the mononuclear species $B(OH)_3$ and $B(OH)_4^-$ bur various ploymeric ions are formed in concentrated solutions, depending on pH, concentration, temperature etc. The species present in a 0.4 *M* solution with increasing pH are

$$B(OH)_3 \longrightarrow B_5O_6(OH)_4^- \longrightarrow B_3O_3(OH)_5^{2-} + B_4O_5(OH)_4^{2-} \longrightarrow B(OH)_4^-.$$

The structures of these anions established from crystalline borates are shown later (borates).

Some other reactions of boric acid are summarised below :



"Aluminium hydroxide" has several forms and stoichiometry. AlO.OH is precipitated by ammonia solution from a hot solution containing aluminium salts. Another form of AlO.OH occurs in the mineral diaspore. True $Al(OH)_3$ is precipitated when CO_2 is passed into a solution containing sodium aluminate :

$$2[Al(OH)_4]^-\,(aq) + CO_2\,(g) \longrightarrow 2Al(OH)_3 + CO_3^{2-}\,(aq) + H_2O.$$

It is also present in the mineral *gibbsite*. Gallium oxide also has two hydrated forms GaO(OH) and $Ga(OH)_3$; indium forms only $In(OH)_3$ while $Tl(OH)_3$ apparently does not exist. Addition of NaOH to Tl(III) salts precipitates the oxide. Aluminium and gallium hydroxides dissolve in excess base to give $M(OH)_4^-$ ions. The anion in dilute ($< 1.5\ M$) solution of "sodium aluminate" above pH 13 may be represented as the tetrahedral $[Al(OH)_4]^-$. At lower pH (8–12), OH-bridged polymeric ions with octahedrally coordinated Al appear to be the main species. Above pH 13 and at concentrations $> 1.5\ M$, dimeric ions $[(OH)_3\,Al\text{-}O\text{-}Al(OH)_3]^{2-}$ are formed (also present in crystalline $K_2[Al_2O(OH)_6]$). $In(OH)_3$ dissolves only in hot 15 *M* alkali. Cooling forms crystalline indates like $K_3[In(OH)_6].2H_2O$ and $Rb_2[In(OH)_5.H_2O]$.

TlOH is soluble in water and is a strong base.

20.3.7 Salts of oxo-acids; aqueous solution chemistry

Borates

A wide variety of metal borates occur in nature, usually in the hydrated form. Fusion of boric acid with metal oxides form the anhydrous borates; crystallization from aqueous solution produces the hydrated forms. The anions in such borates are complex and are based on triangular BO_3 units, tetrahedral BO_4 units or a combination of both. Polynuclear anions are formed by corner sharing of O-atoms among boron oxygen triangles and tetrahedra (see Figure). The overall charge on a given borate ion is equal to the *total number* of terminal oxygens and tetrahedral boron atoms, each contributing one unit of negative charge. The borates are structurally similar to the silicates which are formed by linking of SiO_4 tetrahedra (see group IVA (14)).

The B-O bond length in borates (BO_3^{3-}) is 137 pm, slightly shorter than the B-O single bond length (148 pm) in BO_4^{4-}. This may well be attributed to *p-p* π-bonding from O to B. Since the size of the 2*p* orbital shrinks somewhat from B to O, best 2*p*–2*p* π-overlap is expected in the isoelectronic NO_3^- ion. The CO_3^{2-} ion, also isoelectronic, follows next. Thus the extent of π-bonding among the three isoelectronic ions is expected to decrease as $NO_3^- > CO_3^{2-} > BO_3^{3-}$.

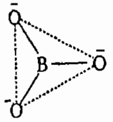
This expectation is supported by the relative bond length shortening in each (See Exercise Q. 24). In order to form polymeric anions, higher reorganization energy would be required by carbonates and nitrates to sacrifice π-interactions within themselves and to establish σ-bonds with neighbours. This is probably the principal factor behind the nonexistence of polycarbonates and polynitrates. Ready formation of gaseous CO_2 and NO_2 (also π-bonded) will also hinder any synthetic route to the polyanions.

Q. 20.3 *The BO_2^- ion occurs only as a ploymer in crystals but there is no CO_2^- ion, while the NO_2^- ion is relatively stable—comment.*

Hints : Draw Lewis structures. The BO_2^- ion has a vacant orbital on boron and is electron-deficient. It accepts electron from the oxygen of neighbour BO_2^- ions, leading to polymerization.

The CO_2^- ion, with one odd electron on carbon, behaves as a free radical and dimerizes to the oxalate ion.

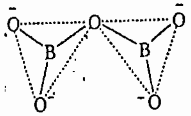
Some simple structural principles based on BO_3 and BO_4 units are illustrated in Fig. 20.17. Many other complex structures are possible.

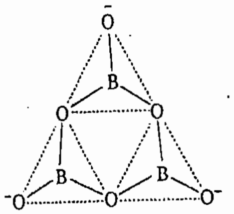


(i) **Discrete BO_3^{3-} units;**

Lanthanide(M) orthoborates : $M^{III}BO_3$.

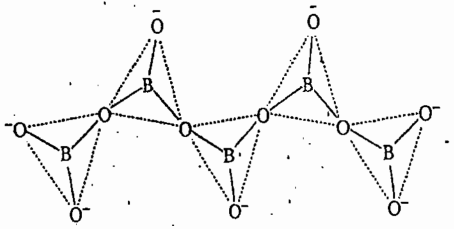
(ii) **$B_2O_5^{2-}$; Two triangular BO_3 units joined by** sharing a corner (the angle at the bridging O may vary) : $Mg_2B_2O_5$, $Co^{II}B_2O_5$, $Fe_2^{II}B_2O_5$.

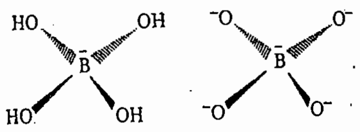




(iii) **$B_3O_6^{3-}$; Three BO_3 units share corners forming a ring :** "$NaBO_2$", "KBO_2" (metaborates) which should be better written $Na_3B_3O_6$ or $K_3B_3O_6$.

(iv) **$(BO_2)_n^{n-}$; Infinite chain of BO_3 units :** $[Ca(BO_2)_2]_n$



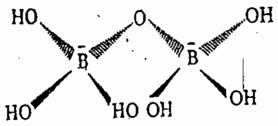


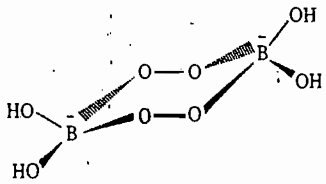
(v) **$B(OH)_4^-$ and BO_4^{5-}; discrete tetrahedral units :**

$Na_2[B(OH)_4]Cl$; Ta^VBO_4.$Cu_2^{II}[(OH)_4]Cl$

(vi) **$[(OH)_3B\text{-}O\text{-}B(OH)_3]^{2-}$**

Two tetrahedral BO_4 units joined by sharing a corner : $Mg[(OH)_3BOB(OH)_3]$





(vii) **$[B_2(O_2)_2(OH)_4]^{2-}$**

Two tetrahedral BO_4 units form a cyclic binuclear group :

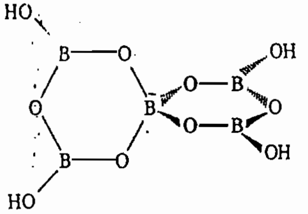
$Na_2[(OH)_2B(O_2)_2B(OH)_2]$, $6H_2O$.

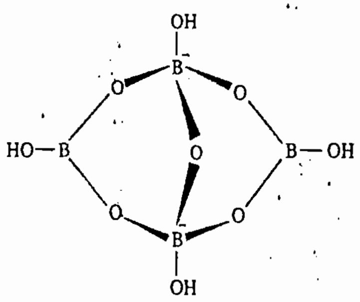
Sodium peroxoborate (also called "sodium perborate"; see later).

(viii) **$[B_5O_6(OH)_4]^-$**

Four BO_3 units linked by a central BO_4 unit to form a spiro anion :

$K[B_5O_6(OH)_4]^-$.





(ix) **$[B_4O_5(OH)_4]^{2-}$**

Two BO_3 and two BO_4 units form the closed anionic structure present in borax, $Na_2B_4O_7$, $10H_2O$. It should be written

$Na_2[B_4O_5(OH)_4]$, $8H_2O$.

Fig. 20.17

Some structural principles of borate anions.

Borax, $Na_2B_4O_7$, $10H_2O$

It is made by boiling the mineral colemanite with sodium carbonate solution.

$$2CaO, 3B_2O_3 + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2.$$

$CaCO_3$ is filtered out. Concentration of the filtrate deposits crystals of borax. The mother liquor containing $NaBO_2$ is again converted to borax by passing CO_2.

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

The structure of the anion in borax has been shown in Fig. 20.17. Aqueous solution of borax reacts alkaline due to hydrolysis to NaOH and H_3BO_3. Since boric acid is weak, borax can be titrated as an alkali against a strong acid using methyl orange (pH range 3.1—4.4).

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

$$\text{or,} \quad [B_4O_5(OH)_5]^{2-} + 5H_2O = 2H_3BO_3 + 2[B(OH)_4]^-.$$

$$2[B(OH)_4]^- + 2H_3O^+ \longrightarrow 2H_3BO_3 + 4H_2O.$$

Borax swells on heating and then sets to a glassy mass on cooling :

$$Na_2B_4O_7, 10H_2O = 2NaBO_2 + B_2O_3 + 10H_2O.$$

Borax bead test

Fusion with metallic salts (which form oxides on heating) forms the metal borates having characteristic colours (borax bead test).

$$B_2O_3 + CuO = Cu(BO_2)_2 \quad \text{green (hot), blue (cold).}$$

The bead becomes dull red and opaque when heated in a reducing flame :

$$2Cu(BO_2)_2 + 2NaBO_2 + C = 2CuBO_2 + Na_2B_4O_7 + CO.$$

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C = 2Cu + 2Na_2B_4O_7 + 2CO.$$

Borax is used in the manufacture of optical and hard glasses and enamels. It is also used in giving glaze to pottery, stiffening candle-wicks and in laundering.

The borate radical (also boric acid) is classed as an *interfering acid radical* in systematic qualitative group analysis of cations since metal borates of analytical groups IIIB, IV and Mg are precipitated in Group IIIA in ammoniacal medium.

Borates/boric acid are removed after Group II by repeated evaporation with conc. HCl (followed by water in some cases) when boric acid volatilizes away.

Peroxoborates

Sodium peroxodiborate, commonly called 'perborate', contains the anion $[(OH)_2B(O_2)_2B(OH)_2]^{2-}$ (Fig. 20.18). It is prepared by (i) action of H_2O_2 or Na_2O_2 on borax solution or (ii) electrolysis of borax solution with Pt-gauze anode in presence of a little Na_2CO_3, (the role of which is not clearly understood). In solution the anion first hydrolyzes to $[B(OH)_3OOH]^-$ and then $[B(OH)_4]^-$, liberating H_2O_2 :

$$[B(OH)_3OOH]^- + H_2O \rightleftharpoons [B(OH)_4]^- + H_2O_2 \qquad K = 0.04.$$

For this reason the compound is used in washing powders.

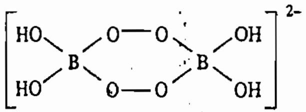


Fig. 20.18
The peroxodiborate anion.

Formerly sodium peroxodiborate was variously formulated as $NaBO_3, 4H_2O$ or $NaBO_2, H_2O_2, 3H_2O$ and classed as a perhydrate or peroxyhydrate i.e., a species containing H_2O_2 of crystallization.

Salts of oxo-acids of Al—Tl

The elements Al-Tl form a wide variety of salts of oxo-acids like nitrates, sulphates, perchlorates (all soluble in water) and phosphates (sparingly soluble). Salts of very weak acids like carbonates (or cyanides) cannot exist owing to extensive hydrolysis (see below).

The aqua ions $[M(H_2O)_6]^{3+}$ are acidic, acidity increasing from Al—Tl.

$$[M(H_2O)_6]^{3+} \rightleftharpoons [M(H_2O)_5OH]^{2+} + H^+ (aq).$$

K_a (approx) : Al 1.1×10^{-5}; Ga 2.5×10^{-3}; In 2×10^{-4}; Tl 7×10^{-2}.

[Sec.20.3.7 *Aqueous solution chemistry*]

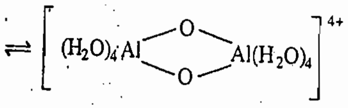
The K_a-values suggest extensive hydrolysis. In fact, salts of weak acids like sulfides, cyanides, carbonates, acetates etc. cannot exist in aqueous solution as the anions will be readily protonated :

$$[Al(H_2O)_6]^{3+} + CH_3COO^- \longrightarrow [Al(H_2O)_5OH]^{2+} + CH_3COOH.$$

$$[Al(H_2O)_6]^{3+} + S^{=} \longrightarrow Al(OH)_3 + H_2S.$$

The $[Al(H_2O)_5OH]^{2+}$ ion also undergoes appreciable dimerization :

$$2[Al(H_2O)_5OH]^{2+} \rightleftharpoons$$



$$K_{300} = 600M^{-1}$$

Several other complex species have been identified in solution as well as in crystals.

Alums

Alums are double sulphates of the general formula $M^IAl(SO_4)_2, 12H_2O$ or $M^I_2SO_4, Al_2(SO_4)_3, 24H_2O$ where M is usually K, Rb, Cs or NH_4; Na and Tl salts may also be obtained but Li^+ appears to be too small to form a stable crystal. Radius of M^+ greater than 100 pm and radius of M^{3+} between 50-70 pm are most favourable for alum formation. This is why sodium alums (r_{Na^+} = 95 pm) are less common than those of K^+ (r = 133 pm). Al may also be replaced by many other trivalent cations not too different in size e.g. Ti, V, Cr, Mn, Fe, Co, Ir, Ga and In. The crystal is made up of $[M^I(H_2O)_6]^+$, $[M^{III}(H_2O)_6]^{3+}$ and two SO_4^{2-} ions; SO_4^{2-} may be replaced by SeO_4^{2-}.

As observed earlier (Table 20.3), the reduction potentials for $M^{3+}(aq) - M$ are negative for M = Al, Ga, In; Al has the highest negative potential, showing that $Al^{3+}(aq)$ ions are most difficultly reduced. This can be related to the highly negative enthalpy of hydration of the Al^{3+} ion. For the remaining elements, the potential increases irregularly since ionization energies also increase from Al to Ga and from In to Tl.

Thallium (I)

The aqueous solution chemistry of thallium naturally includes that of Tl(I). $\overset{o}{E}$ for $Tl^+ (aq)$-Tl is –0.34V, showing that $Tl^+(aq)$ ions are quite stable. In fact, Tl(III) is strongly oxidizing ($\overset{o}{E}_{Tl(III)-Tl(I)}$ = 1.26 V) in aqueous solution. Tl metal dissolves in acids to evolve hydrogen and forming Tl(I) salts. The coating of insoluble TlCl may, however, hinder the reaction with HCl. The hydroxide, nitrate, sulphate, carbonate and fluorides of Tl(I) are soluble in water, but the remaining halides and thiosulphate are insoluble. The Tl(I) ion resembles the Ag(I) and Pb(II) in many respects, for example the solubility of the halides in water, darkening on exposure to light, insolubility of Tl_2S (black) etc. At the same time, it bears many similarities with the alkali metal ions, particularly K^+ and Rb^+. Thus, yellow Tl_2PtCl_6, like K_2PtCl_6, is sparingly soluble in water. The light red hexanitritocobaltate(III) $Tl_3[Co(NO_2)_6]$ ("cobaltinitrite") is insoluble in water, like $K_3[Co(NO_2)_6]$. (*See Exercise, Problem 21*). The radii of K^+ (144 pm), Tl^+ (154 pm) and Rb^+ (158 pm) ions are nearly equal and many of their salts (sulphate, chromate, nitrate, chloride, bromide etc.) are isomorphous. Tl^+ can replace Rb^+ in many alums.

The effect of complexation by halides on the Tl(III)—Tl(I) potential has been mentioned earlier. Tl(I) is also easily oxidized in alkaline media because the potential changes favourably owing to the very low solubility of Tl_2O_3 ($K_{sp} = 10^{-45}$) while TlOH is soluble.

20.3.8 Nitrogen Compounds

Comparison : B—N and C—C bonds

The elements B — In form stable solid nitrides MN. BN has a layer lattice like graphite while the others have a diamond like lattice. Boron also forms several compounds involving B—N bonds which possess many similarities with carbon compounds. The BN group, with 8 valence electrons, is formally isoelectronic with C—C. The electronegativity and covalent radius of carbon is also intermediate between those of B and N. In addition, there exists the possibility of N to B π-bonds involving 2*p* orbitals on both which are comparable in size and energy. However, the B—N bond is expected to be more polar than the C—C bonds, leading to difference in reactivity. Our discussion will be limited to (i) the nitrides, specially boron nitride (ii) amine-borane adducts (formally analogous to alkanes), (iii) aminoboranes (c.f. alkenes) and (iv) borazines (c.f. benzene).

Boron Nitride

Boron reacts with nitrogen or ammonia at 1000°C to form $(BN)_x$.

It may be prepared on a small scale by fusing borax with ammonium chloride.

$$Na_2B_4O_7 + 2NH_4Cl = 2NaCl + H_2O + 2NH_3 + 2B_2O_3$$

$$B_2O_3 + 2NH_3 = 2BN + 3H_2O.$$

Thermal decomposition of boron amide gives pure boron nitride via the imide. (Boron amide is obtained by reacting BCl_3 with NH_3).

$$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl$$

$$2B(NH_2)_3 = B_2(NH)_3 + 3NH_3$$

$$B_2(NH)_3 = 2BN + NH_3.$$

Industrially, boron nitride is prepared by fusing urea with boric acid in an atomosphere of ammonia at 500—900°C.

Boron nitride is a slippery white solid which melts under pressure at 3000°C. It is chemically inert to air, oxygen, hydrogen, chlorine, iodine etc. even on heating. It is decomposed by water (at red heat; gives $B_2O_3 + NH_3$); fluorine ($BF_3 + N_2$) and HF (NH_4BF_4, slowly). It is also decomposed on fusion with KOH or K_2CO_3.

$$2BN + 3H_2O = B_2O_3 + 2NH_3 \qquad 2BN + 3F_2 = 2BF_3 + N_2$$

$$BN + 4HF = NH_4BF_4 \qquad BN + KOH + H_2O = KBO_2 + NH_3$$

$$BN + K_2CO_3 = KBO_2 + KCNO.$$

Comparison with graphite

The common form of boron nitride consists of a layer lattice similar to graphite. In each layer alternate B and N atoms (both sp^2 hybridized) form planar hexagons. The layers are stacked over one another so that the N atom of one layer is directly over the B atom of another layer (difference from graphite where the hexagonal rings in ***alternate layers*** are directly on top of one another). The distance between successive layers is 333 pm (vs 335 pm in graphite). The B—N distance within each layer (145 pm) is also close to the C—C distance in graphite (142 pm) and significantly less than the sum of covalent radii of B and N (88 + 70 = 158 pm), indicating substantial π-bonding within the layer. Boron nitride is sometimes called "inorganic graphite". However, unlike graphite, it is colourless and thus insulator.

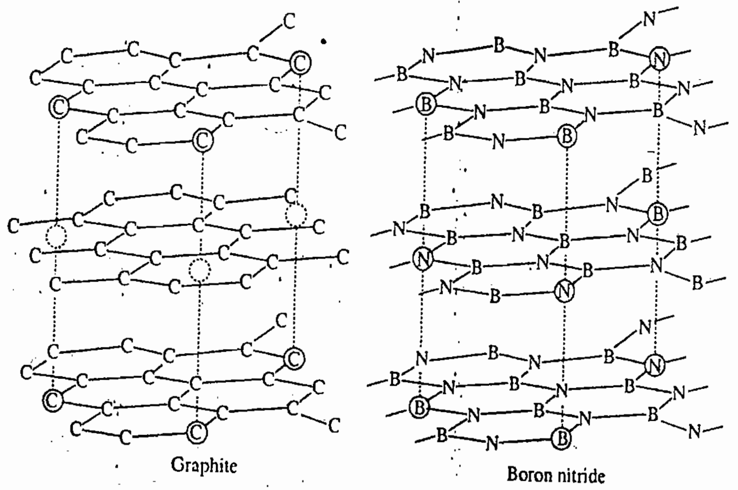


Fig. 20.19

Stacking of B-N layers in boron nitride.

Note the difference in placement of successive layers from that in graphaite.

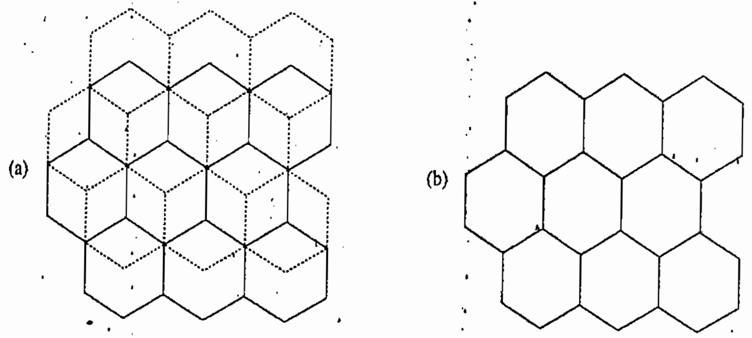


Fig. 20.20

Projection of one layer over another (a) graphite; (b) boron nitride.

Hexagonal BN is converted to a cubic form comparable to diamond (zinc blend type structure) when heated at 1800°C under 85000 atm pressure, preferably in presence of an alkali or alkaline-earth metal catalyst. This extremely hard variety, called *borazon*, is used in cutting diamond.

Nitrides of Al, Ga, In

Only aluminium reacts with nitrogen directly on heating (750°C), forming AlN. AlN is also formed by heating Al_2O_3 and coke in N_2 at 1800°C (Serpek's process of purification of bauxite). GaN is obtained by heating Ga or Ga_2O_3 with NH_3 (600°-1000°C). InN may be obtained by pyrolysis of $(NH_4)_3InF_6$, or heating In_2O_3 in ammonia (630°C). All are stable hard solids but are hydrolyzed with increasing ease from AlN to InN. Thus AlN is hydrolysed by hot dilute alkali to form ammonia. All have the wurtzite structure.

Amine-Boranes

Amine-boranes are Lewis acid-base adducts involving nitrogen-boron donor bonds, e.g., R_3NBX_3, when R = alkyl group or H; X = alkyl group, H or halogen. These are formed by symmetrical cleavage of diborane (section 20.3.2) or may be obtained from ammonium salts :

$$NH_4Cl + LiBH_4 \longrightarrow H_3NBH_3 + LiCl + H_2.$$

They are usually colourless crystalline compounds. Stability of the adduct depends on the B—N bond strength, which, in turn, is determined by several factors like steric hindrance, bond polarity etc. Both B and N atoms in the adduct are typically tetrahedral and the B—N bond length is comparable to the sum of the two covalent radii. Conventionally, the bond is represented as

$$R_3N \longrightarrow BX_3 \quad \text{or} \quad R_3\overset{+}{N} — \overset{-}{B}X_3.$$

However, this does not mean that the nitrogen is positive with respect to the boron atom in the adduct. Rather, it implies that the nitrogen has lower electron density than the nitrogen in the free base (and so on for the boron). In fact, electrophilic reagents always attack the nitrogen atom in adducts while the boron is attacked by nucleophilic reagents.

One important reaction of amine-boranes is that they undergo elimination reactions (of RH or HX) to form *amino-boranes* :

$$(CH_3)_2HN + B_2H_6 \longrightarrow (CH_3)_2H\overset{+}{N} - \overset{-}{B}H_3$$

$$(CH_3)_2H\overset{+}{N} - \overset{-}{B}H_3 \xrightarrow{\text{heat}} (CH_3)_2\overset{+}{N} = \overset{-}{B}H_2 + H_2$$

Similarly, $(CH_3)_2H\overset{+}{N} - \overset{-}{B}Cl_3 \longrightarrow (CH_3)_2\overset{+}{N} = \overset{-}{B}Cl_2 + HCl.$

Me_2NBH_2 is a gas (b.p. 1°C) which gets rapidly hydrolyzed by water, and readily forms a dimer (m.p. 9°C).

Aminoboranes

Aminoboranes contain B—N bonds in which the boron is trigonally hybridized; the lone pair on nitrogen may be donated to a vacant *p* orbital on boron, giving rise to a B—N bond order greater than one. Accordingly, aminoboranes are prototypes of alkenes. The bonding may be expressed in terms of two resonance forms :

$$>B—\ddot{N}< \longleftrightarrow >\overset{-}{B}=\overset{+}{N}<$$

The bond moments of the B—N σ-bond and the dative N—B π-bond largely cancel one another and the compounds have lower dipole moment than suggested by the charge separation shown above. In fact, M.O. calculations show that the N atom has a larger net negative charge than the B atom. The π-cloud imposes rotational barriers about the B—N bond (approx 65-85 kJ mol⁻¹).

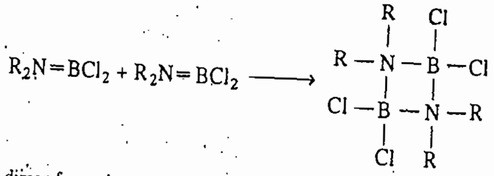
Aminoboranes may be prepared from amine boranes (see above) or by several other straightforward methods, e.g.,

$$R_2NH + BCl_3 \longrightarrow R_2N{=}BCl_2 + HCl \ (R = i\text{-}Pr, \text{xylyl})$$

$$R_2NH_2Cl + MBH_4 \longrightarrow R_2N{=}BH_2 + MCl + H_2 \ (R = H, \text{alkyl, aryl}).$$

The aminoboranes undergo ready substitution and condensation :

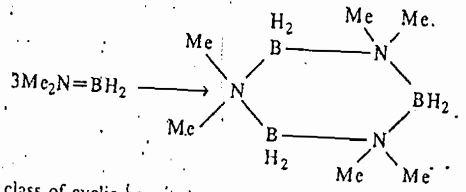
$$Me_2N{=}BCl_2 + 2EtMgCl \longrightarrow Me_2N{=}BEt_2 + 2MgCl_2$$



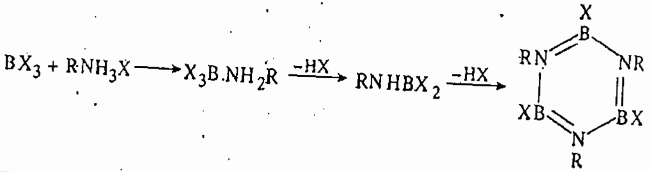
$$R_2N{=}BCl_2 + R_2N{=}BCl_2 \longrightarrow$$

Naturally, dimer formation will be hindered by the presence of bulky groups on either B or N. Thus Me_2NBF_2 dimerizes readily while larger halides are mainly monomers. Trimer formation similarly introduces more crowding of the substituents and hence is much less common. However, H_2NBH_2 and its N-methyl derivatives ($MeHNBH_2$, Me_2NBH_2) are known to form trimers in which the B_3N_3 ring is present in the cyclohexane chair conformation.

The saturated trimeric compounds are called *borazanes* (see Fig. 20-XXIV).



An important class of cyclic boron-nitrogen compounds, borazines, is obtained through elimination of HX or RH from similar cyclic trimers.



20-XXII

Q. 20.4 *The barriers to rotation around the B-N bond are found to decrease as*

$H_2B - NR_2 > HB{-}(NR_2)_2 > B(NR_2)_3$. *Comment.*

Hint : π-bonding decreases as crowding causes departure from planarity.

Borazines

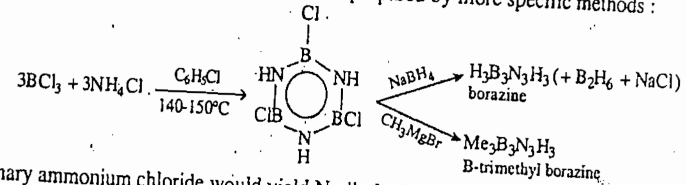
Borazine, $(HB\text{-}NH)_3$, (formerly called borazole) a colourless liquid having a hexgonal planar cyclic skeleton of alternate B and N atoms (20-XXII), was isolated as one of the intermediate products of heating B_2H_6 with NH_3 (the end product was $(BN)_x$).

Preparation

(i) $3B_2H_6 + 2NH_3 \xrightarrow{180°} 2B_3N_3H_6 + 12H_2$

Borazine and substituted borazines are now prepared by more specific methods :

(ii)



(A primary ammonium chloride would yield N-alkyl substituted B-trichloro borazines).

(iii) $MeNH_2{\cdot}BCl_3 + 6Me_3N \xrightarrow{\text{Toluene}} 6Me_3NHCl + Cl_3B_3N_3Me_3$.
(B-trichloro N-trimethyl borazine)

(iv) $3MBH_4 + 3RNH_3^+Cl^- \longrightarrow H_3B_3N_3R_3 + 3MCl + 9H_2$
N-alkylborazine

N, N′,N″-trimethyl B-trimethyl borazine may be prepared from CH_3NH_2 (= $MeNH_2$) and BCl_3 as follows :

(v) $MeNH_3Cl + BCl_3 \longrightarrow Cl_3B_3N_3Me_3 \xrightarrow{\text{LiMe}} Me_3B_3N_3Me_3$.

Properties

Borazine is a colourless liquid (b.p. 55°C) which has many physical properties similr to those of benzene (Table 20.11). It also has an aromatic odour. Pure borazine is light-sensitive and tends to explode unless stored in dark. Substituted borazines may have higher melting and boiling points e.g., $Cl_3B_3N_3Me_3$ melts at 153-156°C.

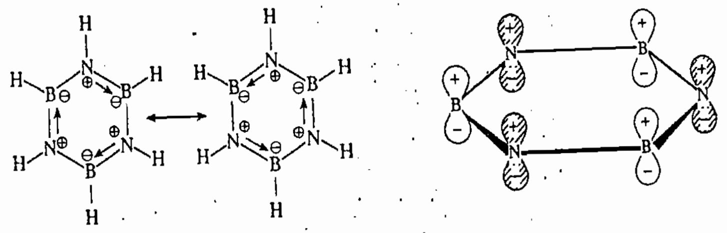
TABLE 20.11

Some properties of borazine and benzene

	Borazine	Benzene
M.P. °C	−57	6
B.P. (centre)	55	80
Critical temperature °C	252	288
Density (liq/b.p.; g cm^{-3})	0.81	0.81
Density (solid/m.p.; g cm^{-3})	1.00	1.01
Surface tension (m.p.; dyne cm^{-1})	31.0	31.0

Structure and bonding

Isoelectronic with benzene, borazine possesses a planar cyclic structure with all B—N distances equal (144 pm). This is close to the B—N distance in boron nitride or the C—C distance in benzene (142 pm). The shortness of the B—N bond in borazine in comparison to that in H_3BNH_3 (156pm) is remarkable. Thus substantial delocalizaion of the lone pair electron of nitrogen to vacant *p*-orbital of boron (both sp^2 hybridized) is suggested, which can be represented by resonance among the valence bond structures shown below (20-XXIII). The corresponding π-overlap is shown on the right.



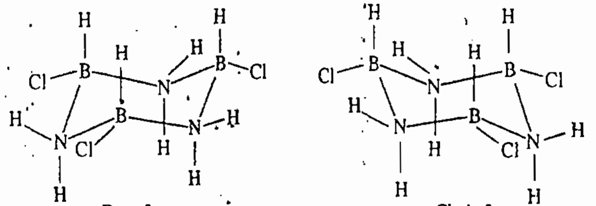
20-XXIII

This similarity in structure and other physical properties has initiated the name "inorganic benzene" for borazine. However, we cannot expect perfect delocalization of the π-electron cloud in borazine since the nitrogen π-orbitals are much lower in energy than the π-bonding orbitals of boron (N has higher nuclear charge). In fact, the chemical m.o. calculations indicate that the nitrogen to boron π-electron drift is actually more than compensated by the boron to nitrogen σ-drift, leaving the nitrogen atom relatively more negative. This is exemplified by the facile addition of polar reagents (H_2O, MeOH, HX etc.) across the B-N bond, the negative groups always adding to boron through nucleophilic attack.

$$H_3B_3N_3H_3 + 3HCl \longrightarrow H_3Cl_3B_3N_3H_6.$$

The electrophile H^+ attaches to the partially negatively charged N atom and the nucleophile adds to the B atom, bearing partial positive charge. Similarly, reaction of chloroborazines with Grignard reagents (RMgX) or hydride source results in the substitution of Cl by the R or H.

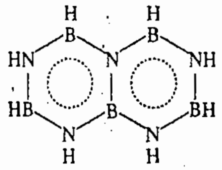
The boron-nitrogen ring loses its planarity in the saturated products (*borazanes*) which are formal analogues of cyclohexane; the chair conformation is probably more stable than the boat (20-XXIV).



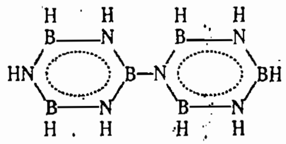
Boat form Chair form

20-XXIV

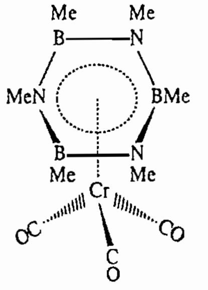
Alkylation at boron also proceeds by nucleophilic attack, (e.g. by CH_3Li), whereas in benzene alkylation is an electrophilic substitution process. Borazine is also slowly hydrolyzed to NH_3 and H_3BO_3. Electrophilic substitution at the borazine ring is not known, but hexamethyl borazine ($Me_3B_3N_3Me_3$.: a very stable solid) reacts with $[Cr(CO)_3(MeCN)_3]$ to form the complex $[Cr(\eta^6-B_3N_3Me_6)(CO)_3]$, resembling one formed by hexamethyl benzene (20-XXVIII). However, there is doubt regarding the planarity of the BN ring in the complex.



20-XXV



20-XXVI



20-XXVII

UV spectral studies reveal that the separation between the π and π* m.o.-s in borazine is significantly greater than in benzene.

29

Thermolysis of borazines produce compounds analogous to naphthalene (20-XXV), biphenyl (20-XXVI) etc.

A B_6-ring in chair conformation is said to be present in the cyclohexaborane $(BNMe_2)_6$.

A phosphorus analogue of borazine has also been prepared (see below).

Compounds containing B—P, B—As etc. bonds

Numerous compounds with B—P, B—As and B—Sb bonds essentially involve the same basic principles as involved in B-N compounds, with obvious modifications for the larger atoms. Thus $R_2P = BR'_2$ are formally analogous to the aminoboranes and tend to polymerize to ring or chain structures. Cyclic $(Me_2PBH_2)_3$ and $(Me_2AsBH_2)_3$ are both highly stable and inert. This has been attributed to drift of electron density from boron to the vacant *d*-orbitals on P/S, which offsets the polarity of the B—P or B—As bond as developed by σ-bonding alone. The adduct $H_3P \rightarrow BH_3$ gives a ring compound which is the analogue of cyclohexane (chair). The cyclic planar compound $(MesBPPh)_3$, where Mes = mesityl and Ph = phenyl, is a phosphorus analogue of borazine with equal B—P distances (184 pm). ^{31}P nmr study also suggests delocalization of electron density from P to B. Difference in size of B and P causes some distortion from ideal trigonal bond angle at both B and P.

The boron atoms in borazine derivatives have been replaced by aluminium to give *alumazines.*

20.3.9 Sulphides

The trisulphide M_2S_3 is formed by all the Group 13 elements on heating with an excess of sulphur. These may also be prepared from the oxides, for example :

$$2B_2O_3 + 3C + 3CS_2 = 2B_2S_3 + 6CO$$

$$Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO.$$

B_2S_3 is a pale yellow solid which sublimes at 200°C in needle-shaped crystals. It is readily hydrolyzed :

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

It has a layer structure containing B_3S_3 six-membered rings and B_2S_2 4-membered rings. Boron also forms a second sulphide B_8S_{16}.

$B_3S_3Br_3$ has a six-membered BS ring with bromine atoms attached to B.

Al_2S_3 (white) and also Al_2Se_3 (grey) and Al_2Te_3 (dark gery) are rapidly hydrolysed in aqueous solution.

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Addition of ammonium bisulphide to an aqueous solution containing Al^{3+} ion precipitates the hydrated oxide.

$$Al_2(SO_4)_3 + 3NH_4HS + 6H_2O = 3NH_4HSO_4 + 2Al(OH)_3 + 3H_2S.$$

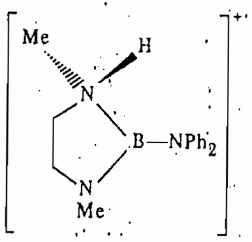
Ga, In and Tl form several sulphides (and selenides etc.) besides the trisulphide. GaS (yellow) has a layer structure with Ga-Ga bonds. InS (red) is similar. In_6S_7 has a complex structure. TlS (black) unlike GaS, is actually $Tl^I[Tl^{III}S_2]$. Tl_2S, TlS_2, Tl_2S_5 and Tl_2S_9 are sulphide and polysulphides of Tl(I). Tl_4S_3 is $Tl^I_3[Tl^{III}S_3]$.

20.3.10. Complex Compounds

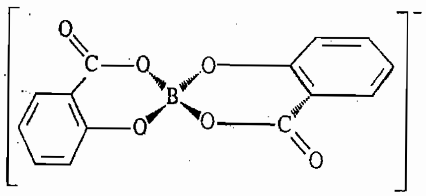
The Group 13(III) elements form a wide variety of complex compounds in different stereochemistry. Crown ether complexes of Al and Tl have also been reported.

We have already come across several complexes formed by boron, for example, BF_4^-, BH_4^- and the chelated oxyderivatives formed by cis-diols (p. 214) — all tetrahedral and anionic. Tetrahedral cationic complexes of boron include the $[Bpy_4]^{3+}$ ion mentioned before (p. 171), $[Ph_2B\ (dipy)]^+$ and may complexes formed by β-diketones, salicylaldehyde, 4-methylpyridine etc.

A planar 3-coordinate boron cation is shown in Fig. 20-XXVIII. Stabilized through N—B back bonding, the cation is best obtained with anions of low nucleophilicity, e.g. $CF_3SO_3^-$.



20-XXVIII



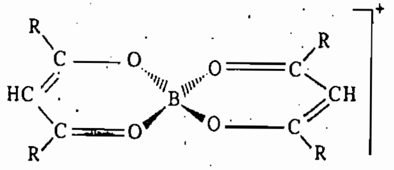
20-XXIX

The halo and hydrido complexes of boron have already been discussed. $[B(C_6H_5)_4]^-$, available as the soluble sodium tetraphenylborate $Na[B(C_6H_5)_4]$ is a valuable reagent for precipitation of potassium and heavier alkali metals. It is prepared by reacting boron triphenyl with sodium phenyl. The bis-salicyalato complex (20-XXIX) has been resolved by fractional crystallization of the strychnine salt.

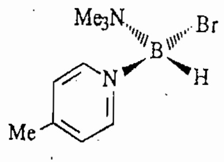
Several tetrahedral cationic boron complexes are also known, e.g.,

$$(C_6H_5)_2BCl + \text{dipyridyl} + AgClO_4 \xrightarrow{MeNO_2} AgCl + [(C_6H_5)_2B(dipy)]^+ClO_4^-$$

The cation is stable towards hydrolysis, but is attacked by base. Reaction of boron trichloride with β-diketones (e.g., acetylacetone, benzoyl-acetone) in ether solution produces cationic complexes like $[B(acac)_2]^+X^-$ (Fig. 20-XXX). Among the simple salts, only the iodide of the bisbenzoylacetonato cation is very stable (m.p. 210°C) while salts of large complex anions like $FeCl_4^-$, $AuCl_4^-$, $PtCl_6^=$ etc. are particularly stable. They are decomposed by water but are soluble in chloroform. The cationic complexes of salicylaldehyde and 4-methyl pyridine (20-XXXI) have been resolved :



20-XXX



20-XXXI

For all group III elements, halide complexes are most numerous, though some complexes with other donor ligands are also known (see later). Some typical examples are shown below. Al and Ga attain hexa-coordination with F^- only, while the larger elements may form 6-coordinate complexes with Cl^- or Br^- also. The tetrahalo complexes are obviously tetrahedral. A solution of Al in aqueous HF contains various aquo-halo species like AlF_4^-, $[AlF_2(H_2O)_4]^+$, $[AlF(H_2O)_5]^{2+}$ etc. The AlF_6^{-3} ion is formed at high fluoride ion concentrations and in crystalline solids.

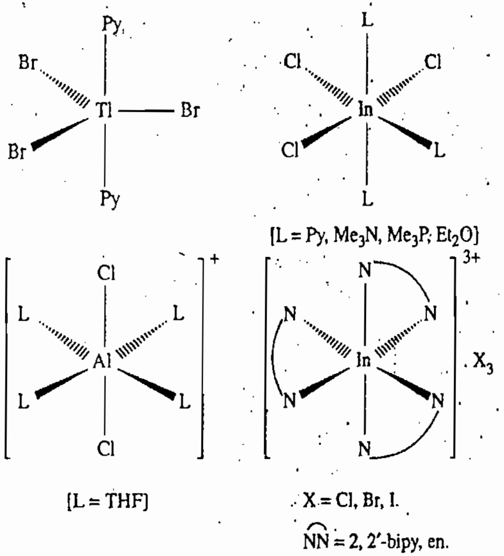


Fig. 20.21

Some complexes of III (13) elements.

The elements of this group also form stable complexes with chelating agents like β-diketones, dicarboxylic acids and 8-quinolinol (8-hydroxy quinoline or *oxine*). Neutral complexes like $Al(oxine)_3$ are insoluble in water but soluble in organic solvents and can be used in analysis (see estimation of Al). The anionic complexes like $[M(oxalate)_3]^{3-}$ may be isolated as salts of large univalent cations.

Crown ether complexes of $AlCl_2^+$ and $TlMe_2^+$ are also known. Few examples have already been given in Fig. 20.4.

20.3.11 Organometallic Compounds

The boron group elements (M) form a large number of compounds with M—C bonds, including the carboranes mentioned earlier. Most important among them are the trialkyls and triaryls, R_3M and the mixed types R_2MX or RMX_2 with halogens and related groups.

Preparation

The alkyls and aryls are conveniently prepared by ready reactions of the trihalides with Grignard and lithium reagents, usually in ether medium :

$$2BF_3 + 6CH_3MgX \longrightarrow 2B(CH_3)_3 + 3MgF_2 + 3MgX_2.$$

$$BF_3 + 3C_6H_5Li \longrightarrow B(C_6H_5)_3 + 3LiF$$

$$GaCl_3 + 3C_6H_5Li \longrightarrow Ga(C_6H_5)_3 + 3LiCl$$

$$AlCl_3 + 4CH_3Li \longrightarrow LiAl(CH_3)_4 + 3LiCl.$$

Boron alkyls can also be made by reacting diborane with alkenes in situ (hydroboration). Aluminium alkyls may be prepared from the chloride using Grignard reagents. On account of their large-scale use as catalysts in polymerization of olefins, they are prepared industrially by direct synthesis

$$Al + \frac{3}{2}H_2 + 3C_2H_4 \longrightarrow AlEt_3$$

The reaction is started by adding preformed AlR_3 which first forms AlR_2H, alkyl aluminium hydride :

$$Al + \frac{3}{2}H_2 + 2AlEt_3 \longrightarrow 3AlEt_2H \longrightarrow \frac{3}{2}AlEt_3$$

Transmetallation, i.e., replacement of a metal (usually Hg) by a more electro positive metal, may also be used :

$$2Ga\,(l) + 3HgMe_2\,(l) \longrightarrow 3Hg + 2GaMe_3\,(l)$$

Thallium trihalides and alkyl (or aryl) Grignard reagents give only dialkyl (or diaryl) thallium halides.

Properties

The trialkyl boron compounds are all monomeric with planar BC_3 skeleton. They are inert towards water, but are spontaneously inflammable in air. The triaryl compounds are comparatively less reactive. As expected, the trialkyl and triaryl compounds act as Lewis acids. BMe_3 is a weaker Lewis acid than the boron halides or BH_3. In forming a tetrahedral adduct with a Lewis base, there is no π-bonding to be disrupted. So the electron-repelling effect of the methyl group and its steric factors seem to hinder adduct formation. BMe_3 does not form an adduct with CO or 2, 6-dimethyl pyridine. Its adducts with donors like Me_3P are also considerably less stable than those with Me_3N. Boron trimesityl (mesityl = 1, 3, 5 - trimethylphenyl) shows no acceptor properties at all.

The aluminium alkyls and aryls are colorless, spontaneously flammable and highly reactive liquids or low melting solids. They react violently with water and alcohols. This may be considered as a consequence of the high carbanionic character of the organic group attached to an electropositive element. The electron deficient Al (or Ga etc.) atom readily forms an adduct with the O-atom of the alcohol (or water); this is followed by a proton transfer to the carbanionic alkyl group :

$$Al_2(CH_3)_6 + C_2H_5OH \longrightarrow (CH_3)_3\,AlOHC_2H_5 \cdots\rightarrow Al(OC_2H_5)_3 + CH_4.$$

Structure of Al_2Me_6

Aluminium trimethyl (Al_2Me_6; m.p. 15°C; b.p. 126°C) has a dimeric structure like that of Al_2Cl_6 with methyl groups replacing Cl-atoms at both terminal and bridge positions, the bridge Al-C bonds being obviously slightly longer (212 pm) than the terminal ones (195 pm)). 3-centre-2-electron description of the bridge bonds appear to be consistent with this structure. Larger alkyl groups (e.g. isopropyl or isobutyl) hinder dimerization.

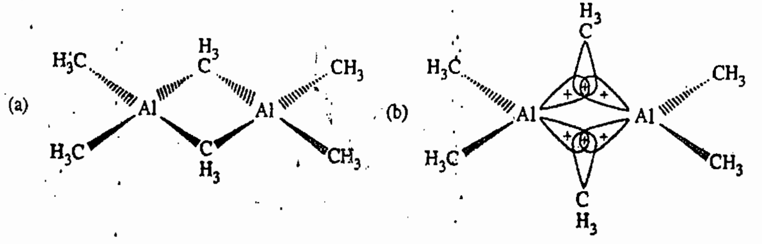


Fig. 20.22

(a) Structure of Al_2Me_6; (b) Bonding overlap in bridges.

The application of organoaluminium compounds in catalysis is discussed separately later.

The trialkyls of Ga, In and Tl are monomeric. Thermal stability as well as chemical reactivity of the compounds decrease from Al to Tl. Tl forms dialkyl salts $[TlR_2]X$ (X = halogen, CN^-, NO_3^-, SO_4^{2-} etc.) which are stable in air and resistant to hydrolysis in acqueous solution. This is consistent with decreasing carbanion character of the organic group. The $[Tl(CH_3)_2]^+$ ion is linear.

When an aqueous solution of TlOH is shaken with cyclopentadiene (C_5H_5), air stable yellow crystals of $Tl(\eta^5\text{-}C_5H_5)$ are obtained. A similar In-analog, but less stable, has also been prepared. In the gas, both compounds are monomeric with pentagonal pyramidal structure with the Tl (or In) atom at the apex (C_{5v} symmetry). They are associated in the solid. $Tl(C_5H_5)$ is useful as a synthetic reagent as it is a milder reducing agent than $Na(C_5H_5)$ and TlCl is insoluble.

Applications : Ziegla-Natta catalyst

The wide application of organoaluminium compounds in polymerization started from the work of K.Ziegler (Germany) in 1955. It was further developed by G. Natta (Italy), both of whom were jointly awarded the Nobel prize in Chemistry in 1963.

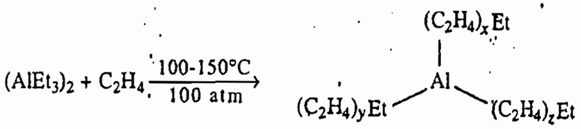
The application of aluminium alkyls in polymerization may be broadly classified into two categories :

(1) Processes involving aluminium alkyls (R_3Al; Ziegler catalysts).

(2) Processes involving aluminium alkyls wih other transition metal compounds, typically $TiCl_4$ (Ziegler-Natta catalyst).

In (1), three major products are aimed at : (a) long chain (C_{14}-C_{20}) unbranched aliphatic alcohols to be used for manufacture of detergents, (b) soft polyethenes (c) isoprene for manufacture of synthetic rubber.

Aluminium alkyls add ethene across the Al-C bonds :



$$(AlEt_3)_2 + C_2H_4 \xrightarrow[100\ \text{atm}]{100\text{-}150°C} Al[(C_2H_4)_xEt][(C_2H_4)_yEt][(C_2H_4)_zEt]$$

Values of x, y and z can be varied with temperature, pressure and time. Normally the value is 6, but it can be as high as 100.

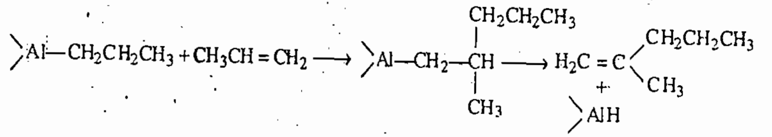
For a typical value of 6 for x, y or z, each Al has three C_{14}– groups associated with it. Controlled oxidation to form alkoxide followed by hydrolysis now gives long chain primary alcohols (C_{14}). Direct hydrolysis of the aluminium alkyls would simply give the alkanes.

$$>Al(C_2H_4)_6Et \xrightarrow{O_2} >Al\text{-}O^-(C_2H_4)_6Et \xrightarrow{H_2O} HO(C_2H_4)_6Et + >AlOH.$$

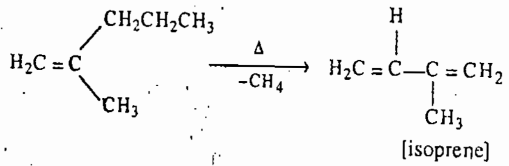
These primary alcohols are converted into $ROSO_3H$, (sulphonic acids) which are used in biodegradable detergents.

The process may also be carried out to produce polythenes with average chainlength of ~ C_{200}. However, these cover a wide range of chain length and the disordered polymers are soft and low melting (<100°C).

Dimerization of propene gives 2-methylpent-1-ene which can be thermally degraded to yield isoprene, required for the production of synthetic rubber.

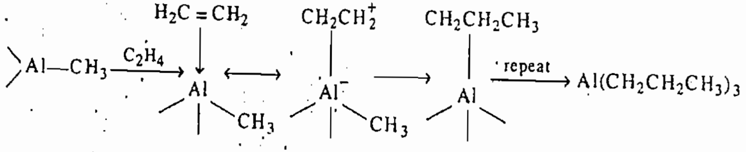


$$>Al-CH_2CH_2CH_3 + CH_3CH=CH_2 \longrightarrow >Al-CH_2-CH(CH_3)(CH_2CH_2CH_3) \longrightarrow H_2C=C(CH_2CH_2CH_3)(CH_3) + >AlH$$



$$H_2C=C(CH_2CH_2CH_3)(CH_3) \xrightarrow[-CH_4]{\Delta} H_2C=CH-C(CH_3)=CH_2$$

The insertion of the olefin in the Al-C bond in R_3Al may be thought to arise from repeated η^2- coordination by the alkene to the aluminium, followed by migration of an alkyl group :



$$>Al-CH_3 \xrightarrow{C_2H_4} \cdots \xrightarrow{\text{repeat}} Al(CH_2CH_2CH_3)_3$$

(2) In the Ziegler-Natta process, a transition metal halide like $TiCl_4$ is usually mixed with Al_2Et_6 in a hydrocarbon (e.g. heptane)—the resulting brown mixture can polymerize ethene even at room temperature and atmospheric pressure. Typical industrial processes work at about 50-150°C and 10 atm pressure. The resulting polythene (i) is a stereo-regular product (for example, in one product all the side chains may lie in the same way) (ii) has a higher density (0.95-0.98 g cm^{-3} vs 0.92 g cm^{-3} for low density polythenes) (iii) possesses greater stiffness and (iv) has higher softening temperature (140-150°C). Such high density polyethenes are now extremely familiar to us in our everyday life. Polypropenes and other copolymers of ethene may be similarly produced.

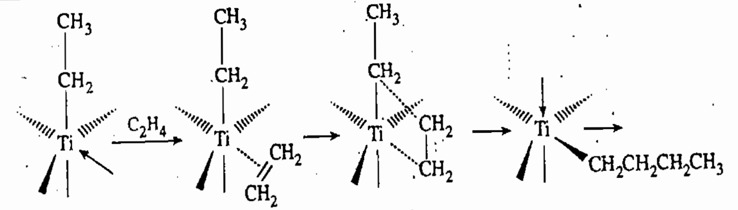
"Second generation" catalysts in the Z-N process include other transition metal compounds also.

A likely mechanism for the heterogeneous surface catalysis in the Z-N process may be exemplified as follows :

(a) $(AlEt_3)_2$ first reduces $TiCl_4$ to a fibrous form of $TiCl_3$ and replaces some of the chlorine atoms with ethyl groups.

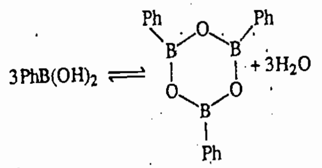
(b) An ethene molecule now coordinates (η^2–) to the vacant site in the nearly octahedral Ti atom on the surface of the catalyst.

(c) The ethene is now interposed between the Ti-C bond with the ethyl group. This extends the C-chain from two to four and creates a further vacancy in the coordination site of Ti. Repeatition increases the carbon-chain length. As the process takes place on a surface, orientation of the attacking olefin is stereo selective. With propylene, $CH_3\text{—}CH = CH_2$, for example, the double bond will attach to the Ti leaving the CH_3 group pointed away from the surface. When the molecule gets inserted between the Ti—C bond after migration, it will always have the same orientation. Such cis-insertion of the alkene is the main reason for the stereoregular products.



Boroxines are cyclic boron-oxygen compounds prepared by dehydration of *boronic acids*, $RB(OH)_2$:

$$Et_2O \rightarrow BF_3 + PhMgBr \longrightarrow PhBF_2 \xrightarrow{H_2O} PhB(OH)_2$$



Boroxines (hence boronic acids) may also be made otherwise, e.g.

$$3(CH_3)_2S \rightarrow BH_3 + 3CO \longrightarrow (CH_3BO)_3 + 3(CH_3)_2S$$

$R_2B(OH)$ compounds are called *boronous acids*.

20.4 DETECTION AND ESTIMATION

Boron

Detection

(i) Borates are usually detected by gently heating the sample with conc. H_2SO_4 and methyl (ethyl) alcohol. The issuing vapour is ignited at the end of a delivery tube; it burns with a green-edged flame. In absence of a borate, the alcohol alone burns with a blue flame.

Conc. H_2SO_4 forms boric acid which reacts with the alcohol giving volatile methyl (ethyl) borate; this burns with a green-edged flame:

$$H_3BO_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O.$$

Notes : 1. HCl cannot be used instead of H_2SO_4; CH_3Cl is formed which burns with green-edged flame.

If halides (X) are present in the sample, HX will be formed by conc H_2SO_4. This will form CH_3X (or C_2H_5X) which also burns with a green-edged flame. In that case the boron-trifluoride test should also be performed (see below).

2. The test should not be performed on a watch glass because Cu, Ba etc. salts may produce a green flame even in absence of a borate.

3. Methyl alcohol is preferred because methyl borate has a lower boiling point.

(ii) *Boron trifluoride test* : A borate is mixed with powdered CaF_2 and made into a paste with a little conc. H_2SO_4. When a little of this paste is taken at the tip of a glass rod and held very close to a flame (not on the flame), the flame is coloured green by the volatile boron trifluoride formed.

(iii) Borates change the blue-violet colour of paranitrobenzene-azochromotropic acid or chromotrope 2B into greenish-blue. Oxidizing agents may be destroyed prior to the test by fuming with solid hydrazine sulfate; fluorides are to be removed as SiF_4 by heating with silicic acid and conc. H_2SO_4.

[Sec. 20.4 Detection and Estimation]

Boron is commonly estimated by distillation of trimethyl borate. About 50 mg of the sample is digested with ~5 cm^3 conc. H_2SO_4 with triple catalyst (Se, $CuSO_4$, K_2SO_4) in a Kjeldahl flask. The clear solution is then transferred to a small r.b. flask with about 50 cm^3 methanol. About 3/4th of the solution is distilled out. The distillate is collected in water. The boric acid formed is treated with mannitol and titrated against standard NaOH solution.

Traces of boron in steels and alloys may be estimated spectrophotometrically using 1,1′-dianthrimide (150 mg in 1000 cm^3 of 98% H_2SO_4); the blue complex has an absorption maximum at 620 nm.

Aluminium

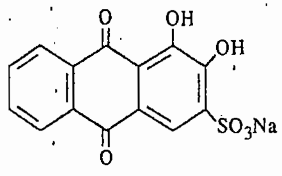
(i) Aluminium salts in aqueous solution form a white gelatinous precipitate of $Al(OH)_3$; this dissolves in excess of the reagent forming sodium aluminate ($NaAlO_2$). On shaking with sufficient ammonium chloride, the precipitate reappears.

$Al(OH)_3$ is not precipitated if sufficient complexing agents like citric -, tartaric -, malic – and sulphosalicyclic acids or sugars are present. These may be decomposed by evaporation with oxidizing acids.

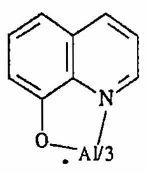
(ii) Alizarin-S (20-XXXII; 0.1 per cent aqueous solution) is used to detect small quantities of aluminium. A drop of the test solution is made sufficiently alkaline with dil. NaOH solution ($NaAlO_2$) and 1 drop of the reagent is added; drops of acetic acid are now added till the violet colour of the reagent disappears, followed by 1 drop in excess. A red precipitate or colour appears if aluminium is present.

Estimation

Aluminium may be estimated by precipitation as $Al(OH)_3$; it has to be heated to at least 1200°C before weighing as Al_2O_3. A more convenient method involves precipitation of aluminium oxinate $Al(C_9H_6ON)_3$, (20-XXXIII; C_9H_7ON = oxine or 8-hydroxy quinoline) using 2-5 percent solution of oxine (in 2*M* acetic acid) in presence of 2*M* ammonium acetate solution. The precipitate is washed with cold water and dried to constant weight at 130-140°C.



20-XXXII



20-XXXIII

Alternatively, the precipitated aluminium oxinate may be dissolved in warm concentrated HCl; the liberated oxine reacts with bromine to form the 5,7-dibromo derivative:

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2H^+ + 2Br^-$$

Each mole of Al(oxine)$_3$ will thus require 12 equivalents of bromine. The bromine is supplied by adding an excess of potassium bromide to the acid solution and titrating with standard potassium bromate solution. Often a slight excess of $KBrO_3$ is added (beyond a yellow colour in presence of methyl red or orange); the excess bromine remaining in solution is then titrated by adding KI.

Aluminium (in steel, for example) may be determined by fluorimetry using Eriochrome Blue Black RC at a pH of 4.8.

Gallium

$Ga(OH)_3$ is precipitated similar to $Al(OH)_3$; but it is a stronger acid and hence weaker base than $Al(OH)_3$ (greater polarizing power of Ga) – so it is soluble in dilute ammonia solution.

Estimation

Gallium(III) may be separated from Zn(II) and In(III) by distillation of $GaCl_3$ at 215°C.

Separation from Al(III) may be achieved by extraction of $HGaCl_4$ (~8*N* HCl) with ether free from alcohol. Fe(III), In(III), V(V) and Zn(II) are also extracted to some extent. Fe(III) may be reduced by Ti(III).

Ga may be selectively precipitated or extracted by cupferron in 5*N* sulphuric acid solution in presence of tartrate; Fe(III), Al(III) and Ti(IV) are thereby separated.

Separation of Ga(III) from Al(III) is also done by oxine (acetate buffer); only gallium oxinate is extracted into chloroform at pH 2.0. The extract has a yellowish green fluorescence; fluorimetry may be carried out for determining traces of Ga.

Indium

Yellow In_2S_3 is precipitated by H_2S from feebly acidic solution. The precipitate is insoluble in yellow ammonium sulphide.

Indium(III) may be separated by extraction of $GaCl_3$ with ether.

Fe(III), Be(II) etc. can be separated by extraction of InI_3 with ether from 0.5-2.5 (*N*) HCl.

Indium may be estimated by precipitation of the hydroxide followed by heating (350-800°) to In_2O_3. It may be titrated like Zn(II) with potassium ferrocyanide.

Separation of In from Zn(II) may be done by precipitation with cupferron (0.6-2*N* HCl); this may be followed by extraction of indium dithizonate at pH 5 — 6.3 with CCl_4 in presence of cyanide. Colorimetric estimation of small quantities of In is thus possible.

Thallium

All thallium salts impart an intense green colour to the Bunsen flame.

(i) Thallium(I) chloride is precipitated in Gr I of qualitative analysis (together with $PbCl_2$, AgCl etc.). It is soluble in hot water; lead may be separated as $PbSO_4$.

From the solution in hot water, yellow TlI may be precipitated with KI. PbI_2 may be kept in solution by adding sodium thiosulphate.

Thallium (I) produces a light red precipitate with "sodium cobaltinitrite" solution and a yellow precipitate of Tl_2CrO_4 with K_2CrO_4 solution, insoluble in dil. HNO_3.

Owing to the slight solubility of TlCl in water, some Tl(I) will escape into later groups. Any Tl(III) present will be reduced to Tl(I) by H_2S in group II. All such Tl(I) will be precipitated as black Tl_2S in group IIIB. The entire group IIIB precipitate is dissolved in dilute HNO_3; H_2S is boiled off and the solution is boiled with SO_2-water. When the resulting solution is poured into excess of sodium carbonate solution, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} are precipitated as carbonates. The Tl(I) in solution may be precipitated by ammonium sulfide solution.

Tl(III) salts in solution do not produce any precipitate with dil HCl or K_2CrO_4 solution, but gives a brown-black precipitate of ($TlI + I_2$) with KI.

Estimation

Thallium may be separated from Cd(II), Zn(II), Ni(II) by precipitation as Tl_2CrO_4. Cu(II), Hg(II) and Ag(I) may thus be separated in presence of cyanide. The precipitate may be weighed for gravimetry. Traces of thallium(I) may be separated as dithizonate between pH 9-12.

Tl (I) may be estimated by titration with KIO_3 in ~ 6*N* HCl medium :

$$IO_3^- + Cl^- + 6H^+ + 2Tl^+ \longrightarrow ICl + 3H_2O + 2Tl^{3+}$$

Tl (III) may be estimated iodometrically (pH < I). If Tl (I) is present, it may be initially oxidized by bromine water, removing the excess with phenol or by boiling for a short time (< 3 min). The liberated I_2 may be estimated by titration with $Na_2S_2O_3$ or by colorimetry in CCl_4.

SUMMARY

The p-block elements : The highest oxidation state shown by the p-block elements equals the sum of s- and p-electrons. In addition they exhibit other oxidation states. Positive oxidation states are more common in groups headed by B, C and N; the heavier members of these groups show the inert pair effect.

The first element in any group differs from the rest as it has the smallest size, highest electronegativity and a valence shell limited to 2*s* and 2*p* shells. They can form strong σ-bonds as well as *p-p* π-bonds. The middle elements show a gradual transition to more electro-positive character. Importance of *p-p* π-bonding decreases but *p-d* π-bonding may be invoked in some cases. The last element is the most metallic in character.

The Group 13(III) consists of B, Al, Ga, In and Tl. Aluminium is the most important element in this group. It occurs mainly as the hydrated oxide bauxite $Al_2O_3, 2H_2O$. India has rich deposits of bauxite. Aluminium is extracted by electrolysis of a molten mixture of bauxite, fluorspar (CaF_2) and cryolite (Na_3AlF_6).

Oxidation state and valence : High ionization energies suggest that the compounds of these elements will be mostly covalent. Solid AlF_3 and $AlCl_3$ are ionic but other halides and the molten chloride are covalent. The M^{3+} ions (M = Al–Tl) may be stabilized in aqueous solution through strong hydration. Coordinated boron cations like $[Bpy_4]^{3+}$ are known. Thlallium forms many salts containing Tl^+ ion.

In spite of the ns^2np^1 electron configuration, the elements except Tl commonly form compounds in the oxidation state III; the energy required in bringing the elements to the trivalent state is more than compensated by the energy gained in the formation of additional bonds. Entropy factors may favour the univalent state in the gaseous phase e.g., $AlCl_3\,(g) + 2Al\,(s) \longrightarrow 3AlCl\,(g)$.

Formation of three single covalent bonds leaves only six electrons in the valence shell of the elements. They tend to make up the deficiency by (i) back accepting non-bonding pairs of electrons from the attached atoms via *p-p* π-bond, as in the boron halides (ii) forming dimers as in the halides Al_2Cl_6 etc. or (iii) forming adducts with suitable donor ligands like py, Me_3N etc.

The apparently bivalent compounds like $GaCl_2$ are actually mixed valence compounds. $Ga^I[Ga^{III}Cl_4]$.

Boron has many similarities with the diagonally related element silicon.

Hydrides and Hydrido complexes : Boron forms diborane B_2H_6 and several higher boranes. All of them involve 3-center 2-electron B—H—B or B—B—B bridge bonds.

Solid aluminium hydride is polymeric. Hydrides of the remaining elements are unstable. The hydrides form stable adducts with suitable donors like the amines, CO as well as the H^- ion. The tetrahydrido borates and aluminates are useful reducing agents.

Halides : Except $Tl^{III}I_3$, Trihalides $M^{III}X_3$ are known for all the elements. Tl(III) is too strongly oxidizing to coexist with I^- and the compound TlI_3 is actually $Tl^{I}I_3$. Complex $[Tl^{III}I_4]^-$ ion is known.

The BX_3 molecules are monomeric involving B—X-bonding. The remaining elements tend to meet their electron deficiency by attaining higher coordination number through halogen bridges. The trifluorides of the elements Al-Tl are ionic but the other halides are relatively volatile having layer lattices containing dimeric molecules.

The trihalides are in general good Lewis acids; they attach neutral donor molecules or anions forming tetrahedral complexes. Acceptor ability generally decreases from B-In. The order of Lewis acidity among the boron trihalides increases from BF_3 to BI_3. Mismatch of size and energy of the larger halogens leads to poorer pi-bonding and hence greater electron deficiency at boron.

Tl (I) forms ionic TlX compounds. Gaseous monohalides MX (M = Al, Ga, In, Tl) may be prepared at high temperatures.

Oxides : All the elements form normal oxide M_2O_3 when heated in oxygen. Tl_2O_3 loses oxygen at ~100°C to form Tl_2O. Ga_2O_3 also forms Ga_2O on heating with Ga at 700°C.

B_2O_3 is dominantly acidic; oxides of Al, Ga and In are amphoteric; basic Tl_2O_3 dissolves in acids to give Tl(III) salts.

$B(OH)_3$ is called boric acid ($pK \sim 9.2$). It acts as a Lewis acid

$$B(OH)_3 + H_2O = [B(OH)_4]^- + H^+.$$

he equilibrium can be displaced nearly completely toward right by chelating the boron with cis-diols.

lOOH, Al $(OH)_3$ etc. are insoluble in water. TlOH is soluble in water and acts as a strong base.

A wide variety of metal borates occur in nature, usually in the hydrated form. They contain triangular BO_3 and tetrahedral BO_4 units. Corner sharing of O-atoms gives rise to condensed borates.

The elements Al-Tl form a wide variety of salts of oxo-acids. Salts of very weak acids like carbonates or cyanides cannot exist owing to extensive hydrolysis. The aqua-ions $[M(H_2O)_6]^{3+}$ are distinctly acidic. Tl (III) is strongly oxidizing ($E°$ Tl(III)–Tl(I) = 1.26V).

Nitrogen compounds : The elements B-In form stable solid nitrides MN. BN has a graphite like layer lattice; others have a diamond lattice. Boron forms a wide variety of compounds containing B—N bonds. The BN group (8 valence electrons) is formally isoelectronic with C—C. The electronegativity and size of carbon is intermediate between those of B and N. These factors and possibility of $2p$-$2p$ π-bond formation gives rise to compounds like amine-borane adducts (c.f. alkanes) aminoboranes (c.f. alkenes) and borazines (c.f. benzene). Borazine $(HBNH)_3$ is a colourless liquid like benzene. It has a hexagonal planar cyclic skeleton of alternate B and N atoms. The B—N bond distances are all equal and shorter than B-N single bond distance. Borazine is called "inorganic benzene" though its chemical reactions are dominated by polarity of B—N bond (ready addition reactions).

Organometallic compounds : The boron group elements form a large number of compounds containing M-C bonds. Most important are the trialkyls and triaryls, R_3M. The trialkyl boron compounds are monomeric with planar BC_3 skeleton. They are weaker Lewis acids than the boron halides or BH_3. They are inert towards water but are spontaneously flammable in air.

The aluminium alkyls and aryls are colourless liquids or solids spontaneously flammable in air. They react violently with water or alcohol—a consequence of the high carbanionic character of the organic group attached to the electropositive atom. Aluminium alkyls, together with transition metal compounds like $TiCl_4$, are important catalysts in polymerization industry, specially in the manufacture of high-density polythene (Ziegler-Natta Catalyst).

EXERCISE

1. *Discuss how the lightest p-block elements differ in physical and chemical properties from the heavier members in the same group.*

   [**Hint :** Read sections 16.4 and 20.1. Give specific examples with reference to structure and electrical properties of B and Al in Gr. 13(III), C and Si in Gr. IV(14) (see Ch. 21) and so on. For chemical properties, give a general discussion (section 20.2.4) followed by specific examples like the hydrides/halides of B vs Al, C vs Si.].
2. *Give the principle of isolation of the elements B, Al, Ga, In and Tl and mention at least one use of these elements (or their compounds).*
3. *Explain why the elements B-In do not commonly exhibit + I and + II oxidation states.*

   Why is Tl an exception to this trend?
4. *Explain why $AlCl_3$ reacts with Al at 800°-1000°C to form AlCl.*
5. *How does one conclude that the compounds $GaCl_2$ and $InCl_2$ do not contain Ga(II) or In(II)?*
6. *Why do you consider the B^{3+} ion unlikely to occur in common compounds of boron? Suggest situations which will favour such species.*
7. *Summarize the trends in relative stabilities of the various oxidation states of the elements in the boron group. Explain the term "inert pair effect" and trace the actual reason for this popular label.*

   Complete the equations for acidic aqueous solutions.

   (*i*) $Tl^{3+} + Al\,(s)$, *excess* $\longrightarrow$

   (*ii*) $In^{+} \longrightarrow$ *(air excluded)*

   (*iii*) $Tl^{+} \longrightarrow$ *(exposed to air)*

   (*iv*) $Tl\,(OH)_3 + HI$ *(excess)* $\longrightarrow$

8. *The ionization potential of boron is slightly less than that of Po (an element toward the end of the oxygen group).*

   Yet Po shows the more metallic character. Comment.
9. *Compare the main aspects of the chemistry of boron, aluminium and silicon.*
10. *Do you expect the following reactions to proceed from left to right in gas phase or hydrocarbon solvent? (Give brief reasons).*

    (*a*) $R_3PBBr_3 + R_3NBF_3 \longrightarrow R_3PBF_3 + R_3NBBr_3$

    (*b*) $4KC_6H_5 + BCl_3 \longrightarrow 3KCl + KB(C_6H_5)_4$

    (*c*) $AsF_3 + BCl_3 \longrightarrow BF_3 + AsCl_3$

    (*d*) $Et_3NGaCl_3 + GaF_3 \longrightarrow Et_3NGaF_3 + GaCl_3$

    (*e*) $Et_3AsBCl_3 + Et_3NGaCl_3 \longrightarrow Et_3AsGaCl_3 + Et_3NBCl_3$

    (*f*) $Me_3NBF_3 + GaCl_3 \longrightarrow Me_3NBCl_3 + GaF_3$

    (*g*) $TlCl + NaI$ *(in water)* $\longrightarrow TlI + NaCl$

    (*h*) $2TlCl_3 + HCHO + H_2O \longrightarrow 2TlCl + 4HCl + CO_2$.

    [**Hint :** Reaction at (d) is not likely to occur owing to high lattice energy of GaF_3. Other reactions may be rationalized from hard-soft acid base concept, lattice energy, or oxidizing character of Tl(III)].
11. *Suggest reactions for the following synthesis :*

    (*a*) B_2D_6, $B(OD)_3$, $B(CH_2CH_2D)_3$ *using* D_2O *as the only source of denterium.*

    (*b*) $B(NMe_2)_3$ *from* BCl_3

    (*c*) $Me_3N_3B_3Me_3$ *from* BCl_3

    (*d*) $Cl_3B_3N_3H_3$ *using* NH_4Cl

    (*e*) $[H_2B\,(NMe_3)_2]^+$ *starting with* B_2H_6

    (*f*) $Cl_3B_3N_3Me_3$ *starting with* BCl_3.

    [Hint : (a) $D_2O \longrightarrow D_2 \longrightarrow NaD$; BF_3 gives B_2D_6; $B_2D_6 + CH_2 = CH_2$

    (b) $BCl_3 + Me_2NH$ (excess) in a hydrocarbon solvent

    (c) $MeNH_2 + HCl \longrightarrow MeNH_3Cl$; BCl_3 gives $Cl_3B_3N_3Me_3$. Then add LiMe.

    (d) $NH_4Cl + BCl_3$

    (e) Direct reaction of B_2H_6 with Me_3N leads to symmetrical cleavage, giving Me_3N-BH_3. $B_2H_6 + NH_3 \longrightarrow [H_2B(NH_3)_2]^+ BH_4^-$. Me_3N now gives $[H_2B(NMe_3)_2]^+ BH_4^-$].
12. *Suggest the most likely explanation for the following :*

    (*a*) BF_3 *reacts with excess NaF in acidic aqueous solution forming* BF_4^- *(aq). The product of reacting* BCl_3 *with excess NaCl is however different.*

    (*b*) *Borazine is more reactive than benzene towards addition of HX.*

    (*c*) $LiAlH_4$ *explodes violently with water, while* $NaBH_4$ *does not.*

    (*d*) *The electrode potential for* Tl^+—Tl^{3+} *system is sensitive to pH and to the presence of complexing anions,*

    (*e*) *Enthalpy of dimerization of the aluminium alkyls* AlR_3 *are* –41, –35, –16 *kJ* mol^{-1} *for* $R = Me, Et$ *and iso-butyl respectively.*

(*f*) AlF_3 *dissolves appreciably in anhydrous HF only when KF is also present. But* AlF_3 *is reprecipitated when* BF_3 *is passed into the solution.*

(*g*) BF_3 *has no dipole moment but* NF_3 *has.*

(*h*) BF_3 *and* BrF_3 *have different shapes.*

(*i*) *2, 6-dimethylpyridine does not form an adduct with* BMe_3 ($Me = CH_3$), *though it behaves as a stronger base than pyridine toward* H^+. *However, it combines with* $AlEt_3$.

(*j*) *6 mol of ionic species are formed in solution per mole of boric acid when it is dissolved in concentrated* H_2SO_4.

[**Hint :** $H_3BO_3 + H_2SO_4 \longrightarrow 3H_3O^+ + B(HSO_4)_4^- + 2HSO_4^-$]

(*k*) $LiBH_4$ *is thermally stable upto 380°C, while* $LiAlH_4$ *decomposes at 100°;* $LiGaH_4$ *at 50°C.*

13. *How does boric acid ionize in aqueous solution? What is the effect of separately adding (i) glycerol (ii)* KHF_2 *to this solution?*

14. (a) *What makes borax a useful primary standard in quantitative analysis? Give a balanced equation representing the reaction involved in the titration of borax. What indicator would you use in such titration?*

(b) *Explain why a solution of borax is a good buffer solution.*

[**Hint :** The stoichiometry corresponds to half-neutralized boric acid; the solution will contain largely H_3BO_3 and $B(OH)_4^-$].

15. *What products are expected from the following reactions under appropriate conditions :*

(*a*) $BF_3 + Et_2O$ (*b*) $BCl_3 + ROH$

(*c*) $BF_3 + H_2O$ (*d*) $B_2H_6 + HCl$

(*e*) $B_2H_6 + LiH$ (*f*) $B_2H_6 + Na$

(*g*) $B_2H_6 + NaBH_4$ (*h*) $Me_2N-BCl_2 + 2PhMgBr$

(*i*) $Et_2NH + BCl_3 \longrightarrow$ *Product heated*

(*j*) $SiF_4NMe_3 + BF_3$ (*k*) $NaBH_4 + SO_2$ (*in presence of NaOH*)

(*l*) $LiBH_4 + CH_3OH$ (*m*) $SiCl_4 + LiAlH_4$

(*n*) $CH_2=CH_2 + Al + H_2$ (*o*) $F_3B{\cdot}NMe_3 + BCl_3$

16. *Draw skeleton structures of* $[Cu^I(MePh_2P)_3(\eta^1-BH_4)]$ *and* $[Cu^I(PPh_3)_2(\eta^2-BH_4)]$.

17. *Discuss the bonding in* B_2H_6. *How can this be extended to cover higher boranes?*

18. *A is a yellowish white deliquescent solid which reacts vigorously with water to produce solution B. Solution B produces a white gelatinous precipitate C when treated with aqueous ammonia solution. C dissolves in excess NaOH from which it is reprecipitated by shaking with solid* NH_4Cl.

Another portion of solution B gives a dirty white precipitate D on treatment with dilute $HNO_3 + AgNO_3$ *solution. D dissolves in excess aqueous ammonia only on heating.*

A dissolves unchanged in dry ether. The solution gives E with LiH; A second product F is obtained when LiH is in excess.

The vapour density of the vapour of A is 267.

Identify the compounds A—F.

19. *Write notes on (i) Ziegler Natta catalysts (ii) Hydroboration (iii) Borohydrides (iv) Lewis acidity trend among boron halides (v) Perborates (vi) Chemistry of Tl(I).*

20. *A white crystalline solid A on fusion with ammonium hydrogen fluoride furnishes an ionic compound B. B on heating with diboron trioxide gives a gaseous product C, which burns with a green edged flame. C on passing through water gives an acidic solution containing D and A is regenerated. On the other hand C reacts with an ethereal solution of sodium borohydride to produce another gaseous product E. E readily reacts with water to regenerate A and produce another gas F that burns with a blue flame. E reacts with dry ammonia gas at low temperature to give an ionic compound G which on heating furnishes a liquid H of molecular weight 80·4 heaving a cyclic structure. Elemental analysis of H corresponds to the empirical formula* BNH_2. *Identify the compounds A to H with reasonable explanation.*

[**Hint :** A = H_3BO_3. Work out the rest.]

21. *White solid A dissolves in water giving an alkaline solution. The solution evolves* CO_2 *on adding dilute* HNO_3; *the neutral solution forms a light red precipitate with sodium hexanitritocobaltate (III) ("cobaltinitrite"). The solution also gives a white precipitate with dilute HCl and a yellow precipitate with KI. Potassium chromate solution also produces a yellow precipitate insoluble in dilute nitric acid. But if the aqueous solution of A is oxidized with a few drops of aquaregia, the resulting solution gives no precipitate with either dilute HCl or* K_2CrO_4 *or* $Na_3[Co(NO_2)_6]$ *solution. But it liberates iodine from a dilute solution of KI.*

Identify A and write the reactions corresponding to each observation.

22. *Complete the reaction sequence given below by putting appropriate substances at A, B, C, D, etc.*

$$\begin{tikzcd}
 & A & E & & \\
B & BF_3 \arrow[l, "Al_2Cl_6"'] \arrow[u, "CH_3MgBr\ ether"'] \arrow[d, "(CH_3)_2O"'] \arrow[r, "D"] & B_2H_6 \arrow[u, "HCl"'] \arrow[d, "H_2O"'] \arrow[r, "NH_3"] & G \arrow[r, "heat"] & H \\
 & C & F & &
\end{tikzcd}$$

Give the structure of H and its reaction with HCl.

[**Hint :** A : Sec., 20.3.11; B : Think about the high lattice energy of AlF_3; C : adduct; D : Page 181; E : Page 184].

23. *Complete the following reactions and identify A and B :*

$$BCl_3 + aniline \xrightarrow[heat]{Benzene} A$$

$$A + HCl \longrightarrow B.$$

24. *Comment on the following bond length data in* MO_3^{n-} *ions where M = B, C and N :*

	B	*C*	*N*
$d_{M\text{-}O}$ (*pm*)	137 (BO_3^{3-})	129 (CO_3^{2-})	122 (NO_3^-)
M—O single bond length (pm)	148 (BO_4^{4-})	143 (*average*)	139 (NO_4^-)
Difference, Δ (pm)	11	14	17
Percent shortening (Δ/d) × 100	8%	10·9%	13·9%

CHAPTER TWENTYONE

ELEMENTS OF GROUP 14(IVA)

C, Si, Ge, Sn, Pb

OBJECTIVES

21.1 Introduction
    Abundance and Occurrence of the Elements [21.1.1]
    Isolation and Use [21.1.2 — 21.1.3]
21.2 General Properties of the Elements [21.2]
21.3 Principal Compounds [21.3]
    (i) Compounds of Graphite [21.3.1]
    (ii) Carbides and Silicides [21.3.2]
    (iii) Hydrides [21.3.3]
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        Aqueous Solution Chemistry [21.3.7]
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        Cyanogen and its derivatives;
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    (xi) Complexes and Clusters [21.3.11]
    (xii) Chemistry of the Fullerenes [21.3.12]
21.4 Detection and Estimation

21

ELEMENTS OF GROUP 14(IVA)

21.1 INTRODUCTION

The first two elements in the carbon group occupy a special position in our life. Carbon, the key element in all living systems, forms more compounds than any other element except hydrogen. Silicon is the second most abundant element (after oxygen) in the earth's crust and is still the principal "building" material in our civilization in the form of stones, sand and clays. The diverse and unique features of a wide range of carbon compounds have necessitated a separate domain of study for such compounds but any rigid demarcation between the so-called organic and inorganic chemistray finds no rationalization from a scientific point of view. Unfortunately, this is being realized rather slowly by the senior chemists while a vast majority of chemists, teachers and of course students are still susceptible to such mania.

The general trend in properties of the elements in this group follows the same pattern as outlined for p-block elements in connection with the boron group. Carbon and silicon are typical nonmetals, followed by germanium, tin and lead with gradually increasing metallic character. The compounds of carbon and silicon are covalent with very few exceptions, while ion formation becomes increasingly favourable for the later elements. Side by side, the typical group valency of 4 becomes gradually less favoured, Pb(IV) being strongly oxidizing in nature. The "inert pair effect" has the same root as discussed in connection with the boron group. The features associated with the first member in a group, viz, inability to octet expansion, importance of *p-p* π-bonding etc. are equally found with carbon, with some additional characteristics which are unique to carbon alone. It has the most favourable combination of charge and size for catenation i.e., linking to other carbon atoms forming chains and rings able to survive in various conditions. In fact, this is the principal reason for the development of so-called "organic chemistry". Clearly, it is not possible here to deal with all aspects of carbon chemistry. Our discussion will be mainly confined to compounds containing C—O, C—N and C—X (halogen) bonds.

21.1.1 Abundance and Occurrence

Carbon is present in the earth's crust to the extent of about 0.8%. Crude oil and coal are the most common forms of combined and free carbon respectively. Flakes of graphite occur in metamorphosed sedimentary rocks like quartz. Diamond occurs embedded in other rocks (e.g., Kimberlite, a dark coloured basic rock from Kimberlin, South Africa) associated with ancient volcanic pipes. Weathering and erosion of such pipes followed by geological action also lead to its accumulation in alluvial gravels.

India and Borneo are the oldest diamond producing countries. Diamond was found in Brazil in 1729 and the South African deposits were discovered only in the later part of the nineteenth century. A large deposit has been discovered in Siberia in the twentieth century. Indian diamonds occur in the southern parts along the coast of the rivers Krishna and Godavari. At present, some diamond is mined at Panna in M.P.

In India, graphite is found mainly in Visakhapatnam, Chattisgarh, Coorg, Travancore, Ajmeer-Merwara and Orissa.

Silicon is second only to oxygen in its abundance (27.6% in the earth's crust) but it is not found free. It has a high affinity for oxygen forming the stable SiO_4 unit which can combine with one another in a number of ways giving rise to a wide variety of silicates (see later). Silica and silicates occur widely in sand, clays and various silicate minerals.

Germanium has no widely occurring ores. It occurs associated with other minerals, particularly zinc and silver minerals (abundance : about 1-2 ppm in earth's crust).

Tin is only slightly more abundant than germanium (≃ 2.1 ppm) but there are specific ores, particularly cassiterite or Tin stone (SnO_2). Other minerals contain Sn(IV). Malayasia, Russian countries, Bolivia, Indonesia, Thailand and China are the major producers of tin. In India tin-stone occurs in Bihar and Orissa.

Lead (13-16 ppm in the earth's crust) is available mostly in the form of galena or PbS. Other minerals also contain Pb(II) e.g. anglesite ($PbSO_4$), cerrusite ($PbCO_3$) etc. USA, Russian countries, Australia and Canada are the major producers of lead. In India, galena containing about 3% Pb (and also a little Ag) is obtained from the Zawar mines at Udaipur (Rajasthan). Lead is also smelted in Andhra and Bihar.

Isotopes

The principal isotope of carbon is ^{12}C. ^{13}C occurs to the extent of about 1.11%. It has a nuclear spin quantum number $\frac{1}{2}$ and can be used in Fourier transform NMR studies. It is also used as a nonradioactive tracer. The atmospheric carbon dioxide contains about 1.2×10^{-10} per cent radio-active ^{14}C ($t_{1/2}$ = 5570 years) produced through *n, p* reaction on nitrogen by thermal neutrons resulting from cosmic radiation. It may also be prepared in a reactor by (*n, p*) reaction on $Li_3{}^{14}N$ and used as a tracer. Its use in radio-carbon dating has been mentioned in chapter 14.

Silicon has three stable isotopes : ^{28}Si (92.23%), ^{29}Si (4.67%) and ^{30}Si (3.10%). ^{29}Si has a nuclear spin quantum number equal to $^1/_2$ and can be used in nmr studies. ^{31}Si can be obtained by neutron irradiation of ^{30}Si; it emits beta-rays with a half-life of 2.6 hours. ^{32}Si is also a beta-emitter ($t_{1/2}$ = 650 years).

Germanium has five stable isotopes of mass numbers 70 (20.5%), 72 (27.4%), 73 (7.8%), 74 (36.5%) and 76 (7.8%).

Tin has as many as ten stable isotopes; their mass numbers and relative abundance (%) are as follows : 112 (0.96); 114 (0.7); 115 (0.35); 116 (14.3); 117 (7.6); 118 (24); 119 (8.6); 120 (32.8); 122 (4.7); 124 (5.94). Sn-119 (nuclear spin 1/2) is used for nmr studies and Mossbauer spectroscopy (see iron, Ch-28).

The stable isotopes of lead are (relative abundance in %) : 204 (15); 206 (23.6): 207 (22.6): 208 (52.5). Pb-207 may be used in nmr studies.

21.1.2 Isolation of the elements

Carbon

Of all the forms of carbon, coke is used in largest quantities. It is obtained by coking or high temperature carbonization of coal — the coal is heated in large ovens in the absence of air.

Natural graphite is obtained in admixture with mica, quartz and silicates. The carbon content is 25% on an average but may be as high as 60%. It is washed by floatation and heated with HCl and HF in vacuum when residual silicon compounds are driven away as SiF_4. Nearly half of the industrial requirement of graphite is met with synthetic graphite. This is made by heating silica with coke in an electric furnace (2500°C) for about 24 hours.

$$SiO_2 + 3C \rightarrow SiC + 2CO \rightarrow C\,(\text{graphite}) + Si\,(g).$$

Natural diamond is also mined in large quantities — more than 18 tonnes a year (924×10^5 carats; 1 carat = 0.2 g). Of this about 30% are used as gems while the rest goes to various industries. Only small size industrial diamonds can be made synthetically by subjecting graphite to 125000 atm pressure at about 3000K. With transition metal catalysts, conversion can be achieved at 70,000 atm pressure and 2000K.

[Sec. 21.1.1

Carbon black is prepared by incomplete combustion of hydrocarbons. Activated carbon is prepared by controlled pyrolysis of organic materials like saw dust or coconut shell (~ 900°C). Activation of the surface is accomplished by adding materials which would oxidize and dehydrate the organic substrate on the surface like NaOH, Na_2CO_3, Na_2SO_4 or chlorides of Ca, Sr, Ba, Zn etc. The small particles provide a very high surface area (> 1000 m^2g^{-1}). The edges of the hexagonal graphite sheets are probably covered with oxygenated groups (–OH, –COOH etc.) which are responsible for the surface activity (see use).

Graphite fibers are obtained when synthetic fibers or asphaltic fibers are subjected to controlled pyrolysis (~ 1500°C). The strong fibers have the same structural principle as graphite but consist of layers of ribbons (in place of sheets in graphite) parallel to the axis of the fiber. The strong bonds in a plane are responsible for high tensile strength and these are used to reinforce plastics (tennis racket, aircraft components etc.).

Isolation—Si] :

Silicon

Silicon is prepared by reducing SiO_2 (sand) with high purity coke in an electric arc furnace. Formation of silicon carbide (SiC) is prevented by using an excess of SiO_2.

$$SiO_2 + 2C = Si + 2CO.$$

The product is nearly 96-97% pure.

This can be purified by converting it to $SiCl_4$ which is purified by distillation and subsequently reduced by Mg or Zn.

$$Si + 2Cl_2 = SiCl_4;\ SiCl_4 + 2Mg = Si + 2MgCl_2.$$

Super pure silicon :

Zone refining

Superpure silicon suitable for electronics industry (impurity less than 1 in 10^9) can be obtained by subjecting such pure silicon to zone-refining. The spongy silicon obtained by reduction of $SiCl_4$ is melted and grown into a cylindrical rod. The rod is placed in a quartz tube filled with an inert gas. It is surrounded by a ring-like heating coil which can be moved from one end of the rod to the other. When the heater melts one part of the rod, impurities dissolve more in the liquid phase. As the heating coil is slowly moved, impurities are carried along with the molten zone and pure silicon crystallizes from the melt. Thus the impurities are transported with the melt to one end which is cut off and discarded.

Other methods of preparing ultrapure silicon are

(i) thermal decomposition of SiI_4/H_2 on a hot tungsten filament.

(ii) reduction of Na_2SiF_6 by sodium :

$$Na_2SiF_6 + 4Na = Si + 6NaF.$$

The Na_2SiF_6 is a bye-product from the manufacture of phosphatic fertilizer from fluorapatite. The highly exothermic reaction is selfsustaining and does not require any additional fuel.

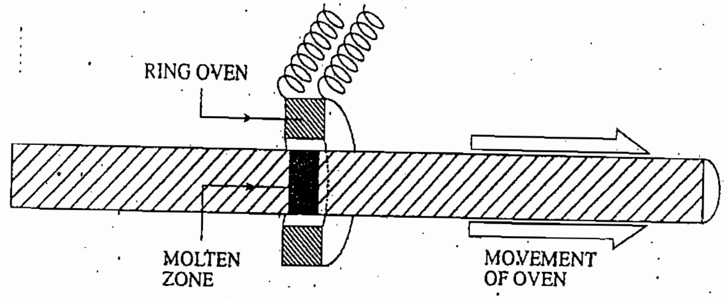


Fig. 21.1 : Zone-refining.

Ferrosilicon, an alloy of Fe and Si highly needed in steel industry is prepared by reducing SiO_2 with coke in presence of scrap iron

$$SiO_2 + Fe + 2C = FeSi + 2CO.$$

Germanium

Germanium was once recovered from coal ash. Now it is mostly obtained from flue dusts from the smelting of zinc.

(a) The flue dust is leached with dil H_2SO_4 and the solution is slowly neutralised by gradual addition of NaOH solution. Precipitation of GeO_2, xH_2O begins at pH 2.4 which is 98% complete at pH 5. $Zn(OH)_2$ starts precipitation at about pH 4. So the precipitate at about pH 5 contains a higher fraction of Ge.

(b) The mixed precipitate is heated with HCl/Cl_2 when volatile $GeCl_4$ (b.p. 83.1°C) distills out and $ZnCl_2$ (b.p. 756°C) is left behind. The $GeCl_4$ is purified by fractional distillation.

(c) $GeCl_4$ is hydrolysed to GeO_2, xH_2O.

(d) GeO_2 is reduced by H_2 (550°C).

(e) Ge is further purified by zone-refining.

Tin

The mineral tin stone contains only 1–5% SnO_2, together with silica and wolframite ($FeWO_4$, iron tungstate). The major steps in the extraction of tin are as follows :

(a) The ore is crushed and washed. Light siliceous matter is largely removed.

(b) The ore is roasted in a current of hot air (in an inclined reverberatory furnace). S and As compounds are driven out. Iron forms mainly Fe_3O_4.

(c) Non-magnetic tin stone is separated from magnetic wolframite and Fe_3O_4 by magnetic separation. The tin concentrate is further washed.

(d) The concentrate, "black tin" (65-90% SnO_2) is reduced with coke at 1200-1300°C :

$$SnO_2 + 2C = Sn + 2CO.$$

Lead

Lead sulfide or galena is concentrated by froth-floatation process and roasted in a limited supply of air to partially convert it to PbO. Self-reduction between unchanged PbS (or added fresh) and the PbO produces lead :

$$2PbO + PbS \longrightarrow 3Pb(l) + SO_2(g).$$

The crude lead contains many impurities like Cu, Ag, Au, Zn, As, Sb and Sn. When the lead is kept molten just above the melting point, copper floats up a solid scum and can be skimmed off. Sn, As and Sb are next preferentially oxidized in a reverberatory furnace and the oxide scum is skimmed off. Silver and gold are more soluble in zinc and are separated with it in the form of a solid crust when the molten metal is slowly cooled from 480°C to below 420°C. The residual zinc may be removed by vacuum distillation or by preferential oxidation in a reverberatory furnace. The lead is finally purified electrolytically using $PbSiF_6$ as an electrolyte.

21.1.3 Use

Carbon

Coke is vital in the extraction of iron and many other metals. Graphite is mainly used in steel-making, metal foundries, refractories, in making crucibles, nozzles etc. and as lubricants. It is also used in brake linings, pencils, brushes of electric motors etc. An important use of graphite is in nuclear reactors as neutron moderators.

Diamond is a valuable gemstone. Industrially it is used in making drills and as an abrasive for cutting and polishing.

Carbon black is largely used in rubber industry to increase the strength of rubbers — particularly those used in making car tyres.

Activated carbon is a very efficient adsorbent — it absorbs organic pollutants from drinking water, noxious gases from the air and so on. It is largely used as a decolorizing agent in sugar industry and in gas purification, including air pollution and gas masks. It is also used in the treatment of sewage water and as a catalyst.

Silicon

Silicon is extensively used in steel making as a deoxidizer. Ferrosilicon is the usual form for this purpose. Steels with high silicon content are corrosion-resistant. Small quantities of ultra-pure silicon are required in electronic industry. Si becomes a *p*-type semiconductor when doped with a Group III element (Al, Ga) and an *n*-type semiconductor when doped with a Group V element (P, As etc.).

Germanium

Germanium is used mainly in making transistors though this use is now declining. Being transparent to infrared rays, Ge is used in making optical parts (prisms, windows etc.) in infrared spectrophotometers.

Tin

Tin is one of the important metals used in early civilizations. It is mainly used as a non-toxic corrosion-resistant coating on steel, particularly in food packaging. Tin alloys have widespread use for various purposes. Some alloys with typical compositions (in parentheses; %) are mentioned below.

Solder	Sn - Pb (33-50% Sn); soldering.
Bronze	Sn - Cu (5-10% Sn), (P, Zn); casting. Gunmetal is Cu - 85% with Sn, Pb and Zn (5% each).
Babbitt	Sn (80 - 90%) : Cu (5%) Pb (0.5%). Heavy duty bearings.
Pewter	Sn (90 - 95%), Sb (1-8%), Cu (0.5-3%). Trays, plates, trophies. An alloy with 90-95% Sn and Pb is used in organ pipes.
Type metal	Pb (80%), Sb (15%), Sn (5%) to Pb (55), Sb (30), Sn (15). Increasing Sb content increases the hardness of the alloy.

Lead

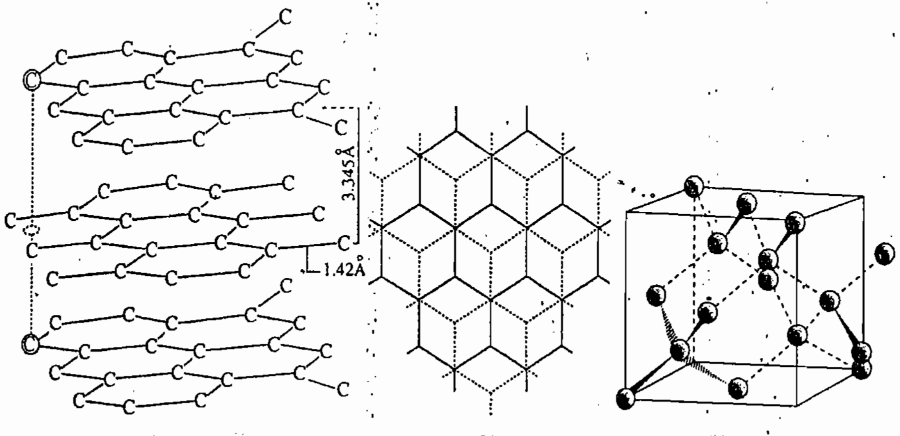
Lead has been used in plumbing since roman civilization. Now this has been stopped due to lead poisoning. The principal use of lead is in making storage batteries, lead based alloys like solder, type metal etc. (see above), cable covering, manufacture of lead tetraethyl (an antiknock additive to petrol but now highly discouraged due to air pollution) and manufacture of pigments.

21.2 GENERAL PROPERTIES OF THE ELEMENTS

21.2.1 Allotropic forms

Carbon has several crystalline allotropic forms — only two of them being common : diamond and graphite (α-graphite). There are four other rare and poorly understood allotropes : β-graphite, Lonsdaleite or hexgonal diamond, chaoite (a very rare mineral) and carbon VI. The last two forms appear to contain a carbyne motif $-C \equiv C - C \equiv C-$ and are closer to diamond in their properties. A recent addition to the range of allotropes of carbon are the *fullerenes*, discrete molecular clusters of even number of carbon atoms (C_n; $n = 30 - 600$, even) arranged in a closed hollow cage (see below). The list of allotropes is going to be further enriched by the discovery of other molecular allotropes involving linear oligomers, monocyclic and bicyclic planar rings and three-dimensional fused ring clusters.

The various amorphous forms of carbon like carbon black, soot etc. are all microcrystalline forms of graphite. Common α-graphite is the most stable form of carbon at ordinary temperature and pressures. Yet diamond structures do not change into graphites as the equilibrium is approached extremely slowly. Graphite consists of a layer structure — in each layer the C-atoms are arranged in hexagonal planar arrangement (sp^2 hybridized) with three σ-bonds to three neighbours and one π-bond to one neighbour. Resonance between structures having alternative mode of π-bonding makes all C—C bonds equal, 141.5 pm, consistent with a bond order of 1.33. The π-electrons are responsbile for the electrical conductivity of graphite. Successive layers of C-atoms are held by weak van der waals force at a separation of 335 pm and can easily slide over one another. In the common α-graphite, *alternate* layers are in phase. In the β-form, every third layer is in phase, giving a rhombohedral arrangement.



(a) (b) (c)

Fig. 21.2

(a) Structure of α-graphite; (b) top-view of the layers in 'a'; (c) structure of diamond.

In diamond, each carbon (sp^3 hybridized) is tetrahedrally surrounded by four other carbon atoms (C—C distance 154 pm). These tetrahedra belong to a cubic unit cell (Fig. 21.2). Natural diamonds commonly contain traces of nitrogen or sometimes, very rarely though, traces of Al (in blue diamonds). In the extremely rare Lonsdaleite allotrope found in certain meteorites, the tetrahedral units are stacked to form a hexagonal wurtzite type lattice.

At room temperature, α-graphite is more stable than diamond; the difference in ΔH_f^0 for the two forms is about 1.9 kJ mol^{-1}. However, graphite can be converted to the more dense diamond form by applying very high pressure, ~ 125,000 atmosphere at about 3000K. In presence of transition metal catalysts (Cr, Fe, Pt), useful rate of conversion may be attained at 70,000 atm pressure and 2000K. The tiny diamonds obtained in this way are mostly used in industry. Larger gem quality diamonds are not economical in comparison to natural diamonds.

Diamond is a transparent hard solid with high refractive index while graphite is a highly reflecting black solid that marks paper (*grapho* = to write). Diamond has the highest thermal conductivity and the lowest known coefficient of thermal expansion (1.06×10^{-6} at room temperature) and molar entropy (2.4 J mol^{-1}K^{-1}) for any element. Some physical properties of the two forms are given in Table 21.1.

TABLE 21.1

Some physical properties of diamond and graphite

	Diamond	**Graphite**
M.P. (K)	~ 4000 (125 kbar)	~ 4000 (9 kbar)
Hardness	10	< 1
Density/g cm^{-3}	3.51	2.2 (petroleum coke) 1.48 (activated C)
Refractive Index (546 nm)	2.41	2.15
ρ (ohm cm)	> 10^{14}	~ 10^{-4}

The chemical reactivity of diamond is much lower than other allotropes of C.

Fullerenes

Introduction

Fullerenes constitute a new series of allotropes of carbon first characterized in 1985 in the cluster C_{60}. There are now several such hollow closed-cage (polyhedral) cluster molecules, C_n (*n* only even in the range 30-600). All of them have structures based on polyhedra formed by fusing pentagons and hexagons (Fig. 21.3), very much comparable to geodesic domes used in architecture. Accordingly, these molecular clusters have been collectively called *fullerenes* or buckminsterfullerenes after architect R. Buckministerfuller, the inventor of geodesic dome.

Preparation

Fullerene-60 or C_{60} was first prepared in 1985 by laser vaporization of graphite (~ 10,000°C) followed by sweeping of the carbon atoms by a blast of high pressure helium gas and rapid coling in a vacuum chamber (Richard Smalley, Rice University, Texas and Harry Kroto, University of Sussex, U. K.; Nobel Prize 1996). Mass spectrometric study revealed that the most abundant and stable species formed in the above experiment was C_{60}, followed by C_{70}. Three years later (1990), W. Kratschmer (Heidelberg) and Donald Huffman (Arizona) showed that such molecular clusters are readily formed in the soot obtained by striking an arc between graphite electrodes (~ 3500°C) at a low pressure of helium gas. Red solutions of the soot in benzene or toluene can be separated chromatographically on alumina giving C_{60} and C_{70} in an approximate ratio of 5 : 1. Pure samples of C_{60} and C_{70} in gram quantities are now available commercially.

Abundance

The C_{60} and C_{70} fullerenes have also been detected as natural deposits in several anthracite belts in Australia, Russia, USA, Canada and New Zealand. These are also likely to be formed in red giant stars, that is, large aged stars which have exhausted their reserves of hydrogen in the core. Fusion of helium nuclei in the core of such stars may produce carbon. Anteras (*Jyestha* nakshatra) is a red giant star.

Many other easy methods of preparing C_{60} and C_{70} fullerenes are now available, for example, pyrolysis of naphthalene vapour in argon (1000°C).

Properties

Thin films of C_{60} are mustard-coloured but in bulk it appears dark brown. Films of C_{70} are red-brown, in bulk grey-black. Solutions of C_{60} have magenta colours while the solutions of C_{70} are dull red. Both the solids have high melting points and they dissolve in organic solvents only slowly, indicating close packing in the crystals.

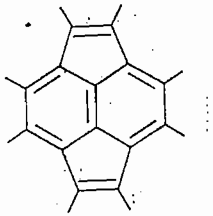
The C-13 nmr spectrum of C_{60} shows a single peak (142.68 pm), suggesting uniform environment for all 60 carbon atoms. However, there are two different C—C bond lengths ~140 pm and ~150 pm (see Fig. 21-1).

Structure and Bonding

Each carbon of a fullerene molecule may be supposed to be sp^2 hybridized, forming three σ bonds to three other carbon atoms. The remaining electron at each carbon is delocalized into a system of molecular orbitals that imparts some aromatic character to the whole molecule. According to one suggested mechanism, the carbon atoms first add in pentagonal and hexagonal patterns which gradually curl under appropriate conditions to form the cage-like structure. To close into a spheroid, a fullerene must have exactly 12 five-membered faces, but the number of six membered faces can vary widely $\left(\frac{1}{2}n-10\right)$. C_{60} has 12 five-membered faced and 20 hexagonal faces; C_{70} has 25 hexaganol faces. In C_{60}, every carbon atom is at the juncture of two six-membered rings and one five membered ring — the six membered rings each containing three double bonds. Thus it has the structure of a truncated icosahedron. The important unit in the structure of C_{60} is the following fragment (21-I). There are two geometrically distinct types of C—C bonds :

(i) those at an edge shared between two fused hexagons (6 : 6 rings) — the bond length is 139.1 ± 1.8 pm. This is also the distance *between* pentagons.

(ii) those at an edge between a pentagon and a hexagon or the bonds *within* a given pentagon are somewhat longer—145.5 ± 1.2 pm.



21-I

Crystals of C_{60} grown from benzene solutions are contaminated with solvent molecules. Pure C_{60} crystals may be grown by subliming the solvent molecules. The unit cell of solid C_{60} consists of a face-centered cubic array of C_{60} molecules in close packing. The molecules can rotate freely at their lattice sites by the thermal energy available at room temperature and can be considered to be spherical. The contact distance obtained from powder X-ray is 1002 pm, which is larger than the diameter of the molecules, 706 pm; the difference of 296 pm may be considered as the van der waals distance between the molecules.

The newly developed chemistry of fullerenes has been discussed in section 21.3.12.

[Sec. 21.2.1
Allotropic forms]

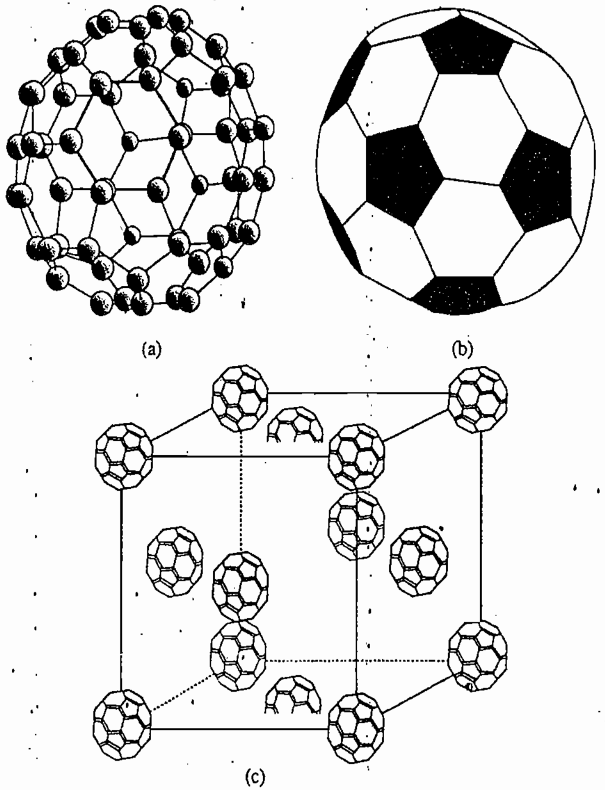


Fig. 21.3 : (a) Structure of C_{60} fullerene; (b) a soccer ball and (c) Face-centered cubic lattice of C_{60}.

Silicon, Germanium, Tin and Lead

Silicon and Germanium crystallize in the diamond form. Si-Si distance in the solid is 235 pm. At very high pressure, a denser distorted form may be produced, but the Si-Si distance remains practically unchanged.

Q. 21.1 *Why silicon is not expected to form an allotrope with graphite like structure?*
[**Hint :** Consider feasibility of *p-p* π-bond]

Tin has two crystalline allotropic forms. The common form at room temperature is the white metallic β-tin having a distorted tetragonal closepacked lattice (density at 20° C = 7.3 g cm^{-3}). The low temperature α-Tin or grey-Sn has a much lower density (5:75 at 20° C).

$$\underset{\text{grey}}{\alpha\text{-Sn}} \xrightleftharpoons{13.2^\circ\text{C}} \underset{\text{white}}{\beta\text{-Sn}}$$

A brittle γ-form is also formed above 161°C.

In earlier days, tin-roofs in winter countries ruptured owing to transition from one form to another with change in density. This was known as *tin-plague*.

Lead exists only in a cubic close packed (FCC) metallic lattice (density 11.34 g cm^{-3}).

21.2.2 Physical Properties

Some important atomic and physical properties of the Group 14(IV) elements are summarized in Table 21.2. The trend in properties may be largely understood from the electron configurations. The effect of inadequate shielding by *d* and *f* electrons is prominent in Ge and Pb.

TABLE 21.2

Some atomic and physical properties of Group 14 elements

		C	Si	Ge	Sn	Pb
Atomic Number		6	14	32	50	82
Electron configuration		[He]$2s^2 2p^2$	[Ne]$3s^2 3p^2$	[Ar]$3d^{10} 4s^2 4p^2$	[Kr]$4d^{10} 5s^2 5p^2$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
Atomic weight		12.011	28.085	72.59	118.69	207.2
Electronegativity (Pauling)		2.5	1.8-1.9	1.8-1.9 (2.0)	1.8-1.9 (2.0)	1.9
Ionization Energy (kJ mol^{-1})	I	1086	786.1	761.5	708.5	715.5
	II	2352	1576.5	1537.0	1411.5	1450.0
	III	4619	3228	3302	2942	3081
	IV	6221	4354	4409	3929	4082
Covalent radius (A°)$^{(a)}$		0.77	1.18	1.22	1.41	1.54
M.P. (°C)		4100$^{(b)}$	1420	94.5	232	327
B.P. (°C)			3280	2850	2623	1751
E° (V) : M^{2+}/M		—	—	—	− 0.14	− 0.13
M^{4+}/M^{2+} $^{(c)}$		—	—	—	+ 0.15	+ 1.7

(*a*) : tetrahedral; (*b*) : = see table 21.1; (*c*) : value refers to $\alpha - PbO_2 - Pb^{2+}$

> Q. 21.2 *The difference in covalent radius between (i) Si and Ge and (ii) Sn and Pb are comparatively smaller than the difference in size between C and Si or Ge and Sn. Comment.*
>
> [**Hint** : Size increase (≈ 50%) from C to Si corresponds to increase in principal quantum number from 2 to 3. The poor shielding characteristics of the less penetrating 3*d* electrons results in much smaller increase in size (0.05 A°; less than 5%) between Si and Ge. The same effect is reinforced by the 4*f* electrons in Pb. The *ns* and *np* electrons in both Ge and Sn are outside $(n-1)d^{10}$ electron configurations. Hence the change in covalent radius between the two elements is more normal (~ 15% increase).]

The melting point of carbon is very high, indicative of the high C—C bond energy and the compact lattice in diamond. Si and Ge also have a diamond type lattice but larger size and weaker bond energy result in lower melting point. Weak metallic bonding is first apparent in tin which shows a sharp drop in melting point. Lead is also a low melting metal. It appears that these two elements do not use all four valence electrons in metallic bonding.

The electronegativities of the elements remain almost unchanged from Si to Pb, again reflecting the effect of poor shielding by *d* and *f* electrons. In fact, the electronegativity of germanium is perhaps slightly greater than that of Si or Sn. Consistent with this, only germanium halides are reduced to hydride by Zn/HCl. Again, SiH_4 is rapidly hydrolysed by water in presence of dilute alkali but GeH_4 or SnH_4 are not. This may be considered to arise from low (or opposite?) polarity of the Ge—H or Sn—H bonds.

[Sec. 21.2.2 Physical Properties]

Band gap

The variation of electrical conductivity among the elements may be understood from the outlines of the band theory of metals (Ch. 7). In an aggregate of *n* atoms with four orbitals and four electrons each, 2*n* bonding orbitals constitute a filled band above which lies an empty band of 2*n* antibonding orbitals. The energy gap between these two bands is large in diamond (> 500 kJ mol^{-1}) and electrons cannot be thermally promoted from the filled to the empty band. Hence diamond (pure) is an insulator. The energy gaps (Δ*E*) in Si, Ge and Sn are 108, 64 and 7.7(α) kJ mol^{-1} respectively, making them good semiconductors. Impurities like Gr III or Gr V elements give rise to *p*-type or *n*-type semiconductors respectively (Ch. 7, section 7.4). A *p-n* junction behaves like a diode while an *n-p-n* junction forms the basis of a transistor.

> **Semiconductors and Transistors**
>
> Modern developments in semiconductor technology began in the 1950s with the introduction of germanium transistors. It was then easier to obtain very pure germanium than very pure silicon. Methods to prepare ultrapure silicon were developed in the late 1960s and silicon transistors are now widely used in view of their superior quality. Other semiconducting materials have also been developed and introduced, mainly from the elements in the neighbouring groups III(13) and V(15).
>
> In chapter 7, we found that semiconductor behaviour depends on the small energy gap between the highest occupied energylevels (valence band) and the lowest unoccupied energy levels i.e., conduction band. With increase in temperature, electrons vacate the valence band and occupy the conduction band. As the energy gap (say Δ*E*) decreases, conductivity increases exponentially with temperature (*T*) as shown by the relation
>
> $$\delta = \delta_o e^{-\Delta E/2kT}$$
>
> where k = Boltzmann constant, δ_o = a parameter characterizing the material. The magnitudes of Δ*E* for C to Sn have been mentioned above. We observe that the band gap decreases sharply from carbon (diamond) to silicon to tin. Diamond is an insulator. Si (pure) is also an insulator at room temperature, resistivity ~ 40 ohm cm at 25°C. If the Si is doped with an element of Group V(15) like P, As or Sb, an *n*-type semiconductor is obtained (section 7.4). Doping with an element of Group III(13) like B, Al or Ga produces a *p*-type semiconductor.
>
> Combination of an *n*-type sample of Si with one of *p*-type gives rise to an *n-p* junction; electrons can flow from *n* to *p* and holes from *p* to *n* and the current passes more easily in one direction than the other. It can act as a diode. Two *n*-type Si separated by a weakly *p*-type Si produces an *n-p-n* junction or a transistor.
>
> Extremely small stable single crystal transistors may be prepared by exposing selected areas on a single crystal *n*-type Si wafer to the vapour of a Group III element when the impurity atoms diffuse to form a layer of *p*-type Si. These areas are then covered with a protective layer of SiO_2 (heating in O_2) which is toughened by exposure to UV radiation. At other desirable places, the layer is etched with HF and exposed to the vapour of a Group V element. In this manner, a patterened deposit of *n-p-n* type Si is obtained which is again covered with a protective layer of SiO_2. Metals are deposited at suitable places (after re-etching) to connect the *n* and *p*-regions into an integrated circuit.
>
> Some of the most widely used semiconductors are now prepared by combining elements from Groups III and V (e.g., GaAs) or II and VI (e.g., CdS). The band gap decreases when heavier atoms are incorporated, e.g.
>
> | | BP | GaP | GaAs | InAs |
> |---|---|---|---|---|
> | Δ*E* (kJ mol^{-1}) | 193 | 218 | 137 | 34.7 |
>
> (Contd. to next page)

GaAs has an extra advantage — its carrier velocity is higher than with silicon. It is the effective average velocity with which an electron moves through the lattice. This is greatly influenced by collision with impurity atoms or with a normal atom which is away from its usual lattice site due to vibrational excitation. This superiority makes GaAs a prospective semiconductor in logic chips. Methods are being developed to obtain highly pure varieties of GaAs (and other semiconductors) by *chemical vapour deposition* (CVD) technique. Volatile compounds like $Ga(CH_3)_3$ and AsH_3 are carried in a stream of H_2 on to a heated substrate where the desired semiconductor compound is deposited, generally as a single crystal film.

The use of GaAs in light emitting diode (LED) is also related to its semiconductor properties. Unlike Si, GaAs is a *direct-gap* semiconductor in which the electrons from the top of the valance band may be excited with photons to the bottom of the conduction band without any change in momentum of the electron. The probability of the reverse transition during deexcitation (i.e., from conduction band to valence band) is also correspondingly higher, with the emission of photons.* In silicon, such radiative transition cannot occur without a change in the linear momentum of the electron. This involves coupling with the linear momentum of the nucleus - thermal motion of the atom is thereby stimulated, making the substance hot.

21.2.3 Chemical Reactivity

Chemical reactivity of the elements of Group 14(IV) increases down the group. E^0 values for Pb(II) — Pb or Sn(II) — Sn are less than that of hydrogen, but the metals cannot liberate hydrogen from acids owing to overpotential (Chapter 9).

Graphite alone can form many compounds by taking up other atoms or ions between the layers whereby the interlayer separation increases. Such intercalation compounds of graphite will be discussed separately. The action of air (oxygen), water, acids and alkalis on the elements are summarized below.

Air

Graphite burns above 700°C (CO).

Diamond burns above 900°C (CO). (See Ellingham diagram, Section 15.2.3)

Si, Ge, Sn burn on strong heating. (At 1400°C, Si also forms SiN and Si_3N_4).

Finely divided lead powder is pyrophoric (combines highly exothermically with oxygen) but the surface is practically inactivated by a thin protective layer of oxide (or chloride, sulphate etc.) PbO is formed above 600° C.

Water

No action in cold by any element.

White hot coke decomposes steam ($CO + H_2$).

Sn reacts with steam to give $SnO_2 + H_2$.

Dil. acids

C, Si, Ge — no action. Sn, Pb dissolve in dilute HNO_3 [$M(NO_3)_2$].

Pb also dissolves slowly in dil. HCl ($PbCl_2$, sparingly soluble).

Pb also dissolves in organic acids like acetic acid, (formic/citric/oxalic) in presence of air.

---

* Doping with phosphorus shifts the transition to red.

Conc. Acids

Diamond is unaffected.

Graphite is oxidized by hot concentrated HNO_3 to mellitic acid, $C_6(COOH)_6$. Hot concentrated HF-HNO_3 oxidizes graphite to graphite oxide.

Silicon reacts with hot concentrated HF-HNO_3 mixture ($SiO_2 + SiF_4$).

Ge dissolves slowly in hot concentrated HNO_3 and H_2SO_4.

Sn liberates H_2 from hot concentrated HCl ($SnCl_2$). Hot concentrated H_2SO_4 gives $SnSO_4 + SO_2$.

Pb does not dissolve in concentrated HCl or H_2SO_4 (insoluble coating).

Aqueous Alkali

Carbon remains unaffected.

Silicon dissolves, slowly in cold and rapidly when heated :

$$Si + 4OH^- = SiO_4^{4-} + 2H_2.$$

Germanium is not attacked.

Sn and Pb form soluble hydroxo compounds with hot alkali solution :

$$Sn + 2KOH + 4H_2O \longrightarrow K_2[Sn(OH)_6] + 2H_2.$$

Halogens

Diamond does not react.

Graphite reacts with F_2 (500°C) forming graphitic fluoride, $(CF)_n$.

Si, Ge form SiX_4, GeX_4, with all halogens on heating (F_2 at room temperature).

Sn reacts with Cl_2/Br_2 in cold, with F_2/I_2 on heating (SnX_4).

Pb gives PbF_2 with F_2 in cold; $PbCl_2$ with Cl_2 on heating.

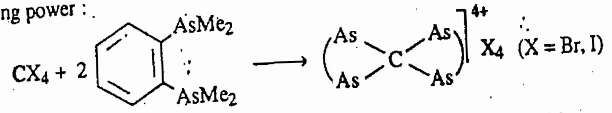
Group Trend

The general trends in the chemistry of the elements of this group follow the typical pattern for *p*-block elements, as observed in the boron group. Starting with the nonmetals carbon and silicon, we arrive, via germanium and tin, at lead which is mostly metallic in character (oxides are amphoteric, though). The oxidation state IV is common for the elements, though tin and lead have significant chemistry in oxidation state II (inert pair effect). The chemistry of carbon is unique in many respect. The main differences in the chemistry of carbon with those of other elements in the group may be attributed to the same general features applicable to the first member in any group in the *p*-block : (i) small size, (ii) high electronegativity, (iii) restriction of valence shell to octet, (iv) strong tendency to *p-p* π-bonding etc. In addition, carbon has a high value for C—C bond energy (see later). Carbon and silicon (like B and Al in Gr. III) have strong affinities for oxygen and fluorine, forming a large number of compounds like carbonates, silicates, fluorosilicates (like borates, aluminates, fluoroborates etc. by B, Al) etc. As such they may be called strong *oxophiles* and *fluorophiles* and considered as "hard" atoms. Lead, on the other hand (like Tl in Gr III) has greater affinity for iodide, sulfide etc. soft anions.

Cationic compounds

The high values of ionization energies suggest that the formation of M^{4+} ions would be rather unlikely for the elements except marginally for Sn and Pb. Also, such ions, if formed, would be strongly polarizing. As such, the major portion of the chemistry of these elements involve covalence. The existence of Sn^{4+} or Pb^{4+} in even

SnF_4/PbF_4 or SnO_2/PbO_2 is not established beyond doubt. As observed in Group 13(IIIA), cations containing carbon and silicon may be obtained in combination with large complexing ligands which increase the effective size of the ion and reduce the polarizing power :



SiI_4 + 6 dmf $\longrightarrow$ $[Si(dmf)_6]^{4+}I_4$. (dmf = dimethyl formamide)

SiI_4 + 6 o-py $\longrightarrow$ $[Si(o\text{-}py)_6]^{4+}I_4$. (o-py = pyridine N-oxide)

Other examples are given in section 21.3.11.

In spite of their ns^2np^2 electron configuration, the lighter elements C and Si do not have any stable bivalent compound under ordinary conditions. Though greater amount of energy is required to bring the elements to the higher valence state (unpairing, promotion, hybridization etc.), the energy released in the formation of two additional bonds more than compensates this. Thus, the enthalpies of formation (298K) of CH_2 and CH_4 are about + 343 and –75 kJ mol^{-1}. However, bivalent species are formed as transient intermediates like the carbene radical (: CH_2) or at high temperatures :

$$CH_2N_2 \text{ (diazomethane)} \longrightarrow \,:CH_2 + N_2 ; \quad Si + SiF_4 \xrightarrow{1150°C} SiF_2$$

For the heavier elements, bond energy values decrease significantly so that the bivalent state becomes comparatively more stable even at room temperature. Very weak M—X bond energy makes MX_2 the only stable species in certain cases, e.g., PbI_2.

$$GeBr_4 + Ge \longrightarrow GeBr_2 \text{ (heat)}$$

$$Sn + I_2 \longrightarrow SnI_2 \text{ (heat in } 2M \text{ HCl)}$$

$$Sn + HX(g) \longrightarrow SnX_2 \text{ (heat; } X = F, Cl)$$

$$Pb + I_2 \longrightarrow PbI_2 \text{ (heat).}$$

$PbCl_4$ decomposes at 50°C to $PbCl_2 + Cl_2$. $PbBr_4$ and PbI_4 do not exist [Br^- and I^- are oxidized by Pb (IV)].

TABLE 21.3

Average bond energies (kJ mol^{-1}; the values are approximate*)

Bond type	M = C	Si	Ge	Sn	Pb
M—M	350	210-250	190-210	105-145	—
M—H	416	323	285	251	205
M—F	485	590	465	—	—
M—Cl	327	400	350	320	244
M—Br	280	310	280	270	—
M—O	336	368	—	—	—

C = C 611, C ≡ C 841.

[Sec. 21.2.3
Group Trend]

The following general observations in Table 21.3 would be helpful.

(i) The energy of M—M bond decreases from C to Sn (sharply from C to Si).

(ii) Strengths of M—H bonds are greater than those of M-M bonds.

(iii) M—H bond strength decreases regularly from C to Sn, as expected from increasingly poor overlap.

(iv) Strengths of bonds to F, Cl, Br or O first increase from C to Si, then fall gradually. This may be due to greater ionic-covalent resonance among the bonds involving Si (greater electronegativity differences) and/or p-d π-bonding to the Si 3d orbitals. From Ge onward, poorer overlap becomes the main reason for decrease in bond strength.

In the covalent gaseous dihalides of tin and lead, the X—M—X bond angles are close to 90° (in $SnCl_2$ it is 95°) as expected for bonding through mainly p-orbitals on M. But the carbene radical has a linear H-C-H arrangement in the ground state, corresponding to sp hybridization of the C-orbitals; this leaves the two unpaired electrons in the two p-orbitals excluded from hybridization. This state is a triplet state (Ch. 3). There exists a singlet state with slightly higher energy in which the electrons are spin-paired and the H—C—H bond angle is 102.4°. However, the stability sequence between singlet and triplet states changes in CF_2 which is diamagnetic with an F-C-F angle of 105°. The F-Si-F angle in SiF_2 is also 102°.

The organometallic compounds of tin and lead appear exception to the inert-pair effect as they almost entirely involve Sn (IV) and Pb (IV).

The explanation of inert pair effect based on covalent bond energy does not apply to ionic compounds. One may say that the extra lattice energy for MX_4 type compounds may not be sufficient to overcome the additional ionization energy required for the process $M^{2+} - 2e = M^{4+}$. However, this is merely a hypothetical case since no simple M^{4+} ions are known with certainty where M is an element of the carbon group. Also there are no solid compounds of C, Si, Ge or Sn in which confirmed M^{2+} ions are present. Only PbF_2 (rutile structure) may be said to be a typical ionic solid. The hydrated Sn^{2+} and Pb^{2+} ions in aqueous solution (e.g. in solutions of respective perchlorates) also undergo extensive and complex hydrolysis forming various hydroxo species, e.g., $[Sn(OH)]^+$, $[Sn_2(OH)_2]^{2+}$, $[Pb(OH)]^+$, $[Pb_3(OH)_4]^{2+}$ etc. (all aquated).

Oxidation state III

There are a few compounds which reflect formal oxidation states between II and IV, but these are generally compounds of mixed valence (like $GaCl_2$). Thus Sn_3F_8 actually consists of $Sn^{IV}F_6$ (oct) and $Sn^{II}F_3$ (pyramidal) units joined by sharing F atoms. However, there are also a few compounds in oxidation state III like

$M[CH(SiMe_3)_2]_3$ (M = Si, Ge, Sn) $M[N(SiMe_3)_2]_3$ (M = Ge, Sn).

Species on the left are rather unstable (half-life ~ 10 min) while others may be stable upto 12 months. The bulky ligands appear to hinder further attack at the radicals.

Catenating power

The unique catenating power of carbon may also be attributed to the intrinsic strength of the C—C bond. This is also greater than the C—O bond strength, making the C—C bond stable towards oxidation. M—M bond strength decreases sharply for M = Si and then further to Sn. These bonds are also considerably weaker than respective M—O bonds; as an example, the Si—O bond is nearly 1.5 times stronger than the Si—Si bond (The S—O bond energy, ≡ 330 kJ mol^{-1}, is similarly stronger than the S—S bond energy, ≡ 226 kJ mol^{-1}). If favoured kinetically or supplied with necessary energy of activation , an Si—Si bond would be exothermically converted to an Si—O

---

* Values vary widely (50 – 100 kJ mol^{-1}) depending upon the compound under consideration.

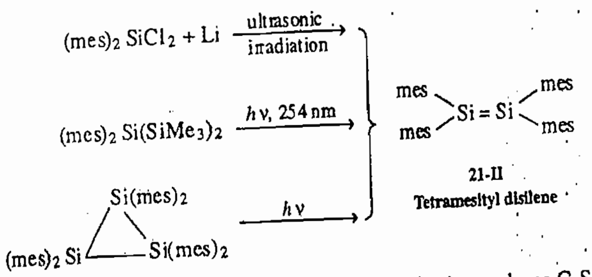
bond. The usual limits in the number of M—M bonds occurring in catenated hydrides and halides of the remaining Gr IV elements are : 11-12 for Si, 9-10 for Ge and 2 for Sn. These figures also result from kinetic rather than thermodynamic stability since even Si_2H_6 is thermodynamically unstable towards decomposition as

$$Si_2H_6\,(g) \longrightarrow SiH_4 + H_2\,(g) + Si\,(s); \quad \Delta G^\circ = -70 \text{ kJ mol}^{-1}.$$

Si=Si and Si=C

A large number of compounds are known in which carbon forms π-bonds with carbon itself or with nitrogen and oxygen. Some kinetic factors must also operate behind the "stability" of such compounds, for ethene is actually thermodynamically unstable relative to the singly bonded polymeric form in polythene. Such *p-p* π-bonds are not favoured for 3*p* (and higher) orbitals due to increasingly poorer overlap (Ch. 16). Thus CO_2 and SiO_2 are structurally completely different species and compounds containing Si = Si or Si = C are not common. Only a few compounds involving such *p-p* π-bonds to Si are now known.

Silenes have been isolated with bulky substituents on the Si atom like the mesityl (2, 4, 6- trimethylphenyl : abbreviated as mes) :



21-II
Tetramesityl disilene

Yellow solid; thermally stable (m.p. 176°C) but air-sensitive. Si—Si distance = 2.16 A° (9% shorter than Si—Si single bond distance). For reactions see section 21.3.

Compounds with Si = C having a planar $C_2Si = CSi_2$ skeleton are also known, e.g., $Me_2Si = C(SiMe_3)(SiMe\ t\text{-}Bu_2)$. Si = N is present in $t\text{-}Bu_2Si = NSi\ t\text{-}Bu_3$. Compounds with Si = P, Si ≡ N have also been reported.

Germenes, e.g., $R_2HCGe = GeCHR_2$ ($R = SiMe_3$) are very unstable.

Multiple bonding of the *dπ-pπ* type are readily formed by silicon using its vacant 3*d* orbital and a filled *p*-orbital of matching π-symmetry, e.g., those on N, O or halogens. Theoretical calculations have indicated that the normally large and diffuse valence shell 3*d* orbitals shrink favourably in presence of electronegative atoms and provide better *d-p* overlap. Some examples of such π-overlap are given below :

(i) $(H_3Si)_3N$ (trisilylamine) is planar while $(H_3C)_3N$ is pyramidal. This is consistent with dative pi-bonding from nitrogen to Si. The N-Si σ-bonds may be supposed to be formed by using sp^2 hybrid orbitals on N (say p_x and p_y, the nuclei being in the XY plane). The lone pair of nitrogen would then occupy the remaining *p* orbital (p_z in this case), which has the right symmetry to enter π-interaction with the vacant 3*d* orbital on Si. The additional bond strength derived from such *p-d* π-bonding now dictates the geometry of the N-Si skeleton. Such delocalization of the nitrogen lone pair (of electrons) would be much reduced in a pyramidal conformation. Carbon does not possess any such low energy vacant orbital suitable for π-bonding and the geometry is determined by σ-bonding alone, making $(CH_3)_3N$ and similar compounds pyramidal. The *p-d* π-bonding also makes trisilylamine a weaker base ; it does not form an adduct with BH_3. Introduction of one or two CH_3 group enhances base character, $MeN(SiH_3)_2$ and $Me_2N(SiH_3)$ forming weak adducts. The weak basic character of $(SiH_3)_3N$ in comparison to $(CH_3)_3N$ is reflected in the fact that instead of forming trisilylammonium salts, it is cleaved by acids :

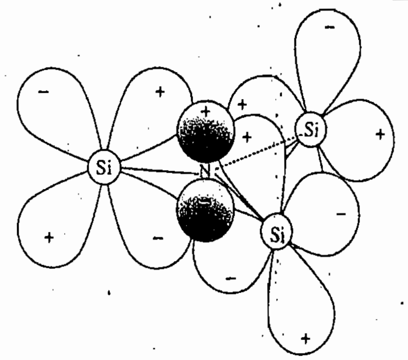


Fig. 21.4

π-overlap in $(SiH_3)_3N$.

$$(CH_3)_3N + HCl \longrightarrow (CH_3)_3\dot{N}H^+Cl^-$$

$$(SiH_3)_3N + 4HCl \longrightarrow NH_4Cl + SiH_3Cl.$$

It has been argued that the planarity of silylamines may also result from electrostatic repulsions between SiH_3 groups. Theoretical calculations, however, indicate small but singificant *p-d* π-bonding in trisilylamine.

Q. 21.3 *$(H_3Si)_3P$ is pyramidal. Comment.*

Hint : P is an element in the third row. The larger 3*p* orbitals appear to be less able to participate in efficient *p-d* π-bonding. Also, lower electronegativity of P is inadequate to induce sufficient +ve charge on Si for significant *d*-orbital contraction.

(ii) Unlike their carbon analogs, H_3SiNCO has a linear Si-N-C-O skeleton in the vapour phase and $(H_3Si)_2NH$ is planar. Here also, the gain in energy by additional *p-d* π-bonding between N and Si may be held responsible for a linear $H_3Si\text{-}N = C = O$ arrangement (*sp* hybridized N atom; one *p*-orbital makes a π-bond with C while the third *p*-orbital with a pair of electrons back-bonds to Si. In crystalline solid H_3SiNCO, packing of the molecules leads to some bending, e.g., ∠Si-N-C = 158° and ∠N-C-O = 176°.

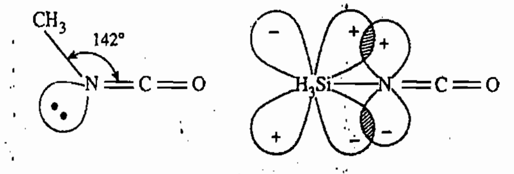


Fig. 21.5

Comparison of the molecular structures of CH_3NCO and SiH_3NCO.

Q. 21.4 *Do you expect H_3GeNCO to have a linear Ge—N—C skeleton?*

Hint : There is no effective π-bonding between N and Ge.

(iii) The bond angles around oxygen in disilyl ethers, $R_3Si\text{-}O\text{-}SiR_3$ are much larger (140°-180°) in comparison to those in $R_3C\text{-}O\text{-}CR_3$. In $(CH_3)_2O$, the bond angle around O is ≅111°, consistent with sp^3 hybridization of the O-orbitals. But in $(SiH_3)_2O$, the angle is 144°. π-bonding between filled oxygen *p*-orbitals and empty silicon *d*-orbitals is favoured by a wider bond angle; in the limit the angle may open to 180° ($R = C_6H_5$). Steric repulsion from the bulky R-groups is also likely to contribute to such bond opening.

(iv) Similar O-Si *p-d* π-bonding is also operative in various other compounds. For example, silanols R_3SiOH are stronger acids than their carbon analogues.

Q. 21.5 *Methyl isothiocyanate, CH_3NCS has a bent C-N-C skeleton while H_3SiNCS has a linear Si-N-C skeleton. Comment.*

Q. 21.6 *Contrary to $(CH_3)_2O$, $(SiH_3)_2O$ does not form adduct with BF_3.*

Hint. O-Si *p-d* π-bonding diminishes the availability of lone pairs of electrons on O.

Hypercarbon compounds

There are numerous situations in which carbon attains coordination numbers greater than four — the bridge carbon atoms in $Al_2(CH_3)_6$ being a ready example (also the alkyl lithiums and carboranes). Such hyper-coordinated carbon compounds may be abbreviated as hypercarbon compounds, though they should not be treated as hypervalent compounds of carbon. The valence of carbon is as usual four in these compounds and limited to four valence orbitals but they may be linked to more atoms. The variety of compounds now known to contain such hypercarbon atoms are carbocations, organometallics, carboranes, carbides and other cluster compounds. In fact, cubic coordination of C in antifluorite Be_2C has been known since 1948. The presence of 6-coordinate carbon in various carboranes was estabilished by Lipscomb in 1964. Albano and others confirmed the presence of 8-coordinated carbon in $[Co_8C(CO)_{18}]^{2-}$ (Fig. 21.6). Besides the examples already cited in previous chapters, we shall encounter more in connection with carbides and carbonyl complexes.

The bonding in such systems may be conveniently described in terms of three center two electron bonds (and other multicenter approaches) together with classical two-center bonds.

Such multicenter σ-bonding may also be involved in compounds containing carbon atoms with four or even fewer number of neighbours and they may be treated at par. Simple molecular orbital treatment also proves quite useful in some of the more symmetrical systems. Thus, the hypercarbon compounds are not remote from mainstream carbon chemistry and their sutudy helps us greatly to understand the mechanisms of many reactions in which carbon atoms become hyper-coordinated in intermediates or transition states.

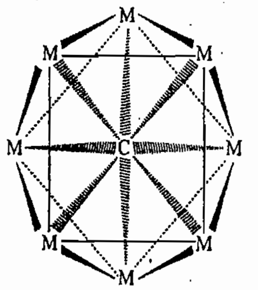
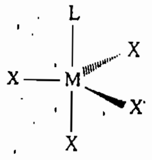


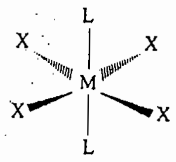
Fig. 21.6
Metal Carbide core in $[Co_8C(CO)_{18}]^{2-}$.

Stereochemistry

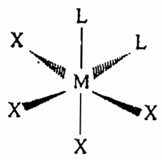
The covalency maximum for carbon is normally four. The compounds are tetrahedral, which is also the geometry of the compounds formed by other elements in the oxidation state IV. However, the later elements in the group may increase their coordination numbers to five and six. Particularly the tetrahalides of these elements add ligands (= L) to form trigonal bipyramidal $MX_4.L$ and octahedral $MX_4.2L$ complexes. Bonding in such complexes may be supposed to involve *d* orbitals on the central atom, but the bonding may also be explained on the basis of three-center four electron bonds. Thus, in a trigonal bipyramid arrangement, the equatorial bonds may be supposed to arise from sp^2 hybrid orbitals on the central atom, while the axial bonds may be described as three center four electron bonds. In an octahedral complex, all six ligands may be treated by such three-center four electron bonds.



21-III (a)
Examples : $GeF_4.NMe_3$

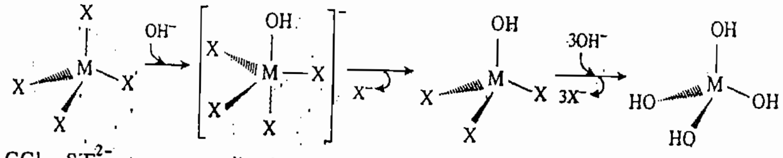


21-III (b)
$SiCl_4.2PMe_3$ (trans)
$GeCl_4.2py$ (trans)



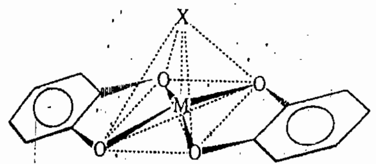
21-III (c)
$SnCl_4.2dmf$ (cis)

Ready hydrolysis of the tetrahalides MX_4 (M = Si, Ge, Sn, Pb) may be considered to proceed via a 5-coordinate intermediate formed by an associative mechanism :

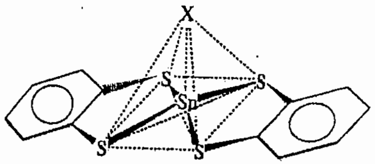


CCl_4, SiF_6^{2-} etc. are coordinatively saturated and formation of such an intermediate presents a high steric activation energy barrier. So these compounds are actually kinetically stable toward hydrolysis (see halides).

In addition to the tbp arrangement in 5-coordinate complexes like MX_5^- or $Me_3SnCl(py)$, certain spiro compounds with O, S and N chelates may also have a square pyramid arrangement;



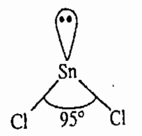
21-IV (a)
$[XSi(O_2C_6H_4)_2]^-$
$[XGe(O_2C_6O_4)_2]^-$



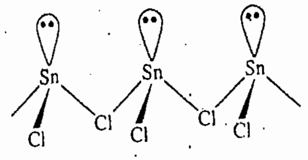
21-IV (b)
$[XSn(S_2C_6H_4)_2]^-$

5-coordination is also present in polymeric R_3SnX compounds of Sn with bridging X.

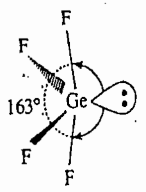
In the divalent state, the elements apparently do not involve the valence shell ns^2 electron pair in bonding. But in most M^{II} compounds, this electron pair seems to participate in bonding through *s-p* mixing, whereby this lone pair attains some *p*-character at the cost of some *s*-character (which implies spherical symmetry) and become directional in nature. Thus these electron pairs are not stereochemically inert. Some examples of Sn (II) compounds are given below.



$SnCl_2$ (gaseous monomer)
21-V



$SnCl_2$ (solid)
21-VI



GeF_2 (solid)
21-VII

The structures of gaseous monomeric dihalides MX_2 may be deduced from Raman spectra and electron diffraction. In crystals, a sterically active lone pair usually gives rise to irregular coordination about the central atom; the electrons presumably occupy apparently empty spaces within the coordination polyhedra formed by the ligands. In GeF_2, for example, the Ge atom has an approximately tbp environment with the lone pair in the equatorial plane and bridged by axial F atoms, resulting in a spiral chain structure. In SnS, each Sn has three S at approximately trigonal pyramidal arrangement and a lone pair in the fourth tetrahedral position; the SnS_3 pyramids are linked by S-atoms resulting in a cross-linked chain structure.

Such lone pairs of electrons naturally give rise to Lewis base character e.g.,

$$BX_3 + SnCl_3^- \longrightarrow [X_3B\ SnCl_3]^-$$

$$PtCl_4^{2-} + 2SnCl_3^- \longrightarrow cis\ [Cl_2Pt\ (SnCl_3)_2]^{2-} + 2Cl^-$$

SnO (blue-black form) and PbO consist of MO_5 units in pseudooctahedral arrangement, the sixth position being occupied by the lone pair.

Q. 21.7 *The ns^2 electron pairs in M (II) compounds (M = group IV element) are lone pairs rather than inert pairs - comment.*

Q. 21.8 *$SnCl_2.2H_2O$ readily loses one molecule of H_2O at 80°C. Explain.*

Hint : Pyramidal $SnCl_2.H_2O$ molecule with a lone pair on Sn. The other H_2O, hydrogen-bonded to the coordinated H_2O, is easily lost.

21.3 PRINCIPAL COMPOUNDS

A major portion of the compounds of carbon is conventionally treated under organic chemistry; they offer certain unique schemes of generalization based on functional groups. For obvious reasons, such compounds cannot be included in the present discussion. The graphitic form is also unique to carbon; consequently some compounds formed by graphite have no analogue among other members in the group. So we shall separately discuss the compounds of graphite. Similarly, silicates and silicones are exclusive to silicon and will be considered separately. The chemistry of fullerenes has been discussed at the end.

21.3.1 Compounds of Graphite

Since the successive layers of graphite are held at a comparatively large distance (335 pm) by weak van der walls forces, a wide variety of reactants can easily penetrate into the graphite lattice giving two principal types of compounds :

(a) Compounds in which the π-electron system of graphite is retained, with consequent retention of electrical conductivity (or even enhancement). The inter-layer separation increases by as much as 10 A°. Such compounds are also called *lamellar compounds* of graphite.

(b) Compounds in which the π-bonding is destroyed and graphite becomes non-conducting. The carbon layers lose planarity and get buckled.

(a) ***Electrically conducting lamellar compounds***

Such compounds are formed by insertion of various atoms (particularly the alkali metal atoms), molecules or ions (e.g., $FeCl_3$) between the graphite layers. They may be prepared by direct reaction, for example, of the alkali metal vapours with graphite at 300°C.

$$\underset{\text{(graphite)}}{C} + K \longrightarrow C_{60}K \xrightarrow{K} \underset{\text{deep blue}}{C_{48}K} \xrightarrow{K} \underset{\text{steel blue}}{C_{24}K} \xrightarrow{K} \underset{\text{bronze}}{C_8K}$$

Li gives C_6Li but Na does not appear to form a product in which the concentration of Na is higher than the stoichiometric ratio in $C_{64}Na$.

Such intercalation compounds may also be prepared electrochemically, i.e., by anodic oxidation or cathodic reduction of graphite in presence of the guest ions :

$$nC + M^+ + e \rightleftharpoons M^+ + C_n^-$$

$$nC + X^- - e \rightleftharpoons C_n^+ + X^-.$$

Solvents like tetrahydrofuran (THF) may also be incorporated within the layers, e.g., $K(THF)C_{24}$.

These lamellar compounds are highly coloured solids with high electrical conductivity. On strong heating, the alkali metal volatilizes unchanged out of the graphite lattice. They ignite in air and react explosively with water.

The C_8M compounds consist of alternate layers of carbon and M atoms, the M atoms being virtually sandwiched between the C_6 rings in the graphite planes, equidistant from the twelve C atoms above and below the M. The separation between two carbon layers in C_8K is 541 pm. The carbon layers are superimposed unlike those in graphite (where alternate layers are superimposed). But the metal atoms in successive layers do not necessarily lie directly over one another. In the lamellar compounds formed by transition metal halides, the graphite layers are stacked in the same alternate fashion as in pure graphite.

The high electrical conductivity of these compounds may arise from transfer of electron(s) from the metal to the π-orbitals of the carbon plane, where they are "free" to move under an electric field. Similarly, it was suggested that incorporated $FeCl_3$ gets partially reduced to $FeCl_2$ but recent Mössbauer study indicates that the Fe atom retains the same tetrahedral environment, as in Fe_2Cl_6 dimer.

(b) ***Graphite compounds which are electrically non-conducting***

Two principal types of compounds are known in this category : graphite oxide and graphite fluoride.

Graphite reacts with fluorine at 400-600°C, when a white compound approximating the composition $(CF)_n$ is obtained. X-ray study shows that in the product the layers of carbon atoms are much more widely separated (≃ 6.6 A° than in graphite. It has been suggested that the carbon atoms in the layer change to sp^3 hybridization adopting the boat or chair conformation and the fluorine atoms are covalently bonded to the carbon atoms. Destruction of the π-electron system makes the compound non-conducting.

"Graphite oxide" is obtained when strong aqueous oxidizing agents like fuming HNO_3 (or, $HNO_3 + KClO_3$) act on graphite. The brown mass on drying has a carbon : oxygen ratio of about 2 : 1, but a small amount of hydrogen is always present. An idealized stoichiometry is C_8O_2OH with the presence of carbonyl (= CO) or tertiary alcoholic $\left(\geq C-OH\right)$ groups.

21.3.2 Carbides and Silicides

Carbon forms binary compounds with most elements. The compounds with elements of similar or lower electronegativity are called carbides. These may be broadly classified as (i) ionic or salt-like carbides, (ii) metallic or interstitial carbides and (iii) molecular or covalent carbides.

1. ***Ionic or salt-like carbides*** : These are formed by the most electropositive metals (Gr I—III); they contain essentially C^{4-}, C_2^{2-} and C_3^{4-} anions, as suggested from their observed hydrolysis to methane, acetylene (ethyne) or methyl acetylene (propyne).

Ion	Example	Product of hydrolysis	General name
C^{4-} :	Na_4C, Be_2C, Al_4C_3	Methane	Methanide (methide)
C_2^{2-} :	Gr 1(IA) and 11(IB) ($M_2^IC_2$) Gr 2(IIA) and 4(IIB) ($M^{II}C_2$) Lanthanide [LnC_2; $Ln_4(C_2)_3$]	Acetylene	Acetylide (ethynide)
C_3^{4-} :	Mg_2C_3	Methylacetylene (propyne)	Allylide (from allylene)

All these compounds are hard high melting solids which may be prepared by direct synthesis. Some typical ionic carbides are described below :

Compound	Preparation	Physical Properties
Be_2C	$BeO + C$ (2000°C)	Brickred solid, antifluorite structure. Decomposes > 2100°C.
Al_4C_3	$Al + C$ (electric furnace)	Pale yellow solid, m.p. 2200°C; complex structure. Formulation as $4Al^{3+} + 3C^{4-}$ ion is questionable due to high charge separation.
CaC_2	$CaO + 3C$ (2200°C)	Colourless solid, m.p. 2300°C. Distorted NaCl structure, C_2 units aligned parallel to each other.

The acetylides may also be prepared by reacting acetylene with (i) the metal in liquid NH_3 (alkali metals) or (ii) the hot metal (500°C; alkaline earth metals). MgC_2 loses some carbon on heating to give Mg_2C_3.

The carbides undergo hydrolysis very exothermically.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2;\ \Delta H = -120 \text{ kJ mol}^{-1}.$$

Calcium carbide has extensive industrial use in producing acetylene for gas welding (at present, acetylene is largely obtained from petroleum). It also fixes nitrogen from air through the formation of calcium cyanamide :

$$CaC_2 + N_2 \xrightarrow{1200°C} CaNCN + C.$$

Calcium cyanamide is widely used as a fertilizer and in making urea and melamine.

Barium carbide absorbs N_2 from the atmosphere to form $Ba(CN)_2$.

The C—C distance in CaC_2 is ≅ 1.2 A°, almost equal to that in acetylene.

Carbides of lanthanoids (Y, Tb, Ce, Pr etc.) and some actinoids (Th, U) with formula MC_2 or $M_4(C_2)_3$ are different. They combine readily with oxygen in air and their hydrolysis produces a mixture of hydrocarbons (C_2H_4, C_2H_6, C_2H_2) and hydrogen. Unlike CaC_2 they are metallic conductors and the C—C distance in them is significantly longer (~ 1.3 A°). One suggested explanation is that they are acetylides of M(III); the metal provides three electrons of which two are utilized in the formation of C_2^{2-} ion while the third electron is transferred to the C_2^{2-} unit (mainly to its antibonding orbitals). This explains the longer bond length as well as the formation of H_2 and other reduced species like C_2H_4, C_2H_6 etc. Further extensively delocalized interaction among the cations and anions is also possible, giving rise to metallic properties.

2. ***Interstitial (metallic) carbides*** : Transition elements (and some of the lanthanides and actinides) form a large number of carbides with a wide range of stoichiometry. In these compounds, C atoms occupy holes or interstices in the metal lattice and as such the compounds retain many of the properties of metals like lustre and electrical conductance. However, the hardness and other properties demonstrate that these compounds contain strong metal carbon bonding. The name "interstitial" gives the erroneous impression that they are not true compounds. They may be prepared by reacting the metal (or oxide) with carbon (or hydrocarbon) at high temperature (≅2000°C).

The interstitial carbides are extremely hard (9-10 on Mohs scale) refractory solids (i.e., infusible or very high melting, 3000°C and above) which are generally unreactive (e.g., to hydrolysis). However, they react slowly with concentrated HF or HNO_3 or when heated in air above 1000°. Carbides of Cr, Mn, Fe, Co and Ni are more reactive; they are rapidly hydrolyzed by dilute acids and sometimes even by water (H_2 + mixture of hydrocarbons).

Empirically it has been found that simple compounds may be formed with C atoms in octahedral holes in the metal lattice only if $r_c/r_M < 0.59$ ...... (Häggs rule), where r_c = covalent radius of C (~ 0·77 A°) and r_M the metallic radius of the metal. Accordingly, when $r_M > 0.77/0.59$ i.e., 1.3A°, carbon atoms may be accomodated readily in the octahedral holes in the close-packed metal lattice. When the carbon atoms occupy all the octahedral holes, the stoichiometry corresponds to MC. Some metals (e.g., Cr, Mn, Fe, Co, Ni) with radii below 1.3A° cannot form MC type carbides — they produce carbides in various stoichiometry having rather complex structures : M_2C (V, Nb, Ta, W), Mn_5C_2, Fe_3C etc.

Many interstitial carbides are industrially very important; TaC and WC are used in making tips of cutting tools for lathes. Fe_3C (cementite) plays a crucial role in determining the quality of steel.

3. ***Covalent Carbides*** : Boron and silicon possess comparable size and electronegativity as of carbon and form very hard covalent carbides.

Boron carbide (B_4C) may be made by reducing B_2O_3 with carbon in an electric furnace. It is a very hard (> 9.5) infusible and inert compound. Its structure is somewhat unusual — boron occurs in the same icosahedral groups of 12 B atoms as in crystalline boron. These are packed with linear C_3 units in an NaCl-type array. It is used as an abrasive and as a shield from radiation.

Reaction of benzene and BCl_3 at 800°C produces a graphite-like boron carbide having stoichiometry close to BC_3.

Silicon carbide, SiC, is manufactured by heating quartz or sand with an excess of coke in an electric furnace (temp. > 2000°C) :

$$SiO_2 + 2C \longrightarrow Si + 2CO;\ Si + C \longrightarrow SiC.$$

It is an extremely hard (9.5 in Moh's scale) infusible solid, pale yellow to colourless when pure. Traces of iron (from sand) and other impurities often make the commercial products coloured — purple, black or green. SiC is unaffected by acids except phosphoric acid and is chemically quite inert. However, it is attacked by Cl_2 (100° C) and alkali (in presence of oxygen/air):

$$SiC + 2Cl_2 \longrightarrow SiCl_4 + C$$

$$SiC + 2NaOH + 2O_2 \longrightarrow Na_2SiO_3 + CO_2 + H_2O.$$

It consists of infinite three-dimensional arrays of Si and C atoms, each surrounded tetrahedrally by four atoms of the other kind. There may be three structural modifications based on diamond or wurtzite structure.

Silicon carbide is widely used as an abrasive under the name **carborundum** and is a *superrefractory*. Al_4C_3, $B_{12}C_3$, TaC and H_fC (m.p. > 3900°C) also belong to this category.

Silicides

Metals may be oxidized by silicon (700°–1200°C) to form silicides; these are also formed by heating a mixture of silicon and the metal oxides in an inert medium :

$$2Mg + Si = Mg_2Si$$

$$6MnO + 5Si = 2Mn_3Si + 3SiO_2.$$

Silicides of Groups I(1) and II(2) elements and of the *d*-elements are semiconductors. They are chemically unstable, being more or less readily decomposed by water and especially by acids.

The silicides of *d*-and *f*-elements generally have a complex stoichiometry like Mo_3Si, Mo_5Si_3, MoSi, $MoSi_2$ which often do not correspond to whole oxidation states of the elements. These silicides may be metallic or semiconductors. Silicides which contain much silicon are resistant to acids and oxidation at high temperature. $MoSi_2$, for example, is insoluble in all acids including aqua regia and HF. It is soluble only in a mixture of HF and HNO_3 and in a solution of alkalis. The melting points of most silicides of *d*- and *f*-elements are very high, for example

Ti_5Si_3 : 2120 V_5Si_3 : 2150 $MoSi_2$: 2050 (°C)

$MoSi_2$ can withstand attack by aggressive media even at temperatures 1600°C–1700°C and is used in electric furnaces. Many silicides are used in making refractory and acid-resistant alloys and as temperature-resistant semiconductors. Several silicides of *f*-elements are used as neutron absorbers in nuclear engineering.

21.3.3 Hydrides

Introduction

The unique catenating property of carbon gives rise to a wide vareity of hydrocarbons, including the aromatic compounds. The stability of 2*p*-2*p* π-bonds adds a further dimension to the hydrogen compounds of carbon which includes C = C and C ≡ C. All these compounds are traditionally and conveniently treated under organic chemistry and will not be discussed here.

The elements Si—Pb form the gaseous hydrides MH_4 with gradually decreasing stability from M = Si to M = Pb, as expected from the steady decrease in M-H bond energy. PbH_4 is extremely unstable. Silicon and germanium form limited number of catenated hydrides M_nH_{2n+2}, $n = 6$ (or 8) for Si and 5 for Ge. The chains may be branched as well. Germanes corresponding to $n = 2$ to 9 have been detected by gas-liquid chromatography (GLC) and mass spectrometry when GeH_4 is subjected to silent electric discharge. There are no analogues of C = C and C ≡ C in simple silicon (and other) hydrides but tetramesityl silenes have been reported (see section 21.2.3).

The magnesium boride used by Stock in preparing boranes (Ch. 20) happened to be contaminated with magnesium silicide. This led him to identify SiH_4, Si_2H_6, Si_3H_8 and Si_4H_{10}. His method of protolysis is no longer important in forming Si-H bonds. Silanes are now more conveniently prepared by

Preparation

(i) reduction of Si-Cl (or Si-Br) bonds with $LiAlH_4$, LiH or NaH in ether solution at low temperatures.

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

$$Si_2Cl_6 + 6NaH \longrightarrow Si_2H_6 + 6NaCl$$

$$Si_3Cl_8 + 8LiH \longrightarrow Si_3H_8 + 8LiCl$$

$$Si_nCl_{2n+2} + LiAlH_4 \longrightarrow Si_nH_{2n+2} + LiCl + AlCl_3\ (n = 1 - 3).$$

(ii) reaction of Si (or ferrosilicon) with anhydrous HX or RX to form chlorosilanes which form silane on heating :

$$Si + 3HCl \longrightarrow SiHCl_3;\quad 4SiHCl_3 \longrightarrow SiH_4 + 3SiCl_4.$$

This method utilizes cheaper starting materials and hence is used for commercial production.

Other MH_4 compounds may be similarly prepared :

(iii) reduction with $LiAlH_4$ or $NaBH_4$

$$GeO_2 + NaBH_4 \xrightarrow[\text{aq. soln.}]{\text{acidic}} GeH_4 + NaBO_2$$

$$SnCl_4 + LiAlH_4 \xrightarrow{\text{ether}} SnH_4 + LiCl + AlCl_3$$

PbH_4 is believed to be formed in traces during the acid hydrolysis of Mg-Pb aloys. It can be made only in traces by cathodic reduction of Pb(II) salts and studied mass spectrometrically. $(CH_3)_3PbH$ is somewhat more stable:

(iv) Higher germanes may be obtained by subjecting GeH_4 to silent electric discharge.

$$GeH_4 \longrightarrow Ge_nH_{2n+2}\quad (n = 2 - 9).$$

(v) Mixed hydrides like $H_3Si\text{-}GeH_3$ have also been prepared by acid hydrolysis of a mixture of Mg_2Si and Mg_2Ge.

(vi). A substituted cyclotrisilane, $\left[(2, 6-Me_2C_6H_3)_2\ Si\right]_3$ [hexakis (2, 6-dimethoxy-phenyl) – cyclotrisilane] has been prepared. The solid compound (m.p. 272°C) is stable to air and moisture, and contains the Si atoms at the corners of an isosceles triangle.

The hydrides are all colourless gases. Unlike the hydrocarbons, silanes spontaneously ignite or explode in air, for example,

$$Si_2H_6 + \tfrac{7}{2}O_2 = 2SiO_2 + 3H_2O$$

Reactivity towards oxygen falls as Si>Ge>Sn. Thus germanes are less flammable in air. It may however be noted that the hydrocarbons also are thermodynamically unstable with respect to carbon dioxide and water but they require ignition. Their stability is, in fact, due to some kinetic block.

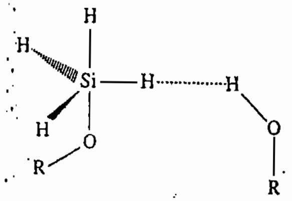
Thermal stability among the silanes decreases with increasing chain length.

The silanes react violently with Cl_2 and are hydrolyzed in contact with traces of aqueous alkali, even that which dissolves from the glass apparatus. But pure silanes do not react with dilute acids or pure water in silica apparatus. Silanes are also good reducing agents [e.g., Fe(III) → Fe(II)].

Some reactions of silanes are summarised below :

O_2 (air)	$Si_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4SiO_2 + 5H_2O$	*(violent)*
	$SiH_4 + 4Cl_2$ (or Br_2) $\longrightarrow SiCl_4 + 4HCl$ ...	*(explosive)*
Cl_2/Br_2	$SiH_4 + Br_2 \longrightarrow SiH_3Br$ or $SiH_2Br_2 + HBr$ ...	*(at -80°C)*
H_2O	$Si_2H_6 + (4+x)H_2O \longrightarrow 2SiO_2, xH_2O + 7H_2$	*(in presence of trace OH^-)*
ROH	$SiH_4 + 4ROH \longrightarrow Si(OR)_4 + 4H_2$	*(in presence of OR^-).*
HX	$SiH_4 + HX \longrightarrow SiH_3X$	*(Al_2X_6 catalyst, X = halogen)*
K	$SiH_4 + 2K \longrightarrow KSiH_3 + KH$	*(diglyme)*

The reactions are consistent with hydridic nature of hydrogen in Si—H bond. Kinetic studies on alcoholysis indicate that the OR^- attacks the Si atom while a hydridic hydrogen is removed by a protic hydrogen in an intermediate like



21-VIII

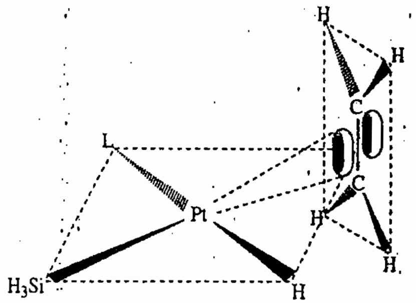
Hydrosilylation

An Si—H bond can add across C = C or C ≡ C bonds in alkenes or alkynes at 300° C or under UV radiation or better, in presence of a platinum complex as catalyst. The reaction, similar to hydroboration (Ch. 20) is called hydrosilylation.

$$H_2C = CH_2 + SiH_4 \xrightarrow[i\text{-PrOH}]{H_2PtCl_6} CH_3CH_2SiH_3.$$

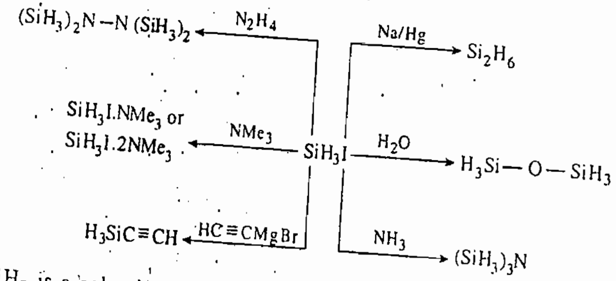
The method is industrially important in the manufacture of silicones.

It has been suggested that the reaction proceeds through an intermediate like

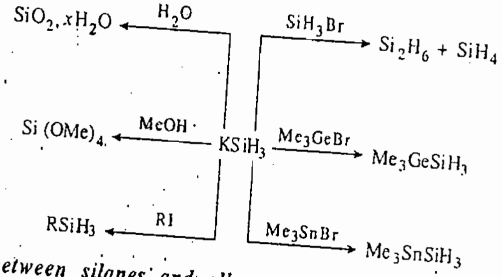


21-IX

SiH_3X (particularly SiH_3I) and $KSiH_3$ have valuable synthetic applications in preparing a wide variety of silicon compounds. SiH_3I is a colourless dense liquid ($\rho = 2$ g cm^{-3}; bp.45.4°C). Some of its reactions are :



$KSiH_3$ is a colourless crystalline solid (NaCl structure) stable up to ~ 200°C. Some of its reactions are :



Differences between silanes and alkanes

The differences in the reactivity between silanes and alkanes may be traced to the following main factors :

(i) Larger size of the Si atom facilitates nucleophilic attack at Si.

(ii) Polarity of the Si—H bond is greater than as well as opposite to that of the C—H bond :

	$\delta^-\ \delta^+$	$\delta^+\ \delta^-$
	C—H	Si—H
Pauling electronegativity	2.5 2.1	1.8 2.1

(iii) Energetically accessible vacant 3*d* orbitals in Si favour adduct formation through expansion of valence shell. This is likely to lower the energy of activation of the reaction intermediates involving Si.

(iv) Si—H bond energy (393 kJ mol^{-1}) is significantly lower than that of either C—H (435 kJ) or Si—O (452 kJ). The Si—Si bond (340 kJ) is also weaker than the C—C bond (368 kJ).

Properties of the hydrides of Ge, Sn and Pb

Stability of the hydrides decrease sharply from Ge to Pb primarily due to decrease in M—H bond energy. The germanes Ge_nH_{2n+2} (n = 1 – 5) are colourless gases/liquids which are less volatile than the silanes. Their properties are more or less similar to those of silane, but they are less reactive. Thus GeH_4 does not ignite spontaneously in contact with air (but SnH_4 does) and is not hydrolyzed by aqueous acid or even aqueous NaOH (30%). GeH_4 reacts with HX to form GeH_3X etc. and with K (or Rb) in liquid ammonia giving white crystalline

$KGeH_3$ (and NH_4^+; GeH_4 is thus an acid in liquid NH_3). SnH_4 decomposes slowly at room temperature ($Sn + H_2$) and remains passive toward dilute aqueous acids and alkalis, but is decomposed by concentrated solutions : Sn + some stannate by alkalis; SnH_3^+, the stannonium ion, and H_2 by acids. SnH_4 is a good reducing agent in organic chemistry (e.g., benzaldehyde → benzyl alcohol or nitrobenzene to aniline).

Stable organohydrides R_nMH_{4-n} (M = Si – Pb) may be prepared by reducing the respective chlorides with $LiAlH_4$.

21.3.4 Halides

Except PbI_4, all four tetrahalides of all the elements are known ($PbBr_4$ is very unstable). Germanium, tin and lead also form stable dihalides. Carbon, and to some extent silicon, form several catenated halides. The fluorinated hydrocarbons and chlorofluorocarbons have many industrial applications. Carbon and silicon also form some oxyhalides.

General discussion

The tetrahalides except SnF_4 and PbF_4 are typically covalent and volatile. SnF_4 (sublimes at 705°C) and PbF_4 (m.p. 600°C) have polymeric structures based on MF_6 octahedra; the M—F bonds are also considerably ionic.

The differences in the hydrolytic behaviour between the carbon and silicon tetrahalides may be traced to the same general principles outlined earlier, i.e., small size and nonavailability of *d*-orbitals in carbon. CF_4, CCl_4 as well as the fluorinated hydrocarbons and chlorofluorocarbons are all very stable and rather unreactive. However, CCl_4 acts as an oxidizing and chlorinating agent at high temperatures. CBr_4 and CCl_4 decompose readily on heating or by the action of uv light. They act as halogenating agents on warming. The tetrahalides of other elements are readily hydrolyzed mainly to $MO_2.xH_2O$ or $M(OH)_4$, but SiF_4 also produces H_2SiF_6. It is possible to isolate a few hydrates of Sn(IV) halides. As usual, the tetrahalides form 5-coordinate (trigonal bipyramidal) and 6-coordinate adducts of the type $MX_4.D$ and $MX_4.2D$ with suitable donors(D).

The dihalides are also covalent except those of Pb(II). They also give rise to several complex species like $SnBr_3^-$, $PbCl_6^{4-}$ and $PbBr_2$ (dimethyl sulphoxide).

Tetrahalides

The tetrahalides of carbon are as follows :

	CF_4	CCl_4	CBr_4	CI_4
State (room temp.)	Colourless gas	Colourless liquid	pale yellow solid	red solid
m.p. (°C)	–185	–23	93	171
b.p. (°C)	–128	76	190	decomposes
Stability	Very stable	Stable, but photo-chemically decomposed.	decomposes slightly on boiling.	decomposes before boiling or by uv light.

They may be prepared by direct or indirect halogenation, e.g.,

$CO_2 + SF_4 \longrightarrow CF_4 + SO_2$
$SiC + 2F_2 \longrightarrow SiF_4 + CF_4$ (Lab. preparation. SiF_4 removed by bubbling through 20% NaOH solution).
$CF_2Cl_2 + F_2 \longrightarrow CF_4 + Cl_2$ (industrial method).
$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$ 30°C; $FeCl_3$ catalyst (industrial)

$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$ 60° C; $FeCl_3$ catalyst
$CCl_4 + 4C_2H_5Br \longrightarrow CBr_4 + 4C_2H_5Cl$
$CCl_4 + 4C_2H_5I \longrightarrow CI_4 + 4C_2H_5Cl$ } $AlCl_3$ catalyst.

The covalent compounds are insoluble in polar solvents but soluble in non-polar solvents like benzene. They are resistant to hydrolysis as the carbon atom is coordinately saturated (all the valence orbitals being engaged) and there are no energetically accessible vacant acceptor orbital (like the 3*d* in Si). CF_4 and CCl_4 are thermodynamically unstable with respect to hydrolysis, as shown by the following negative $\Delta G°$ value :

$$CCl_4\ (l) + 6H_2O \longrightarrow CO_2 + 4H_3O^+\ (aq) + HCl \qquad \Delta G° = -380\ \text{kJ mol}^{-1}$$

$$SiCl_4 + 6H_2O \longrightarrow SiO_2\ (aq) + 4H_3O^+\ (aq) + 4Cl^-\ (aq) \qquad \Delta G° = -290\ \text{kJ mol}^{-1}.$$

The value is much more negative than that for the hydrolysis of $SiCl_4$ (–290 kJ mol⁻¹), although only $SiCl_4$ is very rapidly hydrolyzed. It appears that the formation of a five coordinate intermediate in the initial step of attack at carbon is extremely difficult and the high energy of activation stands against the reaction. If sufficient energy is supplied, for example by superheated steam, then CCl_4 will undergo hydrolysis

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl.$$

Though CF_4 is highly stable, CCl_4 is decomposed photochemically and thermally into CCl_3 radicals and Cl atoms (hence its use in chlorination). The increasing thermal instability of CX_4 compounds from X = F to X = I may be associated with the steady decrease in C—X bond energy but steric crowding around the small carbon atom may be equally responsible. CI_4 decomposes readily to C_2I_4 (tetraiodoethylene) and I_2, presumably in order to overcome the congestion in CI_4 and open the I—C—I bond angle from 109.5° to 120°.

$$2CI_4 \longrightarrow I_2C = CI_2 + I_2$$

Tetrahalides of silicon, SiX_4

The silicon halides may be prepared directly from the elements: SiF_4 is conveniently prepared by heating a mixture of CaF_2 and silica with conc. H_2SO_4 :

$$2CaF_2 + SiO_2 + 2H_2SO_4 \longrightarrow SiF_4 + 2CaSO_4 + 2H_2O.$$

Melting and boiling points of the halides are given below :

	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
M.P./B.P. (°C)	–95/–86 (sub)	–70/57.6	5.2/152.8	120.5/287.5

$SiCl_4$ boils at a lower temperature than CCl_4 (see Q. 19 in exercise of Chapter 7).

Unlike the halides of carbon, the silicon tetrahalides are rapidly hydrolyzed by water and alkali. SiF_4 is only partially hydrolyzed as a secondary reaction occurs between HF and SiF_4 producing hexafluorosilicates SiF_6^{2-} :

$$SiF_4 + 4H_2O \longrightarrow Si\ (OH)_4 + 4HF$$

$$2SiF_4 + 4HF \longrightarrow 2H_2SiF_6.$$

The chloride is rapidly and completely hydrolyzed to Si $(OH)_4$.

SiF_4 also forms adducts with other donor molecules, e.g., $SiF_4.2py$ or, SiF_4 2, 2′-bipyridyl).

Tetrahalides of germanium, GeX_4

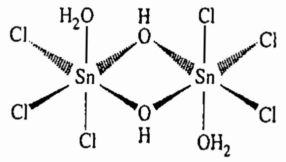
The tetrahalides of germanium are readily prepared from the elements or by the action of aqueous HX on GeO_2. They show the same chemical trend as the silicon compounds. Their physical properties are as follows :

	GeF_4	**$GeCl_4$**	**$GeBr_4$**	**GeI_4**
Nature	Colourless gas	Colourless, fuming liquid	Colourless liquid	Red crystals
B.P. (°C)	−36.5 (sublimes)	83.1	186	~ 400
M.P. (°C)	Sublimes	−49.5	26	146

The tetrahalides are all hydrolyzed but the hydrolysis of $GeCl_4$ is only partial. In 6 – 9 *M* aqueous HCl, several species of the type $[Ge(OH)_nCl_{6-n}]^{2-}$ may be present in equilibrium. $GeCl_4$ can be separated by distillation from solutions in concentrated HCl. The larger size of Ge (than Si) permits the formation of $GeCl_6^{2-}$ as well as other hexacoordinated complexes like GeF_6^{2-} or $GeCl_4$, L_2 (L = tertiary amine or pyridine) or five-coordinated $GeCl_4.L$. Square pyramid environment is found around Ge (IV) in $[(C_6H_4O_2)_2\ GeCl]^-$ [see structure 21-IV (a)].

Tetrahalides of tin, SnX_4

SnF_4 is a hygroscopic white solid ($SnCl_4$ + anhydrous HF) which sublimes at about 700°C. The other SnX_4 compounds are best made by direct union. $SnCl_4$ and $SnBr_4$ are colourless liquids (b.p. 114° and 205°C resp.) while SnI_4 is a bright orange solid (mp 144°C). SnF_4 has a polymeric structure involving octahedral SnF_6 units joined by sharing edges. The halides hydrolyze readily but several hydrates may be isolated, which contain water molecules coordinated to central Sn. Thus the pentahydrate may be written *cis*-$(H_2O)_2\ SnCl_4.3H_2O$; this readily undergoes partial hydrolysis to form a hydroxo-bridged dimer :



21-X

The hydrates containing other donor ligands (or crown ethers) contain the ligands hydrogen bonded to the coordinated water molecules, as in [*cis* $(H_2O)_2\ SnCl_4$. 18-C-6] and [*trans*-$(H_2O)_2\ SnCl_4$.15-C-5]. There appears to be no interaction of the ligand with Sn. Other six coordinate complexes formed by SnX_4 include the octahedral SnX_6^{2-} (X = Cl, Br and also I) and 5-coordinate trigonal bipyramidal $SnCl_5^-$ and $Me_2SnCl_3^-$. Square pyramidal Sn(IV) is present in the anion of the spirocyclic dithiolato complex $[(MeC_6H_3S_2)_2\ SnCl]^-(Me_4N$ salt). The Sn atom is slightly above the plane of the four S-atoms; the Cl atom is at the apex [c.f. 21-IV (b)].

[Sec.21.3.4
Halides]

Q. 21.9 *GeI_4 and SnI_4 are bright orange or red in colour, while other tetrahalides are colourless. Comment.*

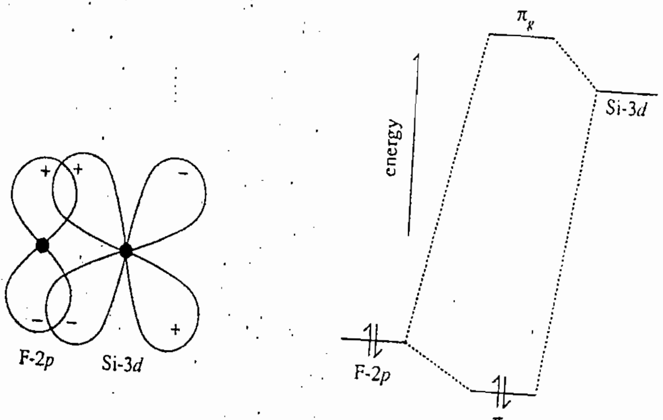
Hint : "Charge transfer"; that is, transfer of electron density from the filled valence shell of the easily polarisable I^- ion to empty acceptor orbitals (*4d*/*5d*) on Ge(IV) or Sn(IV) is intense as the orbitals involved are comparable in size and energy. Absorption in the blue range.

Tetrahalides of lead, PbX_4

PbF_4 (yellow solid, m.p. 600°C) is the only stable lead tetrahalide. It also decomposes to PbF_2 and F_2 on heating. $PbCl_4$, a yellow oil, is stable below 0°; above 50°, it decomposes to $PbCl_2$ and Cl_2. $PbBr_4$ is even less stable and its existence is questionable. PbF_4 can be prepared by the action of F_2 or HF on lead compounds. $PbCl_4$ may be obtained by the reaction of concentrated H_2SO_4 on $(NH_4)_2\ [PbCl_6]$. The stable yellow salts $M_2\ [PbCl_6]$ (M = Na, K, Rb, Cs, NH_4) are obtained by passing chlorine into a saturated solution of $PbCl_2$ in aqueous HCl in presence of MCl.

M-halogen π bonding in tetrahalides

As mentioned in the beginning of this section, the MX_4 tetrahalides except SnF_4 and PbF_4 are typically covalent and volatile. No secondary π bonding can occur in the carbon tetrahalides since carbon has no suitable vacant acceptor orbital in its valence shell. For other elements in the group, theoretical calculations have demonstrated that the normally large valence shell *n*d orbitals on M atoms (Si—Pb) shrink considerably when M is bonded to electronegative halogen atoms. These empty *d*-orbitals on the central Si, Ge, Sn and Pb atoms have the same symmetry as the filled halogen *p*-orbitals. Electron spectroscopy reveals that the halogen *np* lone pairs of electrons in all such tetrahalides are stabilized by π-interaction with the empty *d*-orbitals on the central atoms. The effect is greatest for SiF_4 (Fig. 21.7).



(a)

(b)

Fig. 21.7 : (a) *p-d* π-bonding in SiF_4.
(b) mo energylevel diagram for Si-F back-bonding.

The M—X distances for some tetrahalides are given in Table 21-4, with the sum of respective covalent radii in parenthesis. It may be noted that the actual values are significantly shorter than the sum of covalent radii in the halides of Si, Ge and Sn even allowing for the uncertainties in the values of covalent radii. The discrepancy in CF_4 may be partly eliminated by considering the difference of electronegativity (Section 4.3.3. Shomaker Stevenson relation).

TABLE 21.4

M-halogen distances in tetrahalides (pm)

	C	Si	Ge	Sn
MF_4	132 (141)	154 (181)	167 (186)	—
MCl_4	177 (176)	201 (216)	208 (221)	231 (239)
MBr_4	191 (191)	215 (231)	231 (236)	244 (254)
MI_4	214 (210)	243 (250)	250 (255)	264 (273)

Mixed halides and substituted halides

Mixed silicon halides can be separated and characterized by thermally equilibrating two different tetrahalides :

$$SiCl_4 + SiBr_4 \rightleftharpoons 2SiCl_2Br_2$$

$$nSiX_4 + (4-n)\,SiY_4 \rightleftharpoons 4SiX_nY_{4-n}.$$

The melting and boiling points of the mixed halides usually increase with increasing molecular weight according to the nature of substitution.

A wide variety of tetravalent halides also exist in which the halogen atoms have been partially substituted by hydrogen or organic groups :

$$GeCl_2 + HCl\,(g) \xrightarrow{40°C} HGeCl_3$$

$$SnCl_4 + Sn\,(CH_3)_4 \xrightarrow{heat} 2(CH_3)_2\,SnCl_2.$$

Catenated halides

Carbon, Silicon and germanium also form several catenated halides. Catenation is obviously most extensive in carbon compounds. Thus tetrafluoroethylene polymerizes under pressure into chains of hundreds of carbon atom, $(C_2F_4)_n$:

$$CHCl_3 + HF \xrightarrow{SbF_3,\ SbCl_5\ cat.} CF_2ClH \xrightarrow{700°\ C} X_2F_4 + HCl$$

$$C_2F_4 \xrightarrow{pressure} (-CF_2CF_2CF_2CF_2-)_n.$$

The resulting *polyterrafluoroethylene* (*PTFE*) is a dense, hard white solid plastic stable upto 300° C. It has a greasy feeling when touched and is a good electrical insulator. It is commercially marketted in the names 'Teflon' or 'Fluon'. It is insoluble in most solvents and to both acids and alkalis. Very low coefficient of expansion makes it suitable for coating in non-stick pans and razor blades. Dechlorination of $CF_2ClCFCl_2$ (Zn/EtOH) gives $CF_2{=}CFCl$ (perfluorovinyl chloride) which polymerizes to a transparent plastic commercially known as Kel-F. Polymeric $-SiF_2-$and $SiCl_2$ chains may also be prepared by SiF_4 (or $SiCl_4$ over heated Si) :

$$Si + SiF_4 \longrightarrow (SiF_2)_n$$

Destructive distillation of the polymeric fluoride in vacuum gives several polyfluorosilanes like SiF_4, Si_2F_6, Si_3F_8 and Si_4F_{10}. Species upto $Si_{16}F_{34}$ may be detected by mass spectrometry. Similar chloro and bromo species may be prepared by methods like

$$Si + 3SiCl_4 \xrightarrow{red\ heat} 2Si_2Cl_6$$

$$5Si_2Cl_6 \xrightarrow[Me_3N\ (0.1\ mol\%)]{heat\ with} Si_6Cl_{14} + 4SiCl_4$$

$$Cl_2 + Ca{-}Si \longrightarrow SiCl_4 + Si_2Cl_6 + Si_3Cl_8\ (small) + higher\ species\ (1\%)$$

Ge_2Br_6 may be prepared by refluxing $GeBr_2$ and $GeBr_4$ in toluene :

$$GeBr_2 + GeBr_4 \longrightarrow Ge_2Br_6$$

The compound decomposes to $GeBr_2$ and $GeBr_4$ when heated at 80°C :

$$Ge_2Br_6 \longrightarrow GeBr_4$$

Stability of the dihalides of Ge, Sn and Pb appear to be one of the main reasons for the lack of catenated halides of these elements (weak M—M bond is another principal factor).

For obvious reasons, $X_2M = MX_2$ and $XM \equiv MX$ type halocompounds are unique to carbon, as also are the halogen derivatives of aromatic compounds.

Fluorocarbons and Chlorofluorocarbons (Freons)

These are fluorides or mixed halides of carbon corresponding to different hydrocarbons. They gained industrial importance owing to certain properties arising from larger size of the halogens in comparison to hydrogen and the changed polarities of the C—F of C—Cl bond in comparison to the C—H bond (see later).

Replacement of a C—H bond by a C—F bond releases large amount of heat :

$$\geq C{-}H + F_2 \longrightarrow \geq C{-}F + HF;\quad \Delta H° = -480\,kJ\,mol^{-1}$$

The C—F bond energy being much higher than the C—C bond energy also, uncontrolled fluorination of hydrocarbons would lead to complete decomposition of the carbon skeleton. Controlled fluorination of hydrocarbons may be achieved in a number of ways :

Preparation

(i) Diluting the hydrocarbon vapour with nitrogen or dissolving the hydrocarbon in an inert solvent like CCl_4 (its evaporation will absorb the heat liberated).

(ii) Fluorination with F_2—N_2 mixture in a reactor packed with gold or silver coated copper turnings which act as a quick heat transfer agent and probably at the same time act as a catalyst (via formation of a surface layer of AgF_2 or AuF_3).

(iii) Use of a milder fluorinating agent like CoF_3 at about 150-200°C :

$$C_2H_6 + 12CoF_3 = C_2F_6 + 6HF + 12CoF_2$$

The CoF_2 may be reconverted to CoF_3 by F_2 (350°C).

(iv) Freons or chlorofluorocarbons may be prepared by fluorination of the chloro compound with SbF_3 in presence of $SbCl_5$ (Swart's reaction) or by HF in presence of SbF_3—$SbCl_5$ (See Teflon). Freons represent the whole family of chlorofluorocarbons, though CF_2Cl_2 often goes by the name freon.

Properties

Fluorocarbons may be liquid, gas or solid—their melting and boiling points are not much different from those of the corresponding hydrocarbons (in spite of much higher molecular weight). Rather, some fluorocarbons have much lower b. p. (than corresponding hydrocarbons).

35

Q. 21.10 *Though the molecular weights of fluorocarbons are significantly higher than those of corresponding hydrocarbons, their melting and boiling points are only slightly higher or sometimes even lower. (See Table 21.5). Comment.*

Hint : London forces acting between nonpolar covalent molecules actually depend on polarizability of the molecule (Ch. 7).

TABLE 21.5

Boiling points (°C) of C_nH_{2n+2} and C_nF_{2n+2}

n	1	2	3	5	6	8	10
C_nH_{2n+2}	−161	−88	−44	36	68	125	285
C_nF_{2n+2}	−128	−78	−38	22	51	104	240

The fluorocarbons are remarkably chemically inert - they are unaffected by concentrated acids or alkalis. They dissolve only in nonpolar solvents.

The inertness and stability of fluorocarbons may largely be attributed to

(i) High C—F bond energy (Table 21.3).

(ii) Absence of any suitable acceptor orbital at F (or C) to initiate hydrolytic attack.

(iii) Higher electronegativity of F leaves the C atoms in slightly oxidized state (acquiring δ^+ charge) while in hydrocarbons the C atoms are rather in a reduced state (δ^- charge).

(iv) The size of the F atom being slightly larger than that of the H-atom, F atoms act as a shield to the C skeleton.

(v) Being smallest in size among the halogens, F atoms can replace H atoms in hydrocarbons with least strain or distortion as compared with substitution by larger halogen atoms.

Uses

Fluorocarbons are used as solvents, lubricants and insulators. The chlorofluorocarbons or freons are volatile non-corrosive and non-inflammable gases which are also non-toxic in nature. Hence they found wide use as refrigerants and aerosol sprays. But now it has been definitely established that freons cause severe damage to the ozone layer in upper atmosphere and hence its use has been banned wholly or partially in many countries; a total ban is proposed by 2000 A.D. Freons escaping into the upper atmosphere undergo photolysis to produce free radicals, particularly Cl atoms, which continue to damage the ozone layer in a cyclic manner :

Pollution problem— the ozone hole

$$CFCl_2,\ CF_2Cl_2 \text{ etc.} \xrightarrow{h\nu} \dot{Cl}$$

$$Cl + O_3 \longrightarrow O_2 + Cl\dot{O}$$

$$Cl\dot{O} \longrightarrow \dot{Cl} + O$$

$$Cl\dot{O} + O \longrightarrow \dot{Cl} + O_2$$

Thus, regeneration of the Cl radicals continues to damage the ozone layer. Recombination of the type Cl + Cl ⟶ Cl_2 would require the presence of a third body to dissipate the energy, but such three-body collisions are extremely rare in the upper atmosphere. Hence small amounts of freon can continue to destroy the ozone layers which act as an umbrella to save the earth from harmful UV radiations.

Fluorosilicic acid, H_2SiF_6 is formed in solution by the hydrolysis of SiF_4 and may also be made by dissolving silica in aqueous HF. It is a strong acid in aqueous solution, but pure H_2SiF_6 has not been isolated. Each mole of H_2SiF_6 consumes *six* moles of OH^- ion using phenolphthalein as indicator :

[Sec. 21.3.4 *Dihalides*]

$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O$$

$$Na_2SiF_6 + 4NaOH = 6NaF + Si(OH)_4$$

$$\overline{H_2SiF_6 + 6NaOH = 6NaF + Si(OH)_4 + 2H_2O}$$

Fluorosilicates are prepared from SiF_4 and metal fluorides in aqueous HF. Na, K, and Ba-fluorosilicates are sparingly soluble in water while those of slightly less electro-positive metals like Li, Ca and Sr are soluble in water. A solution of Na_2SiF_6 forms a white crystalline precipitate of $BaSiF_6$ with $BaCl_2$ solution. The precipitate evolves HF and SiF_4 with concentrated H_2SO_4 (distinction from $BaSO_4$).

$$BaSiF_6 + H_2SO_4 = BaSO_4 + SiF_4 + 2HF.$$

The fluorosilicates are also decomposed by heat :

$$Na_2SiF_6 = SiF_4 + 2NaF.$$

Magnesium fluorosilicate is used to harden and polish concrete floors. Na_2SiF_6 is used as an insecticide for chickens.

Dihalides

As mentioned earlier, the divalent state becomes increasingly important from Si to Pb, so that the stability of the dihalides increases as $SiX_2 << GeX_2 < PbX_2$. SiF_2 and $SiCl_2$ are short lived unstable species while GeX_2 onward the compounds are all stable solids.

SiF_2, thermodynamically unstable under normal condition, may be prepared at high temperature, (~1150°C) and low pressure and trapped by chilling in liquid nitrogen temperature to a reddish brown solid.

$$SiF_4 + Si \rightleftharpoons 2SiF_2$$

The solid probably contains polymeric SiF_2 units which undergo cracking on warming to give fluorosilanes SiF_4, Si_2F_6 etc. upto $Si_{16}F_{34}$. $SiCl_2$ has also been prepared by heating Si_2Cl_6 with KSi at 1450° C.

Ge, Sn and Pb form stable solid dihalides which are shown in Table 21.6.

TABLE 21.6

Dihalides of Ge, Sn and Pb

[(a) Colour/mp, °C (sub = sublimes; dec = decomposes). (b) Principle of preparation. (c) Solubility in water (g per 100g).]

GeF_2	**$GeCl_2$**	**$GeBr_2$**	**GeI_2**
(a) white; sub.	pale yellow; dec	yellow (122°)	orange; sub + dec
(b) GeF_4 + Ge (250°)	$GeCl_4$ + Ge (400°)	$GeBr_4$ + Ge	$GeI_4 + H_3PO_2$
SnF_2	**$SnCl_2$**	**$SnBr_2$**	**SnI_2**
(a) Colorless	Colorless (246°)	white (216°)	red (316°)
(b) Sn or SnO + HF	Sn + HCl (*g*)	Sn + HBr (*aq*)	Sn + I_2 (2*M* HCl)
(c) Sol	Very sol (270/15°)	Sol (85/0°)	Less sol (0.99/20°)

PbF_2	$PbCl_2$	$PbBr_2$	PbI_2
(a) Colourless (818°)	White (500°)	Colourless (367°)	Yellow (400°)
(b) $Pb^{2+}(aq) + HX(aq)$	(or NaX, K etc.).		
(c) 0.06/20°	0.7 (0°); 3.2 (100°)	0.5 (0°); 4.7/100°	0.04 (0°); 0.4 (100°)

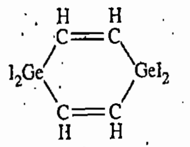
GeF_2 is the most stable dihalide of Ge. $GeCl_2$ disproportionates to Ge and $GeCl_4$ at 1000° C in vacuum, $GeBr_2$ does so at 150°C while GeI_2 disproportionates only when heated above 550°C.

GeF_2 reacts readily with aqueous solutions of alkali metal fluorides to give GeF_3^- which is hydrolytically stable. The ion is oxidized by air in fluoride solutions to GeF_6^{2-} The other dihalides hydrolyze to the yellow Ge $(OH)_2$. The solid dihaldes add Lewis bases (L) to form pyramidal $LGeX_2$:

$$GeCl_2 + Cl^- \longrightarrow GeCl_3^-;\ GeI_2 + R_3P \longrightarrow R_3PGeI_2$$

GeI_2 reacts with acetylene at 140° C to give a compound with the dimeric structure

$2GeI_4 + 2C_2H_4 \longrightarrow$



The halides are readly oxidized to the tetravalent state, for example,

$$GeCl_4 \xleftarrow{Cl_2/20°} GeCl_2 \xrightarrow{Br_2/20°} GeBr_2Cl_2$$

$GeCl_2$ reversibly adds HCl to form the chloroform analogue of Ge:

$$GeCl_2 \underset{-HCl\ (70°)}{\overset{+HCl\ (20°)}{\rightleftharpoons}} GeCl_3$$

The structure of GeF_2 has been mentioned before (p. 260; 21-VII) - the stereochemically active lone pair of electrons occupy an equatorial position in an approximately trigonal bibyramid environment in a fluorine-bridged spiral chain structure with further weak bridging between the chains.

In the gas phase, the dihalide molecules are bent with angles between 90-100°. The tin Sn(II) halides are readily but partially hydrolyzed by water, $SnCl_2$ giving Sn (OH) Cl.

In solutions containing excess halide (X^-) ions, the dihalides readily add halide ions to give pyramidal SnX_3^- ions.

$$SnF_2 + F^- \rightleftharpoons SnF_3^- \qquad pK = 1.$$

Such ions may also persist in crystals e.g., $KSnF_3 \cdot \frac{1}{2}H_2O$ or $CsSnCl_3$; K_2SnCl_4, H_2O is actually $K_2[SnCl_3]\ Cl.H_2O$. However, further condensation and higher coordination number is often found in crystals e.g., $[\overset{II}{Sn_2}X_5]^-$ (X = F, Cl, Br) is $CsSn_2X_5$ or Cs_4SnBr_6.

Solutions of SnF_2 in anhydrous HF are oxidized at room temperature by F_2, O_2 or even SO_2 to a mixed valence compound Sn_3F_8 which contains octahedral $[Sn^{IV}F_6]^{2-}$ and pyramidal $[Sn^{II}F_3]^-$ units packed together.

SnF_2 has been used in some toothpastes, but now it is being replaced by NaF due to toxic nature of tin.

$SnCl_2$ is commonly available as the dihydrate $SnCl_2, 2H_2O$ (see structure). It is widely used as a mild reducing agent ($E°_{aq}\ Sn^{IV}\text{-}Sn^{II} = 0.15$ V, see aqueous solution chemistry), in tinplating, as a sensitizer in silvering mirrors and in the plating of plastics.

The gaseous $SnCl_2$ molecule is bent with a bond angle of 95° (21-V). The lonepair is stereochemically active as shown in the structures of $SnCl_2$ (crystals) (21-VI), $SnCl_2, 2H_2O$ or $SnCl_3^-$.

The dihalides of lead are all stable crystalline salts slightly soluble in cold water but much more soluble in hot water (Table 21.6). $PbCl_2$ and $PbBr_2$ are photosensitive, depositing metallic lead on irradiation with UV rays or even visible light. PbI_2 is photoconductor and decomposes when exposed to green light. The Pb^{2+} ion is partially hydrolyzed:

$$Pb^{2+} + 2H_2O \rightleftharpoons [Pb\ (OH)]^+ + H_3O^+.$$

The tendency to complex formation by adding Lewis base donors is continued to lead. Discrete octahedral $[PbX_6]^{4-}$ ions (X = Cl, Br, I) are present in Cs_4PbX_6.

The distorting effect of the lone pair of electrons appears to be less pronounced in the crystal structures of $PbX_2.PbF_2$ (α-form), $PbCl_2$, $PbBr_2$ form orthorhombic crystals. PbI_2 forms a hexagonal layer lattice like CdI_2. A high-temperature form of PbF_2 (β-form) has the fluorite structure.

Oxohalides

Carbon oxohalides (carbonyl halides) COX_2 are known for X = F, Cl and Br. COI_2 is not known but the mixed halide COFI has been prepared. Other mixed halides like COFCl, COClBr etc. also exist.

Principle of preparation and some physical properties of the compounds are summarized in Table 21.7.

TABLE 21.7
Preparation and properties of COX2

	COF_2	$COCl_2$	$COBr_2$
Preparation	$CO + AgF_2$ $COCl_2 + SbF_3/SbF_5$	$CO + Cl_2$ (activated C)	$CO + Br_2$
Nature	Colourless gas	Colourless gas	Colourless liq.
B.P. °C	−83	7.6	64.5
XCX bond angle	108°	111.3°	110° + 5°
Action of H_2O	$COX_2 + H_2O = CO_2 + 2HX$.		

$COCl_2$ was first prepared by John Davy (1812; brother of Sir Humphrey Davy) through photochemical union between CO and Cl_2 and hence the name **phosgene** (Greek **phos** = light; **genes** = born of). It is a highly toxic gas and is used to prepare isocyanates in the route to polyurethanes. It gives urea with NH_3.

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

The carbonyl halides are planar molecules corresponding to sp^2 hybridized carbon atom with a carbon-oxygen π-bond. The XCX bond angles are notably smaller than 120° (in contrast to isoelectronic BX_3 or CO_3^{2-}) as expected from the presence of the bulky π-electron cloud. However, the bonding seems to be best described by the m.o. approach.

The silicon oxohalides are all single-bonded species which may contain –Si–O–Si– chains or rings. A series of volatile chloro siloxanes $Cl_3Si\text{–}(OSiCl_2\text{–})_n\text{–}OSiCl_3$ have been prepared ($n = 0 - 5$) through controlled hydrolysis of $SiCl_4$ by moist ether or by reacting hot Si (700°C) with $Cl_2 + O_2$. The cyclic tetramers $(SiOCl_2)_4$ and $(SiOBr_2)_4$ have also been prepared by similar methods.

21.3.5 Oxides and Oxoacids

Carbon forms CO, CO_2 and a few other less common oxides; all of these are dominated by strong C—O π-bonds and form gaseous molecules. The importance of π-bonding decreases sharply from Si as may be appreciated from the following bond energy data (kJ mol^{-1})

C—O	C═O	Si—O	Si═O
359	806	466	642

Introduction

The M═C bond energy is more than twice the M—O bond energy when M is C, but for silicon, a system with four Si—O single bonds is more stable than O═Si═O. One can interpret this difference as arising from strong $2p$—$2p$ π-bond in CO_2, but it is also likely that Si—O single bonds are stabilized by d—p π-bonds. Whatever be the explanation, SiO_2 forms a giant macromolecular structure involving SiO_4 units containing Si—O single bonds. GeO_2 follows SiO_2 closely but SnO_2 and PbO_2 commonly form rutile lattice (TiO_2 type : 6 : 3 coordination). The oxides MO_2 become increasingly basic from M = C to M = Pb. Thus CO_2 and SiO_2 are acidic, GeO_2 develops faint basic character while SnO_2 and PbO_2 are amphoteric. PbO_2 is oxidizing in nature. There are no definite hydroxides $M(OH)_4$ though hydrous oxides MO_2, xH_2O are often precipitated as a product of hydrolysis.

CO cannot be regarded as an oxide of divalent carbon though the oxidation number of carbon in it is +2. Silicon forms SiO only at high temperature, but Ge, Sn and Pb form stable oxides of formula type MO having layer lattices. They are slightly more ionic and basic than the corresponding dioxides. Ge^{II} and Sn^{II} are reducing agents.

Lead forms a mixed oxide Pb_3O_4 ($2PbO, PbO_2$; red lead).

Oxides of carbon

CO and CO_2 are the most important and common oxides of carbon. In addition, there are two other stable oxides, C_3O_2 and $C_{12}O_9$ and the unstable oxides C_2O, C_2O_3 and CO_3.

Carbon monoxide

Carbon monoxide is formed by burning carbon in insufficient oxygen. In the laboratory it is obtained by dehydrating formic acid with conc. H_2SO_4. Mixture of CO and H_2, known as **synthesis gas**, is produced industrially by a variety of reactions for use in various organic synthesis (see use).

(a) controlled oxidation or catalytic steam "reforming" of methane (from natural gas) or light petroleum.

(b) gasification of coal with oxygen and/or steam at ≈ 1500°C.

$$C + H_2O(g) \longrightarrow CO + H_2 ; \Delta H° = +131 \text{ kJ mol}^{-1} ; \Delta S° = +134 \text{ kJ mol}^{-1}.$$

CO_2 formed may be removed by washing with monoethanolamine (or sodium arsenite; see CO_2). Sulphur compounds e.g., H_2S, COS (formed from S in natural hydrocarbon or coal) have to be removed carefully (see Group VI) before synthetic use in reactions catalyzed by transition metals. CO in blast furnace gases (with N_2) or in producer gas (see Fuels) may be recovered by complexing with $CuAlCl_4$ in aromatic solvents.

Properties

CO is a colourless, odourless, poisonous gas which is sparingly soluble in water. It burns with a blue flame in air.

$$2CO + O_2 = 2CO_2; \quad \Delta H° = -565 \text{ kJ mol}^{-1}$$

The highly exothermic reaction forms the basis of many gaseous fuels (see Fuels under use).

CO reduces ammoniacal silver nitrate to silver and palladous chloride to palladium :

$$PdCl_2 + H_2O + CO = Pd + 2HCl + CO_2.$$

Test papers soaked in $PdCl_2$ solution turns black on exposure to carbon monoxide.

Estimation

It reduces many metal oxides (see Ellingham diagram). I_2O_5 is reduced to I_2 — the reaction may be used for the detection of CO and also for its estimation by titrating the liberated iodine :

$$I_2O_5 + 5CO = I_2 + 5CO_2 \quad \textit{(Ditte's reaction)}$$

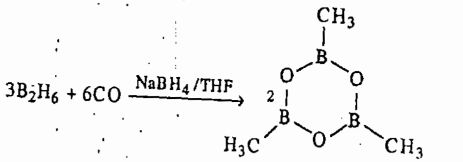
CO may also be estimated by absorption in an acid solution of CuCl after removal of O_2 (alkaline pyrogallate) and CO_2 (KOH);

$$CuCl + CO + 2H_2O = [Cu(CO)Cl(H_2O)_2].$$

Though a neutral oxide, CO reacts with sodium methoxide or fused caustic soda at elevated temperature or under pressure to give sodium acetate/formate :

$$CO + CH_3ONa = CH_3COONa \qquad CO + NaOH = NCOONa$$

Cl_2, Br_2 or liquid S adds to CO forming $COCl_2$, $COBr_2$ or COS. B_2H_6 adds to CO to form BH_3CO, a rare example where CO adds a simple Lewis acid. In presence of $NaBH_4/THF$, however, B-trimethyl boroxine is obtained.



Alkali metals in liquid NH_3 react with CO to produce colourless crystalline salts containing $[OC \equiv CO]^{2-}$ ion

$$2Na + 2CO \longrightarrow NaOC \equiv CONa$$

Although CO is a very weak Lewis base, it acts as a strong ligand to transition metals — nickel forms volatile $Ni(CO)_4$ at ordinary temperature. Many other transition metals form a wide variety of carbonyls under different conditions (see bonding).

This strong complexing ability of CO is respondible for its toxic nature — it forms a bright red complex with haemoglobin (carboxy-haemoglobin) which is nearly 100 times more stable than the oxygen-haemoglobin complex normally formed in oxygen transport. This disrupts the oxygen transport system in the body and may cause unconsciousness to death. Mild poisoning may be rapidly combatted with fresh air/oxygen (see bonding).

CO is not rapidly adsorbed by active charcoal. Hence ordinary gas masks cannot protect one from the gas. Rescue teams in mines are provided with a breathing apparatus which contains a mixture of MnO_2 and CuO that catalytically oxidizes CO to CO_2 in presence of air.

Bonding

The bonding in CO is best represented in terms of the m.o. description (Ch. 7); the conventional valence bond description :C ≡ O: also agrees with the bond order of three — equal to one sigma and two pi bonds, which is consistent with the short C—O distance (113 pm) and high force constant (186 N m^{-1}). However, the HOMO in CO is the 3σ m.o. (only valence shell m.o.s counted) which is largely non bonding in character and is localized near the carbon. Similarly, the LUMO (2π, anibonding) has mainly carbon 2*p* character. Accordingly, CO acts as a π-acid ligand to transition metals, back accepting electron density from filled metal orbitals into its empty antibonding m.o. Since both HOMO and LUMO are localized near carbon, σ-donation to metal in effect makes the carbon partially positively charged which, in turn, enhances its acceptor capacity via back bond. The M—C back-bonding, on the other hand, makes the C an efficient σ-donor. This mutually supporting σ and π-bonding (synergic = working together; Greek *syn* = together; *ergos* = work) is the principal reason for the stabilization of low oxidation states of metals by CO. In $Ni(CO)_4$ and Fe $(CO)_5$ for example, the oxidation states of the metals are zero. This is in keeping with the effective atomic number rule or the 18-electron rule for the stability of 18-electron valence shell configuration of the metal (same number of electrons as in the next inert gas) :

Ni $(CO)_4$: Ni (Z = 28)   4CO groups : 4 × 2 = 8*e*, Total = 36 *e* (Kr)

We shall have more on carbonyls in chapters 27 and 32.

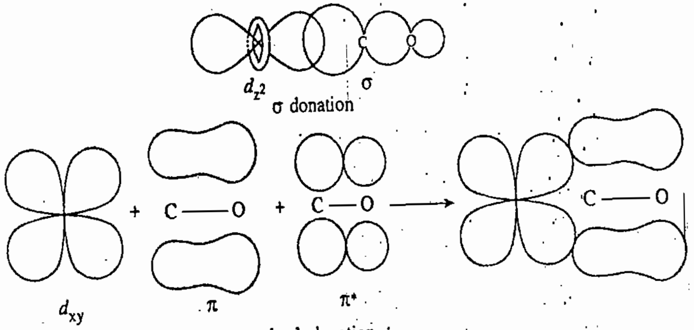
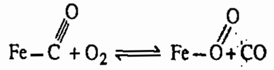


Fig. 21.8

Synergic σ and π-overlap from CO (schematic).

[Sec. 21.3.5 *Carbon monoxide*]

The terminal M—C—O unit in carbonyls is linear to give maximum π-overlap. However, they may be bent when sterically forced, as in carboxy haemoglobin. Haem is Fe(II) complex of protoporphyrin (see Iron) which when free, can bind CO 25,000 times more effectively than oxygen. But when haem is present in myoglobin or haemoglobin, CO is bound only about 100 times as strongly as O_2. Steric crowding froces the Fe—C—O linkage to be bent with a consequent weakening of the Fe—C bond. The equilibrium can be readily reversed with large excess of O_2, which is done with victims of CO poisoning :



$$\text{Fe}-\overset{\text{O}}{\overset{/\!/}{\text{C}}} + O_2 \rightleftharpoons \text{Fe}-\overset{\text{O}}{\overset{/\!/}{\text{O}}} + \text{CO}$$

Q. 21.11 *In spite of the large difference in electronegativity between C and O the dipole moment of CO is very small (0.1 D), with the negative end of the dipole near the less electronegative C—atom. Comment.*

Hint : Consider Lewis structure and m.o. diagram. The nature of distribution of the bond pairs (localized near O) and lone pairs (localized near C, on the HOMO) is complex. The carbon lone pair presumably more than counteracts the efect of the bond pairs (localized near O) and the lone pair on O. Electronegativity considerations are largely based on bond pair electron distribution and do not always lead to correct anticipations. The discrepancy increases more where antibonding orbitals are also occupied.

Q. 21.12 *What conclusion can be drawn from the fact that CO forms large number of carbonyl complexes with transition metals but no stable carbonyl of main group elements are known?*

Hint : It appears that CO is a rather poor σ-donor. The existence of the vast range of transition metal carbonyls may be largely due to stabilization via dative π-back-bonding which appears unlikely for main elements.

Uses

The many industrial uses of carbon monoxide include the synthesis involving water gas and synthesis gas. Pure hydrogen may be obtained by the *Water Gas Shift* (WGS) reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^\circ = -41.2 \text{ kJ mol}^{-1}; \Delta G^\circ = -28.5 \text{ kJ mol}^{-1}$$

The reaction is heterogeneously catalyzed by iron-chromium and zinc-copper oxides. Homogeneous catalysis with transition metal carbonyl complexes and liquid water has also been achieved.

CO is a major constituent of gaseous fuels used in industry including coal gas which is also used as a domestic fuel through pipeline supply. The important fuels containing CO are

(i) **Water Gas :** CO = 42% CO_2 3% H_2 48% CH_4 1% N_2 6% (approx).

It is produced by alternately passing steam and air through a bed of red or white hot coke. The endothermic water gas reaction (see properties) cools the coke bed which is reheated by the air.

(ii) **Producer gas :** CO = 25% N_2 70% CO_2 4% (CH_4, H_2, O_2 etc.).

This is produced by passing air through a bed of red hot coke :

$$2C + O_2 = 2CO \quad \Delta H^\circ = -221 \text{ kJ mol}^{-1}; \Delta S^\circ = +179 \text{ kJ mol}^{-1}.$$

(iii) **Coal gas :** H_2 45-50% CH_4 30-50% CO 5-10% others < 1-5%.

This is obtained by destructive distillation of bituminous coal (high temperature carbonisation).

As mentioned earlier, CO is also used in the extraction of Ni and is involved in the reduction of other metal oxides, for example Fe_2O_3 in the blast furnace.

Synthetic uses

CO can be catalytically reduced by H_2 to a variety of products under varying conditions, e.g.,

$$CO + H_2 \xrightarrow[200\ atm/300°C]{ZnO + Cr_2O_3} CH_3OH$$

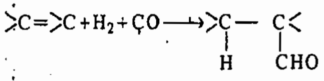
$$CO + H_2 \xrightarrow{Fe,\ Ru\ etc.} CH_4,\ alkanes$$

Fischer Tropsch synthesis

The heterogeneous reduction of CO by H_2 catalyzed by metals (Fe, Co, Ni, Ru etc. on alumina or other support) or by oxides of metals (Co, Cr etc.), known as Fischer-Tropsch synthesis, provides a method for obtaining liquid hydrocarbon fuels from coal as a substitute for natural petroleum. However, the method is still meaningful only when coal is cheap and oil is not available for strategic reasons. By this process, one may obtain a variety of products like CH_4, liquid hydrocarbons, waxy hydrocarbons, methanol and higher alcohols etc. Nickel seems to be best for methanation while cobalt is suitable for higher alkanes. EtOH, CH_3CHO and CH_3COOH are the principal products using Rh. A newly developed catalyst by the Shell company is said to give a waxy product that can be converted to diesel and jet fuel. The methanol obtained by this process may be converted to petroleum hydrocarbons over high silica zeolites. Extensive efforte are being made to find suitable homogeneous catalysts for economically viable reduction of CO by H_2.

Hydroformylation "Oxo process"

CO and H_2 add to olefinic double bonds to produce aldehydes and alcohols in a homogeneous reaction catalyzed by CO_2 (CO)$_8$ (150 — 180°C; 200 — 400 atm) :



$$>C=<C + H_2 + CO \longrightarrow >\underset{\displaystyle H}{\underset{|}{C}}-\underset{\displaystyle CHO}{\underset{|}{C}}<$$

The reaction is called **hydroformylation** (also **oxo** reaction) as it involves addition of H and the –CHO group (formyl), derived from H_2 and CO, to an olefin. The main use of the reaction is in converting propene and higher alk-1-enes to aldehydes and alcohols. In the original process developed using Co-compound, some 15 percent of the olefin is hydrogenated to saturated hydrocarbon and some ketones and alcohols are obtained as by-products. A more effective process using rhodium triphenylphosphine complexes operates under milder conditions (100°C, few atmosphere pressure) with no loss of alkene by hydrogenation.

The mechanism established with $Co_2(CO)_8$ involves the following main steps :

$$H_2 + Co_2(CO)_8 \longrightarrow HCo(CO)_4$$

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$$

$$HCo(CO)_3 + RCH=CH_2 \rightleftharpoons RCH_2CH_2Co(CO)_3$$

$$RCH_2CH_2Co(CO)_3 + CO \rightleftharpoons RCH_2CH_2(CO)Co(CO)_3$$

$$RCH_2CH_2(CO)Co(CO)_3 + H_2 \longrightarrow RCH_2CH_2CHO + HCo(CO)_3.$$

With Rh-complex, the mechanism seems to be essentially the same, the $(Ph_3P)_2RhCO$ group taking the place of $Co(CO)_3$ group.

Carbon Dioxide

CO_2 is also a major industrial chemical which is mainly obtained as a by-product from several industrial processes, for example (a) manufacture of H_2 for NH_3 (b) fermentation industries (c) calcination of limestone and (d) flue gases from coal-based power stations.

(a) $CO + H_2O \rightleftharpoons CO_2 + H_2$ (Water Gas shift Reaction)

(b) $C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 2CO_2$ (anaerobic condition)

(c) $CaCO_3 \longrightarrow CaO + CO_2$

(d) $C + O_2 = CO_2$

CO_2 may be recovered by absorbing in either Na_2CO_3 or ethanolamine solution (Girbotol process) :

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3.$$

$$2NH_2CH_2CH_2OH + H_2O + CO_2 = (HOCH_2CH_2NH_3)_2CO_3.$$

In either case, the gas can be regenerated by warming.

The colourless, odourless (faint pungent smelling) gas can be readily liquefied under pressure; $T_c = 31°C$; $P_c = 72.8$ atm; B.P. –56°C (at 5.3 atm). Expansion from a cylinder leads to deposition of "snow" of solid CO_2 which can be compressed to "dry ice" blocks ("cardice"). It sublimes at –78°C under atmospheric pressure.

CO_2 is fairly soluble in water forming a weakly acidic solution. It is only slowly and partly hydrated to H_2CO_3 (carbonic acid), the bulk being present in the molecular form.

$$H_2CO_3 \rightleftharpoons H_2O + CO_2 \quad K_{298} = [CO_2]/[H_2CO_3] \approx 600$$

The solubility increases remarkably under pressure. Neutralization of the dissolved CO_2 occurs by two different routes depending on pH :

$$pH < 8: \quad H_2O + CO_2 \rightleftharpoons H_2CO_3 \qquad (slow)$$

$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \qquad (fast)$$

The overall reaction follows a pseudo-first order kinetics, since H_2O is always in large excess.

$$pH > 10: \quad CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (slow)$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O \qquad (fast)$$

The overall rate is first order in both CO_2 and OH^-. Between pH 8–10, all equilbria are involved.

The apparent* dissociation constants of H_2CO_3 are (298 K)

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad K_2 = 4.8 \times 10^{-11}$$

[*The equilibrium for the first step assumes that all CO_2 dissolved and undissociated is present as H_2CO_3. It will be erroneous to consider "carbonic acid" as a very weak acid from this value of K_1. Since the major amount of carbon dioxide is present as molecular CO_2 (hydrated), the true dissociation constant K_a would be different :

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+][HCO_3^-]}{[H_2CO_3 + CO_2]} \frac{[H_2CO_3 + CO_2]}{[H_2CO_3]} = K_1 \frac{[H_2CO_3 + CO_2]}{[H_2CO_3]}$$

Since $[CO_2] = 600\,[H_2CO_3]$ (from the value of K)

$$K_a = K_1(600 + 1) = 4.2 \times 10^{-7} \times 601 = 2.5 \times 10^{-4}$$

The corresponding value of pK_a (3.6) is consistent with an acid with the structure $(HO)_2C=O$. (Pauling's formula : $pK_a = 8 - 5n$; $n = 1$). The pH of a saturated solution of CO_2 at 1 atm is 3.7.]

An acid hydrate $CO_2.8H_2O$ can be crystallized from the aqueous solution of CO_2 at 0°C and a pressure of about 50 atm.

Carbonic acid

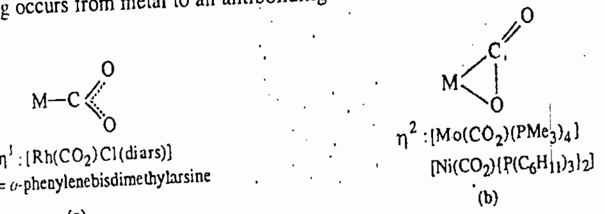
Free carbonic acid has not been isolated, though its acid salts (bicarbonate) and normal salts (carbonate) are well-known. An etherate of probable composition $OC(OH)_2 \cdot O(CH_3)_2$ is obtained by reacting HCl with Na_2CO_3 in presence of dimethyl ether at very low temperatures (–50°C). The white crystalline solid (m.p. –47°C) decomposes at 5°C. H_2CO_3 is believed to be present in the gaseous phase by thermal decomposition of NH_4HCO_3.

CO_2 as ligand

CO_2 is a mild Lewis acid as shown by the formation of carbonates with oxide/hydroxide ions and carboxylic acids with carbanion reagents. The neutral CO_2 molecule also acts as a Lewis base towards metal atoms in low oxidation states :

$$\underset{red}{[Ni^0(PEt_3)_4]} + CO_2 \xrightarrow[\text{1 atm/toluene}]{\text{room temp}} \underset{yellow}{[Ni^0(CO_2)(PEt_3)_3]} + Et_3P$$

Monodentate (η^1), bidentate (η^2), and bridging roles are known. Extensive backbonding occurs from metal to an antibonding π orbital of CO_2.



η^1 : $[Rh(CO_2)Cl(diars)]$
diars = o-phenylenebisdimethylarsine
(a)

η^2 : $[Mo(CO_2)(PMe_3)_4]$
$[Ni(CO_2)\{P(C_6H_{11})_3\}_2]$
(b)

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Reduction

CO_2 can be reduced electrochemically to CO (aq. medium) and $C_2O_4^{2-}$ (in organic solvents such as DMF) :

$$CO_2 + 2H^+ + 2e \longrightarrow CO + H_2O; \quad 2CO_2 + 2e \longrightarrow C_2O_4^{2-}.$$

Electrolysis mediated by platinized TiO_2 or transition metal complexes [e.g. $U\,(bipy)_2\,(CO)_2]^{2+}$ has been carried out to reduce CO_2 to various products like CO, CH_4, CH_3OH, $HCOO^-$ (formate) etc. Reduction of CO_2 to organic compounds under ordinary conditions occurs only in nature during photosynthesis :

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

It is only one from the numerous examples which illustrate the superiority of nature as a skilled chemist.

Structure and Bonding

The CO_2 molecule is linear and symmetrical ($D_{\infty h}$ point group), the C = O bond lengths being 1.16 A°. The central carbon atom, after unpairing of the s-pair of electrons and promotion, may be supposed to use two sp ($s - p_z$ if z-axis is taken as the inter-nuclear axis or rotational axis) hybrid orbitals to form two σ-bonds to the two O atoms. The two singly occupied p-orbitals on C (p_y, p_z) can now give rise to two π-bonds, one with each of the two oxygen atoms (with corresponding singly occupied p-orbitals). There are thus two π-bonds in mutually perpendicular planes. The bonding is best explained in terms of molecular orbital description involving 3 center m.o.s.

Assuming Z-axis as the internuclear axis, the σ-bonding orbitals available for carbon and each oxygen are 2s and $2p_z$. The 2s-orbitals of oxygen are much lower in energy and essentially nonbonding. The C-2s and $2p_z$-orbitals on two oxygen atoms (O_1 and O_2 say) form a pair of σ-m.o.s. ($\sigma_{a_{1g}}$ and $\sigma^*_{a_{1g}}$). The C - $2p_z$ and O - $2p_z$-orbitals form another pair of σ-m.o.s. ($\sigma_{a_{1u}}$ and $\sigma^*_{a_{1u}}$).

Since the 2p orbital of carbon is of higher energy than the 2s orbital, the $\sigma_{a_{1u}}$ m.o. will be of somewhat higher energy than the $\sigma_{a_{1g}}$-m.o.

The two 2p-orbitals on C (p_x and p_y) and the corresponding pairs of atomic orbitals on O can now combine to form one pair of bonding π m.o.; one pair antibonding π m.o. and one pair non-bonding m.o.

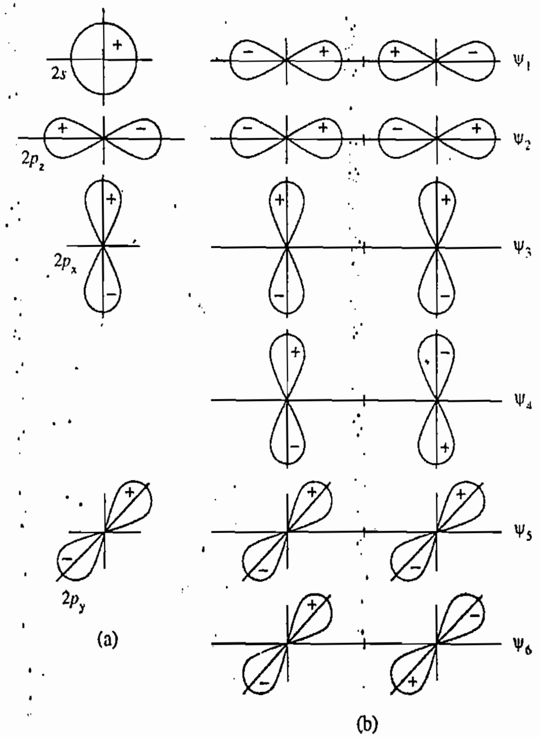


Fig. 21.9 : (a) valence orbitals of the central carbon atom and (b) the group orbitals of the two oxygen atoms.

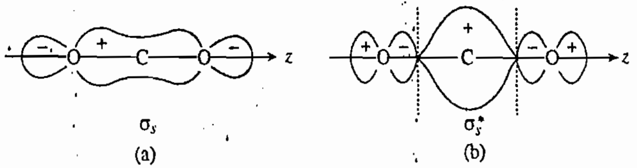


Fig. 21.10 : Combination of carbon-$2p_z$ and ψ_1 of oxygen group forming (a) bonding $\sigma_{a_{1g}}$ and (b) antibonding $\sigma^*_{a_{1g}}$ m.o.s. (vertical lines show nodes).

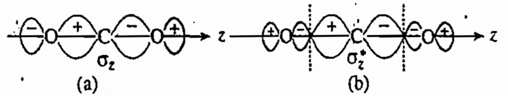


Fig. 21.11 : Combination of carbon $2p_z$ and ψ_2 of oxygen group forming two more σ m.o.s.- (a) $\sigma_{a_{1u}}$ and (b) $\sigma^*_{a_{1u}}$.

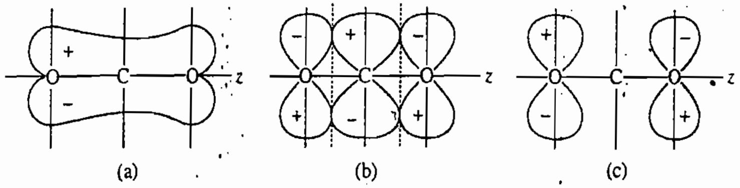


Fig. 21.12 Combination of $2p_x$ orbital of carbon and ψ_3 group of orbitals on oxygen gives (a) a bonding $\pi_{e_{1u}}$ and (b) an antibonding $\pi^*_{e_{1u}}$ m.o. The $2p_y$ and ψ_5 will similarly from another pair of π-m.o. (not shown) and (c) There are no symmetrically suitable orbitals of the central carbon for oxygen group orbitals ψ_4' and ψ_6'. Therefore, the latter act as non-bonding orbitals $\pi^{nb}_{e_{1g}}$ localized near the oxygen atoms. The nonbonding m.o.-arising from ψ_4 is shown in (c).

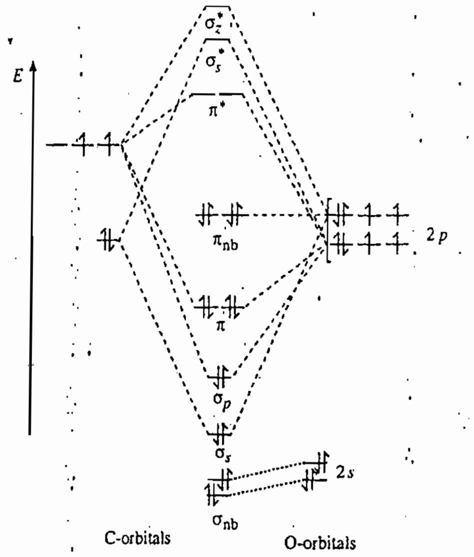


Fig. 21.13

Qualitative m.o. energylevel diagram for CO_2.

The total number of 16 valence electrons (2 × 6 + 4) may now be distributed among the m.o.-s as usual, when the highest occupied m.o. appears to be the non-bonding m.o., essentially localized on the oxygen atom. The total number of m.o.s. (12) is equal to the total number of participating atomic orbitals in the valence shell of the atoms (four on each of the 3 atoms).

Similar bonding schemes apply to isoelectronic linear species like NO_2^+, N_2O, N_3^- etc.

Use

The most extensive use of CO_2 is in refrigeration — of ice-cream, meat, fish etc. Over the last two decades, compressed liquid CO_2 is gradually replacing dry ice for the purpose because of lower production cost and transporting facilities. Liquid CO_2 is also used as a substitute for chlorofluorocarbons in aerosol propellants.

Gaseous CO_2 is extensively used (i) to prepare "soda-water" and other soft drinks (ii) to provide an inert atmosphere for welding (iii) to neutralize alkalis and (iv) in the manufacture of sodium carbonate (washing soda), bicarbonate and urea (via ammonium carbamate).

The Greenhouse Effect

The Greenhouse Effect : There is now a serious concern about the increase of CO_2 content of the atmosphere which is causing a slow rise in global temperature. The effect is called the Greenhouse effect by analogy with the "green-houses" maintained in winter countries by artificial heating. The CO_2 molecules in the atmosphere permit the passage of visible light but absorb strongly in the infrared region, thereby hindering heat radiation from the earth. In the early age of the earth, the concentration of CO_2 in the atmosphere remained more or less steady due to deposition of carbonates (particularly calcium carbonate). But with increased burning of carbonaceous fuels and decrease in forest areas (trees consume CO_2 for photosynthesis), the CO_2 content of the atmosphere has been increasing in an alarmingly higher rate.

It has been estimated that if the present rate of warming continues, average temperature of the earth's atmosphere will rise by about 2.5°C in the next 30 years — resulting in major climatic changes. The polar ice-caps will melt with a consequent rise in sea-level whereby many sea-side localities including some big islands will be completely submerged. Forestation and use of non-fossil fuels as energy source (e.g. wind and atomic energy) seem to be the only remedy, though with doubtful practicability.

Carbon suboxides

C_3O_2 (tricarbon dioxide) is obtained by dehydrating malonic acid with P_4O_{10} at reduced pressure :

$$HOOC.CH_2.COOH \xrightarrow{P_4O_{10}/150^\circ C} O=C=C=C=O + 2H_2O$$

It is a foul-smelling gas (b.p. 6°C) stable at −78°C which polymerizes at room temperature to a yellow solid. At higher temperatures, polymerization produces red (> 100°C) or violet (400°C) solids which decompose to carbon above 500°C. All the polymers appear to contain polycyclic six-membered lactone rings. The C_3O_2 molecule is linear.

C_3O_2 recombines with water to give back malonic acid and reacts with HCl and NH_3 to give the acid chloride or amide of malonic acid :

$$C_3O_2 + 2NH_3 \longrightarrow H_2C(CONH_2)_2 \quad \text{amide}$$

$$C_3O_2 + 2HCl \longrightarrow H_2C(COCl)_2 \quad \text{acid chloride}$$

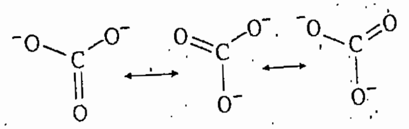
Thermolysis of C_3O_2 probably gives rise to C_5O_2, but this is doubtful. $C_{12}O_9$, a white solid, is another suboxide which is the anhydride of mellitic acid, $C_6(COOH)_6$.

Linear catenated oxides C_nO_2, i.e., OC_nO are stable when n is odd. The system has a total of $(2n+4)$ π m.o.-s (2 per C-atom and 2 per O-atom) to accomodate $(2n+6)$ electrons (2 per C-atom and 3 per O-atom). When n is even, the highest occupied level always contains two electrons in two degenerate π m.o.-s, giving rise to an unstable diradical.

Carbonates, bicarbonates, and peroxocarbonates

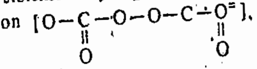
Carbonates and bicarbonates of the alkali and alkaline earth metals have been discussed earlier (Chapters 18 and 19). The lower solubility of alkali metal bicarbonates in comparison to the carbonates owing to extended H-bonding in the former has also been mentioned. Most metal carbonates other than those of the alkali metals are sparingly soluble in water. Carbonates of heavy metals (e.g., Pt, Ba etc.) and highly polarizing cations (Fe(III), Al(III), Pb(IV) etc.) are either unstable or non-existent owing to polarization of the carbonate ion. Similar arguments apply to bicarbonates also.

The carbonate ion is planar, with all C—O distances equal (129 pm). In V.B. terminology this can be rationalized with sp^2 hybridized carbon atom among the canonical forms



In m.o. description we have one filled bonding π-m.o. embracing all four atoms. Both these formalisms suggest a π-bond order $^1/_3$ for each C—O bond, making a total bond order $1\frac{1}{3}$ for each (σ-bond order 1).

Peroxo carbonates

Peroxocarbonates contain an anion in which one 'O' of carbonate or bicarbonate has been replaced by the peroxo group (–O–O–), e.g., the HCO_4^- ion [O–O–COOH]⁻, as in $NaHCO_4 . H_2O$. Alkali metal salts of stoichiometry $M_2C_2O_6$ are known in the solid state which probably contain the anion  $[O-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-O^{=}]$, analogous to the peroxodisulphate ion. $K_2C_2O_6$, blue solid, results from the electrolysis of a solution of K_2CO_3 at –10°C using a high current density. They are hydrolyzed to HCO_3^- and H_2O_2 in solutions :

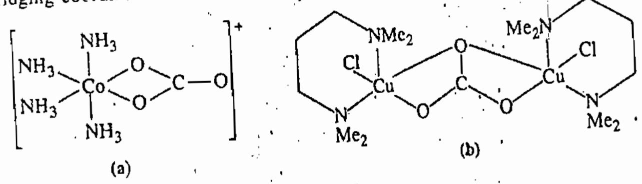
$$C_2O_6^{2-} + H_2O \longrightarrow HCO_4^- + HCO_3^- \ (fast)$$

$$HCO_4^- + H_2O \rightleftharpoons HCO_3^- + H_2O_2$$

Several classical Werner complexes contained the carbonate ion as ligand (e.g., 21-XIIa). Such complexes may also be prepared using CO_2:

$$[Pt(PPh_3)_3] + CO_2 + O_2 \xrightarrow[25°C]{benzene} [Pt(CO_3)(PPh_3)_2] + Ph_3PO$$

Bridging coordination is also known, e.g., in 21-XII b.



(a) (b)

21-XII

Oxides of Silicon

SiO_2 or silica occurs in nature as sand, often coloured yellow or brown due to iron (III) oxides. It is also the major constituent of several rocks e.g., granite and sandstone. Many other minerals, some of which are used as semiprecious gemstones, are basically hydrated SiO_2 : rose quartz (pink), morion (dark brown), amethyst (violet), citrine (yellow) — all containing α-quartz (see later); opal, agate, onyx, jasper and flint — containing poorly crystalline forms of quartz. Finely divided silica occurs in certain mines in Europe and north America known as Kieselguhr (German *Kiesel* = flint, *Guhr* = earthy deposit) and diatomaceous earth (remains of minute unicellular marine algae called *diatoms*). These are largely used in filtration plants, catalyst beds and as abrasives, fillers etc.

Silica also occurs in vegetable and animal organism, e.g. straw of cereals, bamboo cane and sponges.

SiO_2 have different macromolecular structures built up of SiO_4 tetrahedra joined by sharing of oxygen atoms. The two principal forms are *quartz* and *cristobalite*, each having a low temperature α-form and a high-temperature β-form. A third form, **tridymite** (also α and β), is probably a solid solution of silica and impurities like metal oxides (called 'mineralizers'). Some important informations about the three forms are given below (Table 21.8).

TABLE 21.8

Properties of quartz, tridymite and cristobalite

	quartz	**tridymite**	**cristobalite**
(a) *Transition temp α → β* (°C)	573°	120-160	200–280
(b) *do, one form to another* (°C)		$\xrightarrow{867}$	$\xrightarrow{1470}$
(c) *density* (g cm⁻³)	2.65 (α) 2.53 (β)	2.26	2.33
(d) *Si–O dist* (A°)	1.60–1.62	—	1.61
(e) *∠Si–O–Si* (°)	144° (α) 155° (β)	—	147°

The conversions from α to β form involve little structural change and are rapid. But the conversions of quartz to tridymite (867°C) and tridymite to cristobalite (1470°C) are slow as they involve breaking and reforming of bonds which require a high energy of activitation.

At room-temperature, the most stable form (thermodynamically) is α-quartz, in which interlinked SiO_4 tetrahedra form a helical chain. The helices in any one chain may be all right handed or left-handed so that the crystals show enantiomorphism (form non-superimposable mirror images). α-quartz has high optical activity. In cristobalite the Si-atoms are arranged in a diamond like arrangement with O atoms interposed between each pair of Si.

Dense forms of SiO_2 also exist, e.g., *Coesite* (ρ = 2.9 g cm⁻³) and *Stishovite* (ρ = 4.3 g cm⁻³). These may be prepared under very high pressures (35-120 kiloatmospheres) and high temperature (≈ 1300°C). They have also been found in some meteor craters. Both of them revert to normal SiO_2 on heating.

Properties

When heated, silica starts softening above 1500°C and turns into a viscous melt at 1700°C. Before turning into a melt it becomes plastic and can be worked and blown like glass (in an oxyacetylene flame). It is indeed a "glass" in the general sense with an amorphous composition from disordered array of rings, chains and three dimensional units.

Silica is chemically rather unreactive towards acids except HF, H_2, Cl_2 and metals. But it is readily attacked by alkali, fused carbonates, fluorine, and HF. At red heat, it is converted to $SiCl_4$ by Cl_2 in presence of C. Detection of silicates is based on its reaction with HF(CaF_2 + conc. H_2SO_4) to form volatile SiF_4 which subsequently hydrolyzes to a gel of $Si(OH)_4$ and H_2SiF_6 (see detection).

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = 2CaSO_4 + SiF_4 + 2H_2O.$$

Silicates are discussed separately in the next section. "*Amorphous silica*" or *silica gel* is obtained by acid hydrolysis of aqueous sodium silicate, washing the gelatinous "silicic acid" to free from electrolytes, followed by dehydration. The resulting porous mass has a high surface area; it is widely used in chromatography and catalysis as support and also as a dehydrating agent. Silica gel containing cobalt(II) salts is blue when dry but turns pink after absorbing moisture (> 40% of its own weight; it can be reused after dehydration.

Use

Silica is used in making valuable laboratory apparatus including cells, prisms and lenses for use with U.V. light to which it is transparent. Some use of kieselguhr and silica gel have been mentioned earlier. Silica gel is also used in paints and varnishes to provide a matte finish and in food industry as an anticaking agent for cocoa, fruit juice powdered sugar etc. Silica is not poisonous to animals but inhalation of finely divided silica (and silicate minerals like asbestos) damages the lungs and causes silicosis.

High-purity α-quartz is a piezoelectric material used extensively in quartz clocks and similar other devices involving crystal oscillators or electromechanical devices. Such crystals are made synthetically by growing a seed crystal from dilute aqueous NaOH and vitreous silica at 400°C and high pressure (≈ 1700 atm).

Metastable SiO is formed when SiO_2 is heated with Si at high temperature (1250–1300° C) and low pressure (10^{-4} mm Hg). It readily disproportionates to a very low density ($\rho = 1.97$ g cm^{-3}) fibrous form of SiO_2 (W-SiO_2).

$$SiO_2 + Si \longrightarrow 2SiO \longrightarrow W\text{-}SiO_2$$

Oxides of Ge, Sn and Pb

Tin occurs in nature largely as SnO_2 (Cassiterite). GeO_2 and SnO_2 may be prepared by strongly heating the metals in oxygen or with concentrated nitric acid. PbO_2 is made by dissolving red lead (Pb_3O_4) in dilute nitric acid when PbO_2 is left as a residue. Oxidation of lead acetate solution by bleaching powder (heat) provides another method of its preparation :

$$Pb(CH_3COO)_2 + Ca(OCl)Cl + H_2O = PbO_2 + CaCl_2 + 2CH_3COOH.$$

GeO_2 and SnO_2 are white solids, while PbO_2 is chocolate brown. GeO_2 resembles silica and softens before melting (1086°C) and solidifies from the melt as an amorphous glassy form. The quartz, stishovite and crystoballite analogues are also known. The most common forms of SnO_2 and PbO_2 have the rutile structure (TiO_2; 6 : 3 coordination).

GeO_2 is sparingly soluble in water, SnO_2 and PbO_2 are practically insoluble. GeO_2 is weakly acidic, forming germanates (e.g. Na_2GeO_3) with alkalis, and forming $GeCl_4$ with concentrated HCl. SnO_2 is amphoteric as shown by its reaction with fused NaOH and concentrated H_2SO_4 (it is insoluble in all other acids).

[Sec. 21.3.5 *Oxides of Ge, Sn, Pb*]

$$SnO_2 + 2NaOH + 2H_2O = Na_2Sn(OH)_6$$

$$SnO_2 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O.$$

PbO_2 also dissolves in hot caustic alkalis, but forms Pb(II) salts with hot concentrated HCl or H_2SO_4.

$$PbO_2 + 2NaOH + 2H_2O = Na_2Pb(OH)_6$$

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2$$

SnO_2 may be volatilized as violet SnI_4 by heating with NH_4I :

$$SnO_2 + 4NH_4I = SnI_4 + 4NH_3 + 2H_2O.$$

A manifestation of the inert pair effect is shown in the strong oxidizing nature of PbO_2. Besides the reaction with concentrated HCl given above, several reactions are noteworthy :

$$PbO_2 + 2S = PbS + SO_2 \quad \text{(inflames on trituration)}$$

$$PbO_2 + SO_2 = PbSO_4$$

$$5PbO_2 + 2MnSO_4 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

PbO_2 itself decomposes to PbO and O_2 at temperatures above 300°C.

There is no true hydroxide $M(OH)_4$. The gelatinous precipitate resulting from hydrolysis of MX_4 type compounds is best regarded as MO_2, xH_2O ($x > 2$) i.e., hydrous oxides.

Oxides MO

Ge, Sn and Pb form stable divalent oxides MO - stability increasing from Ge to Pb. GeO (Yellow) is obtained by heating (1000°C) GeO_2 with Ge (powder) or by dehydration of $Ge(OH)_2$ ($GeCl_2$ + aqueous NH_3). SnO is best obtained by thermal decomposition of stannous oxalate SnC_2O_4 in absence of air.

$$SnC_2O_4 = SnO + CO + CO_2.$$

It may also be prepared by dehydration of $Sn(OH)_2$ in absence of air. SnO is susceptible to oxidation by air and exists in several modifications — commonly a blue-black tetragonal form.

SnO is more basic than SnO_2, but it is overall amphoteric in nature. It dissolves in acids to give Sn(II) salts. In alkaline solution, the final species seems to be the pyramidal $[Sn(OH)_3]^-$ ion, while condensed basic oxide-hydroxides may be formed in intermediate values of pH, e.g., $[(OH)_2SnOSn(OH)_2]^{2-}$.

"Stannous hydroxide" $[Sn(OH)_2]$ is actually hydrated tin(II) oxide, $SnO_2\,xH_2O$ and is precipitated by adding alkali to aqueous Sn(II) solutions; it dissolves in excess base to form stannites :

$$Sn(OH)_2 + NaOH = Na[Sn(OH)_3].$$

The solution is strongly reducing — it reduces Bi(III) to Bi (black), a reaction used in qualitative analysis of Bi.

$$2Bi(NO_3)_3 + 9NaOH + 3Na[Sn(OH)_3] = 2Bi + 3Na_2[Sn(OH)_6] + 6NaNO_3.$$

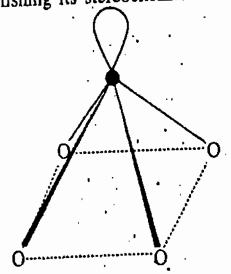
$Sn(OH)_2$ has been prepared by reactions of the following type in non aqueous medium (e.g. THF):

$$2Me_3SnOH + SnCl_2 \longrightarrow Sn(OH)_2 + 2Me_3SnCl$$

PbO has two forms (a) *litharge* (reddish yellow; tetragonal) — stable at room temperature and (b) *massicot* (yellow; orthorhombic) — stable above 488°C. Litharge is prepared by oxidizing molten lead in air above 600°C in a reverberatory furnace and continuously skimming off the molten litharge floating on the surface (m.p. 897°C). Massicot is obtained by heating lead in air.

Essentially basic in nature, PbO dissolves in acids to form Pb(II) salts. But it also dissolves in hot caustic alkali, forming plumbites.

Both SnO and PbO adopt an unusual layer structure in which four O-atoms form the base of a square pyramid with the Sn/Pb at the vertex. The lone pair of electrons on the metal remains on the other side, establishing its stereochemical importance.



21·XIII

Limited addition of dilute alkali to Pb(II) salts in solution forms a white precipitate formally considered as $Pb(OH)_2$; this dissolves in excess alkali to give plumbites. However, true $Pb(OH)_2$ does not appear to exist. The hydrolysis products are now believed to contain condensed polymeric species like $[Pb_6O(OH)_6]^{4+}$.

Red lead

Lead also forms a mixed oxide, Pb_3O_4 (red lead). This is made by calcining litharge in air for about 48 hours within a narrow temperature limit around 340°C.

$$2Pb + O_2 = 2PbO; \quad 6PbO + O_2 = 2Pb_3O_4.$$

Pb_3O_4 decomposes to PbO and O_2 above 470°C. Chemical reactions suggest that the oxide is $2PbO.PbO_2$.

Cold, concentrated or hot dilute nitric acid converts red lead to lead nitrate in solution and leaves an insoluble residue of PbO_2:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

It reacts with glacial acetic acid to form a mixture of $Pb(CH_3COO)_2$ and $Pb(CH_3COO)_4$ which may be separated by crystallization. Lead tetraacetate is an important reagent in organic chemistry (sec. 21.3.7).

Pb_3O_4 is a strong oxidizing agent, oxidizing Mn(II) to MnO_4^- in presence of dilute HNO_3; the equivalent weight corresponds to 1 mol of PbO_2 per mol of Pb_3O_4, i.e., M/2

$$5Pb_3O_4 + 2MnSO_4 + 16HNO_3 = 2HMnO_4 + 2PbSO_4 + 13Pb(NO_3)_2 + 7H_2O.$$

The Pb(IV) atoms form PbO_6 octahedra which are fused into chains by sharing of two opposite edges. The chains are cross-linked by Pb(II), which form pyramidal PbO_3 units.

The oxides of tin and lead have many technical and commercial uses.

SnO_2 is largely used in

(a) **Ceramics Industry :** (i) opacifier for glazes and enamels (ii) pigment base.

(b) **Glass industry :** to toughen glassware with a thin coating of transparent SnO_2 (< 0.1 mm). Thicker films (> 1μm) selectively reflect infrared radiation and provide heat insulation in windows.

(c) **Organic Chemical Industry :** Tin-vanadium and Tin-antimony oxides are used as heterogeneous catalyst in oxidation of aromatic compounds and in the production of acrolein, acrylic acid etc.

Lead oxides are used in

Uses

(a) **Glass and ceramic industry :** PbO is used to make glass with greater density and higher refractive index, together with increased toughness. It is also used in ceramic glazes.

(b) **Storage cell :** Litharge (PbO) or "black oxide" (PbO + Pb) is used in lead storage batteries.

(c) **Pigments :** PbO and Pb_3O_4 ("red lead") are widely used as pigments and in making other pigments e.g. $PbCrO_4$, $CaPbO_2$ (substitute for red lead).

(d) **Oxidizing agent :** PbO_2 is used as an oxidant in chemical industry.

(e) **Ferroelectrics :** Many mixed oxides containing Pb(II) are used as high temperature ferroelectrics e.g., $PbTiO_3$, $PbZrO_3$, $PbNb_2O_6$ etc.

21.3.6 Silicates

Acidic SiO_2 forms silicates when fused with metal oxides, hydroxides or carbonates. The nature and composition of the product varies according to a complicated phase diagram. Fusion of sand with Na_2CO_3 (or K_2CO_3) at about 1400°C forms sodium (or K) silicate which may be dissolved out (from other insoluble products and sand) by hot water under pressure. The thick alkaline solution, *water glass*, contains ions such as $[SiO(OH)_3]^-$ and $[SiO_2(OH)_2]^{2-}$. Such solutions may also be obtained by boiling hydrated silica with concentrated aqueous NaOH (or KOH).

Water glass solutions are used in liquid detergents, as an adhesive for pasting paper and corrugated cardboard, as refractory acid-resistant cements and in making fireproof paints/puttys. Silica gel is also made by modifying sodium silicate solutions.

Solid sodium silicate may be crystallized from the melt (m.p. 1088°C) obtained by fusing sand with Na_2CO_3. A hydrate approximating $Na_2SiO_3, 5H_2O$ may be obtained from the aqueous solution. This is used in slip-casting of porcelain under the commercial name *alkasil*.

Silicate minerals, together with silica and aluminosilicate clays, make nearly 95% of the earth's crust. Various rocks and their breakdown products — sand, soil and clay are mostly silicates. Our building materials - clay, stone or brick as well as cement, concrete, glass and ceramics are also silicates in one form or another. As the earth came to its present form by gradual cooling, the lighter silicate materials crystallized and floated to the top.

The silicate minerals are mostly insoluble due to their extended structure involving different modes of combination between SiO_4 tetrahedral units. A few salient points helpful in understanding the structural principles in silicates are as follows :

1. The strong Si—O bond (ΔH = 466 kJ mol^{-1}) may be considered 50% ionic and 50% covalent from electronegativity difference (3.5 – 1.8 = 1.7; see Ch. 7). It is convenient to treat the structures on an ionic model though the Si^{4+} ion is actually unlikely in view of the high ionization energy involved.

2. The radii of Si^{4+} ion and O^{2-} ions are 0.40 A° and 1.40 A° respectively. The radius-ratio 0.29 is consistent with a coordination number 4 around the Si. A covalent description using sp^3 hybridization of the Si - valence orbitals also leads to the same expectation.

3. The radius of the Al^{3+} ion (0.53 A°) is close to that of the Si^{4+} ion and Al^{3+} can replace Si^{4+} in many silicates. An extra singly charged cation like Na^+ or K^+ maintains electrical neutrality. A pair of ions like ($Na^+ + Si^{4+}$) may also be replaced by isoelectrical ion pairs like ($Ca^{2+} + Al^{3+}$).

4. The SiO_4 tetrahedral units may occur singly or may share one, two three or four O—atoms through corners giving rise to cyclic groups, chains, infinite layers or infinite three-dimensional frameworks. Such sharing always involves corners of different tetrahedra — they never share an edge as that would render the structure unstable.

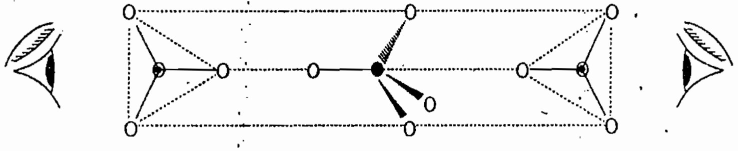
5. The terahedral and octahedral holes resulting from nearly closepacking of the O-atoms are occupied by other metal ions like Be^{2+}, Mg^{2+}, Fe^{2+} etc. The coordination number of the metal roughly follows our expectation from radius ratio for $M^{n+} : O^{2-}$.

	Be^{2+}	Al^{3+}	Mg^{2+}	Fe^{2+}	Ca^{2+}
R_M/r_O	0.25	0.42	0.59	0.68	0.71
C.N.	4	4/6	6	6	8

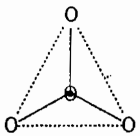
In spite of the limitations of a fully ionic description, the agreements are quite good.

The different structural principles involved in various silicates are summarised below :

The SiO_4 tetrahedron and its two-dimensional representation are as follows :



(i) **No oxygen atom shared** (Orthosilicates, *neso*-silicates)



Discrete SiO_4^{4-} ions :

$M^{II}_2SiO_4$ (M^{II} = Be, Mg, Fe, Mn, Zn)

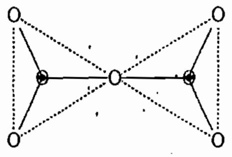
$M^{IV}SiO_4$ (M = Zr).

Olivine : Mg_2SiO_4; about one in ten of the Mg^{2+} ions replaced by Fe^{2+}.

Zircon : $ZrSiO_4$; used as a gem-stone like diamond, but cheaper and softer.

Garnet : $M^{II}_3M^{III}_2$ $[(SiO_4)_3]$; M^{II} = Mg, Ca, Fe^{II}; M^{III} = Cr, Al, Fe^{III}. Used as gemstone, abrasive.

(ii) **One oxygen atom shared** (pyrosilicate, *soro*-silicates)



Discrete $Si_2O_7^{6-}$ ion;

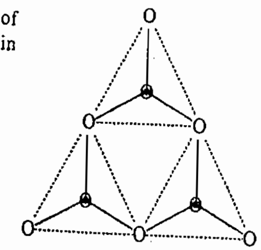
two SiO_2 units joined by sharing an O-atom.

Example comparatively rare.

Thortveitite : $Sc_2Si_2O_7$

(iii) **Two oxygen atoms shared** (closed ring : *cyclo*-silicates; continuous chains : *ino*-silicates)

Each SiO_4 tetrahedron shares an O-atom with each of two neighbouring tetrahedra, resulting in ring or chain anions.

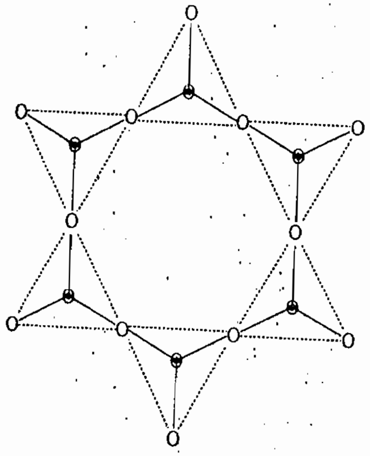


Ring silicates

Two different rings are known :

$Si_3O_9^{6-}$: Three SiO_4 linked together.

Benitoite : BaTi $[Si_3O_9]$



$Si_6O_{18}^{12-}$: Six SiO_4 tetrahedra are linked.

Beryl : $Be_3Al_2Si_6O_{18}$. Emerald has the same formula except that it contains 1-2% Cr, which imparts a deep green colour. Both are used as gemstones.

The rings are arranged one over another in parallel planes and the metal ions lie inbetween. Be is 4-coordinated, Al, Ba are all 6-coordinated.

In beryl, the channels formed by successive rings are permeable to small molecules, e.g. He gas.

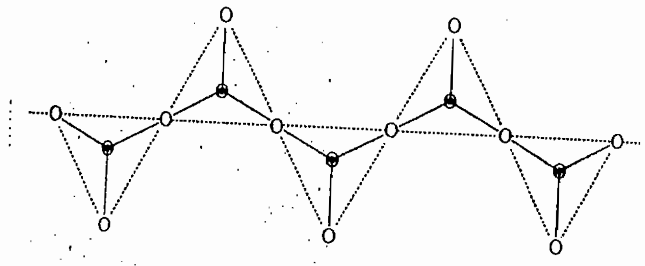
Chain Silicates

The minerals having silicate chains are collectively called *pyroxenes* : $MgSiO_3$, CaMg $(SiO_3)_2$.

Double chains result by joining two simple chains by shared oxygens. Some minerals containing such chains are :

Amphiboles, having anions like $Si_4O_{11}^{6-}$ and others; the asbestos mineral, e.g., *tremolite*, $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$.

Asbestos fibres are mostly used to make roofing sheets and for heat insulation and fire-proof materials. Asbestos dust is very injurious to lungs.



The silicate chains lie parallel to such other; adjacent chains are held by cations between them (electrostatic force). Since the Si—O bonds are strong and directional, it is easier to break the non-directional ionic links; accordingly, the materials cleave parallel to the chains, forming fibres.

(iv) **Three oxygen atoms shared** (sheet silicates; *phyllo*-silicates)

SiO_4 tetrahedra have all three corners attached to three different SiO_4 tetrahedron, resulting in sheet structure.

$$(Si_4O_{10})_n^{4-} : \textit{talc} \text{ (soapstone) } Mg_3(OH)_2Si_4O_{10}.$$

Cations between alternate layers leave only Van der Waals' forces between the corresponding layers, making the mineral very soft. Soapstone derives the name from its slippery feeling.

Talc is used as a dry lubricant. Also used in ceramics, paint, paper and cosmetics (*talcum powder*) industry.

$(Si_3AlO_{10})_n^{5-}$: (Some of the Si atoms replaced by Al); *mica minerals*, e.g., *phlogopite* $KMg_3(OH)_2Si_3AlO_{10}$; *muscovite* $KAl_2(OH)_2Si_3AlO_{10}$.

Replacement of Si(IV) by Al(III) in layers impart an overall negative charge. Electrostatic attraction with the interposed cations makes them much harder than talc. Micas cleave in sheets.

Mica is largely used as electrical insulators. Finely ground mica is used in plastics and rubber as fillers and in ploychromatic and glitter paints.

Clay minerals also belong to this category. They are formed by weathering of igneous rocks. For example, *kaolinite* is formed from feldspars (see next category of silicates) :

$$2[KALSi_3O_8] \xrightarrow{CO_2,\ H_2O} A\lambda_2O_3, 2SiO_2, 2H_2O \text{ (i.e., } Al_2(OH)_4Si_2O_5) + 4SiO_2 + K_2CO_3$$

It consists of electrically neutral layers. *Montmorillonites* have some Al(III) replaced by Mg(II), resulting in small negative charge in the layers. Cations held between the layers are exchangeable. *Fuller's earth* is calcium montmorillonite (used earlier for fulling or cleansing of woollens from grease and dirt, hence the name). *Bentonite* is sodium montmorillonite.

Kaolinite is present in Kaolin or china clay, largely used as a filler in paper and in ceramic industries. Fuller's earth is used to decolorize and deodorize vegetable and mineral oils, fats and waxes. Bentonite is used as drilling mud in drilling oil-wells due to its excellent thixotropic property. The fine plate like particles have '—' charges on the surface and '+' charges on the edges. When undisturbed, the particles align themselves in + – + – |..... orientation, forming a semi-solid gel. On agitation, the alignment breaks and the mass becomes fluid. (*Quick-sand* is a natural example of this phenomenon). Bentonites are also used in foundry sands, mortars, adhesives, puttys and non-drip paints.

Vermiculites are obtained by partial replacement of Mg and Si in talcs by Al. When heated, the mineral dehydrates in a remarkable way by extruding small worm-like structures and hence the name (Latin *vermiculus* = little worm). The porous light-weight residue is used for packing and insulation.

(v) **Four O-atoms shared** (3-dimensional or *tecto*-silicates)

If half the SiO_4 tetrahedra in a layer point upward and the other half point downward, and all the tetrahedra share all four O-atoms with adjacent tetrahedra, we get an infinite three-dimensional network. Since there are no negatively charged terminal oxygen atoms, the whole network becomes electrically neutral and corresponds to $(SiO_2)_n$ i.e., silica.

However, such arrangements acquire an overall negative charge when aluminium atoms replace some of the Si atoms. When a quarter of the Si atoms are so replaced, the unit polymer formula becomes $(AlSi_3O_8^-)$ or $[AlO_2(SiO_2)_3]$; if one half of the Si atoms are replaced, the typical formula similarly becomes $(Al_2Si_2O_8^{2-})$ or $[2AlO_2, (SiO_2)_2]^{2-}$. Additional cations (Na^+, K^+, Ca^{2-} etc.) now occupy holes in the lattice to maintain charge balance. Smaller cations like Fe^{3+}, Cr^{3+} and Mn^{2+} now do not fit the larger cavities. Three groups of minerals contain such three dimensional (3D) aluminosilicate frameworks : (i) feldspars (ii) zeolites and (iii) ultramarines.

Feldspars alone constitute 60% of the earth's crust. Igneous rocks like granite consist of feldspars (with some micas and quartz). The *orthoclase feldspars* like *orthoclase* $K[AlSi_3O_8]$ or $K[AlO_2.(SiO_2)_3]$ and *celsian* Ba $[Al_2Si_2O_8]$ are more symmetrical than the *plagioclase feldspars* like *albite* Na $[AlSi_3O_8]$ and *anorthite* $Ca[Al_2Si_2O_8]$. In the latter, the smaller Na^+ and Ca^{2+} ions do not fit tightly in the lattice cavity and allow for some distortion to take place.

Zeolites

Zeolites* are naturally occurring aluminosilicates having an open three-dimensional structure with loosely held large metal cations and water molecules in spacious honey comb like cavities. Small gaseous molecules like water vapour, ammonia, alcohol, carbon dioxide and small hydrocarbons may also be reversibly trapped by these cavities. The electrostatic binding of the cations increases with increasing charge (actually charge density) : $M^{3+} > M^{2+} > M^+$. Thus a zeolite mineral like $Na_2[Al_2Si_3O_{10}]\ 2H_2O$ (*natrolite*) will exchange two Na^+ ions for a Ca^{2+} ion from a solution containing Ca^{2+} ions (e.g., hard water) :

$$Na_2Ze + CaCl_2 \rightleftharpoons CaZe + 2NaCl$$

The equilibrium may be reversed by using a high concentration of NaCl and the zeolite may be regenerated. This is the principle of water softening by zeolites. Synthetic zeolites and other ion-exchange resins have now taken the place of natural zeolites. Zeolites may also act as molecular sieves as they selectively retain smaller gaseous molecules in their cavities (~ 4 A° in diameter). Such molecular sieves are made by dehydrating zeolites in vacuum at 350°C. They are widely used in gas separation; for example, straight chain hydrocarbons may be trapped and separated from branched chain and aromatic hydrocarbons. They are also used as drying agents. Synthetic zeolites with appropriate pore size have now been prepared in large numbers to suit specific purposes.

Shape-selective heterogeneous catalysis is another interesting application of zeolites as molecular seives. ZSM-5, $Na_3[(AlO_2)_3(SiO_2)],xH_2O)$, is widely used in the selective synthesis of *o*-xylene (1, 2 dimethylbenzene) which is used as an octane-booster in gasoline. It appears that formation of the *meta* and *para* isomers are not favoured by the size and shape of the cavities and tunnels in the catalyst.

The cavities in zeolite structures may also function as a platform for the synthesis of large molecules. Thus, Fe^{2+} trapped in a particular zeolite bed (ion-exchange) may be made to react with phthalonitrile on heating to form iron phthalocyanin — the large molecule cannot escape from the zeolite hole.

Syntehtic zeolites (zeolite-A) are now replacing sodium tripolyphosphate in detergents.

Zeolites may be synthesized by crystallizing aqueous gels of alkaline silicates and aluminates in right proportion at 60°-100°C. In another technique, colloidal silica and technique colloidal silica and finely divided alumina are heated in an autoclave (100 – 200°C) with an aqueous solution of a quaternary ammonium compound e.g., tetrapropylammonium hydroxide. When the resulting mass is heated in air at 500°C, the quaternary ammonium ion is completely burnt away, leaving behind holes in the aluminosilicate framework.

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* *Zein* = to boil, *lithos* = stone. The name was coined by A.F. Cronstedt (1756) becuase the mineral appeared to boil when heated (presumably due to escape of absorbed gas).

Molecular sieves have also been pepared using other materials, for example, phosphorus substituted zeolites, $AlPO_4$ frameworks (ALPO-5), microporous silica (silicalite) etc.

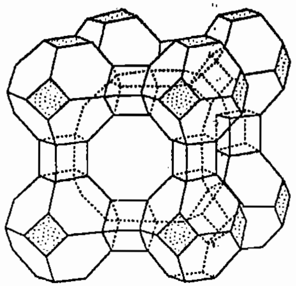

Fig. 21.14
The cage structure in sodalite zeolite.

Ultramarines are also naturally occurring aluminosilicate minerals appreciated for their beautiful colours (for example *lapis lazuli* : splendid blue colour, used in oil paintings). The colour is believed to be associated with the presence of polysulphide ions (S_2^{2-}), but other anions may also be present e.g.

$Na_8\left[(AlSiO_4)_6\right]S_2$ Ultramarine $Na_8\left[(AlSiO_4)_6\right]Cl_2$ Sodalite $Na_8\left[(AlSiO_4)_6\right]SO_4$ Nosean

Synthetic ultramarine is prepared by igniting kaolinite with sodium carbonate and sulphur in absence of air. Typically the colour is blue, though green or red colours may result depending upon the condition (which determines the nature of polysulphide species). Synthetic ultramarines are used in washing white clothes (blueing agent to mask yellow tint) and as a blue pigment in oil-paints and ceramics.

Cement

The common "portland cement"* is essentially a mixture of calcium silicates and aluminates :

dicalcium silicate,	Ca_2SiO_4	or, $2CaO, SiO_2$	$\simeq$ 26%
tricalcium silicate,	Ca_3SiO_5	or, $3CaO, SiO_2$	$\simeq$ 51%
tricalcium aluminate,	$Ca_3Al_2O_6$	or, $3CaO, Al_2O_3$	$\simeq$ 11%
tetracalcium aluminoferrite,	$Ca_4Al_2Fe_2O_{10}$	or, $4CaO, Al_2O_3, Fe_2O_3$	$\simeq$ 1%

A typical composition is as follows :

$$CaO \simeq 70\% \quad SiO_2 \simeq 20\% \quad Al_2O_3 \simeq 5\% \quad Fe_2O_3 \simeq 3\%$$

The setting of cement with water (hence the name hydraulic cement) is initiated by hydration and hydrolysis :

$$2Ca_2SiO_4 + 4H_2O \longrightarrow 3CaO \,.\, 2SiO_2 \,.\, 3H_2O + Ca(OH)_2$$

$$2Ca_3SiO_5 + 6H_2O \longrightarrow 3CaO \,.\, 2SiO_2 \,.\, 3H_2O + 3Ca(OH)_2.$$

The resulting calcium hydroxide, hydrated silicates and aluminates (with Fe_2O_3) slowly crystallize into interlocking crystals over weeks. The initial quick setting ("flash set") due to hydration of tricalcium aluminate is retarded by adding 2-3% gypsum. Cements with higher silica, lower alumina, less alkali and more iron set slowly with low heat of hyration and possess greater resistance to water.

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* from its resembalance, after setting, with the natural limestone from Portland, England (J. Aspdin, 1824).

[Sec. 21.3.6
Glass]

Cement is made by heating (1500°C) a **finely ground mixture** (at least 200 mesh) of limestone, clay etc. in correct composition **in a sloping** rotary kiln. The resulting cement clinker is mixed with ~ 2-5% **gypsum and finely ground.**

High-alumina cement sets quickly and **develops high** strength in a very short period. It is also resistant to saline **water and dilute** mineral acids. A typical composition is

$$CaO \simeq 40\% \quad Al_2O_3 \simeq 40\% \quad SiO_2 \simeq 10\% \quad Fe_2O_3 \simeq 10\%$$

It is prepared by fusing limestone and **bauxite at** $\simeq$ **1400°C.**

The basic slag from iron extraction in **blast furnaces** contains calcium silicate as the principal constituent. *Slag cement* **may be made by** mixing it with limestone and firing.

Glass

Glass is a composite mixture of **aluminosilicates** of sodium or potassium and alkaline earth (usually Ca) as well as other **heavy metals**, e.g. Pb. It is a transparent (or translucent) supercooled liquid which is **formed when** the molten metal silicates solidify without crystallization. The isotropic **amorphous** material has no sharp melting point; it gradually softens on heating and **finally** liquefies. When soft, it becomes plastic and can be blown, moulded or rolled **into sheets**. It can be drawn into short fine fibres to make glass wool or fibre glass. **Laminated safety** glass contains a layer of non brittle plastic material between two thin **sheets of glass.**

Common soda glass contains mainly **sodium** and calcium silicates and is easily fusible. Potassium silicate makes the **glass harder, less easily** fusible and more resistant to attack by chemicals. It is used in making **hard glass test** tubes and other laboratory glasswares. Flint glass contains potassium and **lead silicate** and has a high density and refractive index. It is very soft and is used in **making "cut glasses"** or "crystals" in lamp shades etc. Optical glass is made using some B_2O_3 (and P_2O_5) in place of SiO_2, occasionally with ZnO. Glass containing **boro-silicates** of Zn, Ba or Al are hard and highly resistant to the action of chemicals. They **also** possess very low coefficient of thermal expansion, which makes them suitable for making laboratory glassware ("Jena", "Pyrex", "Borosil", "Corning" etc.). Average composition of some typical glasses are shown in Table 21.9.

TABLE 21.9

Approximate composition of some typical glasses

	SiO_2	Na_2O (K_2O)	CaO (PbO)	Al_2O_3	ZnO	B_2O_3
Soda glass	76	13	11	—	—	—
Potash glass	71	18	11	—	—	—
Flint glass	53	14	33	—	—	—
Jena glass	65	8	—	5	12	10
Corning/Pyrex	81	5	—	2	—	12

Besides these, all glasses may contain little Fe_2O_3 (0.01-0.2%; from SiO_2). Ordinary bottle glass is deeply coloured due to **high** (> 2%) amount of Fe_2O_3. Glass containing a little rare-earth oxides (Ce, Pr etc.) **can absorb UV** radiation.

Glass is manufactured by fusing white sand **with sodium** carbonate and limestone (plus other ingredient where involved) at about **1400°C to clear melt**. Addition of waste glass (*cullet*) helps fusion of the charge. **Heating is continued till** gas bubbles are completely expelled. Arsenious oxide and nitre facilitates **removal of bubble**. Decolourising agents like MnO_2 oxidize Fe(II) to Fe(III); the resulting yellow tint being complementary to the pink tint of Mn(II) silicate, the glass becomes nearly colourless. MnO_2 is therefore called *glassmaker's soap*. Coloured glasses may be obtained by adding different metals or oxides e.g., gold, selenium (ruby red); cobalt oxide (blue); MnO_2 (violet); chromic oxide (green) etc.

The molten mass is gradually cooled to a soft workable condition suitable for blowing or rolling etc. Articles made in this manner have to be carefully "annealed" by slow heating to a temperature just below the softening point and then cooling slowly and uniformly. This is essential for strength and durability of the article.

Ceramics

The ceramic materials (Greek *keramos* = potter's clay) are also essentially silicates processed from various forms of natural clays to suit different purposes. Ceramic technology relates to the manufacture of products like (i) brick, terracotta and sewer pipes (heavy clay products); (ii) chinaware, earthenware and various types of porcelain (whitewares); (iii) firebricks and other refractory products. Bricks are made from ordinary clays containing iron oxides and fired at about 950°C. Kaolin or china clay (Al_2O_3, $2SiO_2$, $2H_2O$) is used in making porcelain — it is mixed with feldspar, flint and other fluxing and refractory ingredients like borax, soda ash, lime etc. The finely powdered mixture is made into a stiff-mud with water and the article prepared from this is fired to a high temperature (≃ 1400°C). Kaolinite ultimately forms a solid solution of mullite ($3Al_2O_3$, $2SiO_2$) and crystobalite (SiO_2) which forms a stoney mass, more or less refractory (heat resisting). A glassy coating or glaze is given to most articles by dipping them in an aqueous suspension of heavy metal oxides like SnO_2 or PbO_2 and firing when a thin coating of easily fusible glass covers the porous ceramic ware. These may be decorated by pigments either before glazing (underglaze) or on top of the glaze (on glaze) with a second firing.

Porcelain finds extensive use in making crockery, floor tiles and as electrical insulators.

Cermets are heterogeneous mixtures of ceramics and metals possessing great resistance to high temperatures, thermal shock, abrasion and corrosion. They are used in nuclear reactors, aircraft jet engines, spacecrafts etc. The metals (or alloys) used are chromium, cobalt, nickel, iron, molybdenum and copper; the ceramic phases may be the refractory oxides as well as carbides nitrides and borides.

(Detection of silica and silicates : see section 21.4).

21.3.7 Oxo-acid Salts of Ge, Sn and Pb : Aqueous Solution Chemistry

Salts of Ge(IV)

Slow emergence of metallic character down the group is shown in the existence of oxo-acid salts and cation chemistry, faintly beginning with Ge. Unstable $Ge(SO_4)_2$ is obtained by heating $GeCl_4$ with SO_3 in a sealed tube at 160°C. The tetraacetate may be prepared by the following reaction (Ac = CH_3CO) :

$$GeCl_4 + 4TlOAc \xrightarrow{Ac_2O} Ge(OAc)_4 + 4TlCl$$

The filtrate, after concentration (low pressure) and cooling, deposits white needle shaped crystals, m.p. 156°C.

Salts of Sn(IV)

Tin(IV) salts of oxoacids are also very few. $Sn(SO_4)_2$, $2H_2O$ may be obtained by treating SnO_2 with hot dilute H_2SO_4 :

$$SnO_2 + 2H_2SO_4 = Sn(SO_4)_2, 2H_2O.$$

The compound is hygroscopic and hydrolyzes in solution to SnO_2.

$Sn(NO_3)_4$ may be obtained by reacting $SnCl_4$ with N_2O_5 (or $ClNO_3$) in nonaqueous medium. It is a volatile solid in which the Sn appears to be eight-coordinated (dodecahedral; NO_3^- acting as a bidentate ligand). The compound readily nitrates organic compounds, presumably via NO_3 radicals.

Salts of oxoacids]

Quite a few Sn(IV) phosphates and phosphato-complexes are well known, for example, $Sn_2O(PO_4)_2$, $Na_2Sn(PO_4)_2$ and the unusual tin(IV) hypophosphite $Sn(H_2PO_2)_4$. The last compound contains Sn (IV) which is oxidizing in nature with the hypophosphite ion which is strongly reducing. The colourless crystals may be precipitated by bubbling oxygen through a solution of SnO in hypophosphorus acid. It is probable that the stability of the compound has kinetic origin.

Tin(IV) compounds are extensively hydrolyzed in aqueous solution. Hydrolysis may be checked by adding sufficient acid. Complex ions like $[SnCl_6]^{2-}$ are present in concentrated HCl solution. Alkaline solutions contain the $[Sn(OH)_6]^{2-}$ ion. Potassium stannate is actually $K_2Sn(OH)_6$ though it is often formulated as K_2SnO_3, $3H_2O$. $Cs_2Sn(NO_3)_6$ may be prepared from Cs_2SnCl_6 and N_2O_4.

Salts of Sn(II)

Sn(II) salts are more numerous and relatively more stable than the Sn(IV) salts. Many of these compounds may be prepared by displacement of Cu(II) from solution by virtue of the higher position of Sn in the electrochemical series.

$$CuSO_4 + Sn \longrightarrow SnSO_4 + Cu \quad \text{(inert atmosphere)}$$

$$Cu(ClO_4)_2 + Sn/Hg \longrightarrow Sn(ClO_4)_2 + Cu$$

$SnSO_4$ is a colourless compound stable in absence of oxygen. It decomposes to SnO_2 and SO_2 around 375°C :

$$SnSO_4 = SnO_2 + SO_2.$$

A basic sulfate and an oxosulfate may be prepared from its aqueous solution with ammonia solution.

$$3SnSO_4 \longrightarrow Sn_3(OH)_2O(SO_4) \xrightarrow{230°} [Sn_3O_2SO_4]$$

Anhydrous $Sn(NO_3)_2$ is not known but a basic nitrate has been prepared by the action of dilute nitric acid on a paste of SnO. It decomposes explosively when heated to 125°C.

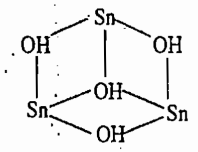
$$Sn_3(OH)_4(NO_3)_2 = 3SnO_2 + 2NO + 2H_2O.$$

Phosphates and phosphato complexes of Sn(II) are well established :

$$Sn_3(PO_4)_2,\ SnHPO_4,\ Sn(H_2PO_4)_2,\ Sn_2P_2O_7 \text{ and } Sn(PO_3)_2.$$

Sn(II) salts in aqueous solution are readily oxidized by atmospheric oxygen, as expected from the low $E°$ value for the system :

$$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq) \qquad E° = 0.15V$$



21-XIV

Sn^{2+} is also extensively hydrolyzed in solution, the principal product being $[Sn_3(OH)_4]^{2+}$ (21-XIV). Tin(II) solutions are therefore kept acidified. A solution of $SnCl_2$ in dilute HCl contains the complex anion $[SnCl_3]^-$.

Salts of Pb(IV)

Lead(IV) is strongly oxidizing in nature and most oxoacid salts of lead contain lead(II). Lead tetraacetate, lead(IV) sulphate and a few complexes like $K_2Pb(SO_4)_3$ are known.

Lead tetraacetate is prepared by cooling a solution of red lead, Pb_3O_4, in hot glacial acetic acid (PbO_2 is insoluble) :

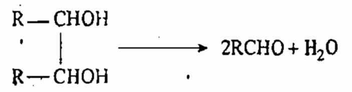
$$Pb_3O_4 + 8CH_3COOH = Pb(CH_3COO)_4 + Pb(CH_3COO)_2 + 4H_2O.$$

Half of the lead (II) acetate can be further converted to the tetraacetate by passing Cl_2 :

$$2Pb(CH_3COO)_2 + Cl_2 = Pb(CH_3COO)_4 + PbCl_2.$$

It may also be prepared by electrolytic oxidation of Pb(II) in acetic acid.

The colourless prismatic crystals (m.p. 175°C) decompose to lead(II) acetate on heating to 195°C. The compound is instantaneously hydrolyzed to PbO_2. It has no measurable conductivity in glacial acetic acid and is soluble in organic solvents like benzene and chloroform. It is used as a strong but selective oxidizing agent in organic chemistry e.g., to oxidize 1, 2 - diols to aldehydes :



$$\begin{matrix} R-CHOH \\ | \\ R-CHOH \end{matrix} \longrightarrow 2RCHO + H_2O$$

The attacking species may be Pb $(OOCMe)_3^+$ or free radicals.

The trifluoroacetate, a white solid, will oxidize even heptane to CF_3COOR; this may be hydrolyzed to obtain ROH.

Lead(IV) sulfate, $Pb(SO_4)_2$ may be made by reacting lead(IV) acetate with conc. H_2SO_4 or by the electrolysis of ≈ 80% H_2SO_4 with lead electrodes below 30°C. Yellow crystals deposit on cooling the solution.

Water decomposes it readily to PbO_2 :

$$Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4.$$

Pb^{4+} does not exist as such in aqueous solution. The $E°$ value for the system

$$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O$$

may be calculated as 1.46 V from other measured $E°$ values.

pH-dependence of the potential for the PbO_2-Pb^{2+} system is noteworthy — the potential decreases with fourth-power of H^+-ion concentration :

$$E = 1.46 - 0.11; pH - 0.0295 \log [Pb^{2+}] \text{ at } 25°C$$

Accordingly, lead(IV) is a strong oxidant in concentrated acid medium only (it oxidizes HCl to Cl_2); in weakly alkaline medium, Cl_2 oxidizes lead(II) to lead(IV), as in the preparation of lead tetraacetate.

Salts of Pb(II)

Lead(II) oxo acid-salts are stable with respect to hydrolysis and oxidation. The salts of large univalent anions are highly soluble, for example, the nitrate, acetate, perchlorate (and tetrafluoroborate). In contrast, salts like the sulphate, selenate, carbonate etc. are sparingly soluble. Some representative solubilities (at temperatures mentioned) are :

	$Pb(NO_3)_2$	$Pb(CH_3COO)_2$	$PbSO_4$	$PbCO_3$
Solubility g L^{-1}	377 (0°C)	197 (0°C)	0.045 (25°C)	10^{-4} (25°C)
Sol. Product (25°C)	—	—	2.2×10^{-8}	1.5×10^{-13}

The soluble lead salts are easily prepared by dissolving $PbCO_3$ or PbO in appropriate acids :

$$PbO \text{ (or, } PbCO_3) + 2HNO_3 = Pb(NO_3)_2 + H_2O$$

(also $HClO_4$, $HClO_3$, $HBrO_3$, CH_3COOH)

The insoluble lead salts are readily precipitated from an aqueous solution of lead(II) nitrate/acetate :

$$Pb(NO_3)_2 + Hg_2SO_4 \longrightarrow PbSO_4 \text{ (similarly } PbSeO_4, PbCrO_4, Pb(IO_3)_2 \text{ etc.)}$$

Lead(II) carbonate, $PbCO_3$ occurs in nature as *cerussite*. It is precipitated from a solution of lead nitrate by $NaHCO_3$ (or CO_2 in presence of Na_2CO_3) at a low temperature : Na_2CO_3 alone and higher temperature tends to form the basic carbonate $2PbCO_3$, $Pb(OH)_2$. This has been used as a white pigment under the name "*white lead*" but is now getting substituted very fast by TiO_2 which is non-toxic and has a better covering power.

Salts of Pb(II)

White lead may be prepared by spraying dilute acetic acid on atomised lead (by superheated steam) in presence of air and CO_2. It may also be prepared electrolytically in a diaphragm cell with lead anodes suspended in sodium acetate solution and iron cathodes in sodium carbonate solution. Lead dissolved out from the anode forms lead acetate which is precipitated as basic lead carbonate by the OH^- and $CO_3^=$ ions coming from the cathode.

Lead acetate crystallising as $Pb(CH_3COO)_2 \cdot 2H_2O$ (*sugar of lead*), was used in medicine as an eye-wash. It is used as a mordant in dyeing and in making other lead compounds e.g. lead chromate (chrome yellow).

Lead sulphate, $PbSO_4$ is often used as the weighable form for gravimetric estimation of lead as it is practically insoluble (1 in 36000) in a mixture of dilute H_2SO_4 and ethanol. It is soluble in hot concentrated H_2SO_4 and in hot ammonium acetate solution :

$$PbSO_4 + 2CH_3COONH_4 = Pb(CH_3COO)_2 + (NH_4)_2SO_4$$

Lead chromate, $PbCrO_4$ forms a beautiful yellow precipitate from K_2CrO_4 and $Pb(NO_3)_2$ solution (solubility product 1.8×10^{-14} at 25°C). It is insoluble in acetic acid, ammonium acetate solution and dilute HNO_3. But it dissolves in conc. HNO_3 and also in concentrated NaOH solution :

$$PbCrO_4 + 4NaOH = Na_2[PbO_2] + Na_2CrO_4 + 2H_2O$$

It is largely used as the pigment *chrome yellow*. Basic lead chromate, PbO, $PbCrO_4$ ($PbCrO_4$ + dil. NaOH) is called "*chrome red*". The yellow and orange coloured compounds may be mixed to get "*chrome orange*".

21.3.8 Nitrogen compounds

Our discussion will be limited to cyanogen (and its derivatives) and the important silicon nitrogen compounds only.

Cyanogen and its derivatives

Cyanogen, $(CN)_2$, the cyanide ion (CN^-), and related species have interested the chemists since early days of chemistry. They also offer a wide route to the systhesis of many industrially important compounds. However, the compounds C_2N_2 and HCN are themselves thermodynamically unstable with respect to oxidation by air, hydrolysis by water or decomposition to the elements. Yet these and the CN^- ion possess appreciable kinetic stability and it is possible to study them extensively.

The cyanide ion, CN^-, with 10 electrons in its valence shell, is expected to have the same gross m.o. description as in CO (and N_2, NO^+) and a bond order 3. Indeed, it is also a strong ligand like CO with vacant antibonding π^* - m.o. suitable for back-bonding.

The CN group has several formal similarities with the halogens : it forms the anion CN^-, the hydracid HCN and the neutral molecule $(CN)_2$ with many properties comparable to those of the halogens, for example :

$$2Cu^{2+} + 4CN^- = 2CuCN + (CN)_2 ; \quad 2Cu^{2+} + 4I^- = 2CuI + I_2$$

(However, CuCN subsequently combines with more CN^- to form $[Cu(CN)_4]^{3-}$).

$$(CN)_2 + 2OH^- = CN^- + OCN^- + H_2O ; \quad Cl_2 + 2OH^- = Cl^- + OCl^- + H_2O.$$

This, and many other groups with similar characteristics are conventionally termed *pseudohalogens* or halogenoids, e.g. SCN, SeCN etc. (see pseudohalogens, Group 17/VIIA).

Preparation

Cyanogen is prepared industrially by catalytic oxidation of gaseous HCN by (a) O_2 (silver catalyst), (b) Cl_2 (activated C or Si), (c) NO_2 (CaO - glass). The NO produced in the last reaction may be recycled.

In a small scale, cyanogen can be prepared by oxidizing CN^- in aqueous solution by Cu(II) or peroxo-disulphate ion.

$$2Cu^{2+} + 4CN^- \longrightarrow 2CuCN + (CN)_2$$

The reaction (80% yield) is facilitated by warming to 60° C. CO_2 formed may be absorbed over solid NaOH. The CuCN produced may be further oxidized by hot aqueous $FeCl_3$:

$$2CuCN + 2FeCl_3 \longrightarrow (CN)_2 + 2CuCl + 2FeCl_2.$$

Dry $(CN)_2$ may be obtained by heating mercury(II) cyanide with $HgCl_2$ (300°C) :

$$HgCl_2 + Hg(CN)_2 \longrightarrow Hg_2Cl_2 + (CN)_2.$$

Cyanogen is a colourless poisonous gas (b.p. — 21°C) with remarkable thermal stability (800°C when pure) in spite of being highly endothermic ($\Delta H_f^0 = +\ 297$ kJ mol^{-1}).

Cyanogen burns in air with a very hot flame - a stoichiometric ratio of $(CN)_2$ and O_2 produces one of the hottest flames known from a chemical reaction (~ 5050°C).

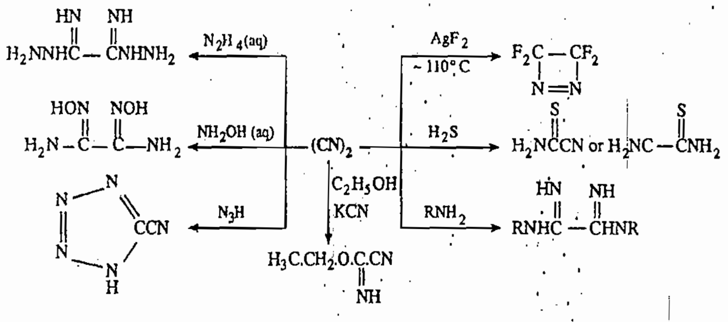
$$(CN)_2 + 2O_2 = 2CO_2 + N_2.$$

Properties

$(CN)_2$ is fairly soluble in water, undergoing slow disporportionation to CN^- and OCN^- which is rapid in basic solution :

$$(CN)_2 + 2OH^- \longrightarrow CN^- + OCN^- + H_2O.$$

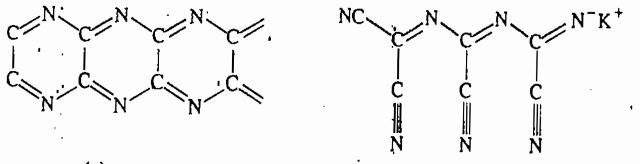
Slow decomposition of $(CN)_2$ in water also produces $(NH_2)_2CO$ (urea) and $H_2NCO.CONH_2$ (oxamide). Cyanogen enters a large number of chemical reactions, many of which are of considerable synthetic interest :



Cyanogen has a linear structure which may be represented as N ≡ C—C ≡ N. The short C—C bond distance (1.38A°) suggests considerable delocalization of the pi-electron clouds.

Cyanogen containing traces of impurities polymerizes on heating (300 - 500°C) to a dark polymeric solid *paracyanogen* [21-XV (a)]; on heating, this depolymerizes to $(CN)_2$ (800°C) and then CN radicals (≈ 850°C. A linear polycyanogen [21-XV (b)] is also formed on interaction of KCN and ICN :

[Sec. 21.3.8
HCN]



(a) (b)

21-XV

Hydrogen cyanide, HCN, is supposed to have been present in the early atmosphere of the earth, taking a vital rôle in the formation of many biologically important compounds. It may be prepared by acidifying an aqueous solution of sodium cyanide. At present it is synthesized by direct ctalytic cooxidation of methane and ammonia in a fast flow system :

$2CH_4 + 2NH_3 + 3O_2 = 2HCN + 6H_2O$ (*Andrussow* process; Pt - Rh; 2 atm / 1000-2000°C).

$CH_4 + NH_3 = HCN + 3H_2$ (*Degussa process*; Pt; 1200°-1300°C).

The products are rapidly removed from the reaction system by quenching.

HCN is formed when $K_4Fe(CN)_6$ is heated with dilute (1 : 2) H_2SO_4 :

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe\,[Fe(CN)_6] + 6HCN.$$

HCN is a colourless highly poisonous volatile liquid (b.p. 26°C).

Strong oriented hydrogen bonding results in a high relative permittivity in the liquid which drops remarkably with increase in temperature (≈ 160 at 0°C to ~ 107 at 25°C). The pure liquid polymerizes vigorously to $HC(NH_2)(CN)_2$ and $H_2N.NC.C = C.CN.NH_2$ as well as higher polymers. It acts as a good non-aqueous solvent in the temperature range −14°C to 26°C. The pure liquid is a strong acid.

HCN is miscible with water and other solvents like Et_2O, EtOH etc. The aqueous solution is very weakly acidic ($pK_a = 9.5$). The solution undergoes slow hydrolysis to formamide and then ammonium formate (rapidly in presence of inorganic acids) :

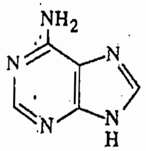
$$HCN \xrightarrow{H_2O} H.CO\,NH_2 \xrightarrow{H_2O} HCOONH_4.$$

It is readily oxidized to $(CN)_2$:

$$\tfrac{1}{2}(CN)_2 + H^+ + e \rightleftharpoons HCN \qquad E^\circ = 0.37\ V.$$

Strong reducing agents reduce it to methylamine :

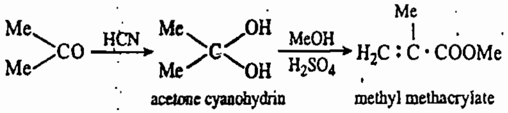
$$HCN + 4H \longrightarrow CH_3NH_2 \quad (Zn/HCl \text{ or } H_2/Pd).$$



21-XVI

Under pressure with traces of water and ammonia, HCN forms adenine (6-amino purine; 21-XVI).

HCN is a very useful synthetic reagent in chemical industry. For example, it adds to alkenes or alkynes, particularly in presence of complexes like $Ni^\circ[P(o\text{-}C_6H_4Me)_3]_4$, a reaction known as *hydrocyanation*. Hydrocyanation of butadiene or acrylonitrile gives adiponitrile or succinonitrile which are used to make 1,4-diaminobutane (hexamethylenediamine) as a route to nylon. The reaction of acetone with HCN forms the basis of manufacturing the polymer of methyl methacrylate (*perspex*).



Uses

HCN is also used to prepare a large number of other cyanogen compounds including acrylonitrile, cyanuric chloride ($C_3N_3Cl_3$; see cyanogen halides), sodium cyanide and various cyano complexes.

Cyanides

The alkali metal cyanides are now prepared by absorbing HCN gas in respective alkali. Prior to the availability of synthetic HCN, sodium cyanide was used to be made via sodamide and sodium cyanamide

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2 \xrightarrow{+C/600°C} Na_2NCN + H_2$$
$$\xrightarrow{+C/800°C} NaCN.$$

Na, K and Rb cyanides crystallize with NaCl structure, Cs and Tl(I) cyanides with CsCl structure. At ordinary temperatures, the cyanide ion may be supposed to be rotating freely with an effective spherical radius of about 1.9 A° (comparable to the Br ion). Alignment to lower symmetry structures may occur at low temperatures.

The alkali cyanides are soluble in water. Mercury(II) cyanide dissolves unionized. Cyanides of Hg(I), Pb(II) and Ag(I) are sparingly soluble.

The cyanides evolve HCN when heated with dilute acids — the reaction was previously used to prepare HCN. Concentrated H_2SO_4 decomposes HCN or a cyanide :

$$2KCN + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + CO.$$

The cyanide ions are readily oxidized by mild oxidizing agents to cyanogen (see before), e.g., by Cu(II). Stronger oxidizing agents like neutral $KMnO_4$ oxidizes it to cyanate (OCN^-) :

$$OCN^- + 2H^+ + 2e \rightleftharpoons CN^- + H_2O \qquad E° = -0.14 \text{ V}.$$

The CN^- ion is isoelectronic with CO (and NO^+) and likewise functions as a strong ligand to metals of the Cr, Mn, Fe, Co, Ni, Cu and Zn groups. The bonding in cyanocomplexes is essentially the same as in carbonyls, but the negative charge on the ion makes it a stronger σ-donor and a weaker π-acceptor. The extreme toxicity of cyanides is associated with their complexation of essential metals in enzymes and haemoglobin. The CN^- ion may also act as a bridge via the nitrogen lone pairs, as is found in infinite polymeric chain structures in crystalline AuCN, $Zn(CN)_2$ or $Cd(CN)_2$; the Prussian blues also contain such chains. Other bridging modes are also possible (see later).

Sodium cyanide is largely used to extract gold and silver through complexation in presence of air. The metals are recovered by reducing the solution with zinc.

$$4M + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na\,[M\,(CN)_2] + 4NaOH \quad (M = Ag \text{ or } Au).$$

Alkali metal cyanates (MOCN) may be easily prepared by oxidizing the cyanide with PbO or PbO_2 in the fused state or in aqueous solution.

$$4KCN + Pb_3O_4 = 4KOCN + 3Pb.$$

[Sec. 21.3.8
Cyanogen derivatives]

Sodium cyanate is manufactured by heating urea with dry sodium carbonate :

$$Na_2CO_3 + 2(NH_2)_2CO \longrightarrow 2NaOCN + 2NH_3 + CO_2 + H_2O.$$

The cyanates are slowly hydrolyzed by water :

$$2KOCN + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

A solution containing ammonium sulphate and potassium cyanate produces on evaporation, ammonium cyanate, NH_4OCN; this isomerizes to urea on heating, the classic discovery by Wohler (1828) :

$$NH_4OCN = (NH_2)_2CO.$$

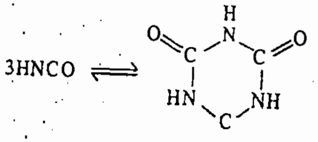
$(OCN)_2$ has not been characterized. Several covalent compounds and metal complexes containing the OCN^- group are known in which either the O or N atom may be linked to the other atom. In general most non-metallic elements seem to be N-bonded, as in $P(NCO)_3$. Such compounds may be prepared from the respective halides by the action of AgNCO in benzene or NH_4OCN in acetonitrile.

Cyanic acid, HOCN ($K = 10^{-4}$, 0°C) is liberated by dilute acids from solutions of cyanates, but it rapidly decomposes to NH_3, CO_2 and H_2O.

Isocyanic acid, HNCO, is a tautomer of cyanic acid and may be obtained by heating urea

$$(NH_2)_2CO \longrightarrow H{-}N = C = O + NH_3$$

HNCO spontaneously and reversibly trimerizes to cyanuric acid :



21-XVII

The isomeric anion CNO^- is present in some fulminates; they are reduced to CN^-, but cannot be prepared by oxidation of the latter. Mercury(II) fulminate may be prepared by reacting the sodium salt of nitromethane with $HgCl_2$.

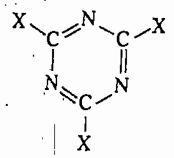
$$HgCl_2 + 2CH_2NO_2^-Na^+ \longrightarrow Hg\,(CNO)_2 + 2H_2O + 2NaCl.$$

It is also formed by the action of alcohol and nitric acid on Hg.

It is a dangerous explosive — used as a detonator.

The OCN^- group of ions are isoelectronic and isostructural with CO_2 and have a linear skeleton.

Cyanogen halides, XCN are also colourless volatile, reactive compounds which tend to form cyclic trimers (cyanuric halides; 21-XVIII).



21-XVIII

Cyanogen chloride, ClCN (b.p. 13°C) may be prepared by the action of chlorine on HCN or by electrolysis of an aqueous solution containing HCN and NH_4Cl. Fluorination of $(ClCN)_3$ gives $(FCN)_3$ which may be cracked thermally to FCN. BrCN may be prepared by reacting Br_2 with MCN in water or CCl_4. ICN is best prepared dry by treating $Hg(CN)_2$ with I_2. Cyanuric chloride and related compounds are widely used in herbicides and dyestuffs.

Cyanogen also forms compounds with other pseudohalogen anions e.g., N_3^-:

$$BrCN + NaN_3 = NaBr + N_3CN.$$

Cyanamide, H_2NCN, a colourless crystalline solid (mp 46°C), results from the action of NH_3 on ClCN. This is prepared by the hydrolysis of calcium cyanamide:

$$CaNCN + H_2O + CO_2 = CaCO_3 + H_2NCN.$$

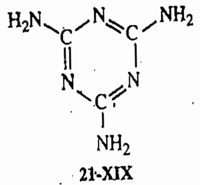
Cyanamide dimerizes to dicyandiamide on heating to 80°C in alkaline solution (*pH* 7-9):

$$2H_2NCN = (H_2N)_2C{=}NCN.$$

This can be obtained directly by boiling CaNCN with water.

At 150°C, cyanamide trimerizes to **melamine** (21-XIX) which is widely used in polymer and plastic industry. This is conveniently prepared by heating urea under pressure (100 atm, 300°C).

$$6H_2N.CO.NH_2 \longrightarrow (NCNH_2)_3 + 6NH_3 + 3CO_2.$$



21-XIX

Cyanamide reacts with H_2S to give thiourea:

$$2NC.NH_2 + H_2S = H_2NCSNH_2 + 2HCN.$$

Linear cyanamide ion, NCN^{2-}, isostructural and isoelectronic with CO_2, is present in solid calcium cyanamide (m.p. 1340°C), which is manufactured by direct nitrogenation of CaC_2 at about 1100° C:

$$CaC_2 + N_2 \longrightarrow CaNCN + C.$$

It is useful as a fertilizer and weed killer, as well as in the production of cyanamides and melamine plastics.

Thiocyanates (e.g. KSCN) are obtained when alkali cyanides are fused with sulfur. The thiocyanate ion, SCN^-, may form a wide range of transition metal complexes, binding through either S or N (see linkage isomerism). A blood red coloration is produced by SCN^- with aqueous Fe(III) [used in the detection of Fe(III)] which is mainly due to the species $[Fe(SCN)(H_2O)_5]^{2+}$:

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5SCN]^{2+} + H_2O.$$

The reaction proceeds further; $Fe(SCN)_3$ and salts of ions like $Fe(SCN)_4^-$ and $[Fe(SCN)_6]^{3-}$ have also been isolated.

Aqueous silver(I) produces a curdy white precipitate of AgSCN with SCN^-; this forms the basis of estimation of silver by *Volhard's method* (see silver, Chapter 29).

Thiocyanates may be oxidized by MnO_2 to thiocyanogen, $(SCN)_2$ (m.p. -7°C) which readily polymerizes irreversibly to brick-red polythiocyanogen. It is also produced by thermal decomposition of some heavy-metal thiocyanates.

$$4HSCN + MnO_2 = Mn(SCN)_2 + (SCN)_2 + 2H_2O$$

$$Pb(SCN)_4 = Pb(SCN)_2 + (SCN)_2.$$

Pure white crystals of thiocyanogen may be obtained by suspending AgSCN in ether or liquid SO_2 and oxidizing with I_2 or Br_2 at low temperature.

In CCl_4 or acetic acid solution, the dimer is stable and has the skeleton

$$N{\equiv}C{-}S{-}S{-}C{\equiv}N.$$

The C—S—S—C group is obviously non-linear. The SCN^- ion is linear.

Pure thiocyanic acid, HSCN has not been characterized, through MeSCN and $Se(SCN)_2$ are known. Isothiocyanic acid, HNCS, is a white solid stable below 0°C. It is produced by reacting KSCN with dry $KHSO_4$. The compound rapidly decomposes at room temperature to HCN and a yellow solid of composition $H_2C_2N_2S_3$.

Selenocyanates may be prepared similar to thiocyanates. The $SeCN^-$ ion is also linear. $(SeCN)_2$ is a yellow powder, polymerizing readily to a red solid.

Silicon-nitrogen compounds

Silicon reacts with nitrogen above 1300°C to form silicon nitride, Si_3N_4. It is usually prepared by heating silica and coke in nitrogen (1500°C).

$$3SiO_2 + 6C + 2N_2 \longrightarrow Si_3N_4 + 6CO.$$

It is also made by other reactions like

$$3Si + 2N_2 \longrightarrow Si_3N_4$$

$$3SiH_4 + 4NH_3 \longrightarrow Si_3N_4 + 12H_2.$$

The compound is extremely hard (9 in Moh's scale), chemically inert and very good insulator — qualities that remain unchanged even above 1000°C. It has a compact structure similar to that of *phenacite* (Be_2SiO_4) in which two-thirds of the Si-atoms in Si_3N_4 structure are replaced by Be. The co-ordination numbers of Si and N are 4 (tetrahedral) and 3 (planar) respectively. The compound finds use as an important ceramic material. *Sialon* ceramics (SiAlON) are made by sintering finely divided Si_3N_4 and Al_2O_3; these are useful in high temperature engine components.

$SiCl_4$ reacts with NH_3 in the vapour phase or in Et_2O to form silylamide, $Si(NH_2)_4$. On heating, this forms the imide $Si(NH)_2$ and then the nitride Si_3N_4.

Various silyl amines may be prepared by reacting halosilanes with ammonia or amines:

$$3SiH_3Cl + 4NH_3 \longrightarrow N(SiH_3)_3 + 3NH_4Cl.$$

$$4SiH_3Br + 5N_2H_4 \longrightarrow (SiH_3)_2NN(SiH_3)_2 + 4N_2H_5Br$$

The stereochemistry of the silylamines differs from that of the carbon-analogs (section 16.4 and 21.2.3). Thus $(CH_3)_3N$ is pyramidal while $(SiH_3)_3N$ or $(SiH_3)_2NH$ have a planar N-Si skeleton.

21.3.9 Sulphides (chalcogenides)

Carbon, silicon, germanium and tin form disulphides MS_2 whose properties vary in accordance with the gradual increase in metallic properties of the elements. PbS_2 is not known owing to strong oxidizing nature of Pb(IV). Stable monosulphides MS are known for Ge, Sn and Pb; CS is unstable even at liquid air temperature.

Carbon forms three sulphides — CS, CS_2, and C_3S_2. Only CS_2, carbon disulphide is chemically important so far.

CS is a very unstable reactive radical formed by the action of high frequency electric discharge on carbon disulphide vapour. It combines with sulphur as well as other chalcogens and halogens (X) to form CS_2, CSSe, CSX_2 etc. C_3S_2 is obtained as a red liquid (m.p. –5°C) by subjecting CS_2 to electric arc or discharge. It polymerizes slowly like C_3O_2. The structure is also supposed to be similar, i.e., $S = C = C = C = S$.

Carbon disulphide is manufactured by reacting methane (in natural gas) with sulphur over heated (600°C) silica gel or aluminium oxide catalyst :

$$CH_4 + 4S \longrightarrow CS_2 + 2H_2S.$$

The gases are easily separated by liquefaction. Previously (prior to 1950's), CS_2 was obtained by reacting sulphur vapour and coke in iron retorts at 750-1000°C. The compound is highly endothermic :

$$C + 2S = CS_2\,(g) \qquad \Delta H \simeq 109 \text{ kJ mol}^{-1}$$

CS_2 is a colourless, volatile and inflammable liquid (b.p. 46°C) with an ether-like odour when pure, though it is usually found with a disagreeable smell due to organic impurities. It has a very low ignition temperature and readily catches fire. The gas is highly poisonous and readily attacks the nervous system. The refractive index of the liquid is remarkably high (~ 1.6). It is almost immiscible with water (~ lg per litre at 20°C) but completely miscible with alcohol, ether and chloroform. It is an excellent solvent for fats, oils, waxes, resins, rubber as well as sulphur, iodine and white phosphorus.

Carbon disulphide undergoes very slow hydrolysis to carbon dioxide and water (> 200°C). It gives carbon tetrachloride with chlorine ($FeCl_3$ catalyst) :

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

CS_2 dissolves in sodium sulphide solution forming sodium trithiocarbonate; aqueous alkali produces a mixture of carbonate and trithiocarbonate :

$$CS_2 + Na_2S = Na_2CS_3.$$

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O.$$

NH_3 reacts with CS_2 to form ammonium dithiocarbamate, $NH_4\,[H_2NCS_2]$.

In presence of Al_2O_3 under pressure, NH_4CNS is obtained which can be isomerized at 160° to thiourea $S = C(NH_2)_2$.

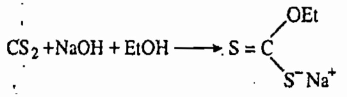
The reactions of CS_2 with SH^-, OR, RNH_2 or R_2NH illustrate nucleophilic attack on carbon :

$$CS_2 + :SH^- \longrightarrow S_2CSH^- \xrightarrow{OH^-} CS_3^{2-} \quad \text{(thiocarbonate).}$$

$$CS_2 + :OC_2H_5^- \longrightarrow C_2H_5OCS_2^- \quad \text{(xanthate)}$$

$$CS_2 + R\ddot{N}H_2 \longrightarrow RHNCS_2^- \quad \text{(dithiocarbamate).}$$

Dithiocarbonic acid, S═C(OH)SH forms a monoethyl ester which is known as **xanthic acid** : S═C(OEt)SH. CS_2 reacts with ethanol and NaOH solution to form sodium xanthate; this is frequently used in concentration of ores by froth-floatation.

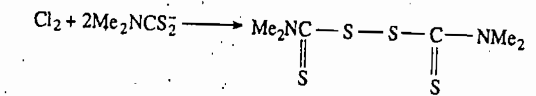


$$CS_2 + NaOH + EtOH \longrightarrow S = C\begin{matrix} OEt \\ S^-Na^+ \end{matrix}$$

With cellulose in place of EtOH, cellulose xanthate is obtained. This is used to prepare viscose rayon or cellophane.

Primary or secondary amines react with CS_2 in presence of NaOH to form dithiocarbamates. The zinc, manganese and iron dithiocarbamates are widely used as fungicides in agriculture.

When a solution of dithio-carbamate is oxidized (by H_2O_2 or $S_2O_8^=$ or Cl_2), one gets *thiuram disulphide* :

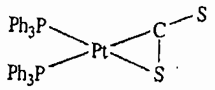


$$Cl_2 + 2Me_2NCS_2^- \longrightarrow Me_2N\underset{\underset{S}{\|}}{C} — S — S — \underset{\underset{S}{\|}}{C} — NMe_2$$

The thiuram disulphides are also strong oxidizing agents; they are used in the vulcanization of rubber and polymerization initiators.

Tetraethylthiuram disulphide renders the body allergic to alcohol (Antabuse).

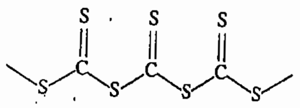
CS_2 is an efficient coordinating ligand to metals. The square planar complexes $M^\circ\,(PPh_3)_2\,(CS_2)$ (M = Pt, Pd) contain bidentate CS_2 with C and S donor atoms (21-XX). Other metals like V, Ni, Fe, Ru etc. also form complexes with CS_2. Unidentate and bridging modes of coordination have also been established.



21-XX

Thiocarbonic acid, H_2CS_3, can be obtained as a red oil, stable at low temperatures, by adding concentrated HCl to a solid thiocarbonate ($CS_2 + SH^-$ in alkaline solution). The thiocarbonates are yellow salts containing the planar CS_3^{2-} ion.

CS_2 polymerizes under high pressure to a black solid with the structure (21-XXI)



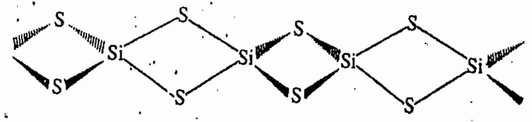
21-XXI

CSe_2 polymerizes spontaneously.

SiS_2 can be obtained by heating silicon in sulphur vapour (100°C). It is a colourless fibrous solid with a chain-structure based on *edge-sharing* of SiS_4 tetrahedra (21-XXII).

At high temperature and pressure, the crystoballite modification is obtained. SiS_2 is rapidly hydrolyzed to SiO_2 and H_2S. Liquid ammonia produces the imide :

$$SiS_2 + 4NH_3 \longrightarrow Si\,(NH)_2 + 2NH_4SH.$$



21-XXII

GeS_2 (white) and **SnS_2** (yellow) are prepared by passing H_2S into aqueous acidic solutions containing Ge(IV) and Sn(IV). GeS_2 has a silica-like structure at high temperatures while SnS_2 has CdI_2 lattice. Both produce thio-salts with alkali-hydroxides, alkali metal sulphides, ammonium bi-sulphide and yellow $(NH_4)_2S_x$. Acidification results in reprecipitation of the sulphides.

$$H_2SnCl_6 + 2H_2S = SnS_2 + 6HCl$$

$$3SnS_2 + 6NaOH = Na_2SnO_3 + 2Na_2SnS_3 + 3H_2O.$$

In presence of sufficient oxalic acid, Sn(IV) forms stable complex ions of the type $[Sn(C_2O_4)_4(H_2O)_2]^{4-}$ which do not precipitate SnS_2 with H_2S. This can be used to separate/distinguish tin from antimonay, since Sb_2S_3 is precipitated in presence of oxalic acid.

Mosaic gold used for gilding is crystalline SnS_2. Golden yellow scales are obtained by heating tin, sulphur and ammonium chloride.

GeS (red brown) is prepared by reducing a suspension of GeS_2 in HCl with excess H_3PO_2. It may also be prepared by heating GeS_2 in a limited supply of H_2. SnS (brown) and PbS (Black) are precipitated by H_2S from aqueous solutions containing Sn(II) or Pb(II) in presence of dilute acids. SnS dissolves in yellow ammonium sulphide $(NH_4)_2S_x$ forming ammonium thiostannate, $(NH_4)_2SnS_3$. On acidification, yellow SnS_2 is precipitated :

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

SnS is insoluble in ammonium sulphide, $(NH_4)_2S$ (colourless). It is also insoluble in ammonium carbonate solution and practically insoluble in alkalis.

PbS is also formed by burning lead in sulphur vapour. It dissolves in hot dilute HNO_3 but is insoluble in yellow ammonium sulphide. It also dissolves in hot concentrated HCl :

$$PbS + 4HCl = H_2PbCl_4 + H_2S$$

GeS and SnS have layer structures like that of black phosphorus, each Ge/Sn having pyramidal coordination of S-atoms and a lone pair of electrons. PbS forms the NaCl structure. Pure PbS is an intrinsic semiconductor. In presence of impurities it develops into *n*-or *p*-type semiconductor. It is also a photoconductor.

GeSe is obtained as a dark brown precipitate from the reaction of H_2Se with $GeCl_2$ solution. Tin reacts directly with selenium (350°) to form SnSe (greyish blue solid).

PbSe may be prepared by the action of H_2Se on a variety of lead compounds ($PbCl_2$, $PbEt_4$ etc.). Reduction of $PbSeO_4$ with H_2 or carbon in an electric furnace is also useful.

The tellurides may be prepared by heating tellurium with the metals in stoichiometric amounts.

21.3.10 Organo compounds of Si, Ge, Sn and Pb

All the elements from Si to Pb form organometallic compounds which involve bonds between elements in the same periodic group — carbon and one of its congeners. In addition to regular tetralkyls and tetraryls MR_4, there are a wide range of compounds of the general formula $R_{4-n}MX_n$ where X may be H, halogen, OR′, NR'_2 etc. A large number of heterocyclic compounds, catenated compounds and a few compounds containing Si=Si and Ge=Ge are also known. As we shall see presently, some of these organo compounds are commercially quite important, for example the silicone polymers and tetraethyl lead.

The organo-compounds are conveniently prepared by reacting the halides with an excess of Grignard or alkyl lithium or aluminium reagents in hydrocarbon solvent e.g. :

$$SiCl_4 + 4LiR \longrightarrow SiR_4$$

$$SnCl_4 + 4RMgCl \longrightarrow SnR_4 + 4MgCl_2$$

$$3SnCl_4 + 4AlR_3 \longrightarrow 3SnR_4 + 4AlCl_3 \text{ (alkyl only)}$$

$$2PbCl_2 + 4RMgX \longrightarrow [2PbR_2] \longrightarrow Pb + PbR_4$$

Excess tetrahalides will produce the alkyl or aryl halides :

$$GeX_4 + nLiR \longrightarrow R_nGeX_{4-n}$$

These are also obtained by heating the tetraalkyls with the corresponding tetrahalides in stoichiometric amounts.

$$GeX_4 + GeX_4 \longrightarrow 2R_2GeX_2;\quad GeBr_4 + 3GeR_4 \longrightarrow 4R_3GeBr.$$

Industrially, a wide range of organosilanes are produced by direct reaction of silicon with alkyl or aryl halides in presence of copper catalyst (~ 10% by weight) at 300° C (E.G. Rochow, 1945).

$$MeCl + Si \longrightarrow Me_2SiCl_2\ (70\%) + MeSiCl_3\ (12\%) + Me_3SiCl\ (5\%).$$

Small amounts of $SiCl_4$, $SiMe_4$, $MeSiHCl_2$ etc. are formed. The relative proportions of various products may be adjusted by monitoring the condition. The exothermic reaction is believed to proceed via the formation of CuMe and CuCl intermediates. Ge and Sn compounds may also be prepared by this method. The alkyl (specially methyl) and phenyl chlorosilanes are very useful in making silicone polymers (see below).

Tetraethyl lead, commercially very important gasoline-additive for anti-knock properties (see use), is manufactured by reacting ethyl chloride with a sodium-lead alloy (80-100°C).

$$4C_2H_5Cl + Pb + 4Na \longrightarrow (C_2H_5)_4Pb + 4NaCl.$$

NaCl and excess sodium are removed by washing with water and tetraethyl-lead is purified by steam-distillation. Only one-fourth of the lead is converted to $(C_2H_5)_4Pb$. An alternative process involves electrolysis of $NaAlEt_4$ with lead anode and mercury cathode :

$$4NaAlEt_4 + Pb \longrightarrow PbEt_4 + 4AlEt_3 + 4Na$$

The sodium may be used to regenerate $NaAlEt_4$ via NaH

$$4NaH + 4AlEt_3 + 4C_2H_4 \longrightarrow 4NaAlEt_4.$$

The reaction of ethyl chloride with lead alone is endothermic. The use of sodium-lead alloy makes the overall reaction exothermic :

$$\begin{array}{l} 4C_2H_5Cl\,(l) + 2Pb\,(s) \longrightarrow (C_2H_5)_4Pb(l) + PbCl_4\,(l)\,;\ \Delta H^\circ = +\,285.77\text{ kJ} \\ PbCl_4\,(l) + 4Na\,(s) \longrightarrow Pb\,(s) + 4NaCl\,(s)\,;\ \Delta H^\circ = -1330.09\text{ kJ} \\ \hline 4C_2H_5Cl\,(l) + Pb\,(s) + 4Na\,(s) \longrightarrow (C_2H_5)_4Pb + 4NaCl\,(s) \\ \qquad\qquad\qquad\qquad\qquad\qquad \Delta H^\circ = -1044.32\text{ kJ.} \end{array}$$

Tetraethyl lead is also formed by reaction of C_2H_5MgBr with $PbCl_2$ (see before).

Catenated organo-derivatives can be prepared by coupling reactions (like Wurtz reaction) or by treating the dihalides with alkylating (or arylating agents) :

$$Me_3SiCl + Me_2SiCl_2 \xrightarrow{Na/K} Me_3Si(SiMe_2)_nSiMe_3 \quad (n = 1-16).$$

$$GeI_2 + (Me_3Al)_2 \longrightarrow Me_3Ge(GeMe_2)_nGeMe_3 \quad (n = 1-22).$$

$$SnCl_2 + C_6H_5MgBr \longrightarrow [Sn(C_6H_5)_2]_6.$$

Organo-compounds containing M=M (silenes, germenes etc.) are discussed separately.

Comparison with boron-group organo-metallics

As mentioned earlier, these organometallic compounds involve bonds between carbon and another element in the same group. Slow variation of electronegativity within the group results in low polarity of the M—C bonds compared to those in Gr 13(IIIA). At the same time, the central atoms in these organometallics four-coordinate while in group III/13 organometallics, the central atoms are usually 3-coordinate. Thus the central atom gets better steric protection in group IV/14. These two factors seem to be largely responsible for the observed reluctance of the organometallics of this group towards hydrolysis and also in general reactivity.

Properties

Nevertheless, the M—C bonds are appreciably stable, as shown by the high bond-dissiciation energies for the Si—C bond — 250-335 kJ mol^{-1}. Accordingly, the compounds possess appreciable thermal stability which decreases from Si to Pb and from aryl to alkyl compounds. Thus, Ph_4Si distills unchanged at 530°C, Ph_4Pb, m.p. 227°C, decomposes at 270°C while Et_4Pb decomposes at 110°C. The catenated compounds are also quite stable but stability falls with increasing size of the elements i.e., from Si—Si to Pb—Pb. Si_2Me_6 is very stable; even $Si_{12}Me_{26}$ can be distilled in air at temperatures around 300°C. In contrast, Pb_2Me_6 blackens in air and higher polyplumbanes are unknown except the thermally unstable red solid $Pb(PbPh_3)_4$. The alkyl chlorosilanes are mobile volatile liquids with similar boiling points : Me_3SiCl 57.7°C; Me_2SiCl_2 69.6°C; $MeSiCl_3$ 66.4°C. Ph_3SiCl is a solid, M.P. 89°C.

The Si—C (and other M—C) bonds are more polar than C—C bonds, carbon forming the negative end of the dipole. This facilitates nucleophilic attack at silicon and electrophilic attack at carbon. Displacement reactions at the central atom usually proceed via the formation of five-coordinate intermediates.

Typical hydrolysis and ammonolysis reactions are as follows :

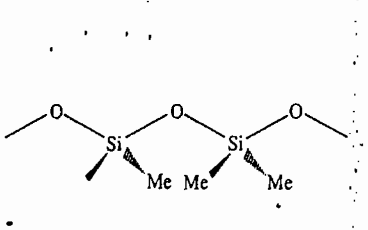
$$Me_3SiCl + H_2O \longrightarrow Me_3SiOH + HCl$$

Me_3SiOH is a volatile liquid (b.p. 99°C). It is more acidic than the corresponding carbon compound—tertiary butyl alchol. Two molecules of Me_3SiOH condense slowly with the elimination of a molecule of water :

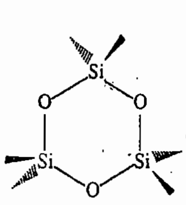
$$2Me_3SiOH \longrightarrow Me_3Si-O-SiMe_3 + H_2O$$

Compounds with Si—O bonds are called *siloxanes.*

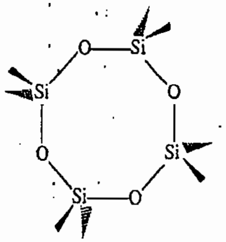
Dimethylsilicon dichloride, Me_2SiCl_2 hydrolyzes to form both cyclic and long chain compounds.



21-XXIII



21-XXIV



21-XXV

Similarly, Ph_2SiCl_2 first forms white crystalline $Ph_2Si(OH)_2$ (m.p. 132°C with decomposition) which undergoes cyclization above 100°C.

Hydrolysis of $MeSiCl_3$ results in a cross-linked polymer. These polymers thus bear structural resemblance to the silicates. Mixtures of methylsilicon halides may be co-hydrolysed to obtain desired polymers. Or the various siloxanes formed through initial hydrolysis may be made to undergo redistribution of $-OSiMe_3$ end-groups with H_2SO_4 as catalyst. These polymeric products are collectively called *silicones* (see later).

Ammonolysis (by NH_3, RNH_2 or R_2NH) similarly produces compounds with Si—N bonds called *silazenes.*

$$Me_2SiCl_2 + NH_3 \xrightarrow{-35°C} (Me_2SiNH)_3 + (Me_2SiNH)_4 \text{ (both cyclic)}$$

$$Me_3SiCl + NH_3 \longrightarrow (Me_3Si)_2NH$$

The bulky methyl groups around the Si atom seem to hinder further protolysis.

Substitution reactions at 4-coordinate Si have been investigated in detail with a large number of optically active organosilicon compounds (see section 15.3.3). We observe that such reactions may proceed with either inversion or retention of configuration, e.g.

$$R_1R_2R_3\overset{*}{Si}H \xrightarrow{Cl_2} R_1R_2R_3\overset{*}{Si}Cl \xrightarrow{LiAlH_4} R_1R_2R_3\overset{*}{Si}H$$

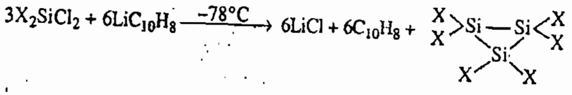
$$[\alpha]_D = \quad +34° \qquad -6° \qquad -34°$$

It has been established from other studies that the first two species on the left have the same relative configuration. Hence the chlorination takes place with retention while the reduction occurs with inversion.

These observations are consistent with the proposed associative reaction path (S_N2) involving five-coordinate Si-intermediate in which the entering and leaving groups occupy axial positions in a trigonal bipyramidal activated complex (section 15.3.3). Since Si can readily form such an intermediate with sufficiently long lifetime (availability of 3*d* orbital), the intermediate can also undergo rearrangement (See BPR. section 15.3.3) to retain the configuration. For the smaller C atom, such an intermediate would involve extremely high energy of activation and hence be short-lived, resulting in inversion.

However, in very few cases other mechanisms may be involved. For example, the racemization of $R_1R_2R_3SiCl$ in CH_3CN (or CH_3NO_2) is believed to occur by an S_N1 mechanism—the $R_1R_2R_3Si^+$ ion formed in a slow step (rate-determining) is stabilized by the highly polar solvent. Recombination in either configuration leads to racemization.

Organosilicon compounds containing Si—Si bonds are now well known, though their chemistry is much less developed than catenated carbon compounds owing to the low Si-Si bond energy. Nevertheless, open-chain, cyclic as well as cage alkyl and arylsilicon compounds have been prepared. For example, a 3-membered ring analogous to cyclopropane may be prepared by reducing dixylylsilicon chloride (xylyl = 2, 6 - dimethylphenyl; X) with lithium naphthalide in ethylene glycoldimethyl ether (glyme)



$$3X_2SiCl_2 + 6LiC_{10}H_8 \xrightarrow{-78°C} 6LiCl + 6C_{10}H_8 + (X_2Si)_3$$

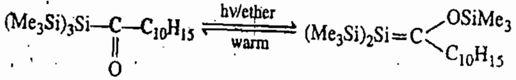
21-XXVI

The compound is stable in presence of air and moisture upto its melting point 272°C. The Si_3 skeleton forms an isosceles triangle (Si - Si 2.42 A° and 2.37 A°).

Cyclohexasilane (m.p. 250°C) may be prepared by similar reductive halide elimination in tetrahydrofuran at 0° C :

$$6Me_2SiCl_2 + 12Li \longrightarrow (SiMe_2)_6 + 12LiCl.$$

Compounds containing Si=C and Si=Si were really challenging to the chemists. Transient species like $Me_2Si{=}C(SiMe_3)_2$ or $Me_2Si{=}CH_2$ were produced thermally or photolytically and detected mass spectrometrically. A stable compound containing Si=C has been prepared by attaching bulky substituent to prevent polymerization :

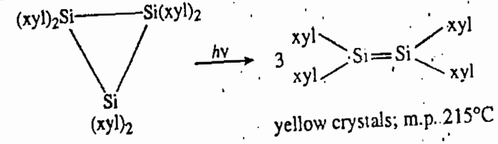


$$(Me_3Si)_3Si-\underset{\underset{O}{\|}}{C}-C_{10}H_{15} \underset{warm}{\overset{h\nu/ether}{\rightleftharpoons}} (Me_3Si)_2Si{=}C\begin{matrix}OSiMe_3\\C_{10}H_{15}\end{matrix}$$

2-adamantyl-2-trimethylsiloxy-1,1-bis (trimethylsilyl)-1-silaethene

The pale yellow crystalline solid (m.p. 92°C) is stable in absence of air, but in solution it very slowly reverts to the mother compound.

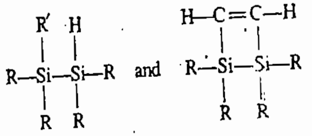
Compounds with Si=Si (disilenes) may be similarly stabilized kinetically against polymerization using bulky groups like mesityl(2,4,6-trimethylphenyl; mes). The tetramesityl disilene forms orange crystals, m.p. 176°C. The xylyl group acts similarly (xylyl - xyl).



yellow crystals; m.p. 215°C

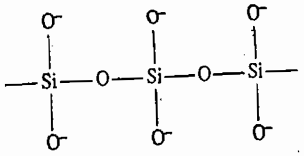
The Si-Si bond length in tetramesityl disilene (2.16 A°) is about 0.2A° shorter than a typical Si-Si single bond distance. The bright colours of the compounds correspond to transition from the π-3p (HOMO) to π^*-3p (LUMO) in the visible region (400 nm) — the separation (≈ 3eV) is much less than the π-2p — π^*-2p separation in alkenes (≈ 6eV which absorb in the UV region (≈ 200nm) and appear colourless.

Halogens and HX molecules add to disiline similar to the alkenes. Even alcohols (R'OH) and alkynes may add to the Si = Si bond giving, for example

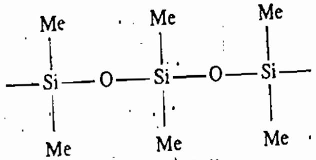


Silicones

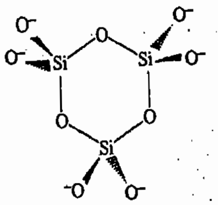
Silicones are organo-silicon polymers having R_2SiO group as the unit building block. R is typically methyl; other groups, particularly phenyl are also involved. The wide range of chain, cyclic and cross-linked silicone polymers are based on structural patterns similar to those in silicates. For example, the O⁻ in silicates have been replace by the formally isoelectronic CH_3 (Me) groups in the dimethyl silicones :



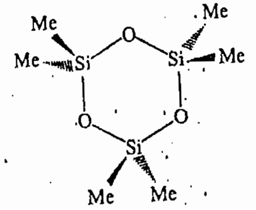
pyroxene



poly dimethyl siloxane
(silicone oil)



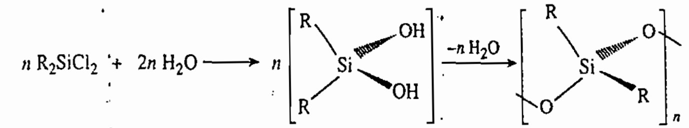
cyclic metasilicate



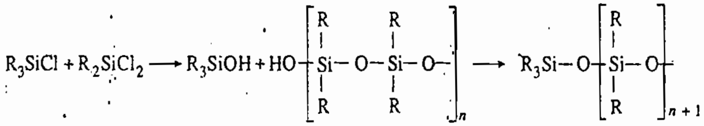
cyclic dimethyl siloxane

Both silicones and silicates are formed due to the reluctance of silicon to form silicon to oxygen double bonds. But the silicates are all solids while the silicones may be oils, greases, rubbers or resins depending upon the extent of polymerization.

The silicone polymers are manufactured from the alkylchlorosilanes (which are obtained by the Rochow process; see before). Hydrolysis of R_2SiCl_2 results in high polymers :



(The corresponding carbon intermediate, $R_2C(OH)_2$, would result in $R_2C{=}O$). Under controlled conditions, cyclic dimethylsiloxanes, $(R_2SiO)_n$, $n = 3 - 6$, may also be formed. The growth of chains in the above hydrolysis may be controlled by carrying out the hydrolysis in presence of varying amounts of R_3SiCl which "seals" the end of the chain by providing an R_3Si - group :



$$R_3SiCl + R_2SiCl_2 \longrightarrow R_3SiOH + HO{-}\left[\begin{matrix} R & & R & \\ | & & | & \\ Si & - O - & Si & - O - \\ | & & | & \\ R & & R & \end{matrix}\right]_n \longrightarrow R_3Si{-}O{-}\left[\begin{matrix} R & \\ | & \\ Si & - O \\ | & \\ R & \end{matrix}\right]_{n+1}$$

Depending on the chain length, the ploymers are liquids, grease like or waxy solids (see properties). A rigid solid polymer may be produced by using $RSiCl_3$ in controlled quantities; this leads to cross-linking of the silicon chains.

The hydrolysis is usually initiated by a small quantity of concentrated H_2SO_4 but KOH may also be used to prepare certain silicone rubbers. Hydrolysis of $PhSiCl_3$ and Ph_2SiCl_2 in toluene produces silicone resins. The polymerization is allowed to proceed to a stage when the product is still soluble in toluene. It is shaped or moulded in this form and heated to 200°C in presence of a catalyst (a quaternary ammonium compound) when cross-linking develops the final 3-dimensional network by condensing the remaining OH groups.

The wide range of silicone polymers are marked by a combination of certain highly desirable properties like :

(i) good resistance to heat, oxidation and attack by most chemicals.

(ii) excellent water repelling character.

(iii) good electrical insulation at high and low temperatures.

(iv) non-stick property.

(v) physiological inertness.

These and other properties of the silicones may be related to their silica like Si—O—Si—O skeleton surrounded by alkyl groups which make them water-repelling.

Uses

Silicone fluids containing straight-chain polymers (20-500 units) are used in making cement work and fibres water-repellant, as dielectric insulating media (in high voltage transformer), hydraulic oils and light duty lubricating oil. Mixed with lithium stearate soaps, they make quality grease for use in high vacuum apparatus. Silicone oils are also useful broad spectrum antifoaming agents—applied from cooking oil to fermentation industries or even in sewage disposal.

Fluids 62%

Rubbers 25%

Silicone rubbers are made by reinforcing straight chain polymers (having 6000 to 600,000 Si units) with fillers like SiO_2 or graphite. They can be "vulcanized" by increasing cross-links through oxidations with benzoyl peroxide. These rubbers retain their quality from –100°C to 250°C. Such rubbers find extensive uses where natural or other synthetic rubbers are disqualified, for example, industrial sealants and adhesives, space suits, medical tubing etc.

Resins 13%

Silicone resins are used in electrical insulations. as laminates for printed circuit boards or in encapsulation resistors, integrated circuits etc. They are also used in coating cooking ware and industrial tyre moulds.

Organo Compounds of germanium, tin and lead

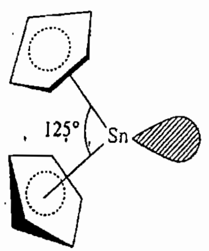
The organocompounds of germanium are similar to the corresponding silicon compounds, though somewhat more reactive and thermally less stable (Me_2GeCl_2 undergoes reversible and incomplete hydrolysis). The Ge—Ge bond is considerably weaker but compounds containing such bonds are stable at moderate temperatures. Ge_2R_6 type compounds may be distilled unchanged (difference of Sn_2R_6); these are also stable towards hydrolysis and ammonolysis. Crystalline cyclic oligomers $(GePh_2)_n$ (n = 4, 5, 6) have also been prepared.

The tetraalkyl tin-compounds also resemble those of silicon and germanium but Sn(IV) shows a greater tendency to attain coordination numbers higher than 4, as shown by formation of octahedral $R_4Sn(bipy)$. Trialkyl tin compounds like R_3SnX (X = ClO_4, F, NO_3 etc.) contain planar R_3Sn^+ (R = Me) ions associated through bridging X groups with the Sn in approximately tbp coordination. In aqueous solution ionization occurs to $[R_3Sn(H_2O)_2]^+$ cation.

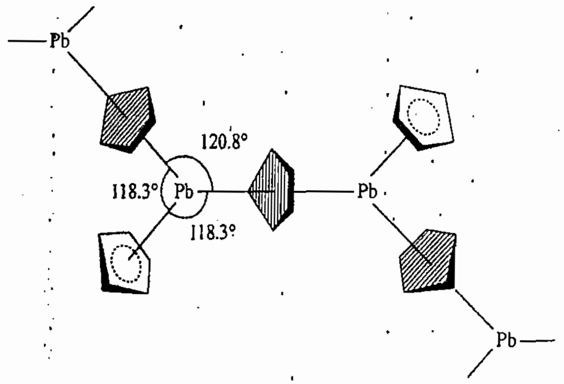
R_3SnX also form 1 : 1 and 1 : 2 adducts with Lewis bases which contain Sn in a tbp environment. Me_2SnF_2 is also polymeric with bridging F atoms, but the coordination around Sn appears to be octahedral. The halogen bridges are extremely weak in the chlorides and bromides which are essentially monomeric. $Me_2Sn(NO_3)_2$ is strictly molecular (nitrate as bidentate). Catenated open chain and cyclic organotin compounds are also numerous. Germenes, stannenes as well as digermenes and distannenes have also been prepared recently. The digermenes and distanneses are however, nonplanar.

In conformity with observed inert pair effect, tin also forms many organometallic compounds containing Sn(II), e.g. R_2Sn and $Sn[CH(SiMe_3)_2]_2$. $Sn(\eta^5 - C_5H_5)_2$ may be prepared as white crystals (m.p. 105°C) from NaC_5H_5 and $SnCl_2$ in tetrahydrofuran. It has a bent structure in the gas phase (21-XXVII) showing the presence of a stereochemically active lone-pair of electrons.

Organotin compounds are of great commercial importance. R_2SnX_2 (typically R = n - octyl; X = laurate, maleate etc.) compounds are used as stabilizers for PVC against discolouring and becoming brittle with time. Bu_2SnX_2 (X = acetate, laurate or 2-ethylhexanoate) is used as curing agent for silicones and as a catalyst in the manufacture of polyurethanes. Tin compounds are also used as anti-fouling paints for marine vessels and agricultural pesticides.



21-XXVII



21-XXVIII

There are a large number of organo-lead compounds containing both Pb(IV) and Pb(II). Tetraethyl lead, $PbEt_4$, is a widely used organometallic compound as gasoline-additive. The tetraalkyls are volatile, monomeric liquids. $PbPh_4$ is a solid (m.p. 227°C) which can be distilled at 240°C under reduced pressure (15 – 20mm Hg). Poor catenating property is shown by the instability of diplumbanes, Pb_2R_6; higher polyplumbanes are unknown except $Pb(PbPh_3)_4$ which is a thermally unstable red solid. Pb $[CH(SiMe_3)_3]_2$ and Pb $(\eta^5 - C_5H_5)_2$ are examples of Pb (II) organo-metallics. The latter has a bent structure in the gas phase like its Sn - analogue; but the solid state contains chains of Pb $(\eta^5 - C_5H_5)$ connected by doubly-coordinating C_5H_5 rings placed perpendicular to the Pb - Pb line (21-XXVIII). Involvement of the lone-pair electron of Pb in linking the chain appears quite likely. $[Pb(AlCl_4)_2 (\eta^6 - C_6H_6)].C_6H_6$ is another organometallic compound of Pb(II) with η^6 - benzene.

Anti-knock compounds

Internal combustion petrol engines operate by spark ignition of a compressed petrol-air mixture. As the compression ratio increases, a point is reached when the fuel gas does not burn smoothly on being sparked; rather the end portion burns with explosive violence, producing a metallic rattle or knocking sound. Such explosions summarily arise from rapid propagation of a series of chain reactions. About 0.01% lead tetraethyl (or tetramethyl) imparts significant anti-knock property to the fuel. $Pb(C_2H_5)_4$ decomposes to produce ethyl radicals :

$$Pb\,(C_2H_5)_4 \longrightarrow Pb\,(s) + 4C_2H_5\cdot\,(g).$$

These radicals function as chain terminators in the hot reaction mixture and prevent explosive combustion responsible for knocking. However, the finely divided lead particles released through the exhaust cause severe pollution problem in view of the very toxic nature of lead. Many countries are now gradually imposing ban on petrol containing lead. Other non-polluting or less polluting compounds are emerging as antiknock compounds—e.g., methyl t-butyl ether, dimethyl carbonate and methanol.

21.3.11 Complexes and Clusters

Complexes

Several complex compounds of the Group IV elements with oxygen, halogen as well as nitrogen, sulphur or phosphonus (and other) donor ligands are known. These are formed in both II and IV oxidation states, the II state being naturally important for Sn and Pb. The coordination numbers are usually 4 (tetrahedral) and 6 (octahedral) but other coordination numbers are also encountered. Some examples have already been given earlier (section 21.2). These may be conveniently classified into the following categories — cationic species, anionic species and neutral species.

Cationic Species : The chemistry of carbocations (carbonium ions) has been extensively studied in organic chemistry. The high ionization energy required to form C^{4+} ion and the high polarizing power of this ion may be favourably modified by complexing with large ligands, as shown in section 21.2.3.

Cationic complexes of Si and Ge are also comparatively few. Some six coordinate octahedral complexes are known like the β-diketonates e.g. $[Si(acac)_3]^+$, tropolonates (= T; SiT_3^+) etc. These are usually prepared by reacting the halides with the ligands in nonaqueous solvents like chloroform :

$SiX_4 + acac \longrightarrow [Si\,(acac)_3]^+X^-$ [X = Cl, $AuCl_4$] $Ph_3SiX + bipy \longrightarrow (SiPh_3\ bipy)^+\ X^-$

$SiI_4 + 6\ dmf \longrightarrow [Si\,(dmf)_6]^+\,[I^-]_4$ $SiI_4 + 6\ O\text{-}py \longrightarrow [Si\,(O\text{-}py)_6]^+\,[I^-]_4$

[*acac* acetylacetone; *bipy* bipyridyl; *dmf* N, N dimethylformamide; *O-py* pyridine-N-oxide.]

Anionic Species : Carbon forms carbanions like $(NC)_3C^-$. We have already come across several six-coordinated fluoro and, mixed halo species. SiF_6^{2-} is formed in the hydrolysis of SiF_4 or by the action of HF on SiO_2. It is stable towards hydrolysis even in basic solution. The Ge and Sn anions, on the other hand, are hydrolyzed by base, while PbF_6^{2-} is hydrolyzed readily by water.

The pentafluorosilicate ion, SiF_5^- (*tbp*) is present in salts like $(R_4B)(SiF_5)$ or $(Ph_4As)(SiF_5)$ which may be obtained through reactions of the type

$$SiF_4 + (R_4N)F \longrightarrow (R_4N)(SiF_5) \quad (\text{in } CH_3OH).$$

Salts of GeF_5^- ion are also known. Ge and Sn also form $GeCl_6^{2-}$ or $SnCl_6^{2-}$ species when their tetrachlorides are treated with HCl or M^ICl. As expected, the $PbCl_6^{2-}$ ion forms only unstable salts which may be obtained by reacting HCl or Cl_2 on $PbCl_2$. $GeCl_5^-$ and $SnCl_5^-$ (*tbp*) may be stabilized with large cations like Ph_3C^+ or Bu_4N^+ :

$$MCl_4 + Bu_4N^+Cl^- \longrightarrow Bu_4N^+ [MCl_5]^- \quad (\text{in } SOCl_2)$$

Other examples of anionic complexes include

octahedral : $[Sn(NO_3)_6]^{2-}$; $[Si(ox)_3]^{2-}$; $[Ge(SO_3F)_6]^{2-}$

trigonal bipyramid : $[Sn(SO_3F)_5]^-$

square pyramid : $[XSi(O_2C_6H_4)_2]^-$; $[XSi(S_2C_6H_4)_2]^-$

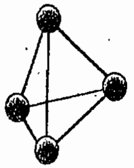
Neutral Species : Several neutral complexes are formed by addition of neutral ligands to the tetrahalides : SiF_4 (bipy), *trans* – SiF_4py_2, $SiCl_4L_2$ (l = py, PMe_3), $GeCl_4py_2$ etc. 5-coordinate (tbp) species like Me_3SnCl (py) are also known. 6-coordinate Sn(II) is present in the bis (β-diketone) adducts of $SnCl_2$.

Cluster Compounds

The heavier members of the group (Ge, Sn, Pb) form highly coloured polyatomic anions when their alkali metal alloys are dissolved in liquid ammonia or 1, 2-diaminoethane (*ethylenediamine, en*). Recently it has been possible to isolate stable crystals containing such anions by use of 2, 2, 2-crypt ligands (Ch–18) :

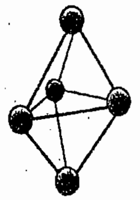
$$2KPb_{2.5} + 2\text{crypt} \longrightarrow [K(\text{crypt})]_2 (Pb_5)$$

Complexation of the alkali metal ion by the cryptate prevents electron transfer from the anion back to the alkali metal on removing the solvent. Derivatives containing M_4^{2-}, M_5^{2-}, M_9^{2-} and M_9^{4-} (M = Ge, Sn, Pb) have been isolated in this manner and studied by X-ray crystallography. Their structures (21-XXIX, 21-XXXII) correspond to valence electron counts with provision for a lone pair on each of the atoms.



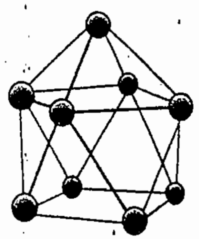
21-XXIX

Tetrahedron Ge_4^{2-}, Sn_4^{2-}



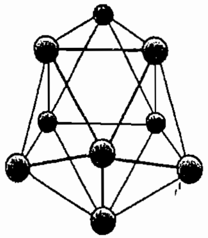
21-XXX

Trigonal bipyramid Sn_5^{2-}, Pb_5^{2-}



21-XXXI

Mono-capped square anti-prism Ge_9^{4-}, Sn_9^{4-}



21-XXXII

Trigonal bipyramid Sn_5^{2-}, Pb_5^{2-}

Electron-count :

		Pb_5^{2-}	Sn_9^{4-}
Total number of valence electrons	:	20	36
Add : number of electrons for charge	:	2	2
		22	38
Less : two *e*-s for each M		10	18
		12	20

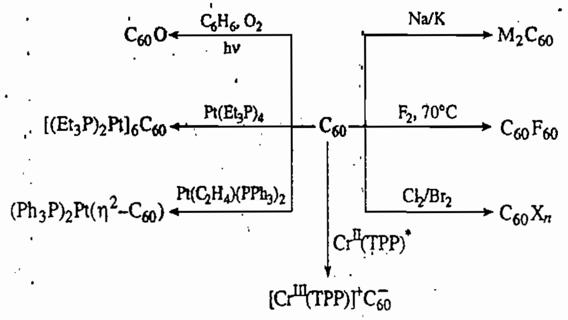
The total number of skeletal electrons for Pb_5^{2-} is thus 12, i.e., 6 pairs. This fits (6 – 1) or 5 atom *closo* - structure.

10 pairs of skeletal electrons in Sn_9^{4-} agree with a mono-capped square anti prism, a *nido* cluster.

21.3.12 Chemistry of the Fullerenes

The chemistry of fullerenes has been emerging rapidly during the last decade; most of the chemistry relates to C_{60} which is by far the most available of all fullerenes. The overall reaction patterns may be interpreted by regarding C_{60} as a series of localized C=C double bonds rather than an aromatic system. This is consistent with the presence of two distinct C—C bond lengths and the detection of only small ring currents in C_{60}. The high reactivity of C_{60} may be related to the non-planarity of the C=C double bonds which introduces some strain in the molecule. Also, each C=C double bond is attached to four electron withdrawing units.

Some reactions of C_{60} are shown schematically in 21-XXXIII. This will be followed by a brief discussion.



*TPP = tetraphenylporphyrin

21-XXXIII

(i) **Reduction :** Birch reduction of a suspension of C_{60} in liquid NH_3/THF by lithium and tertiary butyl alcohol produces light cream coloured solid polyhydrofullerenes ranging from $C_{60}H_{18}$ to $C_{60}H_{36}$.

The last compound may also be obtained selectively as a stable white solid by using a large excess of 9, 10-dihydroanthracene. Primary and secondary amines, for example *n*-$PrNH_2$, ethylenediamine etc. add H and NR_2 groups across the C=C bond to give $C_{60}H_6(NH_2)_6$.

C_{60} can be reduced electrochemically to fulleride anions C_{60}^{n-}, n = 1 – 6; the reduction potentials for n = 1 – 3 are :

$$C_{60} \xrightarrow{-0.33\ V} C_{60}^{-} \xrightarrow{-0.73V} C_{60}^{2-} \xrightarrow{-1.25\ V} C_{60}^{3-}$$

Solutions of C_{60} may be reduced by alkali metals to solid fullerides M_nC_{60}, where n is 1 for M = Rb, Cs but may be 2, 3, 4 and 6 when M = Na, K, Rb and Cs.

A solution of C_{60} in toluene may be reduced by $Na[Mn(\eta^5-C_5Me_5)_2]$ in THF to give crystalline $NaC_{60}.5THF$. The dark purple crystals are extremely moisture and air-sensitive.

Reduction of C_{60}-C_{70} mixtures by lithium gives red-brown solids which give polymethylated fullerenes with CH_3I.

The anhydrous metal fullerides, M_nC_{60}, may be prepared by reduction of C_{60} with vapours of potassium and other alkali metals. With excess alkali metal M_6C_{60} (M = K, Rb, Cs) are formed. The compounds M_3C_{60} are superconducting at reasonably high temperature, the T_c for K_3C_{60} being at 19K. Gradual replacement of potassium by larger alkali metals raises the T_c : 29K for Rb_3C_{60} and 33K for $CsRb_2C_{60}$.

The fulleride anion is also formed in tetrahydrofuran by reduction with tetraphenylporphyrin (TPP) complex of Cr(II) :

$$Cr^{II}(TPP) + C_{60} \longrightarrow [Cr^{III}(TPP)]^+C_{60}^-$$

(ii) **Oxidation :** The C—H bonds of the C_{60} cluster are readily oxidized to C—OH bonds. Such *fullerols*, $C_{60}(OH)_n$ (n = 24—26) can be prepared by aerial oxidation of C_{60} in benzene solution in presence of dilute NaOH; Bu_4NOH acts as an effective catalyst in the process. The fullerols are also formed by hydroboration of C_{60} followed by addition of aqueous alkaline H_2O_2.

When a benzene solution of C_{60} is oxygenated in presence of uv radiation, fullerene epoxide, $C_{60}O$ is formed.

Oxidation of fullerene by halogen is discussed separately.

(iii) **Halogenation :** Solid C_{60} may be slowly fluorinated direct at 70°C to yield $C_{60}F_{60}$ as the ultimate product. Rapid fluorination at 250°C under uv rays gives $C_{60}F_{48}$ as the major product.

Chlorine adds to C_{60} at ~300°C to give polychlorinated products $C_{60}Cl_n$ (n around 24—26). The chlorine undergoes nucleophilic substitution by OCH_3^- :

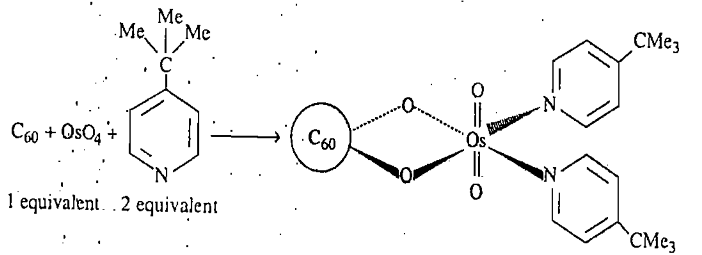
$$C_{60}Cl_n + CH_3OH + KOH \longrightarrow C_{60}(OCH_3)_n + KCl.$$

Chlorination of C_{60} with excess ICl in benzene or toluene at room temperature produces orange $C_{60}Cl_6$.

Bromination of C_{60} with liquid bromine gives $C_{60}Br_{24}$; otherwise bromination in solution (room temperature) gives $C_{60}Br_6$ and $C_{60}Br_8$. Iodine does not add directly to C_{60}.

Both the polychlorides and polybromides can be dehalogenated by strong heating.

(iv) **Adduct formation :** Fullerenes provide a three-dimensional π-system lacking the extensive delocalization present in aromatic systems and can form adducts from fairly localized double bonds. The first characterized adduct was that formed by reacting C_{60} with OsO_4 in benzene containing 4-*t*-butylpyridine :



The crystalline adduct splits into C_{60} on heating in vacuum. X-ray crystallography shows very clearly that the OsO_4 adds to a double bond shared by two six-membered rings. The truncated icosahedron structure of C_{60} was also established from X-ray study of this adduct.

The behaviour of C_{60} (and C_{70}) like alkenes towards transition metals is shown by the formation of η^2-adducts by the π-electrons of a C=C bond :

$$C_{60} + (\eta^2 - C_2H_4)\ Pt\ (PPh_3)_2 \longrightarrow C_2H_4 + (\eta^2 - C_{60})\ Pt\ (PPh_3)_2.$$

$$C_{70} + Ir(CO)Cl(PPh_3)_2 \longrightarrow (\eta^2 - C_{60})\ Ir\ (CO)\ Cl\ (PPh_3)_2$$

η^2, η^2-tetrahapto and η^2, η^2, η^2-hexahapto coordination modes are also known.

(v) **Encapsulation of metal atoms :** The cavity inside the fullerene clusters may be impregnated with metal atoms by soaking graphite in a metal salt solution, followed by drying and vaporization. For example, when graphite is treated with an aqueous solution of lanthanum chloride before drying and vaporizing, the mass spectrum of the products shows the presence of LaC_{60}, LaC_{70}, LaC_{74} and LaC_{82} (in addition to C_{60} and C_{70}). Pairs of C-atoms may now be eliminated from these products to give a closer wrapping of the metal atoms down to LaC_{44}. The compounds are symbolized as La @ C_{60} where "@" indicates that the metal is fully surrounded by the fullerene cage giving endohedral compounds. From esr studies, the suggested description of the compound is La^{3+} @ C_{60}^{3-}.

21.4 DETECTION AND ESTIMATION

Carbon is detected by combustion to carbon dioxide. Carbonates and bicarbonates are also detected through their liberation of CO_2 with acids. Small amounts of CO_2 may be detected by suspending a drop of Na_2CO_3 solution coloured pink with phenolphthalein above the gas (at the tip of a dropper say). CO_2 discharges the pink colour forming $NaHCO_3$. Sulphites etc. may be removed by prior treatment with 20-40 volume H_2O_2. Cyanides may be arrested with $HgCl_2$ solution.

Bicarbonates do not give any precipitate with Mg^{2+} in cold, but the soluble magnesium bicarbonate changes to insoluble carbonate on boiling. Bicarbonates also do not form any precipitate with $HgCl_2$ solution while carbonates give a reddish-brown precipitate of basic carbonate. In order to detect bicarbonates in presence of carbonates, the carbonate (and part of the bicarbonate) is precipitated by adding $CaCl_2$ solution. The filtrate containing calcium bicarbonate turns turbid on making alkaline with a little ammonia solution ($CaCO_3$ is formed).

Carbon in steel may be estimated by combustion to CO_2 in a silica tube at ~ 1100°C followed by absorption of the CO_2 in baryta or soda lime-asbestos ("*Carbosorb*" : self-indicating granules which indicates the degree of absorption by a marked colour-change). Carbonates or bicarbonates may be estimated similarly.

Cyanides may be detected by the formation of a white precipitate of AgCN, soluble in excess silver intrate (K $[Ag(CN)_2]$). They may also be converted to $[Fe(CN)_6]^{4-}$ by boiling with $FeSO_4$ in strongly alkaline medium and detected by the prussian blue colour with aqueous Fe^{3+}.

Cyanides may be estimated by titration against silver nitrate solution. The alkali metal salts of $[Ag(CN)_2]^-$ ion are soluble in water, but after the end point, excess Ag^+ forms an insoluble white precipitate of Ag $[Ag(CN)_2]$. The method is modified by adding I^- ion in ammoniacal solution; yellow AgI indicates the end point against a black background. Alternatively, diphenyl carbazide may be used as an adsorption indicator. The pink colour becomes pale violet on the colloidal precipitate of $Ag[Ag(CN)_2]$ at the end point.

Silica (SiO_2) and silicates form volatile SiF_4 when heated with CaF_2 and conc. H_2SO_4 in a lead crucible (*on asbestos board*). SiF_4 hydrolyzes to an opaque gel of Si $(OH)_4$ in contact with a drop of water supported on a platinum wire loop.

Silicates react with ammonium molybdate in acid solution forming ammonium silicomolybdate $(NH_4)_4$ $[SiO_4.12MoO_3]$ in solution. In acetic acid solution this reacts with benzidine to a blue quinonoid oxidation product and "molybdenum blue". Phosphates and arsenates give similar reactions.

In determining silicon in alloys, the alloy is first attacked with a mixture of H_2SO_4, HNO_3 and HCl and the silica is rendered insoluble by evaoporation to dryness with acid and baking. Steel is attacked with perchloric acid and the silica is rendered insoluble by fuming with the same acid. The silica is washed, dried and weighed.

Germanium is coprecipitated as the hydroxide with Fe(III), Al(III) etc. hydroxides. Ge(IV) forms the yellow complex $[Ge(Mo_2O_7)_6]^{8-}$ ("germani-molybdate") with ammonium molybdate solution in ~ 0.2*N* H_2SO_4. This is then reduced by Fe(II) in 1.5-2 *N* H_2SO_4 to a blue compound which has an absorption maximum at 820-830 mμ. This allows colorimetric determination of Ge(IV).

Tin(II) forms a brown precipitate of SnS from ~ 0.3N HCl medium. The precipitate is soluble in yellow $(NH_4)_2S_x$ and in concentrated HCl. Tin(II) reduces mercury(II) chloride to white mercury (I) chloride and ultimately to grey mercury.

Tin(IV) forms yellow precipitate of SnS_2 from dilute (~ 0.3N) acids. The precipitate is soluble in HCl (conc.), alkali hydroxides, in yellow $(NH_4)_2S_x$ as well as colourless NH_4HS.

Tin in alloys is most conveniently estimated by breaking the alloy with acid mixtures and precipitating tin as hydrated tin(IV) oxide. This can be filtered and ignited to weigh as SnO_2. Alternatively, tin(IV) may be separated from copper, lead, arsenic(III) and antimony(III) by precipitating the latter metals with H_2S in ~ 0.2*M* HCl in presence of HF. The tin-complex is next decomposed by adding boric acid, the H_2S is boiled off and tin is precipitated by "cupferron". The precipitate is ignited to SnO_2 and weighed. A better method is precipitation with N-benzoyl-N-phenyl-hydroxylamine from concentrated HCl solution. The precipitate can be dried at 110°C and weighed as $(C_{13}H_{11}O_2N)_2SnCl_2$.

Tin (II) may be titrated with IO_3^- in strong HCl medium using CCl_4 or $CHCl_3$ till the disappearance of violet colour of iodine in the solvent layer (formation of ICl) :

$$IO_3^- + 2Sn^{2+} + 6H^+ + Cl^- \rightleftharpoons ICl + 2Sn^{4+} + 3H_2O.$$

The titration should be rapid to minimize aerial oxidation of Sn(II). Certain dyes like Amaranth may also be used (red to colourless).

Lead salts in solution form a yellow precipitate of PbI_2 with KI. The precipitate dissolves on boiling but reappears on cooling as bright golden plates. PbI_2 also dissolves in excess KI forming K_2PbI_4. Lead is also precipitated as colourless $PbCl_2$ (soluble in hot water) and black PbS (from acidic solution; soluble in dilute HNO_3).

Lead may be estimated via several insoluble compounds like $PbSO_4$, $PbCrO_4$, $PbMoO_4$. Lead can be selectively extracted into chloroform by diphenylthiocarbazone (dithizone) in presence of ammonia - KCN - Na_2SO_3 at pH ≥ 9.5. The concentration of lead in the extract may be determined by measuring the absorbance at 510 nm.

SUMMARY

Introduction : Carbon, the key element to the life system, forms more compounds than any other element except hydrogen. Silicon is the second most abundant element (after oxygen) in the earth's crust. The general trend in properties of the elements in this group follows the same pattern as outlined for *p*-block elements (Ch. 20). Carbon and silicon are typical nonmetals, followed by germanium, tin and lead with gradually increasing metallic character.

Silicon is prepared by carbon reduction of SiO_2; it is purified by reducing $SiCl_4$. Very pure Si is obtained by zone-refining.

Germanium is recovered from the flue-dust of zinc smelting by leaching with acid, precipitation of $GeO_2.xH_2O$ and reduction (H_2, 550°C). Tin is prepared by carbon reduction of SnO_2. Lead is obtained by self-reduction in partly oxidized PbS.

Besides coke, graphite and diamond, carbon is also very useful as carbon black and activated carbon. Silicon is extensively used in steel making as a deoxidizer (ferrosilicon). Small amounts of ultrapure silicon are used in electronics industry. Tin and lead form a number of useful low-melting alloys.

Silicon and germanium form important semiconductor materials particularly when doped with elements of Group III(13) or V(15).

Fullerenes constitute a new series of allotropes of carbons—these are hollow closed-cage (polyhedral) cluster molecules C_n, where *n* is even in the range 30-600. They have structures based on polyhedra formed by fusing pentagons and hexagons, comparable to a soccer ball for C_{60}.

General Trends : The general trends in the chemistry of the elements follow the typical pattern for *p*-block elements. The high ionization energies make the formation of M^{4+} cations rather unlikely except marginally for Sn and Pb. The lighter elements C and Si do not have any stable bivalent compound under ordinary conditions as the energy released in the formation of four covalent bonds greatly exceeds the energy required to bring the elements to the tetravalent state. For the heavier elements, bond energy decreases significantly and the bivalent state becomes comparatively more stable even at room temperature. Pb(IV) is actually oxidizing in nature.

The unique catenating power of carbon may also be attibuted to the intrinsic high strength of the C—C bond which is also greater than that of the C—O bond, making the C—C bond stable towards oxidation. M—M bond strength decreases sharply for M = Si and then further to Sn. These bonds are also considerably weaker than respective M—O bonds and hence readily susceptible to oxidation.

Carbon forms a large number of compounds containing C = C or C ≡ C π-bonds or their combinations. Poorer overlap forbids stable π-bond formation in Si and higher members in the group. A few compounds containing Si = Si are known with bulky substituents like mesityl (2, 4, 6-trimethyl).

Multiple bonding of the *dπ-pπ* type are readily formed by silicon using its vacant 3*d* orbital and a filled *p*-orbital of matching symmetry, e.g., those on N, O, or halogens. This makes many Si-compounds stereochemically different from their carbon analogues, e.g., $(SiH_3)_3N$ is planar against tetrahedral $(CH_3)_3N$.

Principal Compounds

Compounds of graphite. Graphite may form compounds by accommodating other atoms in the large interlayer space. The π-electron system is retained in lamellar compounds e.g., C_8K and C_6Li. The π-system is disrupted in graphite fluoride and oxide.

Carbides : Ionic or salt-like carbides are fomed by the most electropositive metals (Gr. I - III). They contain essentially $C^{4-}(Al_4C_3)$, $C_2^{2-}(CaC_2)$, $C_3^{4-}(Mg_2C_3)$ ions, hydrolysing respectively to methane, acetylene and methyl acetylene. Metallic or interstitial carbides are formed by many *d*-block elements. C atoms are accommodated in interstices in the metal lattice. Covalent carbides are formed by boron and silicon.

Halides : Except PbI_4, all four tetrahalides of all the elements are known. Ge, Sn and Pb also form stable dihalides. The tetrahalides except SnF_4 and PbF_4 are typically covalent and volatile. The dihalides are also covalent except those of Pb(II). The carbon tetrahalides are hydrolytically stable while other tetrahalides are hydrolyzed to $MO_2.xH_2O$ or $M(OH)_4$. SiF_4 also produces H_2SiF_6.

Oxides and oxoacids : Carbon forms CO, CO_2 and a few other less common oxides (e.g., C_3O_2) all of which are dominated by strong C—O π-bonds. Si—O *p-p* π-bonds are not favourable; SiO_2 is a macromolecular solid with tetrahedral SiO_4 units. The oxides MO_2 become increasingly basic from M = C to M = Pb. PbO_2 is oxidizing in nature. There are no definite hydroxides $M(OH)_4$ though hydrated oxides are precipitated on hydrolysis.

Silicates find extensive use in daily life and industry in various forms. They are made up of SiO_4 tetrahedral units sharing corners to form rings, chains, sheets and 3-dimensional cavities which may act as molecular sieves (e.g., Zeolites).

Oxo-acid salts (Ge, Sn, Pb) : Slow emergence of metallic character down the group is shown in the oxo-acid salts and cation chemistry, slowly beginning with Ge. $Ge(SO_4)_2$ and $Ge(OAC)_4$; $Sn(SO_4)_2, 2H_2O$, $Sn(NO_3)_4$ and Sn(IV) phosphates are noteworthy. Sn(IV) compounds are extensively hydrolyzed in aqueous solution. Alkaline solutions contain the $[Sn(OH)_6]^{2-}$ ion. Sn(II) salts are more numerous and relatively more stable e.g. $SnSO_4$, $Sn(ClO_4)_2$ and $Sn_3(OH)_4(NO_3)_2$. Lead(IV) is present in $Pb(OAc)_4$, $Pb(SO_4)_2$ and $K_2Pb(S_4)_3$. Pb(IV) is a strong oxidant in concentrated acid medium only. Pb(II) oxoacid salts are stable with respect to hydrolysis and oxidation.

EXERCISE

1. *Some physical properties of the Group 4 elements are given below :*

M	M.P. of M (°C)	M.P. of MO_2(°C)	B.P. of MF_4(°C)	B.P. of MCl_4(°C)
C	>4000	–57° (pressure)	–182	77
Si	1410	1730	–95 (sub)	57
Ge	960	1120	–37 (sub)	83
Sn	232	1130	705 (sub)	113
Pb	327	290 (decomp)	MP 600 (decomp)	— (decomp)

Comment on the following observations

(a) *The sharp drop in m.p. from elemental carbon to silicon.*
(b) *The fairly regular decrease in m.p. from Si to Pb.*
(c) *The anomalous m.p. of CO_2.*
(d) *The markedly low thermal stability of PbO_2.*
(e) *The decrease in volatility of the tetrafluorides.*
(f) *The trend in b.p. of the tetrachlorides.*

[**Hints :** (a) Much stronger C—C bonds compared to Si—Si bonds. (b) Bonds become progressively more metallic (c) Ready formation of C=O multiple bond (d) Low stability of Pb(IV).(e, f). Increasing van der Waals' interaction which is variously affected by bond polarity. In the fluorides the F atoms carry negative charge, causing great electrostatic repulsion between neighbouring molecules. This is partly reduced by dative π-bonding from F to Si. π-bonding becomes less important for others and the effect of molecular weight supersedes. π-bonding is also less important in tetrachlorides where the order is influenced mainly by electronegativity differences. C—Cl bonds are less polar than Si—Cl bonds. In $SiCl_4$, intermolecular repulsions outweigh the effect of molecular weight.]

2. *CCl_2 is unknown except as a transient intermediate. Which of the other elements in Group 4 are expected to form stable dichlorides? What are their structures?*
3. *Give examples of a stable carbocation, a carbanion and a free radical. What is a carbene?*
4. *What do you mean by catenation? Why does carbon show much greater tendency for catenation in comparison to (i) Si (ii) N?*
5. *Ethylene (ethene) and acetylene (ethyne) analogs of silicon are rare — explain. Give an example of a compound containing Si = Si bond.*
6. *Write the main steps with conditions for the following conversions. Give balanced equations where involved :*

(i) $SiO_2 \longrightarrow$ *ultrapure Si.* (ii) $GeO_2 \longrightarrow$ *pure Ge.* (iii) $SiO_2 \longrightarrow SiCl_4$
(iv) $PbO \longrightarrow$ *lead tetraacetate.* (v) $SiH_3Cl \longrightarrow N(SiH_3)_3$. (vi) $PbCl_2 \longrightarrow PbEt_4$.
(vii) $SiCl_4 \longrightarrow SiH_4$. (viii) $MeGeCl_3 \longrightarrow MeGeH_3$. (ix) $SiCl_4 \longrightarrow SiMe_4$.

7. *Select the correct answer in each category :*

(a) *the most stable dihalide* : $SnCl_2$, $GeCl_2$, $PbCl_2$
(b) *a tetrahalide that does not exist* : SnI_4, GeI_4, PbI_4
(c) *a pyramidal ion* : SnF_3^-, SnF_5^-, $\cdot CF_3$
(d) *a species with linear N—C—O skeleton* : H_3CNCO, H_3SiNCO, H_3GeNCO.

8. *Describe the reactions (if any), of the following compounds with cold 0.5 N sodium hydroxide solution :*

$$CH_4, SiH_4, GeH_4, SnH_4, Si_2H_6, SiH_3PH_2.$$

[**Hints :** Electronegativity of Si (A—R scale) is lower than that of the other elements; charge separation of the type $\overset{\delta+}{Si}—\overset{\delta-}{H}$ is most favoured and attack by OH^- is easier. Among the simple hydrides MH_4, only SiH_4 reacts appreciably. This is aided thermodynamically by the large difference in energy between Si—O and Si—H bonds. H_2 and silicate anions are formed. SiH_2 reacts similarly, giving seven mols of H_2 per mol. In silylphosphine, OH^- attacks $Si(\delta^+)$ and H^+ attaches to $P(\delta^-)$ giving hydrogen, silicate and phosphine.]

9. *Anhydrous liquid HCN is a non-aqueous solvent. Explain the following reaction that takes place in anhydrous HCN :*

Sulphuric acid is added to a solution of KCN; when the mole ratio of the acid to KCN is 1 : 2, potassium sulfate is precipitated almost quantitatively.

[Hint : Neutralization occurs.

$$2KCN + H_2SO_4 = K_2SO_4(s) + 2HCN.]$$

10. *Comment on the following observations :*

(i) *Carbon compounds of the type $R_2C(OH)_2$ cannot generally be isolated; but compounds like $Et_2Si(OH)_2$ can be isolated which form polymeric substances on dehydration.*
(ii) *$(SiH_3)_2O$ has a flexible Si—O—Si bond angle around 145°.*
(iii) *Addition of aqueous KCN to an aqueous solution of aluminium sulfate precipitates $Al(OH)_3$.*
(iv) *In liquid ammonia, magnesium silicide and ammonium bromide react to form silane.*
(v) *$(CH_3)_3SiOH$ is a stronger acid than its carbon analog.*
(vi) *$(SiH_3)_3N$ and $(CH_3)_3N$ react with HCl to give different products.*

(vii) *$PbSO_4$ is more soluble in aqueous sodium acetate than in aqueous sodium nitrate, even though lead acetate is less soluble in water than lead nitrate.*

(viii) *Stability of MX_4 tetrahalides of Group 4 elements decreases from CCl_4 to $PbCl_4$ and CF_4 to CI_4.*

(ix) *Boiling point of $SiHCl_3$ is less than that of $CHCl_3$.*

(x) *Dipole moment of the compounds MH_3Cl show the following order for different M : C > Si > Ge.*

[**Hints :** (i) Two factors mainly contribute to the stability of silanediols : strength of the Si—O bond and larger size of Si which reduces steric interaction between the two-OH groups.

(ii) O⟶Si dative π-bonding; bond angle increases to improve π-overlap.

(iii) hydrolysis of KCN.

(iv) See liquid NH_3 as solvent, Chapter 12.

(vii) lead acetate is formed which is little ionized.

(x) Bond polarity of C—Cl should be less than that of Si—Cl from electronegativity consideration (C 2.5; Si 1.74; Cl 2.83 in AR scale). But in $SiHCl_3$, dative π-bonding from chlorine to silicon reduces the polarity and outweighs the effect of electronegativity. π-bonding becomes less important for Ge and the bond polarity increases again.]

11. *Give reasons in brief :*

(i) *$SnCl_2$ dissolves in HCl but not in HNO_3.*

(ii) *SnS dissolves in yellow ammonium sulfide but PbS is insoluble.*

(iii) *Ge(II) is a reducing agent but Ge(IV) is not; Pb(IV) is oxidizing but Pb(II) is not.*

(iv) *Diamond is a covalent insulator, graphite is a layered covalent conductor and silicon is a covalent semiconductor.*

(v) *CO and CO_2 are molecular gases but SiO_2 is a high melting solid.*

(vi) *Boiling point of $SiHCl_3$ is less than that of $CHCl_3$.*

(vii) *$SnCl_2$ is readily oxidized by Cl_2 to $SnCl_4$ but $PbCl_4$ readily decomposes to $PbCl_2$ and Cl_2.*

(viii) *$(CH_3)_2CO$ is a volatile liquid while $(CH_3)_2SiO$ is not.*

(ix) *Sn(II) shows reducing behaviour but Pb(II) does not.*

(x) *$SiCl_4$ is readily hydrolyzed but CCl_4 is not.*

(xi) *SiF_2 may be prepared at high temperature by the reaction :*

$$SiF_4 + Si \longrightarrow 2SiF_2.$$

12. (a) *Starting with SiH_4, how would you prepare Si_2H_6, $(SiH_3)_2O$, $(SiH_3)_3N$, SiH_3F, SiH_2Cl_2, $KSiH_3$, $CH_3CH_2SiH_3$?*

(b) *Starting with silica, how will you prepare pure Si, $SiCl_4$ and SiH_4?*

13. *Complete the following reactions*

(i) $Sn^{2+} + PbO_2 + H^+ \longrightarrow Sn^{4+} + ...$

(ii) $Sn^{2+} + air \longrightarrow$

(iii) $Sn + KOH\,(aq) \longrightarrow Sn(OH)_6^{2-} +$

(iv) $Sn + H_2SO_4\,(conc.) \longrightarrow ......(heated)$

(v) $SnS_2 + NaHS + NaOH \longrightarrow Na_2SnS_3 + Na_2SnO_2 +$

(vi) $PbO_2 + Pb + H_2SO_4 \longrightarrow$

(vii) $Pb_3O_4 + HNO_3 \longrightarrow$

(viii) $Sn(OH)_6^{=} + CO_2 \longrightarrow$

(ix) $CH_2OH.CH_2OH + Pb(CH_3COO)_4 \longrightarrow$

(x) $PbCO_3 + PbS \xrightarrow{heat} Pb + SO_2 + CO_2$

(xi) $Cu(ClO_4)_2 + Sn/Hg \longrightarrow Cu + Sn(ClO_4)_2$

(xii) $SnCl_4 + N_2O_5 \longrightarrow Sn(NO_3)_4 +$

(xiii) $CaCN_2 + C + Na_2CO_3 \xrightarrow{fused} NaCN + CaCO_3$

(xiv) $NaNH_2 + C \xrightarrow{500°C} NaCN +$

(xv) $Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 +$

(xvi) $PbO_2 + MnSO_4 + HNO_3 \longrightarrow$

(xvii) $Sn(OH)_4^{=} + Bi(OH)_3 \longrightarrow$

14. (a) *What is the value of n in $[Si_4O_{12}]^{n-}$?*

(b) *Write down one simple chemical method of obtaining CF_4 free from SiF_4 from a mixture of SiF_4 and CF_4.*

(c) *What are fullerenes? Why are they so called?*

(d) *Give one example to illustrate how three-dimensional silicates may act as molecular sieves.*

(e) *What is mosaic gold?*

(f) *Mention one significant physiological action of tetraethylthiuram disulfide.*

15. *How is $PbEt_4$ prepared? How does it cause particulate pollution in air? What measure may be taken to prevent such polluting effect?*

CHAPTER THIRTYTWO

ELEMENTS OF GROUP 15(VA)

OBJECTIVES

22

ELEMENTS OF GROUP 15(VA)

22.1 INTRODUCTION

The elements in this group—nitrogen, phosphrous, arsenic, antimony and bismuth are sometimes collectively called pnictogen (pnicogen) or pnictides from the Greek synonym for choking (nitrogen does not support respiration).

The elements nitrogen and phosphorus are essential constituents of the living system. Peculiarly, the heavier members in the group, particularly arsenic, are extremely toxic.

The chemistry of the elements is similarly interesting. The remarkable tendency of catenation observed in carbon practically disappears in nitrogen; the importance of *p-p* π-bond increases; increased electronegativity leads to significant hydrogen bonding. The chemistry of phosphorus differs in the same way from that of nitrogen as silicon differs from carbon. The remaining elements in the group also gain increasing metallic character (as in Gr14). Arsenic shows some effect of poor shielding by the $3d^{10}$ core and bismuth exhibits inert pair effect to a greater extent than lead.

22.1.1 Abundance and occurrence

Nitrogen is highly abundant (~ 78% by volume and 75% by weight) in air as dinitrogen (N_2), though its abundance in rocks and soils is remarkably low (19 ppm; comparable to Ga, Nb and Li). Only nitrogenous minerals worth mention are KNO_3 (nitre or saltpetre) and $NaNO_3$ (chile saltpeter). These are probably formed via nitric acid resulting from the action of nitrifying bacteria on vegetable and animal remains and leached by water to the subsoil; in the period of desiccation following the rainy season, the salts reascend to the surface by capillary action. Large quantities of nitre are thus left as saline efflorescence on the surface of the soil, together with other salts. Major deposits of nitre occur in Bolivia, Italy, Spain and Russia. Deposits containing mainly $NaNO_3$ are found in Chile. In India, nitre occurs in some regions in Bihar.

Naturally occurring nitrogen consists mainly of ^{14}N; the isotope ^{15}N also occurs slightly, relative abundance $^{14}N/^{15}N \sim 272 : 1$. ^{15}N may be prepared by exchange reactions like

$$^{15}NO\,(g) + {}^{14}NO_3^-(aq) \rightleftharpoons {}^{14}NO\,(g) + {}^{15}NO_3^-(aq)$$

Phosphorus is highly abundant in crustal rocks (≅ 1120 ppm; eleventh position), mostly as orthophosphates of the apatite group, e.g., fluorapatite, $3Ca_3(PO_4)_2$, CaF_2. Over 200 phosphate minerals are distributed in different countries, the major deposits being in Morocco and other African countries, Florida and other North American states, South America, Australia and Asia.

In India, large deposits of phosphatic minerals are found in (i) *Bihar* and *West Bengal* : Hazaribagh, Singhbhum, Dhalbhum, Purulia and adjoining areas. (Total about 1 million ton; 20-25% P_2O_5). (ii) *Tamil Nadu* : About 8 million tonnes of phosphate rocks occur at Tiruchirapalli of which about 2 million tonnes are estimated to occur within 15m depth and considered economically recoverable (15-20% P_2O_5). (iii) *Uttarpradesh* : Fairly extensive deposits occur near Mussoorie.

Small quantities of phosphate rocks also occur in Maharashtra. Large deposits have also been located near Udaipur in Rajasthan.

Phosphorus also occurs in plants and animals where it is an essential constituent of life.

^{31}P is the only stable isotope of phosphorus. Among six known radioactive isotopes, ^{32}P (β-emitter; $t_{1/2}$ = 14 days) is most important. It is produced by (n, p) reaction on ^{32}S or (n, γ) reaction on ^{31}P in nuclear reactors. The isotope is extensively used in tracer studies. ^{31}P has a nuclear spin quantum number $\frac{1}{2}$ and is used in nmr spectrophotometry.

The *elements arsenic, antimony* and *bismuth* have very low abundance in the earth's crust; As < 2ppm; Sb 0.2 ppm; Bi 0.01 ppm. As expected, the elements are chalcophilic in character, and occur mainly as sulphides. Arsenic occurs mainly as *realgar* As_4S_4 and *orpiment* As_2S_3; metal arsenides like NiAs (*niccolite*), CoAsS (*cobaltite*) etc. as well as an oxide (*arsenolite* : As_2O_3) which are widely distributed throughout the world. Orpiment and realgar are found in the morain of Shunkalpa glacier in the Kumaon mountains, though with little economic importance. Small quantities of arsenopyrite (FeAsS) occur near Darjeeling and in the Bhutna valley, Kashmir.

Like phosphorus, Arsenic also has only one stable isotope, ^{75}As.

The principal ore of *antimony* is stibnite, Sb_2S_3. It occurs in China, South Africa, Mexico, Bolivia and Chile. In India, it is found in Kangra valley, though the places are inaccessible. Stibnite also occurs in Visakhapatanam and Hazaribagh.

Antimony has two stable isotopes – ^{121}Sb (57.25%) and ^{123}Sb (42.75%).

Bismuth occurs as Bi_2S_3 (*bismuthinite*), $(BiO)_2CO_3$ (*bismutite*) and Bi_2O_3 (*bismite*). Bi has only one stable isotope (Bi-209). It is the heaviest stable nuclide known for any element.

22.1.2 Isolation of the elements

Nitrogen : It may be obtained in the laboratory by a variety of chemical reactions, though these have little utility except for academic purposes.

(i) $NH_4NO_2 = N_2 + 2H_2O$.

Some NO and HNO_3 are also formed which must be removed by absorbents like $K_2Cr_2O_7$ solution in presence of H_2SO_4.

(ii) $2NaN_3 \xrightarrow{heat} 2Na + 3N_2$ (also barium azide)

(iii) $(NH_4)_2Cr_2O_7 \xrightarrow{heat} N_2 + Cr_2O_3 + 4H_2O$.

The reaction is accompanied by "sparks" and is often used as a model for artificial volcano in popular science exhibitions.

(iv) $3CuO + 2NH_3 \xrightarrow{heat} 3Cu + N_2 + 3H_2O$

(v) $3Cl_2 + 8NH_3\,(aq) \longrightarrow N_2 + 6NH_4Cl$.

Ammonia must be in excess, othewise explosive NCl_3 is formed.

(vi) $3Ca(OCl)Cl + 2NH_3 = 3CaCl_2 + 3H_2O + N_2$.

(vii) $CO(NH_2)_2 + 3NaOBr = N_2 + CO_2 + 2H_2O + 3NaBr$.

Industrially, large amounts of nitrogen are obtained as byproduct during isolation of oxygen by fractional distillation of liquid air. Dinitrogen boils off before O_2 as its b.p. is lower (N_2 : –195.8°C; O_2 : –183.1°C). It usually contains some argon.

Phosphorus : It is obtained by reducing phosphate rock with coke in presence of sand at 1400-1500° C in an electric furnace. The overall reaction may be idealized as

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4.$$

The phosphorus vapour is condensed under water. This is the common "white phosphorus".

When fluorapatite is used, part of the CaF_2 combines with SiO_2 forming the toxic and corrosive gas SiF_4. This may be arrested by water and Na_2CO_3 forming Na_2SiF_6. The phosphate rocks also contain 1-5% Fe_2O_3 which gets converted to liquid "ferrophosphorus" (roughly Fe_2P); this sinks below the slag and can be drained out. This unavoidable loss of P may be partly compensated by some uses of this byproduct (see use).

The preparation/interconversion of other allotropic forms have been discussed later.

Arsenic : It may be obtained by roasting arsenopyrite minerals in absence of air and condensing the sublimate

$$4FeAsS \longrightarrow 4FeS + As_4\,(g) \quad (700°C).$$

Some arsenic is trapped in the sulphide residue. This is converted to volatile As_2O_3 by roasting in air. As_2O_3 is also present in the flue dust from smelting of lead and copper from their sulphide minerals. The As_2O_3 may be trapped by condensation and used as such. It may also be reduced to the element (with C).

Antimony : It is similarly obtained as volatile Sb_2O_3 from roasting of sulphide minerals. The accompanying As_2O_3 is more volatile. The oxide may be reduced with carbon (charcoal) in presence of a flux like Na_2CO_3 or Na_2SO_4. Ores containing 25-40% Sb may be directly smelted in a blast furnace. Ores containing higher percentages of Sb (40-60%) are usually melted without oxidation to Sb_2O_3. This is then reduced with scrap iron :

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS$$

Antimony is also recovered from the flue dust of lead smelting.

Bismuth : It is also a byeproduct of extraction of Pb, Zn or Cu. The sulphide ores may be roasted to form the oxide which may be reduced with charcoal or iron.

22.1.3 Uses of the elements

Uses of nitrogen

Dinitrogen is largely used to provide an inert atmosphere in metallurgy and in various chemical industries like iron and steel industry, petrochemical industry (as a purge) and so on.

Liquid nitrogen is a useful refrigerant. It is used in low-temperature machining and grinding of rubbers and rubber-like substances, preservation of biological specimens and similar low temperature applications.

Large amounts of nitrogen are used in the manufacture of ammonia and calcium cyanamide.

The Nitrogen cycle

There is a continuous interchange of nitrogen between the atmosphere and the biosphere. Nitrogen required for growth of plant and animal life is mostly received through soil as follows :

(i) **The action of bacteria : About 60% of the nitrogen input in the soil is caused by** the action of nitrifying bacteria which convert dinitrogen directly into nitrates or ammonium salts. *Rhizobium* is the most important bacteria in this category which lives symbiotically in the nodules or roots of certain plants (Leguminosae, pea, bean etc.). *Anabena, Nostoc, Azotobacter* and *Clostridium pastorianum* have similar functions. They contain the nitrogen fixing enzyme *nitrogenase*. Traces of transition metals like Fe, Mo, Co and Cu and boron are necessary for the functioning of these bacteria. In one year, about 120 kg. of nitrogen is fixed per acre of fertile land by Rhizobium. The figure is much less (10-0.1) for others.

It has been estimated that the amount of N_2 fixed annually by bacteria is substantially greater than the amount of nitrogen fixed artificially (through Haber process) : 150 million tonnes vs 120 million tonnes (1990 figure).

It is interesting to observe that the nitrifying bacteria can fix nitrogen from the atmosphere under ordinary conditions while our chemistry can at best convert nitrogen to ammonia under 200 atm. pressure and 550°C in presence of catalysts. The enzyme nitrogenase contains two large proteins — one containing four Fe and four S(M.W. ~ 60,000); the other contains 24-32 Fe atom, 2 Mo and a sulphide group (M.W. ~ 2,20,000). It is thought that these proteins form a complex with N_2 before reducing it to NH_3. The first dinitrogen complex was made in 1965 ($[Ru(NH_3)_5N_2]^{2+}$). Other metals, e.g., Ti(II) are now under active consideration (see later). The ammonia is oxidized to nitrate by bacteria like *nitrosomonos* and *nitrobacter*.

(ii) **Artificial fixation of nitrogen** is used to meet the growing need of nitrogen in soil to produce food for the ever-increasing population. The main procedure involves the Haber process for the manufacture of ammonia, which is then converted to nitric acid and other fertilizers.

(iii) **Lightning** in the upper atmosphere leads to the formation of NO and NO_2, which is carried by rain to the soil as HNO_3.

The balance of nitrogen in the atmosphere is maintained by returning the nitrogen to the atmosphere by the following major steps :

(i) **Death and decay of plants and animals, together with animal excretions**, return most of the nitrogen to the soil. Part of this escapes as NH_3; a considerable portion is converted to N_2, N_2O or NH_3 by certain denitrifying bacteria (e.g., *Pseudomonus* and *Achromobacter*).

(ii) **Burning of wood, coal and petroleum** also releases a small amount of nitrogen oxides to the atmosphere.

(iii) **Drainage of surface water** carries some nitrogen into the sea. This helps to support marine life. But part of this is ultimately deposited into sea-beds.

The major human interference in the nitrogen cycle occurs through artificial fixation of nitrogen for the manufacture of fertilizers required to meet the increasing demand of food for the growing human family. This is unavoidable but the leaching of excess nitrogenous fertilizers may lead to excess concentration of salts in water. Nitrates and nitrites are deemed to be potentially hazardous to health in concentrations exceeding 50 mg/litre and 0.1 mg/litre respectively (maximum admissible concentration, MAC). For drinking water, the maximum limit of nitrates is restricted at 10 mg/litre. Side by side, enhanced denitrification can lead to an increase in the concentration of N_2O in the atmosphere; this may damage the ozone layer.

Uses of phosphorus

Phosphorus is mainly used as phosphate fertilizers. About 159 million tonnes of phosphate rock was produced all over the world in 1988. Only a small amount of elemental phosphorus is produced (nearly 1.5 million ton all over the world in 1988), and most of it is converted to pure phosphoric acid. Some phosphorus is converted to P_4S_{10} (used in the preparation of organo-phosphorus compounds) and P_4S_3 (used in match). Phosphorus chlorides, oxochlorides and phosphor bronze are also produced.

Ferrophosphorus (obtained as a byproduct in phosphorus preparation) is used as a filler in high density concrete, in radiation shields for nuclear reactors and in making special steels and cast irons.

The Phosphorus Cycle

The recycling of phosphorus among the biosphere and the earth is much slower than the cycles for other essential nonmetals (e.g., C, N, O, H and S).

(i) Phosphates in rocks are leached very slowly by weathering and carried to lakes and rivers where they support marine life. Some algae and bacteria can even absorb inorganic phosphates directly. Most of the phosphate is reprecipitated and collected in sediments through ages.

(ii) The sediments may be lifted to the surface of the earth by geological action.

(iii) Untreated soil usually contains very little phosphate, mainly as insoluble phosphates of Ca, Al and Fe(III). These are slightly leached in acidic water and taken up by plant roots (as $H_2PO_4^-$). The deficit is supplemented by addition of phosphatic fertilizers — rock phosphates or products made from it. Bone mill and fish mill are also used.

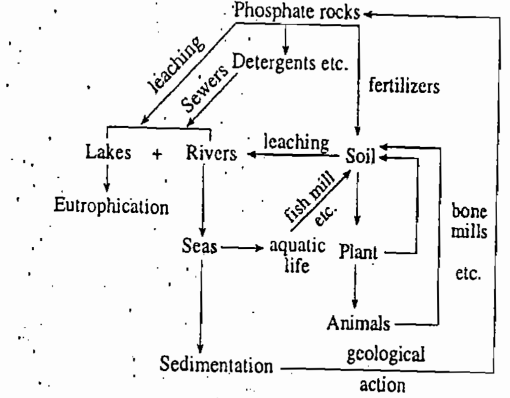
(iv) Phosphates enter the plant and animal kingdom through food chains and play a vital role in the formation of the nucleic acids, metabolic functions via ATP and in the formation of bone, teeth etc. Death and decay of plants and animals return a part of this phosphorus to the soil. Natural decay of bones is an extremely slow process; addition of bone mills and fish mills to soils as fertilizers aids the recycling of phosphorus.

(v) A huge amount of phosphate is used in detergents. This is transported through sewage waters and rivers into the sea where they form sediments. About a million ton of phosphate is thus transported annually.

(vi) The leaching of phosphatic fertilizers by rain water carries annually a few million tons of phosphates to lakes, rivers and seas. A high concentration of phosphates may lead to higher growth of aquatic plants like algae and a shortage in dissolved oxygen, killing fishes and causing slower oxidation of other polluting substances. Such over-nourishment has been called **eutrophication** from its Greek synonym.

TABLE 22.1

Recycling of phosphorus in the biosphere



[Sec.22.1.3 Uses (As, Sb, Bi)]

Uses of As, Sb, Bi

Elemental *arsenic* is used to make various alloys with lead; these are harder and have better castability. GaAs and InAs are now largely used as light emitting diodes (LED), laser windows etc. Arsenic compounds are widely used for controlling weeds and pests (see later).

Antimony is also used in alloying lead and tin for better strength. For example, *type metal* (Pb 55, Sb 30, Sn 15); *antifriction metal* (bearings; Pb 75, Sb 15, Sn 8, Cu 2). Semiconductros like AlSb, GaSb are used in IR devices, diodes etc. Different antimony compounds have many specific uses (see compounds).

Bismuth is used in pharmaceuticals and in making fusible alloys. These low melting alloys are used as safety plugs in boilers and in automatic sprinklers; when the plug melts, water is automatically sprayed over the fire. Some alloys are *Rose's metal* (m.p. 94°C) : Bi 50, Pb 25, Sn 25; *Wood's metal* (m.p. 71°C) : Bi 50, Pb 25, Sn 12.5, Cd 12.5; *Lipowitz metal* (m.p. 60°C) : Bi 50, Pb 27, Sn 13, Cd 10.

The poisonous nature of arsenic compounds has been known since very ancient time. The three major bio-chemical actions of As are coagulation of proteins, complexation with coenzymes and interference with phosphorylation, an important step in the generation of ATP. The usual As level in potable water is within 10 ppb, although reports of much higher As-content (> 100 ppb) are also known. It accumulates in the body and prolonged intake at low level can ultimately give rise to acute poisoning symptoms (see below).

Surprisingly, it has been established recently that arsenic is also an essential trace element for the living system. Although the specific function is yet to be established, it appears quite certain that the element is involved in zinc metabolism in mammals.

Arsenic contamination in Ground Water of West Bengal .

A long stretch of land in West Bengal and adjoining Bangladesh shows arsenic in ground water much above the WHO maximum permissible limit of 0.05 mg l^{-1}, exposing a population of about 30 million in 34,000 km^2 to the threat of severe arsenic poisoning. Such arsenic affected areas extend from the district Malda in the north to the district South 24 Parganas in the south, covering the districts of Nadia, Murshidabad and North 24 Parganas on the eastern bank of the river Bhagirathi and part of the Burdwan district on the western bank—by and large within the upper delta plain of the Bengal basin. More than 800,000 people from 312 wards/villages in these areas are drinking arsenic contaminated water and amongst them at least 175,000 people show arsenical skin lesions. Other symptoms of severe arsenic poisoning (see later) are also frequent in these areas. Typical values for total concentration of arsenic in water samples (mgl^{-1}) from these districts are :

South 24 Parganas	0.05-3.7	*Bardhaman*	0.05-0.64
North-24 Parganas	0.05-1.25	*Murshidabad*	0.05-0.95
Nadia	0.05-1.18	*Malda*	0.05-0.93

The source of the arsenic in the water bearing strata of these regions is definitely geological, though the exact cause is not known with certainty. Arsenic-rich iron pyrites occurs in different layers in the soil of these areas, but the passage of arsenic to the water is not clear since iron pyrites (FeS_2) is insoluble in water. However, pyrites may dissolve in presence of oxygenated water according to the following proposed mechanism :

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2Fe^{2+} + 4HSO_4^-$$

$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

The Fe(III) formed may further catalyze the decomposition of pyrites. It is quite likely that excessive withdrawal of ground water for irrigation might have caused entry of air/oxygen to the underground water, thereby enhancing the decomposition of pyrites and facilitating the passage of arsenic into water. Many other interacting factors like change of pH, redox potential, nature of the soil, use of fertilizers and microbial reactions may also be involved in the process. Concerted efforts of geo-scientists, engineers and environment specialists at different levels have already made some progress in identifying the problem and several projects to mitigate this have also been started. Mass awareness and a coordinated and concerted approach by different bodies is urgently required to arrive at viable area-specific solutions. Proper utilization of surface water (which is available in plenty) in the first step appears essential in this respect.

Arsenic contamination in ground water is not unique to West Bengal. Major cases of arsenic pollution have been reported from Taiwan, Chile, North Mexico and Argentina. The period of occurrence (a), number of people affected (b) and the concentration of arsenic in drinking water (c) are shown below :

	(a)	(b)	(c)
Taiwan	1961-86	100,000	0.1-1.8 mg L^{-1}
Anto fagasta (*Chile*)	1959-70	100,000	0.8 mg L^{-1}
Region Lagunera (*North Mexico*)	1963-83	200,000	0.41 mg L^{-1}
Monte Quemado (*North Argentina*)	1955-	10,000	> 0.2 mg L^{-1}

Other minor incedents of arsenic contamination of groundwater have been reported from Minnesota, USA; Ontario, Canada; Nova Scotia, Canada; New Zealand; Nakajo, Japan; and Millard County, Utah.

Different stages of clinical manifestations of arsenic toxicity are as follows :

(a). *initial stage* : dermatitis, keratosis, conjunctivitis, bronchitis and gastroentritis.

(b) *second stage* : peripheral neuropathies, hepatopathy, melanosis, depigmentation and hyperkeratosis.

(c) *last stage* : gangrene in the limbs and malignant neoplasm.

22.2 GENERAL PROPERTIES

22.2.1 Elemental forms

Nitrogen occurs as the colourless diatomic gas dinitrogen N≡N; it has no allotropes.

Solid phosphorus has several allotropic forms which are mentioned separately. In the liquid and gaseous state below 800°C the unit is the tetrahedral P_4 molecule; dissociation to P_2 units starts above 800°C.

White Phosphorus, the most common form of phosphorus, is a soft waxy solid, m.p. 44°C; b.p. 287°C; density 1.82 g cm^{-3}. It becomes yellow on exposure to light.

White phosphorus is insoluble in water but highly soluble in carbon disulphide (= 880 g per 100 g CS_2 at 10°C), benzene, liquid SO_2, liquid NH_3, PCl_3 and $POCl_3$. On exposure to air, it is slowly oxidized emitting a greenish glow which may be due to PO_2 or $(PO)_2$. Above 50°C, white phosphorus ignites spontaneously in air to P_4O_{10}. It reacts with all halogens (PX_3/PX_5), sulphur (P_4S_n, $n = 3, 5, 7, 10$) and alkali (PH_3, P_2H_4). Concentrated nitric acid slowly oxidizes it to phosphoric acid.

White phosphorus is highly poisonous — even contact with skin or inhalation may cause harmful metabolic disorders.

Structurally, white phosphorus contains the symmetrical tetrahedral P_4 unit with P—P distance 2.21 A° and an interbond angle 60°. Bonding description based on *p*-orbitals suggests that such a bond angle should introduce large strain in the molecule. One should then expect the existence of a cube-shaped P_8 molecule with maximum

p-overlap. However, the transformation $2P_4$—P_8 is unfavourable from entropy consideration; several recent electronic structure calculations also render it enthalpically disfavoured. Photoelectron spectrum of P_4 now shows to a first approximation that the phosphorus $3p$ orbitals are virtually non-bonding. The unit is held by the strongly bonding interaction of the $3s$ orbitals which results in build-up of high electron-density within each triangular face. This interpretation seems to be consistent with the non-existence of cubic P_8.

Red phosphorus is obtained by heating white phosphorus in absence of air at 270-300°C. It is ordinarily amorphous, melting under pressure at 592°C. At 1atm pressure it sublimes at 416°C. It also possesses a much higher density than white P (~ 2.16 g cm^{-3}) and is non-poisonous and insoluble in organic solvents. Its reactivity is much less — it is unattacked by aqueous alkali. It ignites in air only at 250°C and reacts less violently with halogens. The structure is believed to be polymeric with linked P_4 tetrahedra. Various crystalline forms have also been prepared.

$\Delta H°$ for the conversion red P — white P is quite small, only + 17.6 kJ mol^{-1}.

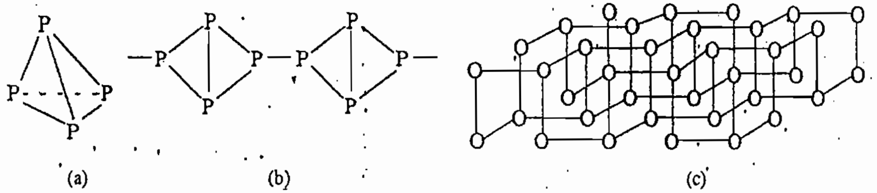


Fig. 22.1

Structure of (a) White phosphorus, (b) Red phosphorus (postulated) and (c) Black phosphorus

Black phosphorus, the least reactive allotrope, results on heating (~200°C) white phosphorus under very high pressure. An orthorhombic form is obtained at ~ 12000 atm pressure; still higher pressures result in rhombohedral and cubic varieties. The densities of these different crystalline forms increase in a parallel fashion : 2.7, 3.6 and 3.9 g cm^{-3} respectively. Black phosphorus resembles graphite in appearance and is semiconducting. The orthorhombic form (m.p. ~ 610°C) consists of a double layer lattice in which each P atom is bonded to three others at ~ 2.23 A°. The bond angles at P are around 100°. The shortest distance between layers is 3.9A°. Black phosphorus does not ignite in air even at 400°C. It is thermodynamically the most stable form; the inertness may also be due to kinetic factors.

The interconversion of white, red and black phosphorus, together with other allotropic forms, are summarized in Fig. 22.2. The conversions have to be carried out in absence of air. Catalysts like mercury favour many of these interconversions.

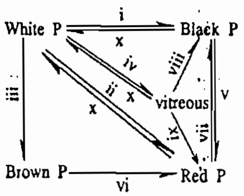


Fig. 22.2

Interconversion among various allotropic forms of phosphorus.

(i)	White	⟶	black	: 220°/pr.
(ii)	White	⟶	red	: > 250° C
(iii)	White	⟶	brown	: vap. cooled rapidly (liq N_2)
(iv)	White	⟶	vitreous	: > 250° C/pr.
(v)	Black	⟶	red	: > 450° C
(vi)	Brown	⟶	red	: > -196° C
(vii)	Red	⟶	black	: 25° C
(viii)	Vitreous	⟶	black	: 400° C/pr.
(ix)	vitreous	⟶	red	: > 450° C
(x)	Any form	⟶	white	: sub (vac).

Arsenic, antimony and bismuth vapours contain the tetramers; rapid condensation of the vapour results in unstable yellow forms of As and Sb which probably also contains the M_4 units. At room temperature the most stable forms of the elements are the lustrous metallic rohombohedral variety, comparable to rhombohedral black phosphorus. The grey solids have corrugated layer lattices in which each atom has three nearest neighbours in puckered hexagonal nets with interbond angles around 96°. The nets stack in such a fashion that three more distant neighbours appear in the adjacent net. Although the expected substantial increase in interatomic distances in each layer from As to Bi is observed, the inter layer distances do not increase proportionately. This is shown by the relatively small increase in the distances to *next-nearest* neighbours (Table 22.2).

TABLE 22.2

Interatomic distances in solid As, Sb and Bi

Distance (pm)	As	Sb	Bi
Three nearest neighbours	251	287	310
Three next-nearest neighbours	315	337	347
Density (g cm^{-3})	58	67	98

There is also a gradual increase in the density of the elements. Though we expect a parallel increase in metallic character, the electrical resistivity of the elements actually shows a marked increase from As to Bi (As 33, Sb 42, Bi 120 μ ohm cm.). All values are higher than that of a poor metallic conductor like Pb (22 μ ohm cm.), that for Bi being even higher than that of nichrome wire (100 μ ohm cm.). The structure of Bi is also not typical of the isotropic bonding normally found in metals. The band structure of bismuth shows a low density of conduction electrons and holes; it is therefore best classified as a semimetal.

All the three elements are brittle solids with colours varying from steel-grey (As) to bluish white (Sb) to dull white (Bi). Molten bismuth expands on solidification, resembling only Ga and Ge among the elements.

Q. 22.1 *Given the following bond dissociation enthalpies (kJ mol^{-1}) : $P \equiv P$ 490; $P-P$ 209; $N \equiv N$ 946; $N-N$ 160, compare the enthalpy changes for the process*

(i) $2P_2(g) = P_4(g)$ (ii) $2N_2(g) = N_4(g)$.

Hints : The process involves replacement of 2 X≡X units by 6 X—X bonds in the X_4 tetrahedron. Energy is released when bonds are formed.

Hence ΔH (i) = $-6 \times 209 + 2 \times 490 = -274$ kJ, ΔH (ii) = + 932 kJ.

Reactions of the elements

Dinitrogen is generally unreactive at room temperature owing to the following reasons (m.o. description KK $1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$).

(i) high $N \equiv N$ bond energy

(ii) large energy difference between the HOMO ($3\sigma_g$) and LUMO ($2\pi_u$).

(iii) symmetrical electron distribution which makes the molecule nonpolar.

N_2 reacts slowly at room temperature with Li and at elevated temperatures with Be, Mg, Ca, Sr, Ba, Al as well as B, Si and Ge to form nitrides. Its reversible combination with hydrogen under pressure and in presence of a catalyst to form NH_3 is well-known. It combines with carbon at red heat (to form cyanogen) and oxygen at 3000°C (to form NO).

Calcium carbide reacts with N_2 at 800°C to form calcium cyanamide :

$$CaC_2 + N_2 = CaNCN + C.$$

N_2 is reduced to NH_3 at room temperature by an alkaline aqueous solution of vanadium (II) sulphate in presence of catechol. Similar reduction may also be effected by an aqueous solution of the cyanocomplex $K_2[MoO(CN)_4(H_2O)]$ and BH_4^-. Reduction to N_2H_4 occurs with $V(OH)_2 - Mg(OH)_2$ suspension :

$$2V(OH)_2 + N_2 + 2H_2O = N_2H_4 + 2VO(OH)_2$$

Room temperature absorption of N_2 by certain transition metal complexes is also interesting as they result in coordination compounds of N_2 :

$$[Ru(NH_3)_5H_2O]^{2+} \xrightarrow{N_2} [Ru(NH_3)_5N_2]^{2+} \text{ ...... (50\% yield).}$$

$$[CoH_3(PPh_3)_3] \longrightarrow CoH(PPh_3)_3N_2 + H_2$$

These coordination compounds have been discussed under section 22.3.10.

Active nitrogen

When nitrogen is passed at low pressure (0.1-2 mm Hg) through an electric discharge, reactive atomic nitrogen is obtained. The formation of such "active nitrogen" is accompanied by a yellow afterglow which persists for several seconds after the discharge is discontinued. Initial recombination of the atoms form excited N_2 molecules. The afterglow corresponds to slow deexcitation of these molecules to ground states N_2 molecules.

Phosphorus is comparatively much more reactive than nitrogen, particularly white phosphorus (see allotropes). The elements As, Sb and Bi also burn in air to form the trioxide M_4O_6 and combine with halogens and some other nonmetals. Non-oxidizing acids have no action on them. Dilute nitric acid converts arsenic to arsenious acid while hot concentrated nitric acid converts arsenic to arsenic acid; but antimony is oxidized to Sb_2O_3. Bismuth, which is more metallic in character, forms the salt $Bi(NO_3)_3$. Unlike phosphorus, the elements As—Bi are unaffected by aqueous alkali. Fused sodium hydroxide attacks arsenic, giving sodium arsenite and hydrogen.

Some relevant equations are :

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2 \quad (conc.)$$

$$P_4 + 20HNO_3 = 4H_3PO_4 + 20NO_2 + 4H_2O \quad (conc.)$$

$$3As_4 + 20HNO_3 + 8H_2O = 12H_3AsO_4 + 20NO \quad (conc.)$$

$$As_4 + 4HNO_3 = As_4O_6 + 4NO + 2H_2O \quad (dilute)$$

$$As_4 + 6H_2SO_4 = As_4O_6 + 6SO_2 + 6H_2O \quad (conc.)$$

$$As_4 + 12NaOH = 4Na_3AsO_3 + 6H_2 \quad (fused)$$

$$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O \quad (hot,\ conc.)$$

$$6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O \quad (hot,\ conc.)$$

$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 4H_2O + 2NO \quad (hot,\ conc.)$$

$$2Bi + 6H_2SO_4 = Bi_2(SO_4)_3 + 6H_2O + 3SO_2 \quad (hot,\ conc.)$$

The elements also form a wide variety of binary compounds with virtually every metallic element. The compounds contain a wide range of structure starting from the simple stoichiometries like Sr_3P_2 or Na_3As, that is phosphides, arsenides etc. However, these compounds do not always contain the simple M^{3-} (i.e., P^{3-} or As^{3-}) ions.

22.2.2 Group Trends

Some important atomic and physical porperties of the elements are summarized in Table 22.3 and Figures 22.3 (a) and 22.3 (b).

TABLE 22.3

Some properties of the elements of Gr 15(VA)

	N	P	As	Sb	Bi
Electron configuration	[He] $2s^22p^3$	[Ne] $3s^23p^3$	[Ar] $3d^{10}4s^2$	[Kr] $4d^{10}5s^25p^3$	[Xe] $4f^{14}5d^{10}$
ΔH^0 (atomization) kJ mol^{-1}	473	315	287	259	207
m.p. °C	−210	44(w)	814*	631	271
b.p. °C	−196	280(w)	615 (sub)	1380	1560
I_1 kJ mol^{-1}	1403	1012	947	834	703
I_2 "	2855	1902	1800	1794	1610
I_3 "	4577	2910	2735	2443	2465
$I_1 + I_2 + I_3$ kJ mol^{-1}	8835	5824	5482	5071	4778
Electronegativity (P)	3.04	2.2	2.18	2.05	2.0
" (AR)	3.07	2.06	2.20	1.82	1.67
Covalent radius (3-*coordinate*; pm)	74	110	122	141	152

* 39 atm pr.

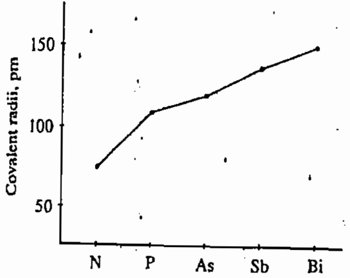


Fig. 22.3 (a)
Variation of M^{III} covalent radius.

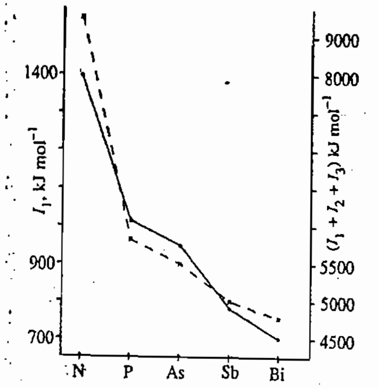


Fig. 22.3 (b)
Variation of (i) I_1 (scale on left) and (ii) $I_1 + I_2 + I_3$ (broken line; scale on right).

The general trend in various properties reflect, as in groups 13 and 14, the effect of underlying $3d^{10}$ core in As and $5d^{10}4f^{14}$ core in Bi. As in previous groups, we expect (i) an increase in metallic character down the group (ii) appearance of inert pair effect in bismuth (iii) non-existence of pentacovalent nitrogen owing to the lack of energetically accessible vacant orbital required for valence expansion (iv) remarkable stability of $2p$-$2p$ π-bonds over $3p$-$3p$ π-bonds (v) aptitude of nitrogen to form H-bonds (vi) involvement of d-orbitals in the chemistry of phosphorus and so on.

The covalent bond energies of the elements support these expectations. Nitrogen forms stronger bonds with hydrogen than phosphorus, but the trend is reversed with chlorine or oxygen. At the same time, stable phosphorus analogues of N_2, NO, HCN, N_3^-, NO_2^+ etc. are absent. These reflect the importance of p-p π-bonding in nitrogen and p-d π-bonding in phosphorus (see later).

TABLE 22.4
Few average covalent bond energies* for N, P, As, Sb and Bi (kJ mol^{-1})

N—N	N—H	N—F	N—Cl	N—O
160	391	272	193	201
P—P	P—H	P—F	P—Cl	P—O
209	322	490	319	340
As—As	As—H	As—F	As—Cl	As—O
180	247	464	317	331
	N = N 418		P = P 310	
	N ≡ N 946		P ≡ P 490	

* (all values are approximate. Wide variation is found in different texts).

The value of E(N ≡ N), (946 kJ mol^{-1} in N_2) is nearly six times E(N – N), (160 kJ mol^{-1} in N_2H_4). The estimated value for E(N ≡ N) is also more than twice E(N – N). This is in marked contrast to corresponding figures for C in Group 14(IV).

C – C	C = C	C ≡ C	
346	598	813	kJ mol^{-1}

The high strength of N ≡ N is certainly derived from efficient σ and π-bonding between the N-atoms. In the m.o. description, enhanced nuclear charge of N helps to lower the energy of the bonding orbitals and thus stabilize the molecule. The lone pair of electrons on each N are at opposite ends of the molecule and do no seem to interact. The marked weakness of the N—N single bond (E = 160 kJ mol^{-1}) in comparison to either C—C or P—P bond is believed to arise from the repulsion between the lone pairs of electrons (which make their first appearance along the period). The bond strength increases remarkably when nitrogen bonds to an atom with no lone pair of electrons like H.

Similarly, the following bond energy comparisons are also interesting (all in kJ mol^{-1}).

$$\text{B—B} < \text{C—C} >> \text{N—N } 160 > \text{O—O } 146 < \text{F—F } 158$$

$$\text{Si—Si } 226 > \text{P—P } 209 < \text{S—S } 226 < \text{Cl—Cl } 242$$

Valence and Oxidation states

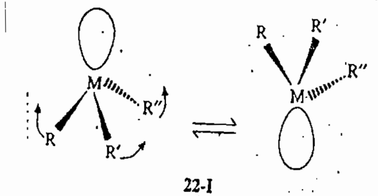
The elements may gain the next noble gas configuration by gaining three electrons and forming M^{3-} ion. However, such electron attachment involves a high positive enthalpy change and is not compensated except by high lattice energies. Thus, the formation of the N^{3-} ion requires 2130 kJ mol^{-1} energy. Accordingly, the nitride ion occurs only in salt-like nitrides of the strongly electropositive metals which afford a high lattice energy. Typical examples customarily cited for such compounds are Li_3N, Be_3N_2, Mg_3N_2, Ca_3N_2, Sr_3N_2, Ba_3N_2 and AlN. Even then, the existence of the monatomic ion with three units of negative charges is not beyond question. There are many other nonionic nitrides (section 22.3.2).

The formation of P^{-3} from P (g) requires only 1450 kJ mol^{-1} energy. Still, truly ionic phosphides are rare, except those of the alkali and alkaline earth metals, e.g., Na_3P and Ca_3P_2. There are other phosphides containing condensed anions like P_7^{3-}. (Section 22.3.2).

Loss of valence electrons by the elements to form cations is also unlikely in view of the high ionization energies involved. The + 5 ions do not exist. With increase in atomic number, we expect Sb^{3+} and Bi^{3+} ions to exist in the crystalline salts $Sb_2(SO_4)_3$ and $Bi(NO_3)_3 \cdot 5H_2O$. But even in these compounds, the metals are strongly coordinated to the anions. Hydrated Bi^{3+} possibly exists in highly acidic solutions of bismuth perchlorate. With slight increase in pH, the dominant species in solution becomes the $[Bi_6(OH)_{12}]^{6+}$ ion (see section 22.3.6). Several other polycations are known. Attempts to stabilize chelated cations of antimony and bismuth by crown ethers have also met little success (see complexes).

Most of the compounds formed by the elements in this group are thus covalent with the elements in oxidation state of either + III or + V. Other formal oxidation numbers are also common, nitrogen covering the wide range from –3 (in NH_3) to +5 (in HNO_3). However, these oxidation states or numbers mainly serve the formalities of balancing redox equations only. The important valence features of the elements concern the number of electron pair bonds formed and the stereochemistries involved.

The MR_3 type compounds are mostly pyramidal with a lone pair of electrons which is sterically active. The molecules undergo rapid inversion (like an umbrella turning inside out and vice versa) in which the M atom oscillates through the plane containing the three R-groups. The potential energy barrier to this inversion (the P.E. is higher when the M atom is in-plane with the R atoms in its transition from one side to another) is small in NH_3, about 23.4 kJ mol^{-1}.



22-I

For $M(CH_3)_3$ compounds, the energies of inversion (kJ mol^{-1}) are

$N(CH_3)_3$	34
$P(CH_3)_3$	133
$As(CH_3)_3$	122
$Sb(CH_3)_3$	112

For NH_3 and amines, the process is very rapid at 20°C, ~10^{11} per second. It is possible to resolve a pyramidal $MR_1R_2R_3$ species into optical isomers if inversion takes place slowly enough (inversion leads to racemization). Calculations show that pure optical isomers can be stable under normal conditions when the energy barrier is at least of the order of 100 kJ mol^{-1}. Hence asymmetric tertiary phosphines and arsines may be resolved. Thus AsMeEtPh (methylethylphenylarsine) has an inversion energy 177 kJ mol^{-1} and can be resolved into the optical isomers.

Three-covalent nitrogen may be planar in a very few cases, as for example, in $N(SiH_3)_3$ and $N(SiMe_3)_3$ where N—Si dative p-d π-bonding is involved (Chapter 21). A planar NIr_3 group is present in the complex $[Ir_3N(SO_4)_6(H_2O)_3]^{6-}$ ion.

The MR_5 type compounds formed by Group V elements often have a trigonal bipyramid structure like PF_5 and PCl_5 (gaseous). The solid halides PCl_5 and PBr_5 have ionic structures like $[PCl_4^+]\,PCl_6^-$ and $[PBr_4^+]Br^-$. SbF_5 and BiF_5 have polymeric structures involving F–M–F bridges. Sb $(C_6H_5)_5$ has a square pyramid arrangement in the solid.

In the trigonal bipyramidal molecule of gaseous PF_5, the two axial bonds are slightly longer than the three equatorial bonds. But the F atoms appear equivalent in the ^{19}F NMR spectra as the axial and equatorial F atoms rapidly interchange their position by a pseudo-rotation (berry pseudo-rotation; section 15.3.3). The activation energy barrier in PF_5 is only about 16 kJ mol^{-1}, resulting in rapid interchange. In PCl_5, the rate is much slower, say once in every three or four hours.

The principal stereochemical patterns of the elements are shown in Table 22.5.

TABLE 22.5

Major stereochemistry of Group 15(VA) elements

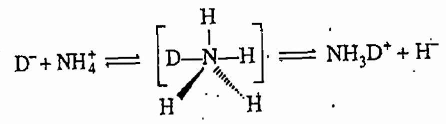
Formal valence	No. of bonds formed	Geometry	Example
3	3	Planar	$N(SiMe_3)_3$
		Pyramidal	NH_3, $AsCl_3$, $SbPh_3$
	4	Tetrahedral	NH_4^+, $AsPh_4^+$
	5	ψ-octahedral	$[SbF_5]^{2-}$
	6	octahedral	$[SbBr_6]^{3-}$
5	4	Tetrahedral	PO_4^{3-}, PCl_4^+
	5	tbp	PF_5, AsF_5, $SbCl_5$, $AsPh_5$
		sp	$SbPh_5$
	6	Octahedral	PF_6^-, $SbBr_6^-$

Distinctive Features of Nitrogen

As observed in groups III and IV, nitrogen at the head of the group has certain distinctive features from the remaining elements in the group. Some of these have been mentioned earlier in this section. Those points may be elaborated as follows :

(i) **Nitrogen has no scope for valence expansion :** We have already discussed the non-availability of energetically accessible vacant orbitals in nitrogen required for valence expansion beyond the 2*s*-2*p* orbitals. The consequent non-existence of compounds like NCl_5 are thus understandable. Phosphorus, on the other hand, has numerous compounds in coordination numbers 5 or 6 readily attained with more electronegative groups like halogenes, OR or phenyl e.g., P $(C_6H_5)_5$, P $(OR)_5$, $[PCl_4]^+$ $[PCl_6]^-$. The bonding in these compounds is most conveniently described in terms of contraction of the *d*-orbitals (which are energetically rather high) followed by hybridization. However, several points may be raised against such bonding modes and other alternatives have also been suggested (e.g., 3-center 4 electron bonds; see PF_5).

Pentacoordinated nitrogen has been speculated in certain reaction intermediates or transition states, (e.g., 22-II), as in the deuteration of NH_4^+ in molten ammonium trifluoroacetate by LiD.



22-II

(ii) **Nitrogen forms very strong** $p\pi$**—**$p\pi$ **bonds.** The reasons for weak π-bonding by 3*p*-3*p* overlap has been discussed before. As a consequence there are no phosphorus analogues of

(a) –N = N– as in difluorodiazene, F–N = N–F and (b) N_3H and N_3^-.

The various oxides of nitrogen are also dominated by nitrogen oxygen *p-p* π-bonds. The two oxides of phosphorus have large number of P—O single bonds (see oxides). The marked differences between the oxoacids of nitrogen and of phosphorus are also largely attributable to this tendency of nitrogen to form strong *p-p* π-bonds. Phosphorus also forms a few compounds of the type $P(OR)_3$, e.g., $P(OMe)_3$ or $P(OPh)_3$; but there are no compounds of the type $N(OR)_3$, nitrogen giving instead O = N(OR).

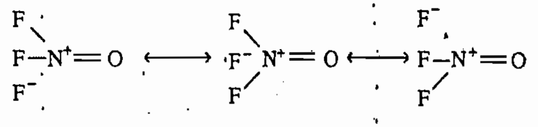
Q. 22.2 *Show that an oxide* N_4O_6 *with a structure similar to that of* P_4O_6 *would be highly endothermic.*

Hints : The reaction $2N_2 + 3O_2 = N_4O_6$ involves breaking of 2N≡N bonds and 3O = O, with the formation of 12 N–O single bonds (see structure of P_4O_6). Using bond energy data ($kJ.mol^{-1}$), 12E (N–O) = 2412 kJ.

$$\begin{aligned} 2E\,(N{\equiv}N) &= 1892 \\ 3E\,(O{=}O) &= \underline{1494} \\ & \quad 3386\ kJ. \end{aligned}$$

The N–O bond length (116pm) in trifluoroamine oxide, ONF_3, is about 26 pm shorter than a single bond. Clearly this cannot be assigned to *d-p* π-bonding. Theoretical calculations show that the 2*p* orbitals of oxygen containing the lone pairs of electrons can π-bond with the filled N–F σ-orbitals. This gives some *pπ-pπ* character to the N—O bond. The importance of the highly electronegative F atom in this case is shown by the fact that the N—O bond distance in $ONMe_3$ is 139 pm, virtually equal to that of a single bond.

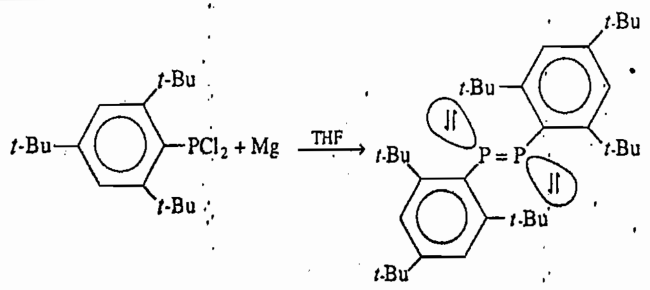
In the amine oxide (R_3NO), the R_3N: moiety acts as a base, and the stability of amine oxides decreases as the donor capacity of R_3N decreases. The N—O bond in such compounds is sufficiently polar, since the N → O electron displacement cannot be compensated by any back donation to N (the 4-covalent N has no scope to receive such backdonated charge). When R = F, i.e. in F_3N:, donor tendency is minimal. Compounds of the type $F_3N \rightarrow BX_3$ are thus unknown. Contrary to this, F_3NO is an isolable compound. The stability may be attributed to delocalization of electrons in accordance with the following canonical structures (22-III) based on oxygen 2*p* electron and the highly electronegative F atom.



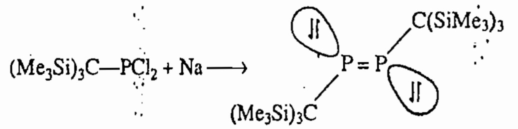
22-III

The short N—O bond distance (116 pm) is consistent with these structures.

Some thermodynamically unstable compounds of phosphorus and arsenic containing multiple bonds have been kinetically stabilized using bulky substituents :



22·IV



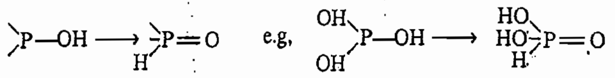
22·V

Cyanide analogues containing C ≡ P have also been obtained as transient species :

$$PH_3 \xrightarrow[\text{40mm Hg pr.}]{\text{carbon arc}} HC{\equiv}P$$

$$CF_3PH_2\,(g) \xrightarrow[20^\circ C]{\text{KOH }(s)} F_2C{=}PH \longrightarrow FC{\equiv}P.$$

(iii) ***p-d* π-bonding is rare with nitrogen** but weak to moderate *p-d* and *d-d* π-bonding play important roles in phosphorus chemistry. This is illustrated by rearrangements like



Similar rearrangement occurs in $P(OMe)_3$ also. The change of the hypothetical $P(OH)_3$ to $HPO(OH)_2$ replaces one P—OH bond by a weaker P—H bond (endothermic by about 138kJ mol^{-1}) but the establishment of the P=O bond overcomes this energy requirement (plus the energy required for valence reorganization). According to one estimate, the energy of this P=O bond is about 544 kJ mol^{-1}. The same tendency of phosphorus is found in the phosphonitrilic halides, $(PNCl_2)_n$ and in phosphine oxides and phosphoryl halides; R_3PO and OPX_3. The filled O-2*p* orbitals interact with the empty 3*d* orbitals on phosphorus, thereby lowering the energy of the "lone pairs" of the oxygen. This has been confirmed by X-ray photoelectron spectroscopy.

Q. 22.3 *X-ray photoelectron spectroscopy shows that the extent of energy-lowering of the oxygen lone pairs of electrons follows the order $OPF_3 > OPCl_3 > OPMe_3$. Comment.*

Hints : Overlap of large, diffuse 3*d* orbitals becomes more effective with greater *d*-orbital contraction in presence of electronegative atoms.

The ability of phosphorus to establish π-bonds by back-acceptance of electrons into its vacant 3*d*-orbitals plays an important part in the bonding of transition metal complexes with phosphorus donor ligands.

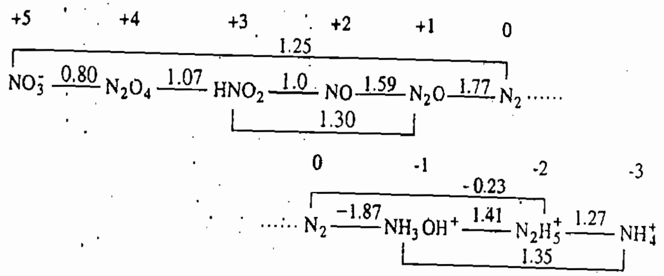
(iv) Nitrogen also differs from the other members of the group (and also from the neighbouring elements C and Si) in being highly electronegative. This results in strong hydrogen bonding in the compounds of nitrogen.

[**Sec. 22.2.2** *Oxidation states*]

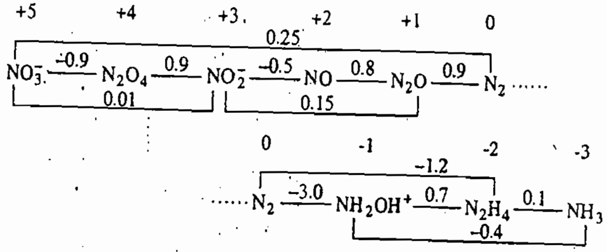
Oxidation state diagram

The oxidation state diagrams of the nitrogen group elements are complicated. The latimer diagrams are given first. These are followed by the oxidation state-free energy diagram (Frost diagram) for acid solution. Nitrogen shows all oxidation states from +5 to −3. Fewer oxidation states are important for others, bismuth showing the least number of oxidation states.

Nitrogen : *Acidic Solution (E° in volts)*

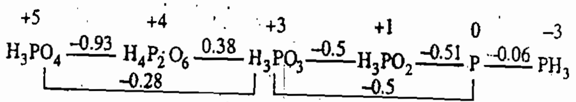


Basic Solution (*E°* in volts)



Phosphorus, arsenic, antimony and bismuth

Acidic solution (*E°* in volts)



$$H_3AsO_4 \xrightarrow{0.56} HAsO_2 \xrightarrow{0.24} As \xrightarrow{-0.23} AsH_3$$

$$Sb_2O_5 \xrightarrow{0.70} SbO^+ \xrightarrow{0.15} Sb \xrightarrow{-0.5} SbH_3$$

$$Bi_2O_5 \xrightarrow{1.6} BiO^+ \xrightarrow{0.32} Bi$$

Basic solution ($E°$ in volts)

$$\overset{+5}{PO_4^{3-}} \xrightarrow{-1.12} \underbrace{\overset{+3}{HPO_3^{2-}} \xrightarrow{-1.6} \overset{+1}{H_2PO_2^-} \xrightarrow{-2.1} \overset{0}{P}}_{-1.73} \xrightarrow{-0.9} \overset{-3}{PH_3}$$

$$AsO_4^{3-} \xrightarrow{-0.67} AsO_2^- \xrightarrow{-0.7} As \xrightarrow{-1.4} AsH_3$$

$$Sb(OH)_6^- \xrightarrow{-0.46} Sb(OH)_4^- \xrightarrow{-0.64} Sb \xrightarrow{-1.34} SbH_6$$

$$Bi_2O_3 \xrightarrow{-0.5} Bi$$

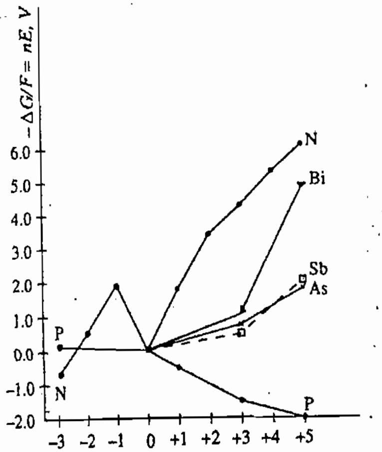


Fig. 22.4

Oxidation state-free energy diagram (Frost diagram) for the elements of Group 15(VA) in acidic solution.

Several features of the oxidation state free energy diagram are noteworthy. The plot for nitrogen is most individual, while the elements P—Bi form a family.

(a) The –III state is most stable for nitrogen; stability of this state decreases gradually to P and As.

(b) The –I state for nitrogen is markedly unstable. Also, the positive oxidation states of nitrogen between O and V are likely to disproportionate in acid solution.

(c) The +V state is most stable for phosphorus, suggesting that P(V), in the form of phosphates, should hardly possess any oxidizing power. The oxidizing nature of N(V) and Bi(V) is also apparent from the plot. As(V) and Sb(V) are expected to be mildly oxidizing. P(III) is reducing; As(III) also acts as a reducing agent.

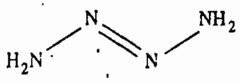
(d) Oxidation states intermediate between –III and +V for phosphorus should tend to disproportionate to PH_3 and P(V).

However, we are already aware of the limitations of thermodynamic correlations in view of kinetic factors. Many thermodynamically favoured reactions may have high reaction barriers resulting in a very slow rate. Redox reactions consuming dinitrogen molecule are slow presumably owing to the inertness of the N ≡ N molecule. Though strange at first sight, the formation of N_2 in solution also appears to be slow due to various reasons and is often sidestepped. Again, nitrites (NO_2^-) are much faster, though weaker oxidizing agent than nitrates (NO_3^-) in dilute solution. In general, oxidation by the oxoanions is favoured by high H^+ ion concentration: perhaps the N—O bond breaking is facilitated by protonation. It has not been possible to rationalize fully the intricate mechanisms by which nitrogen and its oxides take part in redox reactions.

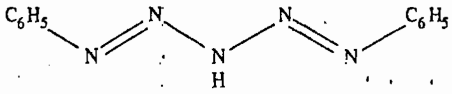
Catenation

Nitrogen differs from carbon in showing much diminished tendency to catenation. Repulsion between lone pairs of electrons and great stability of N≡N makes catenation unfavourable. A few compounds containing chains of N atoms are known (see below). Phosphorus and arsenic have greater tendency to catenation, presumably because of (i) lower repulsion between lone pairs (ii) diminished importance of *p-p* π-bonding and (iii) greater flexibility of bond angle around larger atoms. Accordingly, we have chains and puckered rings containing upto about 22 P or As atoms. Decrease in bond energy disfavours catenation among the heavier members.

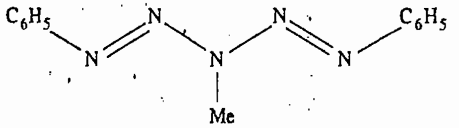
Examples of simple chain compounds of nitrogen are (i) hydrazine $H_2N–NH_2$ and its derivatives, $R_2N–NR_2$, when R = F or organic groups. (ii) Compounds containing multiple bonds like diazenes RN = NR, where R = H, F or organic groups (compounds with R = H are unstable unless coordinated). Hydrazoic acid and the azides contain a chain of three nitrogen atoms. Compounds containing longer chains are increasingly unstable. Organic substituents increase the stability of these polyaza derivatives :



22-VI
(decomposes below 0°C)



22-VII
(explodes near room temp.)



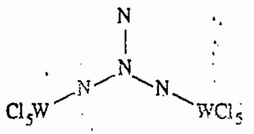
22-VIII
(decomposes at 122°C)

M–M links are known in P_2X_4, P_2H_4, As_2H_4 and $R_2M - MR_2$ compounds where R is an organic group; the compounds of bismuth are extremely unstable. $Me_2As - AsMe_2$ (Cacodyl) has been known since 1760.

A chain containing 8 nitrogen atoms is present in

PhN = N — N(Ph) — N = N = N — N (Ph) — N = NPh

A branched chain planar arrangement of four nitrogen atoms is reported in the tetrazene derivative



22-IX

Phosphorus, and to some extent arsenic, can also form longer chains, rings, nets and clusters. Some typical examples are

$$2\,Et_2PCl + 2Na \longrightarrow Et_2P-PEt_2 + 2NaCl$$

$$nRPCl_2 + nMg \longrightarrow (PR)_n + nMgCl_2 \ (n = 4, 5, 6; R = Me \text{ or } Ph)$$

$$F_3CAsCl_2 + Hg \longrightarrow (F_3CAs)_n \quad (n = 4, 5)$$

$$(CF_3)_2\,SbI + Hg \longrightarrow (CF_3)_2\,Sb-Sb\,(CF_3)_2$$

The compounds with $n = 4-6$ are nonplanar cyclic species.

The allotropic forms of phosphorus amply demonstrate the aptitude of phosphorus for catenation. A large group of polyphosphanes analogous to hydrocarbons are now established : $H_2P-(PH)_n-PH_2$, where $n = 3$ for straight chain compounds but may be as high as 9 for branched chains. Rngs are known in a series of compounds $(PH)_n$, where n may vary from 3 to 10 (see hydrides). The P_5^- ion, isoelectronic with $C_5H_5^-$ (cyclopentadienide), is planar with delocalized charge. This is formed in the following types of reactions :

$$P_4\,(w) + Na \xrightarrow{\text{diglyme}} [Na\,(\text{diglyme})_x]^+\,P_5^-$$

$$P_4\,(w) + LiPh_2 \xrightarrow{\text{THF}} [Li(THF)_x]^+\,P_5^-$$

The existence of a cyclic planar delocalized electron cloud in the ring is supported by the isolation of the novel triple-decker sandwich

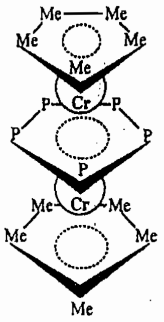
$$(C_5Me_5)\ Cr\ (P_5)\ Cr\ (C_5Me_5)\ (22\text{-}X)$$

in which the C_5Me_5 and P_5 rings are all parallel. A mixed ring P_4CH^- is also similarly planar with delocalized charge. A planar P_6 ring has also been characterized in the triple-decker sandwich

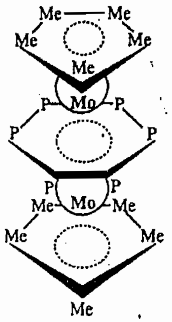
$$(C_5Me_5)\ Mo\ (P_6)\ Mo\ (C_5Me_5).\ (22\text{-}XI)$$

Another sandwich compound involving P_5 ring results from the reaction

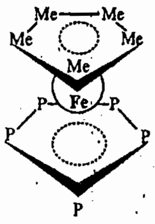
$$P_4 + [C_5Me_5Fe\,(CO)_2]_2 \xrightarrow{\text{heat}} (C_5Me_5)\ Fe\ (P_5)\ (22\text{-}XII)$$



22-X



22-XI



22-XII

22.3 PRINCIPAL COMPOUNDS

The discussion on compounds will follow the same general pattern as before — a general treatment followed by individual compounds. As already explained, the compounds of nitrogen often form a class of their own.

22.3.1 Hydrides

The binary compounds of nitrogen with hydrogen are traditionally classed as hydrides though the electronegativity of nitrogen is higher. Nitrogen forms NH_3, N_2H_4, N_3H and N_2H_2 (di-imide). The last two compounds have no analogues among other members of the group as they contain p-p π-bonds. Hydrides of general formula MH_3 are formed by all the elements, though their stability decreases sharply as the M—H bond energy falls with heavier elements (Table 22.4). While NH_3 begins to break into its elements appreciably around 2000° C, BiH_3 has a half-life of only a few minutes at room temperature. Besides P_2H_4, M_2H_4 type hydrides are known for As and Sb, though insignificant. M_3H_5 and some more catenated hydrides are known for P and As.

MH_5 type hydrides are not known for Group V elements. The non-existence of NH_5 is readily interpreted by the inability of nitrogen to valence expansion. For heavier members, e.g., P, one explanation put earlier concerned the inability of hydrogen to involve d-orbital participation by phosphorus. However, d-orbital participation by these elements is doubtful. The bonding in PCl_5 may be interpreted by considering the formation of two additional axial 3-center 4-electron P—Cl bonds by PCl_3. The extremely low electronegativity of hydrogen does not allow significant $3c$—$4e$ bond formation with phosphorus, dismissing PH_5. At the same time, high dissociation energy of H_2 stands against the formation of such compounds.

MH_3-type hydrides

Before discussing the individual compounds, a brief comparison of these compounds will be made. Some of their physical properties are given in Table 22.6. Data for BiH_3 are lacking due to extreme instability of the compound.

TABLE 22.6

Some physical properties of NH_3, PH_3, AsH_3 and BiH_3

	NH_3	PH_3	AsH_3	SbH_3	BiH_3
M.P. (°C)	−78	−133.5	−116.3	−88	—
B.P. (°C)	−34.5	−87.5	−62.4	−18.4	+ 16.8 (extrapolated)
ΔH_f^0 *(kJ mol⁻¹)*	−46	−9.6 (?)	66	145	278
Proton affinity (kJ mol⁻¹)	−866	−770	—	—	—
Dipole moment (debye)	1.46	0.58	—	—	—
Inversion barrier (kJ mol⁻¹)	24	155	—	—	—
M–H dist (pm)	102	142	152	171	—
<HMH	107.8°	93.6°	91.8°	91.3°	—
$E_{M-H\,(av)}$ *(kJ mol⁻¹)*	391	322	247	255	—

The effect of strong hydrogen bonding in NH_3 is reflected in its relatively high melting and boiling points. We also observe that only the formation of $NH_3\,(g)$ from its elements is significantly exothermic. (The value of PH_3 is somewhat uncertain.) Other hydrides are endothermic. The high negative value of proton affinity for NH_3 and PH_3 suggest the formation of NH_4^+ and PH_4^+ compounds, though the process involves other enthalpy terms, as discussed later.

The sharp fall in MHM bond angle from NH_3 to PH_3 is noteworthy. All the MH_3 molecules are pyramidal with a lone pair of electrons on the central atom. The bond angle of NH_3 can be rationalized by assuming sp^3 hybridization in the valence shell of nitrogen; lone-pair-bond-pair repulsion now slightly diminishes the bond angle. One classical explanation for the decreased bond angle in PH_3 involves larger separation between the H-atoms, thereby causing much less electrostatic repulsion between them. However, the dominating influence on molecular geometry arises from Pauli repulsion between bond pairs of electrons which is many times stronger than the electrostatic repulsion conceived above. The Pauli repulsion varies exponentially with distance and is much less in case of the longer bonds in PH_3 (and AsH_3 etc.). A rather simplified description of the bonding assumes that the central atom uses nearly pure *p*-orbitals in bonding.

All the hydrides are good reducing agents. Their thermal stability decreases steadily —NH_3 is stable to about 2000°C; AsH_3 and SbH_3 decompose to the elements at about 250-300°C; BiH_3 decomposes appreciably above –45°C. As expected, basic character decreases from NH_3 to PH_3 onward. NH_3 and PH_3 can act as good ligands —NH_3 is a hard donor while PH_3 is a soft one.

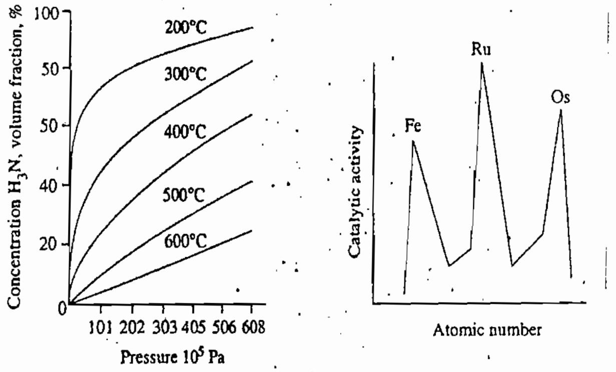


Fig. 22.5

(a) Equilibrium concentration of NH_3 in a mixture (N_2+ $3H_2$) as a function of pressure and temperature. (b) Dependence of the catalytic activity of selected metals in the conversion of N_2 to NH_3.

Ammonia is conveniently prepared by heating any ammonium salt (e.g., NH_4Cl) with a base like $Ca(OH)_2$. A steady supply of NH_3 (*g*) may be obtained by dropping its concentrated aqueous solution on solid NaOH. It is also available in cylinders. Hydrolysis of metal nitrides provides a route to $^{15}NH_3$ or ND_3 :

$$3Mg + {}^{15}N_2 = Mg_3\,{}^{15}N_2 \xrightarrow{H_2O} 2\,{}^{15}NH_3 + 3Mg(OH)_2$$

$$3Mg + N_2 = Mg_3N_2 \xrightarrow{D_2O} 2ND_3 + 3Mg(OD)_2$$

Alternatively, one can reduce NO_3^- or NO_2^- in alkaline medium using Al or Devarda's alloy (Cu 50%; Al 45%; Zn 5%).

Phosphine is readily obtained by heating white phosphorus with aqueous NaOH (or $Ba(OH)_2$). Some P_2H_4 is also formed :

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$

Other reactions have been given later.

Other hydrides may be obtained by reducing the trihalides (with $LiAlH_4$ or $NaBH_4$) or by acid hydrolysis of the alloys with electropositive metals (like Na, K, Ca, Zn).

$$SbCl_3 + NaBH_4 \longrightarrow SbH_3.$$

$$Zn_3Sb_2 + 6HCl \longrightarrow 2SbH_3 + 3ZnCl_2$$

[Sec. 22.3.1 *Hydrides*]

Traces of M_2H_4 (M = P, As, Sb) and M_3H_5 (M = P, As) are obtained as by-products. The yield of BiH_3 is extremely low. It was first detected in traces in radiochemical works (by Paneth) involving $^{212}Bi_2Mg_3$. BiH_3 is now obtained by disproportionation of $MeBiH_2$ at –45°C for several hours.

$$3MeBiH_2 \longrightarrow 2BiH_3 + BiMe_3$$

Over 100 million tonnes of ammonia are now manufactured each year all over the world mainly by direct synthesis (Haber's process)

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \quad \Delta H^\circ = -46 kJ\ mol^{-1};\ \Delta S^0_{298} = -103\ JK^{-1};\ K_{298} = 10^3\ atm^{-2}$$

The process is favoured at high pressure and low temperature (Fig. 22.5). Promoted iron catalyst at 350-550°C is usually used for higher yield and an appreciable rate of conversion. The iron catalyst is prepared by fusing magnetite (Fe_3O_4) with KOH in presence of small amounts of refractory oxides like MgO, Al_2O_3 and SiO_2 and reducing the crushed mass. Nitrogen for the process is obtained by fractionation of liquid air; hydrogen is now obtained by electrolysis of water or by catalytic reforming of natural gas (essentially methane).

$$CH_4 + H_2O \xrightarrow{Ni/750^\circ} CO + 3H_2$$

$$CH_4 + 2H_2O \xrightarrow{Ni/750^\circ} CO_2 + 4H_2$$

Properties

Ammonia is a colourless pungent-smelling gas highly soluble in water owing to extensive hydrogen bonding; the process evolves much heat (≃ 37kJ mol^{-1} of NH_3. Liquid ammonia has a high enthalpy of evaporation (≃ 23.3 kJ mol^{-1}) and can be handled in the laboratory. It is a useful refrigerant and a solvent (Chapter 12). Its dielectric constant (22 at –34°C) is considerably lower than that of water; hence it is a poorer solvent for ionic compounds but better one for organic compounds. Greater complexing ability of ammonia may influence solubility trends, as illustrated by the very high solubility of AgI in liquid ammonia (207 g/100 cm^3 at 25°C).

The low solubility of ionic compounds in liquid NH_3 may be used with advantage for the synthesis of a number of compounds in liquid ammonia

$$AgCl + KNO_3 \longrightarrow AgNO_3 + KCl\downarrow$$

(Silver ions are more strongly ammoniated).

$$[Cr(NH_3)_6]Cl_3 + 3KBH_4 \longrightarrow [Cr(NH_3)_6][BH_4]_3 + 3KCl\downarrow$$

$$[Mg(NH_3)_6]Cl_3 + 2KBH_4 \longrightarrow [Mg(NH_3)_6][BH_4]_2 + 2KCl\downarrow$$

- KBH_4 dissolves unchanged in liquid NH_3, but gets hydrolyzed in water. The KCl may be filtered out and the pure tetrahydroborates can be crystallized.

$$R_3GeH + K(am) \longrightarrow \tfrac{1}{2}H_2 + KGeR_3 \begin{cases} \xrightarrow{R_3GeCl} R_3Ge{-}GeR_3 + KCl\downarrow \\ \xrightarrow{R_3SnCl} R_3Ge{-}SnR_3 + KCl\downarrow \end{cases}$$

- Ge–Ge and Ge–Sn bonds established.

$$K_2[Ni^{II}(CN)_4] + 2K(am) \longrightarrow K_4[Ni^0(CN)_4]$$

$$Mn_2(CN)_{10} + 2Na(am) \longrightarrow 2Na[Mn^{-1}(CO)_5]$$

- Unusually low oxidation states of metals are produced.

Aqueous solutions of amonia are weakly basic :

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq);\ K_{298} = 1.8 \times 10^{-5}\ mol\ dm^{-3}$$

The undissociated "ammonium hydroxide" molecule "NH_4OH" is not known to exist in such solutions. Weakly bonded hydrates have been isolated at low temperatures containing three-dimensional H-bonded network of H_2O molecules cross-linked by NH_3 molecules; e.g., $NH_3.H_2O$ (m.p. 194.1 K); $2NH_3.H_2O$ (m.p. 194.3K).

Concentrated aqueous solutions of ammonia ("liquor ammonia") contains about 35% NH_3 by weight, sp. gravity 0.88. Common supplies are approximately 17*N*. Bottles of liquor ammonia develop high pressure, particularly in summer. They should be cooled under the tap/and covered with a towel before opening. **Liquor ammonia is extremely damaging to the eyes.**

Ammonia burns in air to N_2 : $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.

In presence of a Pt or Pt–Rh catalyst at 750° – 900°C, NO is produced. This can be oxidized further to NO_2 as an industrial route to HNO_3 (*Ostwald process*).

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

A mixture of CH_4 and NH_3 (and O_2) forms HCN and H_2 (or H_2O) over a platinum catalyst at 1200° – 1500°C (see HCN; Chapter 21).

NH_3 burns in F_2 to NF_3. Excess chlorine gives NCl_3, while excess ammonia produces N_2 and NH_4Cl. Reaction of Cl_2 with excess aqueous ammonia also produces N_2. Chloramine is formed as an intermediate at pH > 8. At pH 3–5, $NHCl_2$ is formed. At pH>3, NCl_3 is produced.

$$NH_3 + OCl^- \rightleftharpoons NH_2Cl + OH^- \quad pH > 8$$

$$2NH_2Cl + H^+ \rightleftharpoons NHCl_2 + NH_4^+ \quad pH\ 3 - 5$$

$$3NH_2Cl + H^+ \longrightarrow 3NCl_3 + NH_4^+ \quad pH < 3$$

Carbon at red heat reacts with ammonia to give NH_4CN (+H_2). Phosphorus similarly gives PH_3 (and N_2), while sulphur reacts to form N_2S and N_4S_4.

Metal oxides like PbO or CuO are readily reduced by ammonia at red heat. Sodium metal reacts to form sodamide $NaNH_2$. Ca, Mg, Zn etc. react with ammonia at 900 – 1000°C to form their nitrides.

Aqueous ammonia solution is used in selective precipitation of metal hydroxides in qualitative analysis. The effective concentration of OH^- ion in solution may be controlled by suppressing the dissociation of ammonia in presence of ammonium salts, usually NH_4Cl, when only the hydroxides of Fe(III), Cr(III), Al(III), lanthanides etc. are precipitated; Mg^{2+}, Zn^{2+} etc. are not precipitated under such conditions (see solubility product; Ch. 11).

Ammonia forms a number of stable complexes with many metals ions, e.g. Cu (II) and Ag(I) :

$2CuSO_4 + 2NH_4OH = CuSO_4.Cu(OH)_2 + (NH_4)_2SO_4$ (bluish white ppt. of basic copper sulphate.)

$CuSO_4.Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH = 2[Cu(NH_3)_4]SO_4 + 8H_2O$ (deep blue solutions.)

$2AgNO_3 + 2NH_4OH = Ag_2O + 2NH_4NO_3 + 2H_2O$ (initial white ppt, changing to brown.)

$Ag_2O + 4NH_3 + H_2O = 2[Ag(NH_3)_2]OH$ (colourless solution.)

The action of aqueous ammonia on $HgCl_2$ provides an example of **ammonolysis**—mercury displaces hydrogen forming direct covalent bonds to nitrogen :

$$Hg^{2+} + 2NH_3 \rightleftharpoons [Hg\text{–}NH_2]^+ + NH_4^+$$

Quite a number of products have been reported since long in the reaction of Hg(II) with aqueous NH_3 but their identity have been established only recently with definite structural information from physicochemical studies (Chapter 30).

Mercury (I) disproportionates when treated with ammonia into Hg and Hg(II). The Hg(II) reacts further with NH_3 to give "aminomercuric" compounds as above. Liberated Hg turns the products black.

$$Hg_2Cl_2 + 2NH_3 = 2HgNH_2Cl + Hg + NH_4Cl.$$

Phosphine

In addition to alkaline disproportionation of white phosphorus, several methods exist for the preparation of phosphine.

(i) $PH_4I + KOH(aq) = PH_3 + KI + H_2O$.

The method gives very pure phosphine, PH_4I is easily obtained by reacting white P with iodine.

(ii) $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$

(iii) $4H_3PO_3 = PH_3 + 3H_3PO_4$ (Also by $LiAlH_4$ in Et_2O).

Yield of PH_3 is high (≃ 97% at 205 – 210°C.

(iv) $PCl_3 + 3LiH = PH_3 + 3LiCl$.

Phosphine is a poisonous, colourless gas with a faint garlic smell. It is slightly soluble in water (26 ml per 100 ml at 290 K, 1 atm) but highly soluble in organic liquids like CS_2 and CCl_3COOH.

The proton affinity of PH_3 (*g*) is 770 kJ mol^{-1} (cf. 866 kJ mol^{-1} for NH_3 (*g*).)

Aqueous solutions of PH_3 react neutral as a result of extremely weak ionization :

$$PH_3(aq) + H_2O \rightleftharpoons PH_4^+(aq) + OH^-(aq) \qquad K_{298} \simeq 10^{-28}$$

$$PH_3(aq) + H_2O \rightleftharpoons PH_2^-(aq) + H_3C^+(aq) \qquad K_{298} \simeq 10^{-29}$$

Its feeble basic character is shown by its reaction with liquid HCl to give $PH_4^+Cl^-$ (sparingly soluble). Other phosphonium salts are also known (see below). In liquid ammonia, phosphine dissolves to form $NH_4^+PH_2^-$ and reacts with potassium to KPH_2. It also forms adducts with different Lewis acids e.g., $H_3B.PH_3$, $F_3B.PH_3$, H_3PAlCl_3 etc.

Phosphine is often contaminated with P_2H_4 which is spontaneously flammable in air. Pure phosphine ignites in air around 150°C.

$$PH_3 + 2O_2 = H_3PO_4$$

PH_3 forms H_2S and a mixture of phosphorus sulfides on heating with S. In presence of aqueous HCl, phosphine reacts with formaldehyde to form tetrakis(hydroxymethyl) phosphonium chloride (*hydrophosphorylation*); this is the major ingredient for permanent flame-proofing of cotton with urea-formaldehyde or melamine-formaldehyde resins.

$$PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]Cl.$$

Phosphine is also a strong reducing agent; solutions of metal ions like Ag(I) and Cu(II) are reduced to the phosphides or the metals :

$3CuSO_4 + 2PH_3 = Cu_3P_2 + 3H_2SO_4$ (black ppt)

$6AgNO_3 + PH_3 = Ag_3P.3AgNO_3 + 3HNO_3$ (yellow)

$Ag_3P.3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3PO_3$ (black).

Phosphine and substituted phosphines form complexes with many transition metals e.g., $Cr(CO)_3(PH_3)_3$. It is likely that $P \rightarrow M$ σ bonding is reinforced by $M \rightarrow P$ π-bonding using a vacant *d*-orbital on P. However, the extent to which σ-bonding and π-bonding reinforce each other is not fully established.

AsH_3, SbH_3 and BiH_3

These hydrides are also colourless poisonous gases. Their increasing thermal instability is shown in the *Marsh's test* : a mixture of AsH_3 and SbH_3 is passed through a tube which is heated at a particular point. SbH_3 begins to decompose on approaching the hot region and deposits a black mirror of metallic Sb on the tube; AsH_3 requires a higher temperature and hence deposits black As beyond the hot region.

The gases are insoluble in water and exhibit no basic properties. They are strong reducing agents :

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

With concentrated $AgNO_3$ solution, yellow soluble $Ag_3As; 3AgNO_3$ is formed initially.

SbH_3 similarly gives a precipitate of black silver antimonide. With excess of $AgNO_3$, this decomposes into silver and Sb_2O_3.

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$$

$$2Ag_3Sb + 6AgNO_3 + 3H_2O = 12Ag + Sb_2O_3 + 6HNO_3.$$

BiH_3 is extremely unstable.

Ammonium salts

Ammonia readily combines with protonic acids forming stable ammonium salts. Nearly all ammonium salts are colourless and soluble in water, with a few exceptions like the "cobaltinitrite", hexanitritocobaltate(III), $(NH_4)_3[Co(NO_2)_6]$ (yellow); the hexachloroplatinate (IV), $(NH_4)_2[PtCl_6]$ (yellow) and the acid tartrate, $NH_4.H.C_4H_4O_6$ (white).

Solutions of ammonium salts of strong acids are slightly acidic due to hydrolysis (Ch. 11) :

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_h = K_w/K_b \approx 5.5 \times 10^{-10} \text{ (298 K)}$$

Thus an 1*M* solution will have a pH around 4.7

Ammonium salts are strong acids in liquid NH_3 :

$$Mg + 2NH_4^+ = Mg^{2+}(am) + 2NH_3 + H_2$$

In crystals, the NH_4^+ ion has a radius of about 1.5 A° (6 coordinated), equal to that of Rb^+. The structures of ammonium salts are thus often similar to those of K, Rb and Cs. Structures may be different when strong hydrogen bonding is involved, e.g., NH_4F has the wurtzite structure.

Ammonium salts of volatile acids sublime with dissociation; those containing oxidizing anions decompose on strong heating, with oxidation to N_2O or N_2.

$NH_4Cl\,(s) = NH_3\,(g) + HCl\,(g) \qquad \Delta H = 177 \text{ kJ mol}^{-1}$.

$NH_4NO_3\,(s) = NH_3\,(g) + HNO_3\,(g) \qquad \Delta H = 171 \text{ kJ mol}^{-1}$.

$NH_4NO_3\,(s) = N_2O\,(g) + 2H_2O\,(g) \qquad (\sim 200°C)$.

$2NH_4NO_3\,(s) = 2N_2\,(g) + O_2\,(g) + 4H_2O\,(g) \qquad (> 250°C)$.

$(NH_4)_2Cr_2O_7\,(s) = N_2\,(g) + Cr_2O_3\,(s) + 4H_2O\,(g)$

Ammonium fluoride, on fusion, forms ammonium bifluoride :

$$2NH_4F = NH_3 + NH_4HF_2.$$

Ammonium Chloride (*Sal-ammoniac*), NH_4Cl, may be prepared by neutralising ammonia with HCl. It is usually made by subliming a mixture of ammonium sulphate and sodium chloride, or obtained as a by-product in the Solvay process of manufacturing sodium carbonate. It is a white crystalline solid which readily sublimes. It is highly soluble in water with considerable lowering of temperature. It is used as a reagent in the laboratory, in drycells of the Leclanche type and as a flux in tinning or soldering metals. The oxide films on the metal surface are dissolved out, leaving a clean metal surface for firm bite. Ammonium chloride is also used in medicine, dyeing and calico-printing.

The salt was known to the ancient Hindu Chemists as *Nishadal*. The Arabs prepared it by heating Camel's dung.

Ammonium Sulphate $(NH_4)_2SO_4$, is prepared by passing NH_3 (*g*) with CO_2 into a suspension of gypsum in water :

$$CaSO_4 + 2NH_3 + H_2O + CO_2 = CaCO_3 + (NH_4)_2SO_4$$

It is also obtained as a byproduct in the manufacture of coal gas.

It forms transparent crystals highly soluble in water. It is converted to ammonium bisulphate on heating : $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$.

It is used as a fertilizer and in preparing other ammonium salts.

Ammonium nitrate NH_4NO_3, is prepared from ammonium sulphate by double decomposition in aqueous solution :

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3$$

Being more soluble, NH_4NO_3 crystallizes later. The white crystalline deliquescent solid decomposes explosively on strong heating (see before) due to the rapid formation of 7 moles of gaseous product per mole of solid. It is used as an explosive (e.g., **ammonal** and **amatol** contain NH_4NO_3 with Al and T.N.T. respectively) and as a fertilizer.

Calcium ammonium nitrate (*CAN*, nitrochalk) is a superior fertilizer to ammonium nitrate as it is non-explosive and easy to handle. It is also more soluble in water than $(NH_4)_2SO_4$ and prevents development of acidity in the soil. It is prepared by mixing ammonium nitrate with chalk ($CaCO_3$) and the slurry is made into small pellets covered with soapstone to arrest moisture.

Ammonium nitrite, NH_4NO_2, may be prepared by evaporating a solution of NH_4Cl and $NaNO_2$ in vacuum. NH_4NO_2 sublimes as a colourless crystalline solid which is highly deliquescent and explosive (decomposing to $N_2 + 2H_2O$).

Ammonium carbonate (Sal volatile), $(NH_4)_2CO_3$ is prepared by heating NH_4Cl (or sulphate) with powdered chalk. The sublimate contains a mixture of $(NH_4)_2CO_3$ with the bicarbonate NH_4HCO_3 and ammonium carbamate NH_2COONH_4. These are converted to $(NH_4)_2CO_3$ by digesting with concentrated aqueous ammonia for several hours at about 12°C. The white crystalline solid sublimes readily in air and is used in "*smelling salt*".

"Ammonium sulfide" : Ammonium bisulphide NH_4HS is formed in solution by passing H_2S in dilute aqueous ammonia. The colourless solution liberates sulphur on exposure to air; the sulphur dissolves in excess bisulphide to form yellow ammonium sulphide solution, $(NH_4)_2S_x$. It is also obtained by passing H_2S into aqueous ammonia in presence of suspended sulphur powder. It dissolves sulphides of As, Sb and Sn forming thiosalts :

$$As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + (3x-5)S$$

Note : Ammonium ion cannot coexist in aqueous solution with anions of very weak acids, e.g., the sulphide ion. A solution with a high enough pH to allow appreciable concentration of S^{-2} ion has a high concentration of OH^- ion; this does not allow appreciable concentration of NH_4^+ ions.

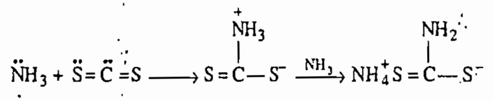
Ammonium carbamate, $NH_2COO^- NH_4^+$ is a white solid formed by reacting dry NH_3 with dry CO_2. It is converted to urea on heating to 130-150° C under about 35 atm pressure.

$$2NH_3 + CO_2 \longrightarrow NH_2COONH_4 \longrightarrow CO(NH_2)_2 + H_2O.$$

The compound is highly soluble in water; the aqueous solution hydrolyses to ammonium carbonate :

$$NH_2COONH_4 + H_2O \longrightarrow (NH_4)_2CO_3.$$

Ammonium dithiocarbamate results from the addition of ammonia to carbon disulphide :



$$\ddot{N}H_3 + \ddot{S}=\ddot{C}=S \longrightarrow S=\underset{}{\overset{\overset{+}{N}H_3}{C}}-S^- \xrightarrow{NH_3} NH_4^+S=\overset{NH_2}{C}-S^-$$

It forms ammonium thiocyanate, NH_4SCN on heating.

Ammonium salts have wide industrial and laboratory uses. Ammonium perchlorate is an important oxidizer in solid propellants for rocket fuels.

Phosphonium and arsonium salts

Only phosphorus and arsenic in Group VB form MH_4^+ ions similar to NH_4^+, though much less readily than nitrogen. The formation of an "onium" halide $MH_4^+X^-(s)$ by a reaction of the type

$$MH_3(g) + HX(g) \longrightarrow MH_4^+X^-$$

involves several energy terms like (i) strength of M—H bond (ii) strength of H—X bond (iii) lattice energy of MH_4X and so on. Very weak Sb—H bond seems to be primarily responsible for the nonexistence of SbH_4^+ or BiH_4^+ salts. For As, the energy balance favours $AsH_4^+Br^-$ and $AsH_4^+I^-$ but the fluoride and chloride are not formed, presumably because of the high H—F or H—Cl bond energy.

Q. 22.4 *PH_4I is thermally most stable among the phosphonium halides. Comment.*

Ans. : We may consider the formation of MH_4X salts in terms of proton affinities of $MH_3(g)$ (see B—H cycle for NH_3, chapter 6). Among the various PH_4 compounds (X = halogen), the thermodynamic tendency of $PH_3(g)$ to react with HX (g) would be favoured by (construct B—H cycle) :

(i) low H—X bond energy
(ii) high electron affinity of X
(iii) high lattice energy of $PH_4X(s)$

The H—X bond is weakest for X = I. Electron affinity of Cl is highest among the halogens. Highest lattice energy is expected for X = F. But with a large cation like PH_4^+ ($\approx Cs^+$, the gain in lattice energy along the series $PH_4I < PH_4Br < PH_4F$ is rather slow, while the increase in bond energy from HI to HF is much higher. Electron affinity does not influence the energy factor significantly. The total energy balance thus favours th formation of PH_4I. PH_4I is obtained as colourless crystals on mixing gaseous PH_3 and HI. PH_4Cl, obtained at low temperatures, is unstable above -30°C. PH_4Br decomposes at 0°C (see Problem 10.2 inside Chapter 10).

The proton affinity of $PH_3(g)$ is greater than that of $H_2O(g)$. Yet phosphonium halides are decomposed by water owing to the higher hydration enthalpy of H_3O^+ (again a consequence of the larger size of PH_4^+).

$$PH_4I(s) + H_2O \longrightarrow H_3O^+ + I^- + PH_3(g)$$

The MH_4^+ ions are tetrahedral. In PH_4^+ ion, the P—H distance is 1.414A°, as against 1.44A° in PH_3.

Tetra-substituted onium salts with alkyl or aryl groups are well known for all the elements :

$$MR_3 + RI \longrightarrow MR_4^+I^- \ (M = N, P, As, Sb)$$

For bismuth, only $BiPh_4^+$ ion is known.

Salts containing partially substituted NH_4^+ cations are formed directly from primary, secondary or tertiary amines

$$RNH_2 + HCl \longrightarrow RNH_3^+Cl^-$$
$$R_2NH + HCl \longrightarrow R_2NH_2^+Cl^-$$
$$R_3N + HCl \longrightarrow R_3NH^+ Cl^-$$

The tetraalkyl and aryl onium ions are often useful in chemistry when large univalent cations are required.

Onium salts containing halogen, alkoxy etc. groups are also well known :

$$NF_3 + SbF_3 + 2F_2 \xrightarrow{200°C/100\ atm} NF_4^+SbF_6^-$$
$$AsF_3 + AsCl_3 + Cl_2 \longrightarrow AsCl_4^+AsF_6^-$$
$$PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]^+ Cl^-$$

Hydrazine

Hydrazine is prepared by controlled oxidation of ammonia (in excess) by alkaline solution of sodium hypochlorite; the overall reaction is

$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

The reaction first leads to rapid formation of chloramine, NH_2Cl.

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

The chloramine then produces hydrazine by either of the following paths :

(a) Slow nucleophilic attack of NH_3 followed by rapid neutralization :

$$H_3N + NH_2Cl \longrightarrow [H_3N\text{-}NH_2]^+ + Cl^- \quad (slow)$$
$$N_2H_5^+ + OH^- \longrightarrow H_2N\text{-}NH_2 + H_2O \quad (fast)$$

(b) Rapid formation of a chloramide ion, $NHCl^-$, followed by slow nucleophilic attack of NH_3 :

$$NH_2Cl + OH^- \longrightarrow NHCl^- + H_2O \quad (fast)$$
$$NHCl^- + NH_3 \longrightarrow N_2H_4 + Cl^- \quad (slow)$$

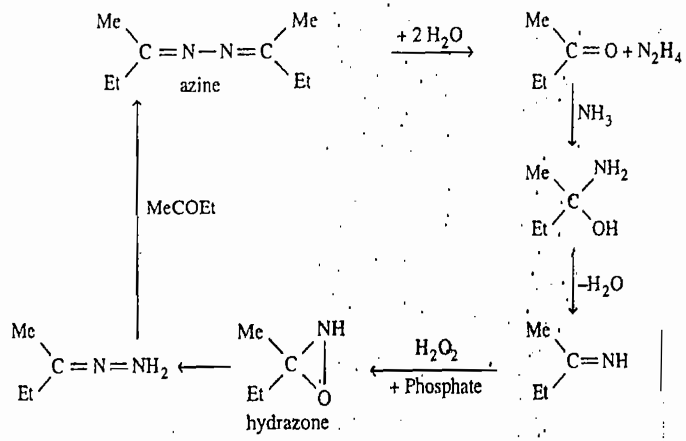
A side reaction tends to destroy hydrazine :

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl \quad (fast)$$

The reaction is catalyzed by traces of heavy metal ions (e.g., Cu^{++}). Addition of gelatin or glue suppresses this reaction by complexing the metal ions and increases the yield of hydrazine.

In the laboratory, freshly prepared sodium hypochlorite solution is added to 20% ammonia solution containing about 1% gelatine. The solution is boiled for about half an hour, cooled and acidified with dilute H_2SO_4. Hydrazinium sulphate crystallizes out on adding alcohol. This may be distilled with concentrated KOH solution in an all glass apparatus under reduced pressure; hydrazine hydrate (N_2H_4, H_2O; b.p. 119°) distills out. This may be distilled with solid NaOH to obtain anhydrous hydrazine.

Industrially, hydrazine is prepared by the same reaction but at a higher temperature (≃ 150°C and pressure in a very short time (≃ 1 second. Urea may also be used instead of ammonia. The use of NaOCl may be avoided by using a regenerative cycle involving butan-2-one and an azine :



The azine precipitates from aqueous solution. This is filtered and hydrolyzed separately.

Methyl hydrazine and dimethyl hydrazine may be prepared by reacting chloramine, NH_2Cl, with methylamine or dimethylamine.

Properties

Anyhydrous hydrazine is a colourless fuming liquid with a faint ammoniacal odour. It is an endothermic compound. Many of its physical properties are comparable to those of water (and partly to NH_3, H_2O_2) :

M.P.	B.P.	Density (*l*)*	Dielec. constant*	ΔH_f^0	ΔG_f^0
2°C	113.5°C	1 g cm^{-3}	51.7	50.6 kJ mol^{-1}	149 kJ mol^{-1}

* at 25°C.

In spite of its endothermic nature, pure hydrazine and its aqueous solutions are kinetically stable. It burns in air producing much heat :

$$N_2H_4\,(l) + O_2\,(g) = N_2\,(g) + 2H_2O\,(l) \quad \Delta H^\circ = -622 \text{ kJ mol}^{-1}$$

[Sec. 22.3.1 *Hydrazine*]

This is the basis for extensive use of hydrazine (and its alkyl derivatives) as rocket fuel.

N_2H_4 may be considered to have been formed by replacing an H-atom of NH_3 by an $-NH_2$ group. Accordingly, it is expected to be a weaker base than NH_3. It is in fact a weak bifunctional base :

$$N_2H_4\,(aq) + H_2O = N_2H_5^+\,(aq) + OH^- \qquad K\,(25°C) = 8.5 \times 10^{-7}$$

$$N_2H_5^+\,(aq) + H_2O = N_2H_6^{2+} + OH^- \qquad K\,(25°C) = 8.9 \times 10^{-16}$$

Hydrazinium salts of $N_2H_5^+$ are stable in water, but those of $N_2H_6^{2+}$ are extensively hydrolyzed (note the *K*-value). Such salts are less soluble than those of $N_2H_5^+$ and may be crystallized from solutions containing large excess of the acid. Sulphuric acid forms three salts – $[N_2H_5]_2SO_4$; $[N_2H_6]\,SO_4$; and $[N_2H_6]\,[HSO_4]_2$.

Reducing property

Hydrazine is a strong reducing agent, particularly in basic solution. It is usually oxidized to N_2 but NH_3 and N_3H are also obtained under various conditions. A high negative reduction potential suggests that N_2H_4 should be a stronger reducing agent in basic solution than in acid medium.

Acid solution : $N_2 + 5H^+ + 4e = N_2H_5^+$ $\quad E^\circ = -0.23V$

Basic solution : $N_2 + 4H_2O + 4e = N_2H_4 + 4OH^-$ $\quad E^\circ = -1.16V$

N_2H_4 precipitates gold, silver and platinum from their salt solutions. An alkaline solution of Cu(II) (Fehling's solution, e.g.) is reduced to Cu_2O in cold, and to metallic copper when hot :

$$4AuCl_3 + 3N_2H_4 = 4Au + 3N_2 + 12HCl$$

$$4CuO + N_2H_4 = 2Cu_2O + N_2 + 2H_2O$$

Estimation

The 4-electron oxidation is quantitative with some oxidants and offers a method for the estimation of hydrazine in dilute aqueous solution. In the reaction

$$N_2H_4 + KIO_3 + 2HCl \longrightarrow N_2 + KCl + ICl + 3H_2O$$

the IO_3^- is first reduced to I_2 which imparts a violet colour to little CCl_4 added to the mixture. The end point is detected by the complete discharge of iodine colour from the CCl_4 layer (thorough shaking is necessary) when I_2 is oxidized to ICl (see Problem 22.7).

Use of N_2H_4 enriched in ^{15}N shows that in the acid medium oxidation of N_2H_4 to N_2, both the N-atoms of N_2 originate in the same molecule of N_2H_4.

Besides this 4-electron change, N_2H_4 may also undergo 1-electron oxidation (e.g., with Fe(III), Ce(IV) or MnO_4^-) and 2-electron oxidation (e.g., with H_2O_2 or HNO_2) :

1-electron : $NH_4^+ + \frac{1}{2}N_2 + H^+ + e = N_2H_5^+$ $\quad E^\circ(\text{acid}) = -1.74$ V

$NH_3 + \frac{1}{2}N_2 + H_2O + e = N_2H_4 + OH^-$ $\quad E^\circ\,(\text{base}) = -2.42$ V

2-electron : $\frac{1}{2}NH_4^+ + \frac{1}{2}N_3H + \frac{5}{2}H^+ + 2e = N_2H_5^+$ $\quad E^\circ(\text{acid}) = -0.23$ V

$\frac{1}{2}NH_3 + \frac{1}{2}N_3^- + \frac{5}{2}H_2O + 2e = N_2H_4 + \frac{5}{2}OH^-$ $\quad E^\circ(\text{base}) = -0.92$ V

Hydrazine may also act as an oxidizing agent in acid medium

$$N_2H_5^+ + 3H^+ + 2e \rightleftharpoons 2NH_4^+.$$

But the reaction is slow. $TiCl_3$ is oxidized to $TiCl_4$. Zinc and hydrochloric acid also reduces hydrazine to ammonia.

$$N_2H_4 + Zn + 4HCl = 2NH_4Cl + ZnCl_2.$$

In acid solution, hydrazine is not oxidized by air, as revealed by the potential $E°$ $(N_2 - N_2H_5^+) = -0.23$ V. In basic solution, N_2H_4 is oxidized by air and O_2, specially when catalyzed by multivalent metal ions :

$$N_2H_4\,(aq) + 2O_2 = N_2 + 2H_2O_2\,(aq)$$

$$N_2H_4 + 2H_2O_2 = N_2 + 4H_2O \quad \textit{(in presence of } M^{n+} \textit{ ions)}$$

The reaction forms the basis of *deaeration* of water used in high pressure boilers— the dissolved oxygen is converted to N_2 and H_2O, reducing corrosion.

Structure and Bonding

Both the nitrogen atoms in N_2H_4 may be supposed to be sp^3 hybridized, each having a lone-pair of electrons in one of the hybrid orbitals. One hybrid orbital from each N forms the N—N bond; the remaining orbitals are engaged in N—H bonding. The N—N bond distance is 1.47 A° and the bond energy is estimated at 160 kJ mol^{-1} assuming the N—H bond energy to be the same as in NH_3.

IR and electron diffraction indicates that in the gaseous state, N_2H_4 is almost exclusively present in the **gauche** conformation, the two "halves" of the molecule being rotated by ~95° along the N—N bond. The HNH bond angles are 108°.

Note : P_2H_4 has the same gauche conformation in the gas phase but solid P_2H_4 has the staggered conformation. N_2F_4 exists in both forms.

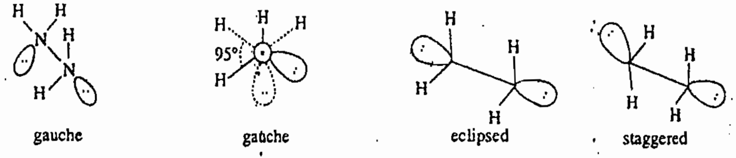


Fig. 22.6

Various conformations of N_2H_4.

Use

(a) Hydrazine is largely used as a rocket fuel. The methyl derivatives $MeNHNH_2$ and Me_2NNH_2 are also used in combination with it. Liquid O_2, N_2O_4 or H_2O_2 may be used as the oxidant.

(b) Hydrazine finds extensive use as a versatile reducing agent e.g., to prepare silver and copper mirrors and in the precipitation of platinum metals from solutions. Its application in deaeration of boiler water is also based on its reducing action on dissolved O_2 in air—the products $(N_2 + H_2O)$ are harmless and do not increase the amount of dissolved solid. Na_2SO_3, used previously, increased the concentration of Na_2SO_4. N_2H_4 has an extra advantage : it reduces the surface Fe_2O_3 to hard coherent Fe_3O_4, and thus inhibits corrosion.

1 mole N_2H_4 (32 g) consumes 1 mole dissolved O_2 (32 g). With an usual concentration of O_2 in the boiler feed-water at ~ 0.01 ppm. the theoretical requirement of N_2H_4 is 1 kg per 100,000 tonnes of feed-water (Na_2SO_3 required = 8 kg).

(c) Hydrazine and its derivatives are finding wide applications in the synthesis of several organic derivatives, medicines, herbicide, insecticide etc. Isonicotinic hydrazine, $C_5H_4NCONHNH_2$, is an antitubercular drug.

(d) Hydrazine is also a widely used blowing agent in foam rubber industry.

Similarity between hydrazine and H_2O_2

Hydrazine bears the same relation to NH_3 as does hydrogen peroxide to H_2O.

(i) Their structures are comparable (see structure of H_2O_2 also).

(ii) Both are associated in the liquid and solid states through hydrogen bonding.

(iii) The O-atoms in H_2O_2 and the N-atoms in N_2H_4 are tetrahedrally hybridized.

(iv) The two compounds decompose in the same manner :

$$3N_2H_4 = N_2 + 4NH_3;\ 2H_2O_2 = 2H_2O + O_2$$

(v) Both N_2H_4 and H_2O_2 may act as oxidizing and reducing agents, e.g. in acid medium :

$$N_2H_5^+ + 3H^+ + 2e = 2NH_4^+ \qquad \textit{oxidizing}$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O \qquad \text{''}$$

$$N_2H_5^+ = N_2 + 5H^+ + 4e \qquad \textit{reducing}$$

$$H_2O_2 = O_2 + 2H^+ + 2e \qquad \text{''}$$

Examples of reactions are given in the text.

Diphosphine, P_2H_4 (As_2H_4, Sb_2H_4)

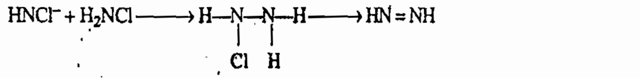
Diphosphine is formed in minor quantities in many reactions used to prepare phosphine e.g., white P with aqueous NaOH or water on calcium phosphide. P_2H_4 may be condensed in a cold trap. It is also made by passing PH_3 through an electric discharge (5-10 kV). It is a colourless volatile liquid (b.p. 51° C ?), thermally unstable above room temperature and spontaneously inflammable in air. Water decomposes it slowly. On storage, P_2H_4 decomposes to form polymeric amorphous yellow solids with varying compositions around P_2H. It has no basic properties. As already mentioned, it exists mainly in the gauche form.

As_2H_4 $(H_2AsO_3^- + BH_4^-)$ and Sb_2H_4 $(SbCl_3 + BH_4^-)$ are even more unstable.

Unstable hydrides of nitrogen

Diazene, N_2H_2, is unstable above – 180°C and is formed (together with NH_3) by microwave discharge on gaseous N_2H_4. Oxidation of hydrazine in solution by two-electron oxidants like O_2, peroxides etc. also produces N_2H_2 as a transient intermediate. It may also be formed by the action of alkali on chloramine :

$$OH^- + H_2NCl \longrightarrow HNCl^- + H_2O$$



$$HNCl^- + H_2NCl \longrightarrow \underset{}{H-\underset{Cl}{\underset{|}{N}}-\underset{H}{\underset{|}{N}}-H} \longrightarrow HN=NH$$

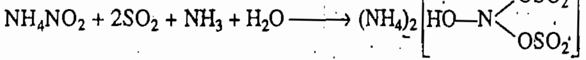
The compound is diamagnetic and decomposes mainly to N_2, H_2 and N_2H_4. Both cis and trans forms are known.

Interaction of NH_3 on a silver zeolite produces Ag (1) - complexes of triazene, N_3H_5 and cyclotriazene, N_3H_3. Some other unstable hydrides like N_4H_2 and N_4H_4 are also known.

Hydroxylamine, NH_2OH

Hydroxylamine is closely related in structure and properties to both ammonia and hydrazine. It may be prepared by reduction of nitrites, nitric acid or NO. Acid hydrolysis of nitroalkanes also produces hydroxylamine.

(a) **Raschig synthesis :** Sodium or ammonium nitrite solution is reduced with SO_2 at low temperature (0°C). At first hydroxylamido-*N*, *N*-disulphate is formed which undergoes hydrolysis to hydroxylammonium sulfate.



$$NH_4NO_2 + 2SO_2 + NH_3 + H_2O \longrightarrow (NH_4)_2\left[HO{-}N\begin{matrix}OSO_2^-\\OSO_2^-\end{matrix}\right]$$

$$(NH_4)_2[(HO)N(OSO_2)_2] + H_2O \longrightarrow (NH_4)[(HO){-}NH(OSO_2)] + NH_4HSO_4$$

$$2(NH_4)[(HO)NH(OSO_2)] + 2H_2O \longrightarrow (NH_3OH)_2SO_4 + (NH_4)_2SO_4$$

The hydroxylammonium sulfate may be converted to NH_2OH by ion-exchange or ammonolysis with liquid ammonia. The less soluble salts Na_2SO_4 or $(NH_4)_2SO_4$ crystallize first. Excess ammonia may be removed under reduced pressure.

(b) Anhydrous hydroxylamine may be prepared by reacting hydroxylamine hydrochloride with sodium methoxide (both in methanol).

$$[NH_3OH]^+Cl + CH_3ONa = NH_2OH + CH_3OH + NaCl.$$

The insoluble NaCl is filtered off. Methyl alcohol is separated by distillation under reduced pressure (40 mm).

Alternatively, a suspension of hydroxylammonium chloride in butanol may be treated with NaOBu :

$$[NH_3(OH)]Cl + NaOBu \longrightarrow NH_2OH + NaCl + BuOH$$

NaCl may be removed by filtration : NH_2OH is precipitated on adding diethyl ether and cooling.

(c) Electrolytic reduction of cold (≈ 0-5°C) nitric acid (≈ 50%) with amalgamated lead electrodes (high H_2 overvoltage) in 50% H_2SO_4/HCl medium produces hydroxylamine in the cathode compartment.

$$HNO_3 + 6H^+ + 6e = NH_2OH + 2H_2O \longrightarrow [NH_3(OH)]_2SO_4 \text{ or } [NH_3OH]Cl.$$

The hydroxylammonium sulphate may be converted to the chloride by adding $BaCl_2$ (Na_2SO_4 is precipitated).

(d) Hydrogenation of NO gives NH_2OH in acid solution (Pt/charcoal catalyst).

$$2NO + 3H_2 + H_2SO_4 = [NH_3(OH)]_2SO_4.$$

(e) Commercially, hydroxylamine may be prepared by hydrolysis of nitroethane (obtained by gas phase nitration of ethane present in natural gas).

$$C_2H_4 + N_2O_4 = O_2NCH_2CH_2NO_2$$

$$O_2NCH_2CH_2NO_2 + H_2SO_4 = CO + CO_2 + [NH_3(OH)]_2SO_4$$

Properties

(i) Pure hydroxylamine forms colourless, odourless deliquescent crystals melting at 33°C (b.p. 58° C at 22 mm Hg). It explodes on heating — even at room temperature the solid or its concentrated solution disproportionates appreciably

$$3NH_2OH = N_2 + NH_3 + 3H_2O; \quad 4NH_2OH = N_2O + 2NH_3 + 3H_2O.$$

NH_2OH has a high dielectric constant (~ 78) and is readily soluble in water or alcohol, but only slightly in ether or benzene.

(ii) Replacement of one H in NH_3 by OH or of one H in H_2O by NH_2 results in NH_2OH. Its aqueous solution is less basic than NH_3 or N_2H_4 :

$$NH_2OH\,(aq) + H_2O = NH_3OH^+ + OH^- \quad K\,(298) = 6.6 \times 10^{-9}$$

Salts of the cation are known, e.g., $[NH_3OH]Cl$, m.p. 151° C; $[NH_3OH]NO_3$ m.p. 48°C, $[NH_3OH]_2SO_4$ m.p. 170°C. These are hydrolyzed in aqueous solution.

In absence of water, NH_2OH may also act as a very weak acid.

The salts $Ca(OH)(ONH_2)$ and $Ca(NH_2O)_2$ are known. They explode on heating.

(iii) The oxidation state of nitrogen in NH_2OH is intermediate and it may act both as an oxidizing or reducing agent.

It reduces Fe(III) to Fe(II) in acid solution (in presence of alkali Fe(II) is oxidized). In alkaline medium Fehling's solution, ammoniacal silver nitrate, iodine and mercury(II) chloride are reduced.

$$2NH_2OH = N_2O + H_2O + 4H^+ + 4e.$$

$$2NH_2OH + 4OH^- = N_2O + 5H_2O + 4e.$$

$$2NH_2OH + 4CuO = N_2O + 2Cu_2O + 3H_2O.$$

$$2NH_2OH + 4Fe^{3+} = N_2O + 4Fe^{2+} + H_2O + 4H^+.$$

Reducing property

The formation of N_2O in most oxidations by NH_2OH demonstrates the importance of kinetic over thermodynamic factors. Thermodynamically (Latimer diagram), N_2 seems to be the product of oxidation of NH_2OH by weak oxidizing agents. It appears that deprotonation of NH_2OH first gives NOH radicals which form hyponitrous acid HON = NOH; this decomposes into N_2O and H_2O.

$$NH_2OH \longrightarrow NOH + 2H^+ + 2e; \quad NOH + NOH \longrightarrow H_2N_2O_2 \longrightarrow H_2O + N_2O.$$

More powerful oxidizing agents like BrO_3^- oxidize NH_2OH to HNO_3.

Hydroxylamine acts as an oxidizing agent and gets reduced to ammonia.

$$NH_2OH + 2H^+ + 2e \longrightarrow NH_3 + H_2O$$

$$NH_2OH + H_2O + 2e \longrightarrow NH_3 + 2OH^-$$

In strongly acid medium, it oxidizes stannous chloride to stannic chloride, SO_2 to ammonium sulphate and hydrogen iodide to iodine.

$$NH_2OH + SnCl_2 + 2HCl = SnCl_4 + NH_3 + H_2O$$

Oxidizing property

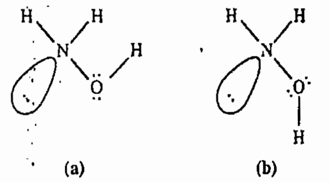
In alkaline medium, hydroxylamine oxidizes ferrous hydroxide, sodium arsenite and hydrogen peroxide :

$$2Fe(OH)_2 + NH_2OH + H_2O = 2Fe(OH)_3 + NH_3$$

$$Na_3AsO_3 + NH_2OH = Na_3AsO_4 + NH_3.$$

Structure and Bonding

The bonding in hydroxylamine corresponds to *sp*³ hybridized N-atom with one orbital occupied by a lone pair of electrons. The N—O distance is 1.47 A°, consistent with a single bond. Two configurational isomers -cis and trans, are possible, with several intermediate gauche conformations :



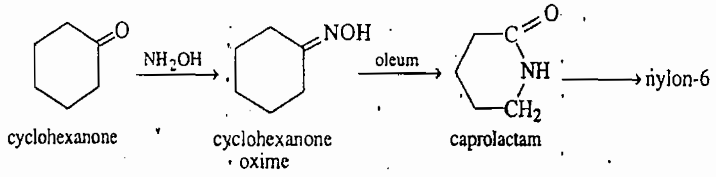
22-XIII

Use

Hydroxylamine is generally used as a reducing agent, e.g., (i) antioxidant in photographic developers (ii) reduction of Cu(II) in the dyeing of acrylic fibres.

Hydroxylamine sulphate absorbed on silica gel is used as an absorbent in combustion analysis for gases like N_2O, NO and N_2O_4.

Its ability to form oximes with carbonyl group is used in the manufacture of *caprolactam*—an important intermediate in the production of polyamide fibres (e.g., nylon).



Hydrogen azide (hydrazoic acid, HN_3)

Though a hydride of nitrogen in the formal sense, HN_3 is quite different from NH_3 and N_2H_4. It was first prepared by the oxidation of aqueous hydrazine with nitrous acid (Curtius, 1890) :

$$N_2H_5^+ + HNO_2 \longrightarrow HN_3 + H^+ + 2H_2O$$

Other oxidizing agents like H_2O_2, HNO_3, $S_2O_8^{2-}$, ClO_3^- also produce HN_3.

Pure HN_3 is best obtained by

(i) carefully distilling sodium azide with dilute sulphuric acid to obtain a solution of HN_3 (*explosive*; b.p. = 37°C).

(ii) fractionating the solution and dehydrating over fused calcium chloride, followed by redistillation.

Sodium azide is prepared by adding powdered $NaNO_3$ to fused $NaNH_2$ (175°C) or by passing nitrous oxide over molten $NaNH_2$ (190°C) :

$$N_2O + 2NaNH_2 = NaN_3 + NaOH + NH_3$$

$$NaNO_3 + 3NaNH_2 = NaN_3 + 3NaOH + NH_3.$$

Industrially, this reaction may also be carried out using liquid NH_3 as a solvent, NaN_3 may also be obtained without isolation of $NaNH_2$

$$3H_2O + 4Na + NH_3 = NaN_3 + 3NaOH + 2N_2$$

Silver, lead and Hg(I) azides may be obtained as insoluble precipitates from a solution of sodium azide.

Chlorine azide (ClN_3), a dangerously explosive gas, is formed when a mixture of NaN_3 and NaOCl is acidified with acetic acid.

Bromine azide BrN_3, an orange explosive liquid, is formed from NaN_3 and bromine. IN_3, a pale yellow explosive solid is similarly obtained. CF_3N_3 is made as follows :

$$CF_3NO + N_2H_4 \longrightarrow F_3CN = NNH_2 + H_2O.$$

$$F_3CN = NNH_2 + Cl_2 \longrightarrow CF_3N_3 + 2HCl.$$

Properties

(a) HN_3 is a colourless liquid (or gas, b.p. = 37°C) with an irritating odour. The liquid as well as its vapour (even in concentration <1 ppm in air) are deadly poisonous. Both the liquid and the vapour explode on heating or with a violent shock

$$2HN_3 = 3N_2 + H_2$$

(b) It is a weak acid, slightly stronger than acetic acid :

$$HN_3 \rightleftharpoons H^+ + N_3^- \quad K = 2.8 \times 10^{-5} \ (25°C)$$

The aqueous solution dissolves certain metals like Zn. Cu and Fe with the formation of azide, N_2 and NH_3. Only a little H_2 is evolved with Mg.

$$Cu + 3HN_3 = Cu\,(N_3)_2 + N_2 + NH_3$$

(c) HN_3 is quantitatively oxidized by HNO_2 or HOCl.

$$HN_3 + HNO_2 = N_2 + N_2O + H_2O$$

$$2HN_3 + HOCl = 3N_2 + HCl + H_2O$$

HN_3 may be estimated by titration with sodium nitrite solution using ferric chloride as an indicator – this gives a red colour with HN_3.

HN_3 is also oxidized quantitatively by I_2 in presence of sodium thiosulphate as a catalyst.

$$2HN_3 + I_2 = 3N_2 + 2HI$$

(d) The azides of alkali and alkaline earth metals are ionic in nature, while those of transition metals display both ionic and covalent chracter. The ionic azides are non-explosive; they decompose quietly on heating (150–300° C). LiN_3 gives Li_3N and N_2 but others give the metals and N_2. Very pure N_2 is prepared by heating $Ba\,(N_3)_2$

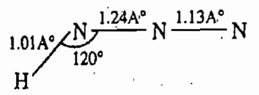
$$Ba\,(N_3)_2 = Ba + 3N_2$$

Covalent azides (of heavy metals and ClN_3 etc.) are dangerously explosive. The stability of the azide ion may be explained in terms of favourable Lewis structures (see bonding). However, certain organic azides are reasonably stable, for example CF_3N_3 explodes only at 330°C.

(e) The azide ion has many similarities with halide ions (and cyanide etc.) and is often termed a *pseudohalide*. The azides of Ag(I), Hg(I) and Pb(II) are insoluble in water, similar to their halides. The compounds ClN_3, BrN_3 etc. are similar to interhalogens. However, the corresponding pseudohalogen molecule $(N_3)_2$ has not been isolated.

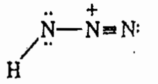
Structure and Bonding

In HN_3, the N-N-N group is linear and the structure is

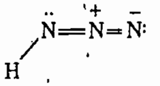


22-XIV (a)

This is also true for covalent azides. Resonance contribution from the following structures appears consistent with the unequal N—N distances.



22-XIV (b)



22-XIV (c)

The central N-atom may be considered to use *sp* hybrid orbital for bonding. The N-atom linked to the H-atom may be supposed to use sp^3 hybrid orbitals in structure (b) and sp^2 hybrid orbitals in structure (c). Alternatively, one may invoke 3-centre two-electron bonding molecular orbitals extending over all three N atoms.

The azide ion is symmetrical and linear with both N—N distances equal to 116pm. Valence bond consideration suggests the resonance structures

$$:\overset{-}{\ddot{N}}=\overset{+}{N}=\overset{-}{\ddot{N}}: \longleftrightarrow :N\equiv\overset{+}{N}-\overset{2-}{\ddot{N}}: \longleftrightarrow :\overset{2-}{\ddot{N}}-\overset{+}{N}\equiv N:$$

The explosive nature of covalent azides in contrast to ionic azides has been attributed to the relatively greater stability of the azide ion in ionic azides and to the loss of symmetry in the covalent compounds. However, it is not yet certain whether the explosive azides AgN_3 and $Pb(N_3)_2$ are fully covalent. The first ionization energy of Ag is 235 kJ mol^{-1} greater than that of sodium and this may largely account for the observed difference in the enthalpy of formation of AgN_3 and NaN_3, + 310 kJ and +21kJ mol^{-1} respectively. In any case, AgN_3 has a high positive enthalpy of formation.

Use

The azides are particularly useful in the explosive industry. Lead azide is extensively used in detonators.

Q. 22.5 *25.0 cm^3 of 0.0497 M solution of hydroxylamine was boiled with excess ferric alum solution in H_2SO_4. The Fe(II) formed required 24.7 cm^3 of 0.1007(N) $K_2Cr_2O_7$ solution. Guess the product formed on oxidation of hydroxylamine.*

Ans. : NH_2OH added = 25 × 0.0497 mmol = 1.2425 mmol.

Fe^{2+} formed = 24.7 × 0.1007 meq. = 2.4873 meq.

$\therefore$ 1.2425 mmol $NH_2OH \equiv$ 2.4873 meq.

or, 1 mol $NH_2OH \equiv$ 2 equivalent.

The O.N. of nitrogen must have increased by 2 units; the O.N. of N in the product is $-1 + 2 = +1$. The compound formed is likely to be N_2O.

Q. 22.6 *25.0 cm^3 of a 0.02 M solution of hydrazine was reacted with excess potassium ferricyanide (hexacyanoferrate(III)) in alkaline medium. The hexacyanoferrate(II) was subsequently oxidized to hexacyanoferrate (III) by 19.8 cm^3 of 0.1008 (N) $KMnO_4$.*

What might be the product of oxidation of hydrazine?

Ans. : N_2H_4 added = 25 × 0.02 mmol = 0.5 mmol.

$[Fe(CN)_6]^{4-}$ formed = 19.8 × 0.1008 meq = 1.9958 meq

$\therefore$ 0.5 mmol $N_2H_4 \equiv$ 1.9958 meq

or, 1 mol $N_2H_4 \equiv$ 4 eq (approx)

$\therefore$ O.N. of each N atom must have increased by 2 unit. Hence O.N. of N in the product $= -2 + 2 = 0$.

It should be N_2.

Q. 22.7 *0.1062 g sample of hydrazinium sulphate was taken in 9N HCl medium, 5 c.c. of CCl_4 added, and the mixture titrated with 0.023 M KIO_3 solution, shaking until the organic layer was just decolorized.*

33.3 c.c. of KIO_3 solution was required.

Find the per cent purity of the hydrazine sulphate.

Ans. : In strong HCl medium, the reaction is

$$IO_3^- + N_2H_4 + 2H^+ + Cl^- = ICl + N_2 + 3H_2O$$

or, 1 mol $IO_3^- \equiv$ 1 mol N_2H_4 (here $N_2H_5HSO_4$)

Here, IO_3^- required = 33.3 × 0.023 mmol = 0.7659 mmol

$\therefore$ 0.1062g sample contains 0.7659 mmol of $N_2H_5HSO_4$ i.e., 0.7659 × 130 mg = 0.09957 g.

$\therefore$ Per cent purity = 9.957 ÷ 0.1062 = 93.76%.

22.3.2 Nitrides, Phosphides and Arsenides

Nitrogen and phosphorus, and to a less extent arsenic, form binary compounds with a large number of elements in the periodic table which are conventionally called nitrides, phosphides etc. The formation of the M^{3-} ion by the elements is highly endothermic and at the same time the large diffuse electron cloud of the anion is highly susceptible to deformation. Lattice energy is often inadequate to form a stable ionic crystal and the compounds are seldom ionic. Since no general pattern can be readily developed, we discuss nitrides, phosphides and aresenides separately.

Nitrides

Nitrides are commonly classified as

(a) *Salt-like nitrides* : Alkali and alkaline earth metals, Be, Mg, Al, Zn.

(b) *Covalent nitrides* : Non-metals like B, P, S.

(c) *Metallic or interstitial nitrides* : Transition metals.

(a) *Salt-like or ionic nitrides* have formula consistent with normal metal ions and the nitride ion N^{3-}. The hydrolysis of these ions into ammonia and metal hydroxide agrees with such formalism but this cannot be taken as a direct "proof" of their ionic nature. Only Li among the alkali metals and the alkaline earth metals combine directly

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with N_2 on heating. Others may be prepared by heating their amides or by heating the metal in NH_3 or otherwise, e.g.,

$$3Ca + N_2 = Ca_3N_2$$

$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2$$

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$$

The ionic nitrides are solids with a wide variety of thermal stability and colour. Li_3N is ruby-red having a melting point 548°C with decomposition. Be_3N_2 melts at 2200°C while Mg_3N_2 decomposes above 271°C; Ba_3N_2 has a high m.p. at 1000°C. The nitrides of Gr II metals are all colourless.

The nitrides are readily hydrolyzed by water :

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

The N^{3-} ion has been assigned a radius of 146pm (O^{2-} : 1.40pm, F^- : 133 pm). Li_3N has a hexagonal ionic structure. Nitrides of the M_3N_2 type are anti-isomorphous with oxides of M_2O_3 type — the metals occupy the positions of oxide ions and the nitrogen atoms occur at the position occupied by the metals in the oxide structure.

(b) *Covalent Nitrides* of the nonmetallic elements are discussed under the elements. Boron nitride, cyanogen and sulphur nitrides are some of the important compounds in this category. The covalent nitrides MN of Gr 13(III) elements are structurally related to isoelectronic graphite, diamond and SiC. The compounds display a gradation in bonding from covalent to partially ionic to essentially metallic.

(c) In the *metallic nitrides* of the transition metals, the nitrogen atoms frequently occupy the interstices in the close-packed metal lattice. They often do not have an exact stoichiometry but the formula types MN, M_2N and M_4N are closely approached.

These are usually prepared by heating the metal (or its compounds) in active nitrogen, nitrogen or NH_3.

$$2ZrCl_4 + N_2 + 4H_2 = 2ZrN + 8HCl$$

The metallic nitrides are usually opaque, very hard substances with metallic properties like electrical conductivities. These suggest that the electronic band structure of the metal still persists in the compounds. The melting points of the compounds are very high, e.g.,

	TiN	VN	CrN
M.P. (°C)	2950	2050	1770

The hardness of the compounds also lie around 9 in Moh's scale. They are chemically very inert (like the borides and carbides), but slow hydrolysis with acids may be observed.

$$2VN + 3H_2SO_4 = V_2(SO_4)_3 + N_2 + 3H_2$$

The hardness, melting point and chemical inertness of the metal nitrides open the possibility of their use in making crucibles, high-temperature reaction vessels and thermocouple sheaths. Some metal nitrides are also used as heterogeneous catalysts, e.g., iron nitride in Fischer Tropsch hydriding of carbonyls.

The N^{3-} ion can also act as a ligand, particularly to the heavier transition metals. It is one of the strongest π-donors, as shown by the very short M—N distance, about 0.4-0.5 A° shorter than M—N σ-bond distances : typical examples are $[VCl_3N]^-$, $[WCl_5N]^{2-}$. Bridging nitride ligands are also known.

Phosphides

Phosphides are known for a large number of metals in a wide range of stoichiometry and structure. These are mostly prepared by heating the metal with suitable amount of red phosphorus at high temperature in an intert atmosphere (or in an evacuated sealed tube). Electrolysis of molten alkali metal phosphates containing appropriate metal oxides or halides is also used. Other typical reactions involve reaction of a metal (or its compound) with PH_3, reduction of phosphate with C etc.

Alkali and alkaline earth metals form phosphides with some degree of ionic bonding (also lanthanoids). The common formula are M_3P (Li, Na), M_3P_2 (Be, Mg, Zn, Cd), MP (La, Ce) and Th_3P_4. These compounds are hydrolyzed by water or dilute acid to give PH_3. However, they should not be considered to contain the discrete P^{3-} ion. The phosphides of transition metals have formula which bear no relationship with the usual oxidation states of the metals. Their structures may contain phosphorus atoms as well as P_2, P_4 rings or even chains or layers of phosphorus atoms. The metal-rich phosphides ($M/P > 1$) are usually hard and brittle but refractory i.e., they have high thermal stability and are generally chemically inert. On the other hand, the phosphorus-rich phosphides containing P_4 or higher units have much lower melting points and thermal stabilities. The monophosphides MP have comparatively higher melting point and thermal stabilities.

Arsenides (Antimonides and Bismuthides)

Arsenides, antimonides and bismuthides are also known for a large number of metals in several complex structures and stoichiometries. Compounds of formula M_3E and M_3E_2 are known for the more electro-positive metals of Gr I and II respectively. However, the stoichiometry is again not an indication of the presence of E^{3-} ions. Other stoichiometries like LiAs, NaSb, LiBi are also known. They have complex structures, some containing parallel infinite spirals of As or Sb atoms. The compounds often possess metallic lustre and electrical conductivity.

The structure of nickel arsenide is often used as a reference (Fig. 22.7). Each As atom has six Ni as nearest neighbours at the corners of a trigonal prism; each Ni atom has six As atoms as nearest neighbours at 243 pm. There are also two more Ni atoms at a slightly larger distance (252 pm). Ni—Ni bonding is most likely to run throughout the structure, accounting for the observed electrical conductivity of the compound. The total structure may be described as hexagonal closepacked As atoms with Ni atoms in the octahedral holes.

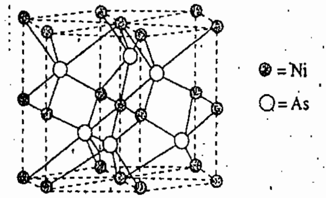


Fig. 22.7

Structure of nickel arsenide.

The structure is very common for transition-metal arsenides, antimonides, sulphides, selenides and tellurides.

22.3.3. Halides

The normal trihalides MX_3 are formed by all the elements in the group, though NBr_3 and NI_3 are extremely unstable. As nitrogen is unable to achieve a stable coordination number of five, no pentahalides of the general formula NX_5 are known. However, NF_3 can be converted to the N(V) species NF_4^+ :

$$NF_3 + 2F_2 + SbF_3 \longrightarrow [NF_4^+][SbF_6^-]$$

Pentahalides are known for the elements phosphorus to bismuth, but the decreasing M—X bond energy as both M and X become larger can hardly stabilize the M (V) state; consequently fewer pentahalides are known with the larger members in the group and with heavier halogens.

Besides, few lower halides are known for nitrogen and phosphorus (Table 22.7). N_2F_2, difluorodiazine has a N=N bond and is known in both cis and trans forms (see later).

TABLE 22.7

Halides of Gr. V(15) elements (m.p./b.p. in °C)

	Fluorides	Chlorides	Bromides	Iodies
N	NF_3 (b.p. 129)	NCl_3 (b.p. 71)	NBr_3	(NI_3)
	N_2F_4	—	—	—
	N_2F_2	—	—	—
P	PF_3 (b.p. 102)	PCl_3 (b.p. 76.1)	PBr_3 (b.p. 173.2)	PI_3 (m.p. 61.2)
	P_2F_4	P_2Cl_4	P_2Br_4	P_2I_4
	PF_5 (b.p. 85)	PCl_5 (sub. 162°)	PBr_5	PI_5
As	AsF_3 (b.p. 63)	$AsCl_3$ (b.p. 103.2)	$AsBr_3$ (m.p. 31.2) (b.p. 221)	AsI_3 (m.p. 140)
	AsF_5 (b.p. 53)	$AsCl_5$	—	—
Sb	SbF_3 (m.p. 292)	$SbCl_3$ (m.p. 73.2)	$SbBr_3$ (m.p. 97)	SbI_3 (m.p. 171)
	SbF_5	$SbCl_5$	—	—
Bi	BiF_3 (m.p. 725?)	$BiCl_5$ (m.p. 233.5)	$BiBr_3$ (m.p. 219)	BiI_3 (m.p. 409)
	BiF_5 (m.p. 154)	—	—	—
		$Bi_{24}Cl_{28}$		

Mixed halides are also formed by some of the elements. Thus all the molecular chloro-fluorides MCl_xF_{5-x} are known where M = P or As; however, the compounds of arsenic are extremely unstable.

Bismuth alone in the group forms a subhalide $Bi_{24}Cl_{28}$ containing clusters of Bi atoms.

The difference in the chemical properties of the halides may be largely traced to the general changes occurring from nitrogen to phosphorus and so on. The formation of different products on hydrolysis by NCl_3 and PCl_3 is already known :

$$NCl_3 + 3OH^- \longrightarrow 2NH_3 + 3OCl^-$$

$$PCl_3 + 3OH^- \longrightarrow HP(O)(OH)_2 + 3Cl^-$$

The non-availability of any suitable acceptor orbital in nitrogen and the reversed polarities of $\overset{\delta-}{N}—\overset{\delta+}{Cl}$ and $\overset{\delta+}{P}—\overset{\delta-}{Cl}$ bonds appear to be the chief reason. The nitrogen halides are also kinetically reluctant to hydrolysis similar to the halides of carbon. They also do not from complex anions. The general trend in properties of the compounds is more or less the same as in Gr IV. Bismuth develops much metallic character, as shown, by the salt-like character of BiF_3. The fluorides of all other elements are gases or volatile liquids and solids. BiF_5 has an infinite chain polymer of BiF_6 octahedra.

The trihalides of P, As, Sb and Bi can be made by direct combination of the elements with the halogen. The pentahalides may be obtained by reacting excess halogen. The nitrogen trihalides are obtained by reacting ammonia with excess of the halogens. Except NF_3, these are endothermic and explosive. NI_3 is known only in combination with NH_3.

The trihalides MX_3 are all pyramidal with a lone pair of electrons on M. The bond angles and dipole moment of NF_3 indicate that the lone pair of electrons occupy an sp^3 hybrid orbital and its moment partly cancels the moments of N—F bonds ($\mu = 0.2$ D only). The covalent trihalides of other elements have bond angles close to 90°. The gaseous pentahalides have trigonal bipyrimidal disposal of valence orbitals. In mixed chlorofluorides like PCl_3F, the F-atoms occupy axial positon (See Ch.7 and 15). Crystalline phosphorus pentachloride is ionic $PCl_4^+ PCl_6^-$. Phophorus pentabromide, on the other hand has an ionic formulation like $PBr_4^+ Br^-$. The loss in lattice energy due to larger anion radius of PBr_6^- is not compensated by the energy released in forming the PBr_6^- anion (steric congestion).

Halides of nitrogen

Nitrogen trifluoride, NF_3, is prepared by eletrolysis of NH_4F in anhydrous HF. Small amounts of N_2F_2 are produced in this process. NF_3 is also formed by reacting NH_3 with F_2 diluted with N_2 in a copper packed reactor. Other fluorides like N_2F_4, N_2F_2 are also formed — the nature of product depends on the $F_2 : NH_3$ ratio and other conditions.

It is a colourless, stable gas ($\Delta H^\circ = -109$ kJ mol^{-1}), unaffected by water or most other reagents at ordinary temperature. It reacts readily with $AlCl_3$ at 70°C

$$2NF_3 + AlCl_3 = N_2 + 3Cl_2 + 2AlF_3$$

The high lattice energy of AlF_3 together with the large N ≡ N bond enrgy seems to drive the reaction. NF_3 does not appear to have any donor properties. In presence of F_2, it combines with strong Lewis acids under pressure, uv radiation at low temperature or glow discharge, to form tetrafluoroammonium salts :

$$NF_3 + F_2 + BF_3 \longrightarrow NF_4^+ BF_4^-$$

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4^+ AsF_6^-$$

The NF_3 molecule is pyramidal with a very small dipole moment (see Chapter 7).

Nitrogen trichloride, tribromide, triiodide

NCl_3 is formed by the action of chlorine on a concentrated and slightly acidic solution of ammonium chloride; it may be continuously extracted into CCl_4.

It is a pale yellow explosive oily liquid (b.p. ~ 71°C), endothermic (ΔH_f^0 = 232 kJ mol^{-1}) and very reactive. The difference in the heats of formation of NF_3 and NCl_3 arises from the differences in N—F vs N—Cl as well as F—F and Cl—Cl bond energies. It is slowly hydrolysed to NH_3.

NCl_3 is pyramidal with Cl-N-Cl angle ~107° 45′ and N—Cl distance = 175 pm.

NBr_3 is prepared similar to NCl_3. The reaction of I_2 with concentrated aqueous ammonia at ordinary temperature produces black explosive crystals of $NH_3.NI_3$. The crystal contains zigzag chains of NI_4 tetrahedra sharing corners. The chains are linked by NH_3 molecules between them.

Other fluorides of nitrogen

N_2F_4, tetrafluorohydrazine, is prepared by heating NF_3 with Cu :

$$2NF_3 + Cu = CuF_2 + N_2F_4 \quad (400°C).$$

It is a colourless reactive gas (b.p. −73°C, $\Delta G°$ (298) : + 81 kJ mol^{-1}) which readily dissociates into difluoroamino radical :

$$N_2F_4 = 2NF_2$$

The odd electron radical has been shown to be bent with the odd electron in relatively pure π M.O. The reactions of N_2F_4 gives products formally derived from this free radical :

$$2NF_2 + 2RSH \longrightarrow RSSR + 2HNF_2$$

$$N_2F_4 + Cl_2 \longrightarrow 2NF_2Cl$$

$$N_2F_4 + RCHO \longrightarrow NHF_2 + RCONF_2$$

In this respect, N_2F_4 resembles N_2O_4 rather than N_2H_4.

It is hydrolysed by water, initially extremely slowly. In HF, it forms the cation $N_2F_3^+$ with strong Lewis acids :

$$N_2F_4 + 2SbF_5 \longrightarrow N_2F_3^+ [Sb_2F_{11}]^-$$

N_2F_4 (*g*) contains nearly equal amounts of gauche and trans forms at room temperature.

N_2F_2, difluorodiazene, results from the reaction of N_2F_4 with $AlCl_3$ at − 70°C :

$$2N_2F_4 + 2AlCl_3 = N_2F_2 + N_2 + 2AlF_3 + 3Cl_2.$$

The trans-form (b.p. −111.4°C) so obtained changes to the cis-form (b.p. −106°C) on warming which is the dominant species around 25°C and is more reactive. It reacts with glass containers completely in about 2 weeks to form SiF_4 and N_2O. The cis-form alone reacts with AsF_5 to form $[N_2F]^+ [AsF_6]^-$.

Trihalides of Phosphorus

Phosphorus trifluoride, PF_3 is best made by fluorination of AsF_3, ZnF_2 or CaF_2. It is a colourless, odourless gas (b.p. 102°C which is highly toxic owing to the formation of a complex with hemoglobin (like CO). It is hydrolyzed slowly by water, but rapidly in presence of alkali.

$$PF_3 + 3H_2O = H_3PO_3 + 3HF$$

PF_3 forms many complexes with transition metals, e.g., $Pt(PF_3)_4$, $Pd(PF_3)_4$, $Ni(CO)_n(PF_3)_{4-n}$ (n = 0 – 4). These complexes may be obtained by direct reaction of PF_3 with metals (at high temperatures and pressures) or metal salts or by fluorination of PCl_3 complexes. In addition to σ donation of the lone pair of electrons on phosphorus to the metal, the complexes also involve back donation of electron density from filled metal orbitals to empty acceptor *d*-orbital on phosphorus via π-bonding.

The P–F distance in PF_3 is 1.56 A° and the F–P–F angle is 96.3°.

[Sec. 22.3.3 *Phosphorus halides*]

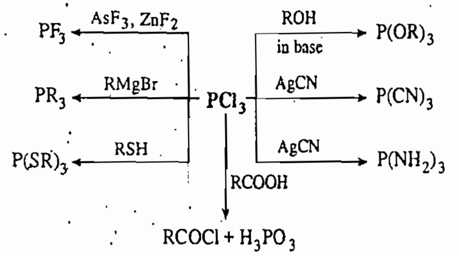
Phosphorus trichloride, PCl_3 is the most important trihalide of phosphorus. It is made by direct synthesis — about 280,000 tonnes are produced per year all over the world. It is a colourless liquid (b.p. 76°C) which fumes strongly in moist air and is readily hydrolyzed by water, with partial oxidation :

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl \quad (\text{some } H_4P_2O_3)$$

It undergoes a wide variety of reactions, namely, substitution, oxidation, reduction as well as addition.

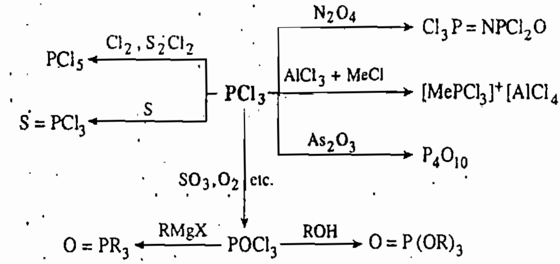
Substitution

The chlorine atoms are readily substituted through a large number of reactions, e.g.

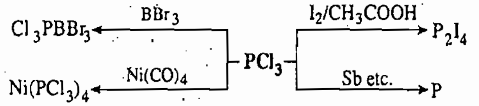


Oxidation.

Some typical reactions are shown below :



Reduction and Adduct formation



PCl_3 is the starting material for organophosphorus compounds which are largely used as oil additives, plasticizers, flame retardants, manufacture of insecticides and fuel additives (see reactions of $POCl_3$ under oxochlorides).

The Cl—P—Cl bond angles in PCl_3 are 100° with P—Cl distances pf 204 pm.

Phosphorus tribromide and triiodide

The preparation and properties of PBr_3 and PI_3 are similar to those of PCl_3. PBr_3 is a colourless liquid, b.p. 173.2°C. The P—Br distances are 2.22A° and Br-P-Br angles 101°. PI_3 forms red hexagonal crystals, m.p. 1-2°C, which decompose above 200°C. PI_3 is gradually finding use in abstracting oxygen atoms from different compounds. In presence of triethylamine, it converts primary nitroalkanes, RCH_2NO_2 and aldehyde-oximes (RCH = NOH) to nitriles (RCN). Sulphoxides and selenoxides (R_2SO or R_2SeO) are converted to sulphides or selenides, R_2S and R_2Se respectively at (or below) room temperature by a solution of PI_3 in CH_2Cl_2.

Trihalides of Arsenic, Antimony and Bismuth

All four trihalides are known for each of the three elements. The trifluorides are prepared by the action of HF on the respective trioxide M_2O_3 (M = As, Sb, Bi). Direct reaction of the element or its oxide with F_2 produces the pentafluoride. Since AsF_3 is rapidly hydrolyzed, it is prepared in an anhydrous condition :

$$As_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2AsF_3 + 3CaSO_4 + 3H_2O$$

Other trihalides may also be prepared using concentrated aqueous HF.

The trichlorides and tribromides of As and Sb may be prepared by directly reacting the halogen with As/Sb or their oxides. $AsCl_3$ is prepared conveniently by distilling As_2O_3 with conc HCl. Bismuth trihalides are not readily hydrolyzed, and so may be prepared by dissolving Bi_2O_3 in concentrated aqueous HX.

The trihalides have varying physical and chemical properties. Some physical properties are given in Table 22.8 It may be observed that except AsF_3 and $AsCl_3$ (which are colourless liquids), all other trihalides are solids. The sharp drop in the magnitude of ΔH_f^0 after fluorides is noticeable.

$AsCl_3$ and $SbCl_3$ have convenient liquid range (Table 22.8), low viscosity coefficients ($AsCl_3$: 1.23 centipoise at 20°C; $SbCl_3$: 2.6 centipoise at 75°C) and fairly high dielectric constants (13 and 33 respectively) combined with good solvent properties. These facts make them suitable as nonaqueous solvents for various reactions. Their self-ionization

$$2MCl_3 \rightleftharpoons MCl_2^+ + MCl_4^-$$

seems to be negligible in view of the very low conductivities (K = 10^{-7} ohm^{-1} cm^{-1}).

The trihalides are in general hydrolyzed by water. $SbCl_3$ and $BiCl_3$ produce the oxochlorides SbOCl and BiOCl consistent with the increasing electropositive character of the elements.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

TABLE 22.8

Some physical properties of the trihalides of As, Sb and Bi

	State (25°C)	M.P./°C	B.P./°C	ΔH_f^0 kJ mol^{-1}
AsF_3	Colourless liquid	−6	63	−957
SbF_3	Colourless crystals	390	~345	−916
BiF_3	Grey-white powder	650	900	−900
$AsCl_3$	Colourless liquid	−16	130	−305
$SbCl_3$	White, deliquescent crystals	73.4	223	−382
$BiCl_3$	White, deliquescent crystals	234	441	−379
$AsBr_3$	Pale-yellow	31	221	−197
$SbBr_3$	White, deliquescent crystals	96	288	−259
$BiBr_3$	Yellow, deliquescent crystals	219	462	−276
AsI_3	red, crystals	140	~400	−58
SbI_3	red, crystals	171	401	−100.4
BiI_3	green-black crystals	409	~542	−150

AsX_3 and SiX_3 react with alcohols and alkoxides to form arsenite or antimonite esters/halide esters :

$$AsCl_3 + EtOH \longrightarrow (EtO)AsCl_2 + HCl$$

$$AsCl_3 + 2NaOEt \longrightarrow (EtO)_2AsCl + NaCl$$

The trihalides of As and Sb are feeble electron pair donors but they act as good acceptors, particularly with halide ions and amines. AsF_3 forms complexes with alkali metal fluorides :

$$KF + AsF_3 \longrightarrow K^+[AsF_4]^-$$

SbF_3 gives a wide range of complex haloanions (see complex halides).

Both AsF_3 and SbF_3 are good fluorinating agents, particularly SbF_3 (*Swarts reagent*) :

$$Cl_3CCCl_3 + SbF_3 \longrightarrow FCl_2CCl_2F$$

$$SiCl_4 + SbF_3 \longrightarrow SiCl_3F,\ SiCl_2F_2,\ SiClF_3$$

$$R_3PS + SbF_3 \longrightarrow R_3PF_2$$

The arsenic trihalides give pyramidal AsX_3 molecules in the gas phase. The X—As—X bond angles lie in the range 96°–100°. The solids also contain this structure, $SbCl_3$ and $SbBr_3$ are also similar. The iodides contain the atoms of As/Sb in octahedral interstices in hexagonal closepacked lattice of I atoms.

BiF_3 has an ionic structure with the bismuth in nine-coordination (tricapped trigonal prism). $BiCl_3$ has a molecular lattice but the environment of the Bi atom corresponds to eight-coordination with 5 further Cl-atoms at 3.2–3.4 A°. The molecule itself also appears to be slightly distorted.

Pentahalides

Phosphorus pentafluoride, PF_5 may be prepared by fluorinating PCl_5 (by AsF_3, say). Thermal decomposition of hexafluorophosphate salts like $NaPF_6$, $Ba(PF_6)_2$ or the diazonium salt also forms PF_5. The gas is thermally stable but chemically very reactive. It is a very strong acid which forms complexes with F^-, amines, ethers etc. It fumes in air due to hydrolysis to the oxofluoride

$$PF_5 + H_2O = POF_3 + 2HF$$

The PF_5 molecule has a trigonal bipyramid structure in which the axial P—F distances (1.58A°) are longer than the equatorial P—F distances (1.53A°) in electron diffraction studies. However, the bonds appear all equivalent in ^{19}F nmr spectrum on a milli-second scale. This can be explained by Berry pseudorotation (Ch. 15).

Formerly, the bonding in this and many similar compounds was explained in terms of sp^3d hybridization of the valence orbitals of the central atom. Though mo. calculations do require the inclusion of *d*-orbital functions, the total *d*-orbital population in PF_5 appears to be only about 0.6 electrons. The idea of σ-bonding involving *d*-orbitals is thus not even approximately correct. The involvement of *d*-orbitals appears to be in the form of $p\pi$-$d\pi$ backbonding from filled fluorine 2*p*-orbitals.

The bonding in PF_5 may be explained in terms of

(i) three usual 2-center-2-electron covalent P—F bonds in the equatorial plane. The P-atom may interchange the *s*-pair with a p_z electron and use sp^2 hybrid orbitals in the xy plane.

(ii) two 3-center-4-electron P—F bonds in the axial plane. Combination of two F $2p_z$ a.o.s and the $3p_z$ a.o. on P gives rise to three m.o.s : one bonding, one nonbonding and one antibonding (c.f. HF_2^- ion, Fig. 17.10 p 100). The four available electrons occupy the bonding and nonbonding m.o.-s. Effectively, only the two electrons in the bonding m.o. hold the three atoms. The bonds are thus expected to be longer than the equatorial bonds.

Phosphorus pentachloride, PCl_5, is prepared directly from the elements or by passing chlorine into well-cooled PCl_3. It is vigorously hydrolyzed by water :

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

PCl_5 sublimes at 163°C but melts under pressure at 167°C. It is molecular in the gas and liquid phases but may ionize in polar solvents like CH_3CN or nitrobenzene; the actual mode of ionization depends mainly on concentration :

$$2PCl_5 = [PCl_4^+] + [PCl_6^-]$$

$$PCl_5 = [PCl_4^+] + Cl^-.$$

Crystalline PCl_5 consists of tetrahedral PCl_4^+ and octahedral PCl_6^- ions. These ions are also known in other environments as in the $PCl_5 - TiCl_4$ system where one gets $[PCl_4]_3$ $[TiCl_6]$ $[PCl_6]$. $CsPCl_6$ has been prepared.

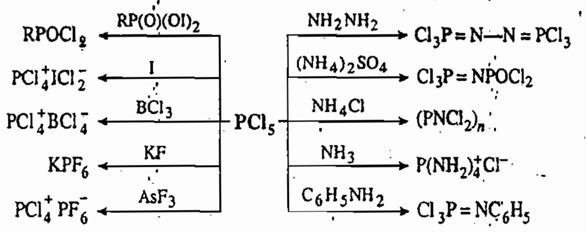
PCl_5 is a widely used chlorinating agent; it converts carboxylic acids to acid chlorides. Concentrated H_2SO_4 forms sulphuryl chloride, SO_2Cl_2

$$HO.SO_2.OH + 2PCl_5 = ClSO_2Cl + 2POCl_3 + 2HCl.$$

Zinc, cadmium, gold and platinum are converted to their chlorides on heating with PCl_5 :

$$PCl_5 + Zn = PCl_3 + ZnCl_2.$$

PCl_5 enters a wide variety of reactions many of which are of considerable technical importance. Some reactions are summarized below; PCl_5 as a strong Lewis acid, forming adducts with pyridine, pyrazine etc.



Phosphorus pentabromide and pentaiodide

PBr_5 forms reddish-yellow rhombohedral crystals which start decomposing above 0°C to PBr_3 (*g*) and Br_2 (*g*). No liquid is known. The crystalline solid normally has an ordered lattice of $[PBr_4^+]$ $[Br^-]$. Rapid cooling of the vapour to 15K produces a disordered lattice containing $[PBr_4]^+$ $[Br_3^-]$ and PBr_3.

PI_5 is not wellknown, though it has been prepared in 1978 by the action of HI, LiI, NaI etc. on PCl_5 dissolved in CH_3I. It forms brown black crystals melting at 41°C. In solution, the compound appears to be $[PI_4^+]$ I^-.

[Sec. 22.3.3 *Pentahalides*]

Pentahalides of arsenic, antimony and bismuth

Arsenic, antimony and bismuth form pentafluorides while only arsenic and antimony pentachlorides are known. The nonexistence of other pentahalides may be correlated to the oxidizing nature of the elements in + 5 oxidation state.

The pentafluorides may be prepared by reacting fluorine with the elements or with As_2O_3 or Sb_2O_3. $AsCl_5$ has been prepared only in 1976 by reacting $AsCl_3$ with liquid chlorine at −105°C under uv radiation. It decomposes above −50°C to $AsCl_3$ and Cl_2. The compound gives Raman spectra closely similar to those given by PCl_5 and $SbCl_5$. $SbCl_5$ is quite stable up to ~ 140°C and is made by reacting $SbCl_3$ with Cl_2.

The melting and boiling points of the pentahalides are given in Table 22.9.

TABLE 22.9

Melting/Boiling points of the pentahalides of As, Sb and Bi

	AsF_5	SbF_5	BiF_5	$AsCl_5$	$SbCl_5$
M.P./°C	−80	8.3	154.4	−50 (?) (decomp)	4
B.P./°C	−53	141	230	—	140 (decomp)

AsF_5 is more or less similar to PF_5 in structure, but SbF_5 appears to be associated through F-bridges even in the gaseous state. The viscous liquid probably contains linear polymers containing 6-coordinate Sb with F-bridges; the solid contains cyclic tetramers (Fig. 22.8). Liquid SbF_5 is similar to glycerol in consistency with a high viscosity (40 cp at 20°C).

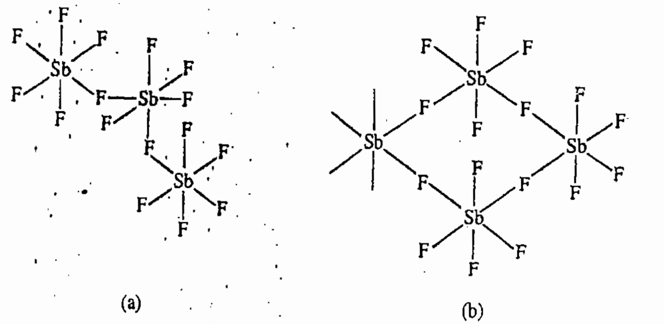


Fig. 22.8

(a) Linear polymer of SbF_5 liquid (schematic); (b) Tetrameric unit in solid SbF_5.

BiF_5 forms white needle-shaped crystals containing infinite linear chains of BiF_6 octahedra which are trans-bridged and stacked parallel to each other.

The pentafluorides are strong fluorinating and oxidizing agents. They are also potent fluoride ion acceptors, forming MF_6^- or more complex anions. AsF_5 and SbF_5 ionize in liquid HF to give conducting solutions :

$$2AsF_5 + 2HF \longrightarrow H_2F^+ + As_2F_{11}^-$$

$$SbF_5 + 2HF \longrightarrow H_2F^+ + SbF_6^-$$

The $As_2F_{11}^-$ ion can be isolated as its salt with Et_4N^+. The strong F^- ion acceptor capacity of SbF_5 ion enhances the acidity of liquid HF and HSO_3F—giving rise to superacids (Ch. 10). The acidity is enhanced further by addition of 3 or more moles of SO_3.

BiF_5 is also an extremely reactive compound. It reacts violently with water forming O_3, OF_2 and a brown residue which is probably a hydrated oxide fluoride containing Bi(V). Above 50°C, it converts paraffin hydrocarbons to fluorocarbons. UF_4 is fluorinated to UF_6 (150°), Br_2 to BrF_3 + BrF_5 and Cl_2 to ClF (> 180°).

The remarkable instability of $AsCl_5$ in contrast to PCl_5 and $SbCl_5$ may be related to the remarkably poor shielding effect of the $3d^{10}$ core on the nuclear charge; this lowers the energy of the 4*s* orbital in all the elements which follow – Ga, Ge, As, Se and Br. The highest oxidation state thus becomes difficult to be attained in these elements. There is as such no evidence or reason to believe that the As—Cl bond in $AsCl_5$ is unduly weak. The effect becomes significant again after the filling of the 4*f* subshell, as is observed in the non-existence of $BiCl_5$.

Lower Halides

P_2F_4, P_2I_4, As_2I_4 and Sb_2I_4 are well-characterized. P_2Cl_4 and P_2Br_4 are also known, though not so well characterized.

P_2F_4 is obtained in high yield by the following reaction at room temperature under reduced pressure :

$$2PF_2I + 2Hg \longrightarrow P_2F_4 + Hg_2I_2$$

It is a colourless gas (b.p. – 6.2°C), reacting with O_2 to form F_2POPF_2. Hydrolysis of P_2F_4 also gives the same product. The P—P distance is 2.28 A°, P—F distances 1.6 A° and the FPF angles nearly 99°. The FPP angles are slightly less, ~ 95.4°.

P_2Cl_4, obtained as a colourless oil (m.p. –28°C), in low yield by microowave discharge through PCl_3 at 1.5 mm (Hg) pressure, decomposes slowly at room temperature. Hydrolysis in basic solution gives P_2H_4 and $P_2(OH)_4$. P_2Br_4 has been reported to be formed in a C_2H_4 – PBr_3 – Al_2Br_6 system.

P_2I_4 forms red triclinic needles which may be obtained by the action of I_2 on (a) red phosphorus (180°C) or (b) white phosphorus in solution in CS_2, or (c) PCl_3. Hydrolysis of P_2I_4 yields various phosphines and oxoacids of phosphorus, together with a little hypophosphoric acid : $(HO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{P}(OH)_2$. Br_2 cleaves the P—P bond, giving $PBrI_2$. The molecule of P_2I_4 has the trans-centrosymmetric structure.

As_2I_4 (red crystals, m.p. 137°C) is formed on heating requisite amounts of As and I_2 in a sealed tube (260°C) in presence of octahydrophenanthrene. Though stable to 150°C in an inert atmosphere, the compound disproportionates on standing to AsI_2 + As. It also undergoes ready hydrolysis and oxidation. Sb_2I_4 is much less stable.

No halide of the stoichiometry Bi_2X_4 is known. BiCl is supposed to be present in the vapour above heated Bi–$BiCl_3$ mixture. The black solid may be represented as $Bi_{24}Cl_{28}$; it contains two metal clusters –Bi_9^{5+} ions, together with four $BiCl_5^{2-}$ and one $Bi_2Cl_8^{2-}$ ion. The compound is stable in vacuum below 200°C. It hydrolyses rapidly to oxochloride and disproportionates in presence of ligands which coordinate strongly to $BiCl_3$.

Oxohalides of Nitrogen

Nitrogen forms two different types of oxohalides : (i) nitrosyl halides, XNO (X = F, Cl, Br) and (ii) nitryl halides XNO_2 (X = F, Cl).

(i) **Nitrosyl halides** are formed by reacting NO with the appropriate halogen or by reactions like

$$NO + AgF_2 \longrightarrow FNO + AgF ; \quad N_2O_4 + KCl \longrightarrow ClNO + KNO_3$$

Some of their physical properties are summarized in Table 22.10 Their stability decreases as FNO > ClNO > BrNO. BrNO decomposes (~ 7%) at room temperature and 1 atm pressure into Br_2 + NO. They are also decomposed by water to HNO_3, HNO_2, NO and HX. They are powerful oxidizing agents and attack many metals forming metal fluorides. They combine with suitable fluorides and chlorides to form salts of NO^+

$$FNO + AsF_5 \longrightarrow NO^+ AsF_6^-$$
$$ClNO + SbCl_5 \longrightarrow NO^+ SbCl_6^-$$
$$NOCl + AlCl_3 \longrightarrow NO^+ AlCl_4^-$$
$$NOF + PF_5 \longrightarrow NO^+ PF_6^-$$

The nitrosonium ion is similar in size to the ammonium ion; many nitrosonium salts are thus isomorphous with corresponding ammonium salts.

Like aqua regia, aqueous solutions of XNO dissolve metals through the formation of HNO_2 and HNO_3 :

$$XNO + H_2O \longrightarrow HNO_2 + HX; \quad 3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O.$$

TABLE 22.10

Few characteristics of XNO and XNO_2 compounds

Compound	Colour	M.P.(°C)	B.P.(°C)	Structure	
FNO	Colourless	–133	–60	bent, F$\hat{N}$O F—N N—O	= 110° = 1.52 A° = 1.13 A°
ClNO	Orange-yellow	–62	–6	bent, Cl$\hat{N}$O Cl—N N—O	= 116° = 1.95 A° = 1.14 A°
BrNO	red	–56	0	bent, Br$\hat{N}$O Br—N N—O	= 114° = 2.14 A° = 1.15 A°
FNO_2	Colourless	–166	–72	planar, O$\hat{N}$O F—N N—O	= 125° (?) = 1.35 A° = 1.23 A°
$ClNO_2$	Colourless	–145	–15	planar, O$\hat{N}$O Cl—N N—O	= 131° = 1.84 A° = 1.20 A°

(ii) **Nitryl halides** may be regarded as derivatives of HNO_3 ($HONO_2$) in which a halogen atom replaces OH. They are prepared as

$$N_2O_4 + 2CoF_3\,(s) = 2FNO_2 + 2CoF_2\,(s) \qquad 300°C$$
$$ClSO_3H + HNO_3\,(anhydrous) = ClNO_2 + H_2SO_4 \qquad 0°C$$

Both are decomposed by water :

$$XNO_2 + H_2O \longrightarrow HNO_2 + HOX \longrightarrow HNO_3 + HX$$

They form salts containing NO_2^+, the nitronium ion :

$$FNO_2 + BF_3 = NO_2^+ BF_4^-$$

Nitrosyl hypofluorite, ONOF is formed by the reaction of NO_2 and F_2 at −30°C.

Fluorine and chlorine nitrates, FONO₂ (b.p. −46°C) and **ClONO₂** (b.p. 22°C) have been prepared by the reactions

$$F_2 + HNO_3 \longrightarrow FONO_2 + HF$$

$$ClF + HNO_3 \longrightarrow ClONO_2 + HF$$

Both are explosive.

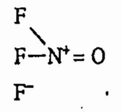
Trifluoroamine oxide, F₃NO, (b.p. −87°C) has been prepared in a number of ways :

$$3FNO + 2IrF_6^- \longrightarrow 2NOIrF_6^- + F_3NO.$$

$$2NF_3 + O_2 \longrightarrow 2F_3NO \text{ (electric discharge)}$$

$$FNO + F_2 \longrightarrow F_3NO \ (h\nu, 25°C)$$

It reacts with NO rapidly to give FNO. Fluoride ion acceptors like AsF_5 (SbF_5) react with it to give salts containing NF_2O^+ cation. The electronic structure of the compound may be written as $F_3N \rightarrow O$. But the short N—O bond (1.16A°) suggests, contributions from structures like (p 345)



Oxohalides of Phosphorus

All four **phosphoryl halides** X_3PO are known (X = F, Cl, Br, I). The phosphorus(III) halides readily form an additional P═O bond.

$$PCl_3 + \tfrac{1}{2}O_2 = POCl_3 \text{ (room temp).}$$

$$P_4O_{10} + 6PCl_5 = 10\,POCl_3$$

$POBr_3$ can be made similarly. POF_3 is better made by fluorination of $POCl_3$ with a metal fluoride. Iodination of $POCl_3$ with LiI gives POI_3.

Melting and boiling points of the compounds are as follows :

	POF_3	$POCl_3$	$POBr_3$	POI_3
M.P./°C	−39	1.25	55	53
B.P./°C	−40	105	192	-

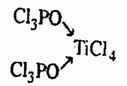
The phosphoryl halides are readily hydrolyzed to phosphoric acid (+ HX). The halogens may be successively replaced by alkyl or aryl groups (Grignard reagent), by alkoxo groups (alcohols), by RNH (amines) and so on, giving a large number of organophosphorus derivatives and phosphate esters.

$$O = PCl_3 + 3C_2H_5OH \longrightarrow O = P(OC_2H_5)_3$$

Triethyl phosphate is used in producing systemic insecticides. Several other phosphate esters are also produced in kilotonne scales for use as plasticizers, petrol additive etc. Tritolyl phosphate is a petrol additive; triuryl and trioctyl phosphates are used as plasticizers; tri-n-butyl phosphate is used in solvent extraction.

$POCl_3$ acts as a donor toward metal/nonmetal acceptors, e.g.,

$$Cl_3PO \longrightarrow BCl_3 \qquad Cl_3PO \longrightarrow FeCl_3$$



$$(Cl_3PO)_2 \rightarrow TiCl_4$$

The very strong complex $Cl_3PO - Al_2Cl_6$ has been utilized to remove Al_2Cl_6 from adducts with products in Friedel-Crafts reactions.

All phosphoryl halides have pyramidal PX_3 groups with an oxygen atom along the fourth corner of a distorted tetrahedron. The P—O distances (~ 1.55 A°) indicate appreciable double bond character.

Polyphosphoryl (and thiophosphoryl) fluorides and chlorides are known. Pyrophosphoryl chloride, $Cl_2P(=O)$—O—$P(=O)Cl_2$, is a colourless oily liquid, b.p. 215° (dec); it is prepared by passing Cl_2 into a suspension of P_4O_{10} and PCl_3 in CCl_4.

Oxohalides of As, Sb, Bi

Few oxo halides of the MOX type are known; AsOF (?); SbOF, SbOCl; BiOF, BiOCl, BiOBr, BiOX.

AsOF has not been fully characterized but is reportedly formed when As_4O_6 is heated with AsF_3 in a sealed tube at 320°.

SbOF and SbOCl result from controlled hydrolysis of $SbF_3/SbCl_3$. Thus, when a solution of Sb_2O_3 in concentrated HCl is diluted with water, the solution turns milky due to the precipitation of SbOCl.

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

However, other oxide halides may be formed with excess water e.g., $Sb_4O_5Cl_2$. The latter is also formed by heating Sb_2O_3 with $SbCl_3$ to 75°C in vacuum. The solids have complicated layer structures. SbOCl consists of polymeric sheets formed by linking Sb atoms through O and Cl bridges with composition like $[Sb_6O_6Cl_4]^{2+}$ held between layers of Cl^- ions.

Bismuth oxohalides BiOX are similarly precipitated from partial hydrolysis of BiX_3 compounds. BiOF and BiOI are also formed when BiF_3/BiI_3 are heated in air. They have complex layer lattice structures and are white except BiOI which is brick-red. BiOI decomposes above 300°C; heating BiOCl or BiOBr above 600° C gives oxide halides of composition $Bi_{24}O_{31}X_{10}$.

Except Cl_3AsO, there is no definite oxohalide of the type X_3MO. $AsOF_3$ is known only as a polymer. $AsCl_3$ cannot be made by hydrolysis of the highly unstable $AsCl_5$ or by the action of O_2 on $AsCl_3$. It was made only in 1976 by ozonization of $AsCl_3$ in $CFCl_3/CH_2Cl_2$ at −78°C. The white monomeric solid is unstable above −25°C, forming $As_2O_3Cl_4$, a polymeric solid.

$$3AsOCl_3 \longrightarrow AsCl_3 + Cl_2 + As_2O_3Cl_4$$

$AsOCl_3$ contains an As═O double bond.

Complex Halides

The halides of Gr 15(V) act as Lewis acids to form a number of halo-complexes, commonly in the coordination number six. The pentahalides are particularly stronger Lewis acids. Thus, PF_3 does not form the PF_4^- ion, but PF_6^- may be made in aqeous medium by reacting phosphoric acid wih concentrated HF. It may be precipitated with large organic cations. Solid KPF_6 may be prepared by heating PCl_5 with KHF_2. Treatment of PCl_5 with AsF_3 in $AsCl_3$ solution gives the mixed halide PF_3Cl_2 having the structure $[PCl_4]^+ [PF_6]^-$. It sublimes with decomposition at 130°C.

AsF_3 forms complexes with both KF and SbF_5 — having compositions $K^+[AsF_4]^-$ and $[AsF_2]^+ [SbF_6]^-$ respectively.

SbF_3 also combines with alkali metal fluorides to yield complexes with a wide range of anions, e.g.,

K_2SbF_5 : square pyramid SbF_5^{2-} ion.

KSb_2F_7 : SbF_3 and SbF_4^- ion; the latter has a roughly tbp geometry with a lone pair of electrons in an equatorial position.

$KsbF_4$: cyclic $Sb_4F_{16}^{4-}$ anion in which four SbF_5 groups each share two F atoms.

$CsSb_2F_7$: F-bridged $[F_3Sb—F—SbF_3]^-$ ion.

Lewis acidity among the pentafluorides increases in the order

$$SbF_5 > BiF_5 > AsF_5 > PF_5.$$

AsF_5 forms complexes like $KAsF_6$ and $NOAsF_6$ with octahedral $[AsF_6^-]$ group. SbF_5 acts as a very powerful fluoride ion acceptor and forms a large number of salts containing $[SbF_6]^-$, $[Sb_2F_{11}]^-$ or $[Sb_3F_{16}]^-$ ions with unusual cations like O_2^+, XeF^+, ClF_2^+ and NF_4^+. Bismuth (V) also forms a number of hexafluoro complexes like

$$BiF_3 + F_2 \xrightarrow{\text{in } BrF_3} BrF_2^+ BiF_6^- \xrightarrow{Ag/BrF_3} Ag^+BiF_6^-$$

Even the very unstable $AsCl_5$ is known to form a number of 6-coordinate complexes; the $AsCl_5$ is formed in situ :

$$AsCl_3 + Cl_2 + NEt_4Cl \longrightarrow NEt_4^+ AsCl_6^-$$

$$AsCl_3 + Cl_2 + R_3PO \longrightarrow AsCl_5 (R_3PO).$$

$SbCl_5$ forms an adduct with ICl_3 which has a chain structure : the structure is intermediate between $[ICl_2]^+ [SbCl_6]^-$ and $[SbCl_4]^+ [ICl_4]^-$.

Partial oxidation of $SbCl_3$ with Cl_2 in presence of CsCl gives dark blue Cs_2SbCl_6. An analogous reaction forms the black salt $(NH_4)_2SbBr_6$. Both the compounds are isomorphous with K_2PtCl_6 but they do not contain Sb(IV) since they are diamagnetic. They are probably mixed valence compounds containing Sb(III) and Sb(IV) i.e., $[SbBr_6]^{3-}$ ion (Sb – Br = 2.79 A°) and $[SbBr_6]^-$ ion (Sb – Br = 2.56 A°). Both the ions are octahedral, though $[SbBr_6]^{3-}$ has an unshared pair of electrons. Either the 5s pair is stereochemically inert or six 3-center-2-electron bonds are involved.

22.3.4 Oxides

General Discussion

The elements in Group (VB)15 form oxides in their usual III and V states, though Bismuth (V) oxide is unstable and ill characterized. Nitrogen also forms N_2O, NO and NO_2 (N_2O_4) containing nitrogen in I, II and IV states. The oxides of nitrogen are all gaseous with N—O p-p π-bonds dominating over their structures; as such they have no analogues among the remaining elements in the group. They are also slightly endothermic (remember the high N≡N bond energy and the stable m.o. configuration of N_2).

However, they are involved in many redox reactions involving nitrogen compounds where kinetic factors often play a significant role for their existence.

High values of electronegativity, N≡N bond energy and ionization enthalpy make it difficult to oxidize nitrogen directly—only NO is formed from N_2 and O_2 under the aotion of electric spark at high temperatures. N_2O_5 may be made by dehydrating HNO_3 or by the action of FNO_2 with excess $LiNO_3$. The gas consists of discrete N_2O_5 molecules with N—O—N bonds but the solid is ionized with a planar NO_3^- ion and a linear NO_2^+ (nitronium) cation. Higher oxides of nitrogen (e.g., NO_3 and N_2O_6) have been reported $(O_3 + N_2O_5)$ but very little is known about them.

The reaction for direct synthesis of NO, i.e.,

$$\tfrac{1}{2} N_2 (g) + \tfrac{1}{2} O_2 (g) = \dot{N}O (g)$$

has $\Delta H°$ (298 K) = + 90 kJ, $\Delta S°$ (298 K) = 9 JK^{-1} and K (298 K) = 5×10^{-31}. The positive value of ΔS implies that ΔG can be negative at high enough temperature according to the relation

$$\Delta G = \Delta H - T\Delta S$$

For all other oxides of nitrogen, ΔG is positive at all temperatures (Fig. 22.9), as expected from a negative ΔS value. Other nitrogen oxides therefore cannot be prepared by direct synthesis.

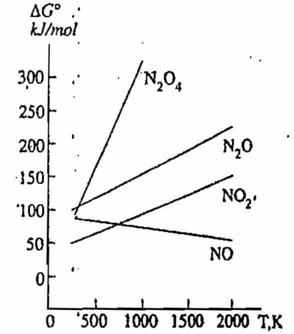


Fig. 22.9
Dependence of the standard free energies of formation of nitrogen oxides on temperature.

Phosphorus is readily oxidized to P_4O_{10} when burnt in excess of air. The vapour, as well as the solid and liquid forms have structures based on PO_4 tetrahedra (see later).

The pentoxides of As, Sb and Bi (M_2O_5) may be prepared by oxidizing the elements or the trioxides, but increasingly powerful oxidizing agents are needed from As to Bi. Bi_2O_5 readily loses oxygen and is not obtained in a stoichiometric form. As_2O_5 is a solid with a polymeric structure containing AsO_4 tetrahedra and AsO_6 octahedra sharing corners. Structures of Sb_2O_5 and Bi_2O_5 are not known but they are likely to be based on MO_6 octahedron.

N_2O_5 loses oxygen above 0°C to form N_2O_4. The pentoxides of As, Sb and Bi also lose oxygen on heating with increasing ease. N_2O_5 is strongly acidic and a strong oxidizing agent. It dissolves in water to form HNO_3. P_4O_{10} is also acidic, forming

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H_3PO_4 and other acids, but it is not oxidizing in nature. Acidity of the pentoxides decreases among the heavier members : Sb_2O_5 reacts with alkali to form antimonates containing $Sb(OH)_6^-$ units. $NaBiO_3$ is also known. Oxidizing nature of the pentoxides increases again from As to Bi in keeping with the emergence of inert pair effect.

Among the trioxides, N_2O_3 is the least stable; it is also the least stable one among the oxides of nitrogen. It is formed as a blue solid when an equimolar mixture of NO and NO_2 is condensed at low temperature. In the gas phase it completely dissociates into NO and NO_2. It is the anhydride of HNO_2. Phosphorus(III) oxide results when phosphorus is burnt in a limited supply of oxygen. The vapour corresponds to the formula P_4O_6 which is related structurally to the P_4 tetrahedron in elemental phosphorus (see later). The oxide is acidic (giving H_3PO_3) and reducing in nature. Arsenic, antimony and bismuth burn in air to form As_4O_6, Sb_4O_6 and Bi_2O_3 respectively. The first two oxides have structures similar to P_4O_6 in the solid and gas phase, but a second solid form is also known, specially with Sb. Bi_2O_3 exists in several solid forms, containing mostly BiO_6 units in a distorted prism arrangement. Acidity of the oxides decreases from As – Sb, Sb_4O_6 is amphoteric and Bi_2O_3 is basic.

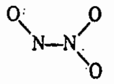
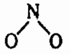
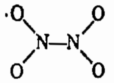
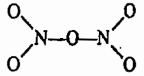
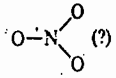
Phosphorus also forms a series of mixed oxides P_4O_x (x = 7, 8, 9) containing formally P(III) and P(V). The structures may be derived by gradually adding terminal oxygen atoms to the P_4O_6 structure.

Oxides of nitrogen

Some physical properties of the oxides are summarized in Table 22.11

TABLE 22.11

Oxides of nitrogen

Formula	Nature	M.P./B.P.(°C)	ΔH_f^0 (298) kJmol^{-1}	Structure (gas)
N_2O (Dinitrogen monoxide)	Colourless gas not very reactive.	m.p. −90.8 b.p. −88.5	82	N—N—O
NO (nitrogen monoxide)	Colourless gas, paramagnetic. mod. reactive.	m.p. −163.6 b.p. −151.8	90.2	N—O
N_2O_3 (Dinitrogen trioxide)	Blue solid, diss into NO and NO_2 in gas phase.	m.p. −101	—	
NO_2 (nitrogen dioxide)	Brown gas, paramagnetic; reactive.	—	—	
N_2O_4 (Dinitrogen tetroxide)	Colourless liq, diss.into NO_2 in gas.	m.p. −11.2 b.p. +21.15	9.2	
N_2O_5 (Dinitrogen pentoxide)	Colourless solid. $NO_2^+NO_3^-$; unstable in gas.	m.p. 32	− 43.1 (s) 11.3 (g)	
NO_3, N_2O_6	Not isolated pure. Indicated by absorption spectrum. Paramagnetic.			 (?) (planar)

[Sec. 22.3.4 *Nitrogen oxides*]

Dinitrogen monoxide (N_2O, nitrous oxide)

It is obtained by carefully heating molten ammonium nitrate (250–260°C) :

$$NH_4NO_3 = N_2O + 2H_2O.$$

Some N_2 and NO are also formed. The latter may be removed by passing through a solution of iron (II) sulphate. Chlorides catalyze the decompostion to N_2. But almost pure N_2O is obtained by heating NH_4NO_3 solutions in HNO_3 or H_2SO_4 with small amounts of Cl^-.

The reaction is an example of *comproportionation* (p 241 Vol I) in which the cation is oxidized by the anion. It is probable that NH_4NO_3 first dissociates into NH_3 and HNO_3. HNO_3 then undergoes autoprotolysis forming NO_2^+ :

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

$$NH_3 + NO_2^+ \longrightarrow [H_3NNO_2]^- \longrightarrow NNO + H_3O^+$$

This is supported when the reaction is carried out using ^{15}N.

$$^{15}NH_4NO_3 = {}^{15}NNO + H_2O$$

$$NH_4\,{}^{15}NO_3 = N^{15}NO + H_2O.$$

N_2O is also formed by thermal decomposition of hyponitrites and various other reactions.

N_2O is a colourless gas fairly soluble in cold water but insoluble in hot water. It supports combustion by dissociation to oxygen above ~ 600°C. At room temperature, the gas is relatively inert towards alkali metals, halogen or ozone. Kinetic factors must be dominant, because reduction potentials suggest strongly oxidizing nature in either acidic or basic medium

$$N_2O\,(g) + 2H^+\,(aq) + 2e \rightleftharpoons N_2\,(g) + H_2O \qquad E^\circ = +1.77V\ (pH = 0)$$

$$N_2O\,(g) + H_2O + 2e \rightleftharpoons N_2\,(g) + 2OH^- \qquad E^\circ = +0.94V\ (pH = 14).$$

At high temperatures, N_2O reacts with H_2 ($N_2 + H_2O$), many nonmetals and some metals :

$$10N_2O + P_4 = P_4O_{10} + 10N_2$$

$$N_2O + Cu = CuO + N_2$$

Hot molten sodamide reacts with N_2O to give sodium azide, N_3Na :

$$NaNH_2 + N_2O = NaN_3 + H_2O\ (200°C)$$

N_2O can also act as a ligand :

$$[Ru\,(NH_3)_5\,(H_2O)]^{2+} + N_2O\,(aq) \longrightarrow [Ru\,(NH_3)_5\,(N_2O)]^{2+} + H_2O$$

The N_2O molecule has the assymmetric linear structure

$$N \overset{1.13A°}{\text{———}} N \overset{1.19A°}{\text{———}} O.$$

The bond orders calculated are N—N : 2.73 and N—O 1.61. Lewis structures consistent with its low dipole moment (μ = 0.166 D) are

$$\overset{(-)}{:\ddot{N}:}\ \overset{(+)}{:N:}\ :\ddot{O}: \quad \text{and} \quad :N::\overset{+}{N}:\overset{-}{\ddot{O}}:$$

The central N-atom may be supposed to use *sp* hybrid orbitals to form two σ-bonds to N and O on two sides. The two *p*-orbitals excluded from hybridization form two pi-bonds to N and O in structure (a) and to N only in structure (b).

Nitrous oxide was given the name "laughing gas" by its inventor Davy (1799) as it produced hysteric laughter on inhalation. It has been *much* used as an anaesthetic but has now been discontinued due to certain undesirable side-effects. Its principal use is as aerosol propellants and as aerating agent for whipping cream.

Nitrogen monoxide (NO, nitric oxide)

Nitrogen (II) oxide is formed in several reactions involving nitrous and nitric acids or their salts :

$$3Cu + 8HNO_3\ (1:1) = 3Cu\,(NO_3)_2 + 2NO + 4H_2O$$

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 = Fe_2\,(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

$$3KNO_2\,(l) + KNO_3\,(l) + Cr_2O_3\,(s) = 2K_2CrO_4 + 4NO.$$

It is produced by catalytic oxidation of ammonia in the Ostwald process for the synthesis of HNO_3 via NO_2.

Direct combination between N_2 and O_2 takes place only at very high temperatures (~ 3000°C) and is not commercially viable. The reaction

$$N_2 + O_2 \longrightarrow 2NO$$

cannot ocur by simple electron-transfer between the HOMO and LUMO of the reactants. The HOMO in N_2 is a σ m.o. and is not suitable for positive overlap with the LUMO on O_2 which is a π* m.o. (Fig. 22.10). The HOMO on O_2 (π* m.o.) matches in symmetry for overlap with the LUMO on N_2 (also a π* m.o.), but such electron transfer is opposed by the higher electronegativity of oxygen. As such, higher-lying m.o.-s must be involved in reacting N_2 and O_2, which would make the activation energy very high.

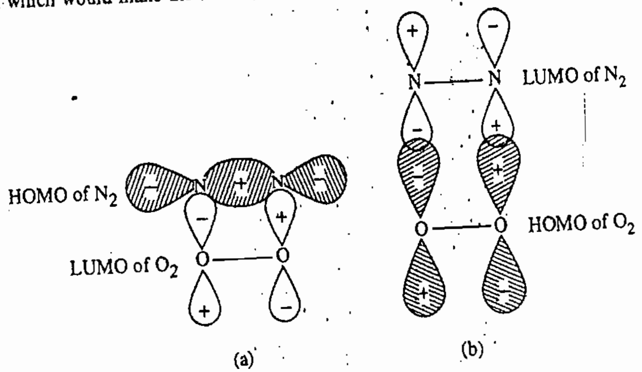


Fig. 22.10

Schematic overlap between m.o.-s of N_2 and O_2 :

(a) the σ_{2p} HOMO of N_2 makes unfavourable overlap with the π* LUMO of O_2;

(b) the π* LUMO of N_2 and π* HOMO of O_2 match for overlap but electron transfer is unlikely from electronegativity consideration.

[Sec. 22.3.4 *Nitrogen oxides*]

NO is a neutral oxide and does not react with acids and alkalis. It is a colourless paramagnetic gas which shows little tendency to dimerize. It is only slightly soluble in water.

NO reacts instantly with O_2 (NO_2) and with halogens F_2, Cl_2 and Br_2 to form nitrosyl halides XNO (See Oxohalides, Section 22.3.3). Strong oxidizing agents like $KMnO_4$ (acid) or I_2 oxidize it to HNO_3 :

$$3MnO_4^- + 5NO + 4H^+ = 3Mn^{2+} + 5NO_3^- + 2H_2O$$

The reaction is quantitative and may be used for the analysis of NO.

NO is reduced to NH_2OH by Cr(II) or Sn(II) in acid solution. SO_2 reduces it to N_2O. A cold solution of iron (II) sulphate absorbs NO and turns brown due to the formation of the complex $[Fe\,(NO)(H_2O)_5]^{2+}$ ion. NO forms a wide range of coordination compounds with transition metals — such nitrosyl complexes will be discussed separately.

NO is usually a poor supporter of combustion in spite of its endothermic nature. Its decomposition to N_2 and O_2 does not occur at an appreciable rate below about 1000°C. It decomposes to N_2O and NO_2 at much lower temperatures (30-50°C) under pressure :

$$3NO \rightleftharpoons N_2O + NO_2 \qquad \Delta H = -3 \times 51.8\ kJ.$$

Since NO is an endothermic compound, its formation is favoured at high temperatures and the gas is present in exhausts from cars and aeroplane.

The gas is only slowly converted to NO_2 since the reaction has a rate law second order in NO — proceeding via a transient dimer $(NO)_2$ which subsequently collides with a molecule of O_2. Accordingly, NO accumulated in the upper atmosphere is likely to decompose the protective ozone layer

$$O_3 + NO \longrightarrow O_2 + NO_2.$$

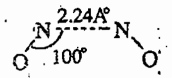
Since NO is endoergic, scientists are trying to develop a catalyst which would decompose it into N_2 and O_2 at the exhaust source. It has been observed that under laboratory conditions, Cu(II) in a zeolite bed (ZSM-5) catalyzes the disproportionation of NO into N_2 and O_2 (Iwamoto et al, 1986).

The molecule NO is described better by the m.o. approach. The m.o. description is similar to that of N_2 or CO with an additional electron in the antibonding level :

$$KK\ 1\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2\, 1\pi_u^4\, 2\pi_g^1 \quad or \quad KK\ 1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 1\pi_u^4\, 1\pi_g^1.$$

The bond order is 2.5. The bond length (1.15 A°) is actually shorter than typical double bonded NO species (1.20 A°) and decreases significantly in NO^+ (1.06 A°) formed by removal of the last electron in the antibonding π* -m.o. The N–O stretching frequency increases from around 1877 cm^{-1} in NO to about 2320 cm^{-1} in NO^+.

Though gaseous NO shows no sign of dimerization, partial dimerization occurs in liquid NO. The solid has been shown to consist of dimeric units by X-ray diffraction. Weak association in the solid is revealed by the relatively long N—N distance (22-XV) and the low heat of dimerization, 15.5 kJ mol^{-1}. The dimer is diamagnetic, showing the absence of unpaired spins but it has feeble intrinsic temperature-independent paramagnetism (explained later in connection with magnetic properties of transition metal compounds).



22-XV

The notable reluctance of gaseous NO to dimerize in comparison to NO_2 shows that the odd electron in the π^* m.o. of NO has greater delocalization. Also, we observe that dimerization of NO to O = N–N = O results in no change in the total bond order from two NO molecules (2 × 2.5 = 5).

Salts of the nitrosonium ion

Removal of the odd electron from the π^* orbital in NO requires about 900 kJ mol^{-1} energy. The resulting nitrosonium ion NO^+ has an extensive chemistry. The ion is readily formed in several reactions in anhydrous conditions :

$$NOCl + AlCl_3 \longrightarrow NO^+ AlCl_4^-$$

$$NOCl + SbCl_5 \longrightarrow NO^+ SbCl_6^-$$

$$N_2O_3 + 3H_2SO_4 \longrightarrow 2NO^+ + 3HSO_4^- + H_3O^+$$

$$N_2O_4 + 3H_2SO_4 \longrightarrow NO^+ + NO_2^+ + 3HSO_4^- + H_3O^+$$

$$N_2O_3 + 2HClO_4 \longrightarrow 2NO^+ClO_4^- + H_2O$$

$$N_2O_3 + 2HBF_4 \longrightarrow 2NO^+BF_4^- + H_2O$$

$NO^+HSO_4^-$ was an important intermediate in the old lead chamber process of manufacture of sulphuric acid. Electrolysis, conductivity studies and cryoscopic data support the salt-like composition of this and other nitrosonium compounds. The NO^+ ion is intermediate in size between H_3O^+ and NH_4^+ and is isoelectronic with CO. $NO^+ ClO_4^-$ and $NO^+BF_4^-$ have the same structure as the corresponding NH_4^+ and H_3O^+ compounds. Like CO, NO^+ forms several transition metal complexes e.g., the brown $[Fe(H_2O)_5NO]^{2+}$ mentioned earlier.

The nitrosonium salts are readily hydrolyzed :

$$NO^+ + H_2O \rightleftharpoons H^+ + HNO_2.$$

Dinitrogen Trioxide, N_2O_3

It is obtained as a blue liquid only at very low temperatures (–30°C) by condensing equimolar amounts of NO and NO_2. Its dissociation into NO and NO_2 begins to be significant above –30°C. It condenses to a pale blue solid at –100°C.

Liquid N_2O_3 appears to undergo self-ionization to some extent :

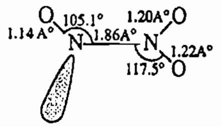
$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

As shown above, N_2O_3 readily forms salts of the nitrosonium ion (NO^+).

It is the formal anhydride of nitrous acid and forms nitrites with alkali :

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

Spectral studies reveal that the molecule has nearly the same planar structure (22-XVI) in the solid as well as other states. The N—N bond is unusually long (1.86 A°) in comparison to the N—N single bonds in for example, $H_2N–NH_2$, 1.47A°. The compound is diamagnetic and hence contains no odd electrons.



22-XVI

Nitrogen Dioxide and Dinitrogen Tetroxide (NO_2 and N_2O_4).

The two oxides coexist in equilibrium at the liquid and gaseous state

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g) \quad K = 1.4 \times 10^{-5}\ mol\ dm^{-3}\ (30°C).$$

The solid (m.p. –11° C), colourless and diamagnetic, is entirely N_2O_4. The pale yellow liquid contains about 0.01% NO_2 at the freezing point. At the boiling point (21°C), the deep brown liquid contains about 0.1% NO_2 while the deep brown vapour contains 15% NO_2. The vapour darkens with rise in temperature; at about 100°C, it contains ~ 90% NO_2. Dissociation is nearly complete at 140°C, above which the colour becomes lighter owing to reversible dissociation into NO and O_2.

A mixture of the gaseous oxides is readily obtained by heating heavy metal nirates (e.g., Cu^{II}, Pb^{II}, Ba^{II} etc). Oxidation of NO in air and reduction of concentrated nitric acid and nitrates (by metals or other reducing agent) also generate these gases.

The gases are acidic in nature, forming nitrous and nitric acids with water. The nitrous acid subsequently decomposes to HNO_3 and NO, particularly on warming :

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

$$2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O.$$

The gases are highly reactive and oxidizing in nature, attacking many metals, including mercury, at room temperature. The aqueous solution is comparable in strength to bromine :

$$N_2O_4 + 2H^+ + 2e = 2HNO_2 \qquad E° = + 1.07\ V$$

$$NO_2 + 2HCl \longrightarrow NOCl + H_2O + \tfrac{1}{2}\,Cl_2$$

$$NO_2 + 2HCl \longrightarrow NO + H_2O + Cl_2 \ \text{(heating; also with HBr).}$$

$$NO_2 + 2KI + H_2O \longrightarrow NO + 2KOH + I_2.$$

NO_2 reacts with fluorine and chlorine, forming nitryl fluoride and chloride :

$$2NO_2 + F_2 \longrightarrow 2NO_2F; \quad 2NO_2 + Cl_2 \longrightarrow 2NO_2Cl$$

N_2O_4 undergoes self-ionization endothermically, the major species being NO^+ and NO_3^-

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad K = 7 \times 10^{-8}\ mol\ dm^{-3}\ (30°C)$$

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad K = 10^{-22}\ mol\ dm^{-3}\ (30°C).$$

In anhydrous acids extensive dissociation takes place; it is almost complete in anhydrous HNO_3 :

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-.$$

In concentrated H_2SO_4 it yields both nitrosonium and nitronium ions :

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-.$$

The electrical conductivity of liquid N_2O_4 increases considerably when mixed with solvents of high dielectric constant (e.g., nitromethane, ε = 37) or donor solvents (*D*) like MeCOOEt, Et_2O, Me_2SO etc. Solvated nitrosonium cation is produced :

$$N_2O_4 + nD \rightleftharpoons [D_nNO]^+ + NO_3^-.$$

Typical reactions in liquid N_2O_4 are :

Acid-Base : $NOCl + AgNO_3 \longrightarrow AgCl + N_2O_4$

Acid : $2NOCl + Sn \longrightarrow SnCl_2 + 2NO$

Solvolysis : $CaO + 2N_2O_4 \longrightarrow Ca(NO_3)_2 + N_2O_3$

Systems involving liquid N_2O_4 and an organic solvent dissolves relatively noble metals to form nitrates, often solvated (by N_2O_4). For example, in $MeNO_2$ or MeCOOEt

$$Cu + 3N_2O_4 \longrightarrow NO\,[Cu(NO_3)_3] + 2NO$$

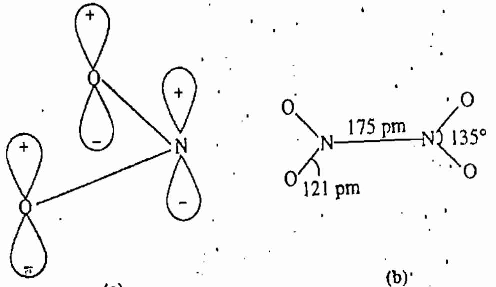
The crystalline solid contains NO^+ ions and polymeric nitrato anions. On heating, it loses NO_2 to give anhydrous $Cu(NO_3)_2$.

Together with NO, N_2O_4 and NO_2 are also produced in combustion and are of concern in atmospheric pollution. The equilibrium mixture of NO and NO_2 ("*nitrous fumes*") is used as a selective oxidizing agent in organic chemistry.

NO_2 is a radical with one unpaired electron. The O–N–O angle is 134°. It can lose its odd electron ($\Delta H = 928$ kJ mol^{-1}) to give the nitronium ion, NO_2^+. Nitronium salts have been discussed later.

N_2O_4 is a planar molecule (22-XVII) with a rather long N—N bond (1.75A°; in N_2H_4 it is 1.47 A°). The bonding in each NO_2 fragment may be described by assuming sp^2 hybridization by the N-atom : one hybrid orbital contains the odd electron; the other two make σ-bonds with *p*-orbitals on the two O-atoms.

The *p*-orbital on N excluded from hybridization combines with similar orbitals on the O-atoms to produce a delocalized π-bonding extending over the entire skeleton.



22-XVII

The unpaired electron thus appears to be more localized on the N-atom (than in NO), leading to ready dimerization. The N—N bond is long because of delocalization of the bonding electron pair of the whole molecule and large repulsion between the doubly occupied m.o.'s of NO_2. The barrier to rotation about the N—N bond has been estimated to be around 9.6 kJ mol^{-1}.

M.O. description of angular triatomic molecules

The molecular orbital approach for anuglar triatomic molecules involving π-bonds may be illustrated with NO_2 as an example (H_2O, discussed in Chapter 23, has only σ-bonds). For simplicity, we assume that the 2*s* atomic orbitals on the two oxygen atoms are essentially non-bonding as they are much lower in energy than the nitrogen atomic orbitals. Then we are left with 2*s*, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on N and the $2p_x$, $2p_y$, and $2p_z$ a.o.-s on each of the two O atoms.

The NO_2 molecule possesses C_{2v} symmetry. If we choose the *z*-axis as the C_2 axis and the *x*-axis perpendicular to the molecular plane, the *yz* plane will be the molecular plane. Overlap considerations now show that there will be five σ-m.o.-s : two bonding, two antibonding and one non-bonding. Without entering into details of the symmetry properties of the orbitals, we may refer to Fig. 22.11(a) for the nature of σ-overlap involved in the above m.o.-s. For convenience, the axes of the oxygen atoms have been so oriented that the *z*-axis for each O is directed toward the N atom. The nitrogen 2*s* and $2p_z$ have been combined first (*sp* hybrid), followed by overlap with the O-2*p* orbitals. (The results will be the same if linear combination of all three a.o.-s are taken directly). This gives three σ-m.o.-s. The p_y a.o. on N also gives rise to one bonding and one antibonding m.o. [Fig. 22.11(b)].

The $2p_x$ orbitals on all three atoms, perpendicular to the molecular plane, may now combine to give three π m.o. *s* : one bonding, one antibonding and a non-bonding one [Fig. 22.11 (c)].

The $2p_y$ a.o. on each oxygen remains non-bonding.

The approximate energy level diagram for the molecule is shown in Fig. 22.11 (d).

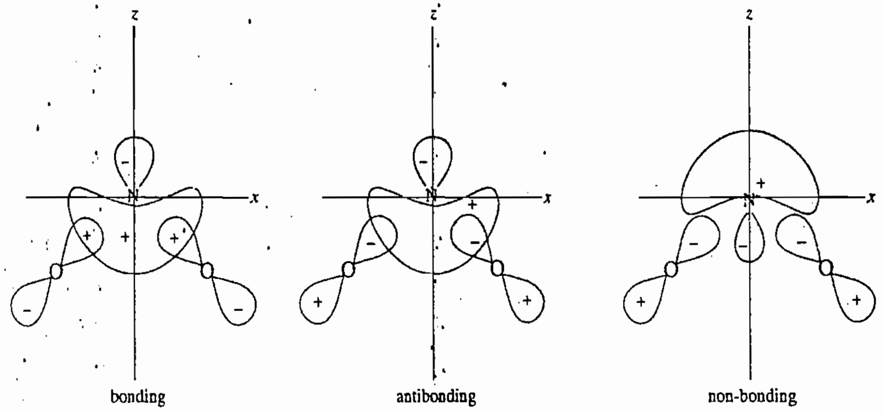


Fig. 22.11 (a)

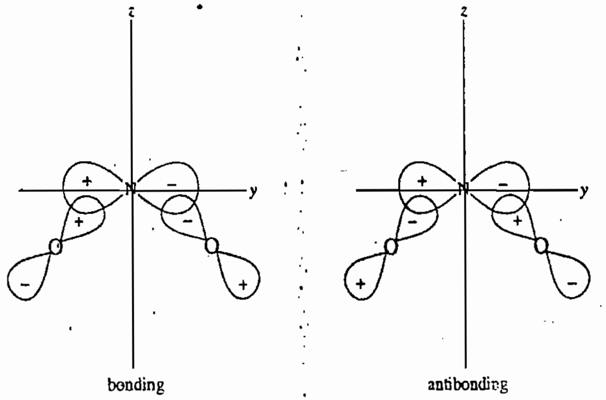


Fig. 22.11 (b)

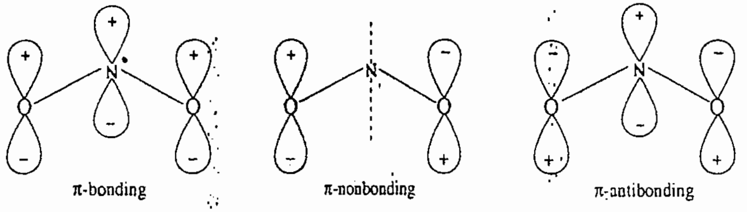


Fig. 22.11 (c)

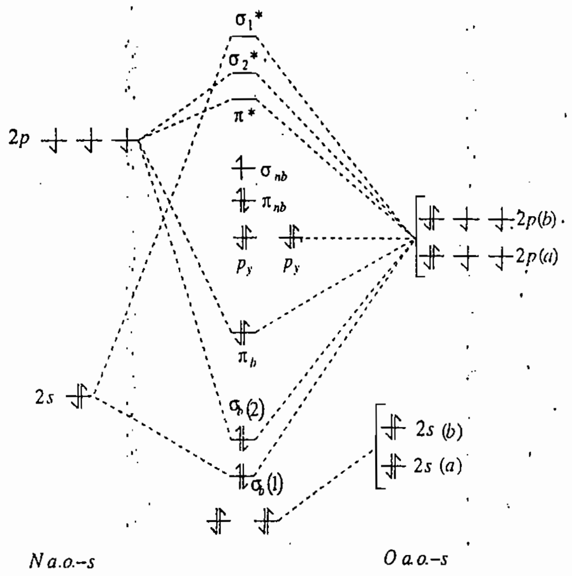


Fig. 22.11 (d) : Molecular orbitals in NO_2.

Fig. 22.11(a)—(c) Sketches for some of the combinations,
(d) m.o. energy level diagram.

(The molecules Cl_2O, O_3, SO_2, OF_2, ClO_2, NO_2^- etc. may be treated in the same manner).

The seventeen valence electrons may now be placed to obtain an average bond order of 1.5 for each N—O bond. Out of the six electrons in bonding m.o.-s, four are in σ m.o.-s and two are in the π m.o. This may be considered equivalent to 1σ-bond and $\frac{1}{2}$ π-bond between each N and O. We remember that in case of nitric oxide, the N—O bond is equivalent to 1σ-bond and 1.5 π-bond (total bond order 2.5). This is consistent with the observed N—O distances in the two cases, NO_2 : 1.20 A°; NO : 1.13A°. The ready dimierization of NO_2 is also consistent with this m.o. description — the extent of π-bonding and hence delocalization is less than in the case of NO and the odd electron is in a σ m.o. (though nonbonding) localized near N, while in NO the odd electron is in an antibonding π-m.o.

Dinitrogen Pentoxide (N_2O_5)

It is obtained by dehydration of concentrated nitric acid by P_4O_{10} at low temperature (–10°C) :

$$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + N_2O_5$$

A more convenient preparation involves reaction between FNO_2 and $LiNO_3$.

Nitronium salts]

It is obtained as a colourless crystalline deliquescent solid which sublimes at 32.4° C (1 atm) but is unstable as a solid as well as in the gas phase above room temperature. It readily produces nitric acid with water. Ionic dissociation occurs in anhydrous H_2SO_4, HNO_3 or H_3PO_4 :

$$N_2O_5 + 3H_2SO_4 \rightleftharpoons H_3O^+ + 2NO_2^+ + 3HSO_4^-$$

This and similar reactions provide a route to nitronium salts (see later).

With H_2O_2, N_2O_5 produces nitric and pernitric acids :

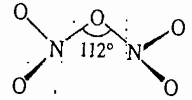
$$H_2O_2 + N_2O_5 \longrightarrow HONO_2 + HOONO_2.$$

It is a strong oxidizing agent :

$$I_2 + N_2O_5 \longrightarrow I_2O_5 + N_2$$

$$Na + N_2O_5 \longrightarrow NaNO_3 + NO_2$$

The structure of the gaseous molecule at low temperature (–11°C) is shown in 22-XVIII.



22-XVIII

N–O (bridge) = 1.5 A°
N–O (term) = 1.2 A°
<NON = 112°
<ONO = 133°

The compound is also molecular in solution in CCl_4, $CHCl_3$ or $OPCl_3$. Solid N_2O_5 consists of linear NO_2^+ (N–O = 1.15 A°) and NO_3^- ions (planar, N–O = 1.24 A°).

The nitronium salts

Crystalline nitronium salts containing NO_2^+ ion are formed in the reactions of N_2O_5 in strong anhydrous acids or acid anhydride, often in nitromethane solution.

$$N_2O_5 + HSO_3F \longrightarrow NO_2^+ FSO_3^- + HNO_3$$

$$N_2O_5 + HClO_4 \longrightarrow NO_2^+ ClO_4^- + HNO_3$$

$$2SO_3 + HNO_3 \longrightarrow NO_2^+ HS_2O_7^-$$

In this last reaction HNO_3 is apparently a base, functioning as $NO_2^+OH^-$. The nitronium disulphate $[NO_2]_2^+[S_2O_7]^=$ is formed in nitromethane. Nitronium fluoroborate and fluorosilicates are formed by reacting N_2O_5 with the fluorides in presence of HF in nitromethane :

$$N_2O_5\,BF_3 + HF = NO_2BF_4 + HNO_3$$

$$2N_2O_5 + SiF_4 + 2HF = (NO_2)_2SiF_6 + 2HNO_3$$

These crystalline compounds are thermodynamically stable. They, however, decompose at 100–150°C except $[NO_2]_2$ (S_3O_{10}) which boils at 200°C without decomposition. They are very reactive, being rapidly hydrolyzed by water. They are strong electrophilic reagents — NO_2^+ is the attacking agent in the nitration of organic compounds.

As expected, the nitronium ion is linear and symmetrical, $O = N^+ = O$; the N-atom may be supposed to involve *sp* hybrid orbitals in σ-bonding the O-atoms.

NO_3 has not been isolated as a pure compound, but its integrity as an independent chemical species is revealed by its absorption spectrum during decomposition of O_3 catalyzed by N_2O_5.

N_4O and N_4O_2 are actually unstable azides of NO^+ and NO_2^+ respectively, i.e., $NO^+N_3^-$ and $NO_2^+N_3^-$. They are formed in solution when sodium azide acts on nitrosyl or nitronium salts in an organic solvent. N_4O decomposes at –50°C, and N_4O_2 decomposes above –10°C.

Oxides of Phosphorus

Phosphorus trioxide, P_4O_6

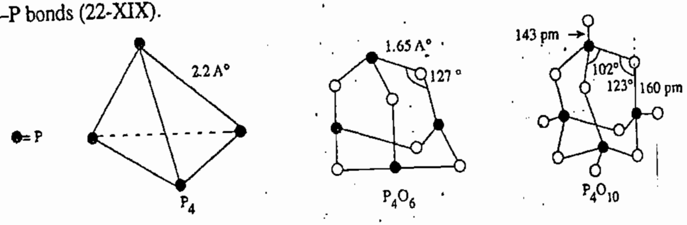
P_4O_6 is called phosphorus trioxide due to historical reasons. Its molecular structure agrees with the present formula. It is produced by burning white phosphorus in an oxygen-deficient atmosphere, e.g., gentle heating (≃ 50°C) of P_4 in ≃75% O_2 at low pressure (~ 90 mm Hg). The conversion is low, around 50%, and it is difficult to separate the white phosphorus completely by distillation. The white phosphorus may be changed to red by the action of uv rays; the P_4O_6 may then be dissolved out in an organic solvent (e.g., benzene or thf).

P_4O_6 forms low-melting white crystals, m.p. 23.8°C, b.p. 175°C, which are stable to oxygen at room temperature (but only when free from even traces of white phosphorus). It burns when heated in air. On heating in a sealed evacuated tube at 200–400°C, it disproportionates into red P and oxides of varying composition, P_4O_n, $n = 7–10$.

P_4O_6 is an acidic oxide and gets hydrolyzed by excess of cold water to H_3PO_3, phosphorous acid. With hot water, PH_3, H_3PO_4 and elemental P are the main products, presumably formed by disproportionation of H_3PO_3.

P_4O_6 reacts vigorously with chlorine or bromine to form oxohalides; iodine reacts in a sealed tube to form P_2I_4.

The structure of P_4O_6 has the same tetrahedral symmetry as found in the P_4 unit in elemental phosphorus; the P_4 lattice expands to accommodate O-atoms inbetween each P—P bonds (22-XIX).



22-XIX

Phosphorus pentoxide, P_4O_{10}

This oxide has also retained its historical name. It is obtained by burning phosphorus in excess oxygen. The white crystalline solid may be purified by sublimation at 360°C (1 atm) when the common hexagonal crystalline form containing P_4O_{10} molecules (22- XIX) is deposited.

[Sec.22.3.4
Phosphorus oxides]

P_4O_{10} has strong affinity for water with which it forms phosphoric acids. It can extract water even from concentrated H_2SO_4 which itself is a dehydrating agent. It dehydrates H_2SO_4 to SO_3, HNO_3 to N_2O_5, $RCONH_2$ to RCN and so on. P_4O_{10} is usually dispersed over glass wool to prevent the formation of surface crusts by hydrolysis products. Phosphoric acid is largely manufactured from P_4O_{10}.

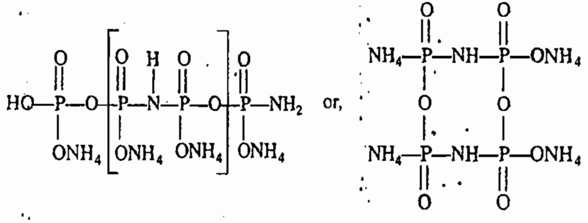
With alcohols and ethers, P_4O_{10} similarly gives phosphate esters, in which one or more OH groups in H_3PO_4 [$O = P(OH)_3$] are replaced by OR groups :

$$P_4O_{10} + 6EtOH \longrightarrow 2O = P(OH)_2(OEt) + 2O = P(OH)(OEt)_2;\ (65°C)$$

$$P_4O_{10} + 6Et_2O \longrightarrow 4O = P(OEt)_3\ \ (heat).$$

On stronger heating, ethanol may be dehydrated to ethene.

P_4O_{10} reacts vigorously with NH_3 to form condensed linear or cyclic amidopolyphosphates of a wide composition range depending upon the conditions, e.g.,



The condensed polymers can sequster ions like Ca^{II} and hence their use in industry in water softening.

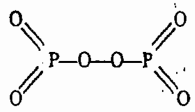
The common hexagonal form of P_4O_{10} contains tetrahedral molecules which persist in the gas phase also. The structure is again related to that of P_4 tetrahedron - with changed dimensions from those of P_4O_6 and one terminal O-atom from each P (22-XIX). The bridging P—O bonds are evidently longer (1.60 A°) than the terminal P—O bonds (1.43 A°) having considerable double bond character. Other crystalline (orthorhombic) and glassy forms of P_4O_{10} may be obtained by heating the hexagonal variety (400 - 450°C). All, however, contain PO_4 units.

The oxides P_4O_x with $x = 7$, 8 and 9 have structures derived from P_4O_6 with successive addition of terminal oxygen atoms.

These are formed by heating P_4O_6 in a sealed tube at temperatures 200°—400°C. P_4O_7 may also be made at room temperature from a solution of P_4O_6 in tetrahydrofuran using Ph_3PO as catalyst.

An oxide of composition PO may be prepared by slowly refluxing $POBr_3$ with Mg in diethyl ether. Its structure is probably polymeric. It reacts with water to give PH_3.

P_2O_6, phosphorus peroxide, is obtained as a violet solid by passing $P_4O_{10} + O_2$ through a heated discharge tube at low pressure. The compound liberates O_2 when heated (130°C) under reduced pressure. It liberates I_2 from KI and hydrolyzes to peroxophosphoric acid. It may have a peroxobridged structure :



22-XX

Oxides of As, Sb and Bi

Arsenic(III) oxide As_4O_6 is formed by burning the element in air. In industries, it results from the roasting of sulphide ores containing arsenic (e.g., arsenopyrite, FeAsS). It is a white solid, slightly soluble in water 0.2 g per 100 g at 25°C). The acidic solution contains "arsenious acid" H_3AsO_3 or As $(OH)_3$. It is a weak acid :

$$As(OH)_3 \rightleftharpoons H^+ + [AsO(OH)_2]^- \qquad K_a = 6 \times 10^{-10}\ (25°C)$$

In basic soluions, anions as $[AsO\ (OH)_2]^-$, $[AsO_2\ (OH)]^{2-}$ and $[AsO_3]^{3-}$ are present. As_4O_6 also dissolves in dilute HCl :

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

The solubility first decreases with increase in acidity (minimum 11.6 g per 100 g in 3M HCl) but then increases probably due to the formation of chloro-complexes.

Arsenious oxide is a reducing agent and is readily oxidized to As(V) by ozone, H_2O_2, halogens, hypochlorite, Fe (III) etc. The actual potential of the system depends largely on the pH (Section 9.2.6).

$$AsO_4^{3-} + 2H^+ + 2e \rightleftharpoons AsO_3^{3-} + H_2O \qquad E_0 = 0.56\ V$$

$$As_4O_6 + 4Cl_2 + 10H_2O = 4H_3AsO_4 + 8HCl$$

$$As_4O_6 + 4FeCl_3 + 10H_2O = 4H_3AsO_4 + 8FeCl_2 + 8HCl.$$

I_2 may be estimated quantitatively by As_4O_6 as primary standard (dissolved in dilute NaOH) in presence of sodium bicarbonate (section 9.2.6). Borax-boric acid or Na_2HPO_4-NaH_2PO_4 buffer may also be used.

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

Fehling's solution is reduced to red Cu_2O (boiling) :

$$2Cu^{++} + AsO_3^{3-} + 4OH^- = Cu_2O + AsO_4^{3-} + 2H_2O.$$

As_4O_6 is reduced to black elemental arsenic on heating with charcoal, or in solution by Sn(II) or on boiling with copper foils and HCl :

$$As_4O_6 + 6SnCl_2 + 12HCl = As_4 + 6SnCl_4 + 6H_2O \qquad (\textit{Bettendorff's test}).$$

$$As_4O_6 + 12Cu + 12HCl = As_4 + 12CuCl + 6H_2O.$$

As_4O_6 may be reduced to AsH_3 by KBH_4 in alkaline solution.

The common crystalline form of arsenious oxide and its vapour upto 800°C contains As_4O_6 molecules isostructural with P_4O_6. At higher temperatures, partial dissociation into As_2O_3 begins. Another crystalline variety (monoclinic) of the oxide has a lattice structure of AsO_3 pyramids joined through oxygen atoms.

Arsenious oxide is highly poisonous - lethal dose ~ 0.1 g. It is a cumulative poison, i.e. it accumulates in the body, particularly in hairs and nails.

Arsenic Pentoxide, As_2O_5 is difficult to obtain by direct reaction of arsenic with O_2. Oxidation of As or As_2O_3 with concentrated nitric acid results in arsenic acid. The hydrated crystals may be dehydrated by heating at 200°C to obtain As_2O_5 as a white deliquescent solid. It is also formed by heating As or As_2O_3 with O_2 under pressure.

The oxide loses oxygen when heated to about 300°C to form the trioxide. It is deliquescent and highly soluble in water forming arsenic acid.

$$As_2O_5 + 3H_2O = 2H_3AsO_4.$$

It is a strong oxidizing agent, liberating chlorine form HCl.

$$As_2O_5 + 10HCl = 2AsCl_3 + 5H_2O + 2Cl_2$$

The structure of As_2O_5 consists of equal numbers of AsO_6 octahedra and AsO_4 tetrahedra linked by sharing corners.

Antimony Oxide Sb_4O_6 is prepared by heating antimony in oxygen. The white powdery solid becomes yellow on heating. It is insoluble in water and amphoteric in nature. It dissolves in bases to produce solution of antimonate(III) ("antimonites"). Only a few metaantimonites and polyantimonites are known eg. $NaSbO_2$, $NaSb_3O_5$, H_2O and $Na_2Sb_4O_7$. Sb_4O_6 is insoluble in dilute nitric or sulphuric acids, but dissolves in hot concentrated sulphuric acid to form $Sb_2\ (SO_4)_3$. It also dissolves in dilute HCl and in tartaric acid.

Sb_4O_6 is oxidized by I_2 and may be titrated in tartaric acid soluion :

$$Sb_4O_6 + 4H_2O + 4I_2 = 2Sb_2O_5 + 8HI$$

The vapour of antimony (III) oxide consists of Sb_4O_6 molecules similar to P_4O_6. This is also present in the cubic form of the solid (upto about 570°C). At higher temperature, a polymeric orthorhombic form containing Sb_2O_3 is obtained which melts at about 655°C.

Sb_4O_6 is used in large quantities (over 10,000 tonnes yearly) in industry as flame retardant in fabrics, paper, paints, plastics, adhesives and rubbers.

Antimony pentoxide, Sb_2O_5, is obtained as a yellow powder by the action of oxygen at high pressure and temperature on Sb_2O_3. It is also formed by hydrolysis of $SbCl_5$ with aqueous ammonia followed by delydration of the product at 275°C. It is almost insoluble in water but reddens damp litmus. Fusion with KOH yields potassium antimonate, $KSb(OH)_6$ (see oxoacid salts). Sb_2O_5 also dissolves in cold HCl to give $SbCl_5$ which liberates I_2 from KI. The structure consists of octahedral SbO_6 groups.

SbO_2 is formed as a white insoluble powder on heating Sb_4O_6 or Sb_2O_5 in air at 900°C. It consists of octahedral Sb^VO_6 and pyramidal $Sb^{III}O_4$ units.

Bismuth trioxide Bi_2O_3 is obtained as a pale yellow powder by burning bismuth in oxygen. It is insoluble in water and alkalis and has no acidic character. It dissolves in acids to give solutions of salts containing Bi(III) cations. From this $Bi(OH)_3$ is precipitated by ammonia and alkali solutions. The oxide exists in several structural modifications. The common monoclinic variety stable at room temperature (up to or 700°C) has a polymeric layer structure. A cubic form is obtained above this temperature which melts at about 825°C.

The oxide is used to make some optical glasses and to give white glaze on porcelain.

Bi_2O_5 has never been obtained pure. Action of strong oxidizing agents like Cl_2 on a suspension of Bi_2O_3 in concentrated alkali gives a red-brown powder which rapidly loses oxygen at 100°C. The solution also precipitates hydrated "Bi_2O_5" on acidification with dilute nitric acid. The oxide dissolves in sulphuric and nitric acids liberating oxygen and in hydrochloric acid liberating chlorine :

$$Bi_2O_5 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O + O_2$$

22.3.5 Oxoacids and their salts

The oxo-acids of nitrogen involve nitrogen-oxygen p-p π-bonding. There are no direct analogues of these acids among phosphorus, arsenic etc. elements as they cannot form strong p-p π-bonds with oxygen. Phosphorus has a rich chemistry of condensed phosphates.

Oxo-acids of nitrogen

Nitric acid appears to be the only stable oxo-acid of nitrogen. Among other weak as well as unstable oxo-acids, some are known in solution and/or as salts. The principal oxoacids are summarized below.

TABLE 22.12

Oxoacids of nitrogen

$H_2N_2O_2$ Hyponitrous acid	Weak acid, HON = NOH. Reduction of *aq* $NaNO_2$ (Na-Hg) $\longrightarrow$ $Na_2N_2O_2$ (see text).
$H_2N_2O_3$ Hyponitric acid (Oxyhyponitrous)	Known in solution and salt. $NH_2OH + BuONO_2 + NaOMe$ in MeOH at 0°C $\longrightarrow Na_2[ON = NO_2]$ Sodium hyponitrate (trioxodinitrate); *Angeli's salt.*
$H_4N_2O_4$ Nitroxylic acid (hydronitrous)	Explosive. Reduction of $NaNO_2$ (Na in liq. NH_3) $\longrightarrow$ $Na_4[O_2NNO_2]$ (deep yellow).
HNO_2 Nitrous acid.	Unstable weak acid. Stable salts (See text).
HOONO Peroxonitrous acid	Unstable intermediate during oxidation of NO_2^- to NO_3^- by H_2O_2. The ion (yellow) is stable in alkaline medium but pure salts not isolated.
HNO_3 Nitric Acid	Stable strong acid (See text).
$HOONO_2$ Peroxonitric acid	Unstable. HNO_3 or N_2O_5 + 90% H_2O_2. No solid salts known.
H_3NO_4 (Orthonitric acid; unknown)	Na_3NO_4 and K_3NO_4 prepared in 1977. $NaNO_3 + Na_2O$ (heated to 300°C for 7 days). X-ray study shows regular Td symmetry in NO_4^{3-} ion (N–O = 1.39 A°).

Hyponitrous acid : Hyponitrites may be prepared by reduction of aqueous $NaNO_2$ or $NaNO_3$ with Na-Hg (or Mg-Hg).

$$2NaONO + 4H \longrightarrow NaON = NONa$$

The reduction is carried out by shaking in a separating funnel for about an hour. The mercury is then run off and the solution filtered. The filtrate gives crystals of $Na_2N_2O_2$, $5H_2O$ in a vacuum desiccator over conc. H_2SO_4. These are washed with alcohol and ether to anhydrous $Na_2N_2O_2$ which is fairly stable in air. An aqueous solution of $Na_2N_2O_2$ precipitates yellow $Ag_2N_2O_2$ with silver nitrate.

The free acid is obtained by treating silver hyponitrite with anhydrous HCl in ether. The AgCl is filtered out and the ether evaporated (vacuum), when white crystals of $H_2N_2O_2$ are obtained.

Crystalline hyponitrous acid is explosive when dry; the acid is stable in solution but slowly decomposes to N_2O on acidification. (pH < 4).

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

(But N_2O is not the anhydride of the acid). Decomposition is very fast (minutes) between pH 4-14 due to base catalyzed decomposition

$$HONNOH \longrightarrow HONNO^- \longrightarrow OH^- + N \equiv N = O.$$

$H_2N_2O_2$ is a weak dibasic acid, $pK_1 = 6.9$, $pK_2 = 11.6$ (comparable to "carbonic acid"). Both acid and normal salts are known, e.g., Ba $(HN_2O_2)_2$ and $Na_2N_2O_2$.

The salts and esters of the acid decompose on heating :

$$3Na_2N_2O_2 = 2NaNO_2 + 2Na_2O + 2N_2 \ldots\ldots \text{(explosively at 200°C).}$$

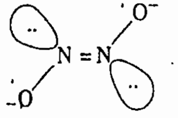
Hyponitrites are reducing agents :

$$[ONNO]^{2-} + 3I_2 + 3H_2O \longrightarrow NO_3^- + NO_2^- + 6HI$$

$$5[ONNO]^{2-} + 8MnO_4^- + 24H^+ \longrightarrow 10NO_3^- + 8Mn^{2+} + 12H_2O$$

It is likely that the oxidation of ammonia to nitrite or N_2O in nature proceeds through hydroxylamine and hyponitrous acid.

The dimeric nature of hyponitrous acid is supported by several factors : (i) existence of acid and normal salts; (ii) decomposition to N_2O (also N_2 from esters and salts); (iii) cryoscopic data (iv) zero dipole moment of the diethyl ester and (v) Raman and infra-red spectroscopic studies. Points (iv) and (v) also confirm the *trans* configuration (C_{2h}) of the hyponitrite ion (22-XXI).



22-XXI

The structure is consistent with sp^2 hybridization of both N-atoms. The *p*-orbital excluded from hybridization forms a π-bond between the N atoms.

$H_2N_2O_2$ is isomeric with *nitramide*; $H_2N{-}NO_2$ (see later).

Nitrous acid : The free acid is very unstable and unknown in the liquid state. A dilute aqueous solution may be obtained by adding dilute H_2SO_4 to an ice-cold solution of barium nitrite (see below for preparation).

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HNO_2$$

When the presence of other salts does not interfere, a solution may be obtained simply by acidifying $NaNO_2$(aq) below 0°C.

HNO_2 gas may be prepared by the rapid equilibrium

$$NO + NO_2 + H_2O = 2HNO_2 \qquad K\ (293K) = 1.56\ atm^{-1}$$

Nitrites may be pepared by mild reduction of nitrates or by absorbing "nitrous fumes" in aqueous alkali. Other nitrites may be made by metathesis :

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO\ (melt)$$

$$Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2\ (aq)$$

$$Ba(OH)_2 + NO + NO_2 \longrightarrow Ba(NO_2)_2 + H_2O\ (aq)$$

$$NaNO_2 + AgNO_3 \longrightarrow AgNO_2 + NaNO_3\ (aq)$$

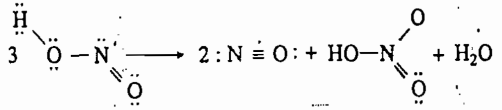
Nitrites of alkali and alkaline earth metals, Ag, Tl(I), NH_4 as well as of Co(II), Ni(II), Hg(II) etc. are known. The salts usually have faint yellow tinge but those of Co(II), Ni(II) and Hg(II) are often highly coloured indicating essentially covalent assembly of the polarizable nitrite group. The role of polarization is also reflected in the varying thermal stability of the salts (compare to the carbonates/bicarbonates) (Q. 22.8).

Q. 22.8 *$NaNO_2$ (m.p. 284°C) and KNO_2 (m.p. 441°C) may be fused without decomposition but $Ba(NO_2)_2$ decomposes above 220°C; $Mg(NO_2)_2$ decomposes slowly even at room temperature; $AgNO_2$ above 140° and $Hg(NO_2)_2$ above 75°. Comment.*

Nitrous acid is a weak acid [pK_a (298K) = 5.2]. Its aqueous solution is unstable — decomposition is rapid when heated :

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + H_2O + 2NO$$

This disproportionation of HNO_2 is accompanied by a net increase in π-bonds keeping the number of N—OH bonds unchanged. Assigning a π-bond order of 1.5 for NO, we get (2 × 1.5 + 1) i.e., 4 π-bonds at the cost of 3 π-bonds. The effective repulsion between the lone pairs of electrons on N and O is also reduced. The redox behaviour of HNO_2 also follows from this approach — it may be oxidized to HNO_3 or reduced to NO.



$$3\ H{-}\ddot{O}{-}\ddot{N}{=}\ddot{O} \longrightarrow 2:N\equiv O: + HO{-}N(=O){=}\ddot{O} + H_2O$$

Nitrous acid and nitrites can behave both as an oxidizing and a reducing agent :

oxidizing : $HNO_2 + H^+ + e = NO + H_2O \qquad E° = 1.0\ V$

reducing : $NO_3^- + 3H^+ + 2e = HNO_2 + H_2O \qquad E° = 0.94\ V$

HNO_2 oxidizes Fe(II), I^-, As(III) and Hg (in presence of H_2SO_4) and itself gets reduced to NO :

$$2KI + 2KNO_2 + 2H_2SO_4 = 2K_2SO_4 + I_2 + 2NO + 2H_2O$$

$$2Hg + 2KNO_2 + 2H_2SO_4 = Hg_2SO_4 + K_2SO_4 + 2NO + 2H_2O$$

Sn(II) reduces it to $H_2N_2O_2$ ($H_2O + N_2O$), SO_2 reduces it to NO and N_2O; and H_2S reduces it to NH_3. Hydrazinium salts are converted to azides which react further with HNO_2 :

$$HNO_2 + N_2H_5^+ \longrightarrow HN_3 + H_2O + H_3O^+$$

$$HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2O.$$

Use of ^{15}N shows that all the nitrogen from HNO_2 forms the middle nitrogen atom in N_2O :

$$HN_3 + HO^{15}NO \xrightarrow{-H_2O} [NNN^{15}NO] \longrightarrow NN + N^{15}NO.$$

Nitrous acid and nitrites appear to be kinetically faster oxidizing agents than HNO_3/NO_3^- in dilute aqueous solution in spite of comparable reduction potential values (see under nitric acid). Thus, a dilute aqueous solution of $NaNO_2$ readily liberates iodine from iodides in acid medium, whereas dilute HNO_3 (< 2M) or nitrates do not give this reaction.

The rate of oxidation by NO_2^- is greatly enhanced in presence of acids which help formation of the nitrosonium cation :

$$HNO_2\,(aq) + H^+\,(aq) \longrightarrow NO^+\,(aq) + H_2O$$

The NO^+ cation acts as a Lewis acid and readily combines with the species undergoing oxidation, essentially an electron-rich Lewis base. Thus, at low pH the oxidant in nitrite is a different species, NO^+, while at higher pH the species is NO_2^-.

Urea, sulphamic acid and ammonium chloride reduces HNO_2 to N_2 — the reactions are used in analysis to destroy nitrites in presence of nitrates.

Nitrites behave as reducing agent to strong oxidizing agents like H_2O_2, Br_2, $KMnO_4$ - acid (*estimation*) :

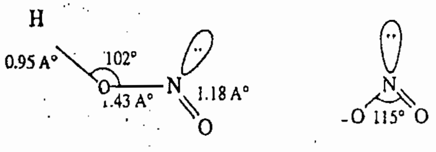
$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O.$$

Silver bromate is quantitatively reduced to silver bromide (*gravimetric estimation*) :

$$AgBrO_3 + 3HNO_2 = AgBr + 3HNO_3.$$

HNO_2 participates in a large number of interesting reactions in organic chemistry, particularly those involving aliphatic and aromatic amines. These are not discussed here.

The structure of the gaseous HNO_2 molecule has been established through microwave spectroscopy. It has the planar *trans* configuration shown (22-XXII a). The nitrite ion is planar (22-XXII b), consistent with sp^2 hybridization at N.



(a) (b)

22-XXII

Sodium nitrite is mildly toxic. Earlier it has been widely used for curing meat. It is now largely used in the synthesis of hydroxylamine and in making azo dyes.

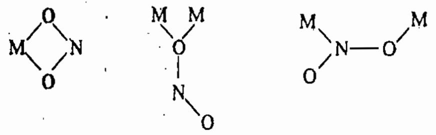
The NO_2^- ion can coordinate to metals either through N ("nitro" complexes) or through O ("nitrito" complexes) e.g.,

$[Co(NH_3)_5NO_2]^{2+}Cl_2$ *yellow*

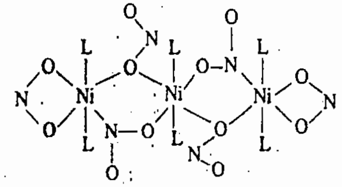
$[Co(NH_3)_5(ONO)]^{2+}]Cl_2$ *red*

The nitrito form is usually less stable and tends to get converted to the nitro isomer (See linkage isomerism). Chelating and bridging modes of coordination are also known.

The nitrite ion can coordinate in three other ways, shown schematically as :



All three of these coordination modes are present in the complex salt $Ni_3(3\text{-methylpyridine})_6(NO_2)_6$:



22-XXIII

Nitric acid : This is one of the most widely used heavy chemicals (see use) produced in millions of tonnes each year. The laboratory preparation involves distillation of $NaNO_3$ or KNO_3 with concentrated H_2SO_4. It is manufactured by catalytic oxidation of NH_3 by Ostwald process : (i) air with ~ 10% (vol) NH_3 is passed quickly (0.001 s time of contact) over (ii) Pt gauze catalyst (10% Rh reduces loss of Pt) at (iii) ~ 850° C and (iv) 5 atm pressure. (v) The NO formed gets automatically oxidized to NO_2 by excess air. This is (vi) absorbed in water (~ 40°C) to yield 60% solution of HNO_3. This may be concentrated by distillation to about 68.5% by weight (constant-boiling mixture or azeotrope; 122°C).

This is the commercial acid of specific gravity 1.414. It may be concentrated to 98% by distillation with conc. H_2SO_4 or conc. $Mg(NO_3)_2$ solutions.

Pure HNO_3 can be obtained by reacting KNO_3 with 100% H_2SO_4 at 0°C and removing the HNO_3 by vacuum distillation.

Pure nitric acid is a colourless liquid, freezing point – 41.6°C and boiling point 82.6°C (1 atm), sp. gravity 1.5. The pure acid and its concentrated aqueous solutions undergo photochemical decomposition and turns brown by absorbing the liberated NO_2

$$4HNO_3 \xrightarrow{h\nu} 4NO_2 + 2H_2O + O_2.$$

Pure HNO_3 has a high dielectric constant ($\varepsilon = 50 \pm 10$ at 14°C) and is a good ionizing solvent for electrolytes. It has the highest self-ionization among the pure liquid acids :

autoprotolysis : $2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$

rapid loss of H_2O : $H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$

overall : $2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$

Addition of water represses the autoprotolysis. At –10°C, conductivity decreases from 3.67×10^{-2} to 1.08×10^{-2} (both $ohm^{-1}\ cm^{-1}$) at 1.75 molal H_2O but again rises due to increased ionization as

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

Anhydrous nitric acid is a good ionizing solvent for electrolytes but solubility is mainly limited to salts producing NO_2^+ or NO_3^- ions.

N_2O_4 ionizes almost completely in anhydrous HNO_3 to give NO^+ and NO_3^- (no evidence for NO_2 or NO_2^+ by Raman spectroscopy).

In dilute aqueous solutions (below 2*M*) nitric acid behaves as a typical strong acid and has little oxidizing power. Dissociation is nearly 93% at 0.1*M* concentration. Only magnesium and manganese liberate hydrogen from very dilute solutions of nitric acid.

Q. 22.9 *In concentrated sulphuric acid, HNO_3 behaves as a base. Write the ionization steps.*

Ans. :

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$
$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$
$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$
$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

[Sec. 22.3.5 Oxoacids]

In concentration greater than 2*M*, nitric acid is a powerful oxidizing agent and attacks most metals except gold, platinum, iridium, rhodium and rhenium. Cr, Al, Fe (and to some extent Cu) are rendered passive by the concentrated acid due to formation of an oxide film. In its reaction with metals, the metal is usually converted to the nitrate and nitric acid is reduced to NO_2 (hot concentrated), NO (cold 1 : 1) or N_2O (cold very dilute). Tin, arsenic, antimony and a few transition metals are converted to their oxides. The concentrated acid also oxidizes S (SO_2), C (CO_2), I_2 (HIO_3) and P (H_3PO_4). A mixture of conc. HNO_3 (3 vol) and conc. HCl (1 vol) is known as *aqua regia* and dissolves gold and platinum metals through the action of nascent chlorine and ClNO aided by the complexing ability of the Cl^- ion.

Q. 22.10 *Tantalum (Ta) and a few metals are quite resistant to HNO_3 but dissolve rapidly if HF is also present. Suggest an explanation.*

Hint : Stable complex species like TaF_6^- are formed.]

A dilute solution of nitric acid (< 2*M*) or nitrates does not liberate iodine from acidified iodide solution but a dilute solution of HNO_2 or a nitrite readily does so. $E°$ for the half-reactions.

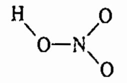
$$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O \qquad E° = 0.94\ V$$

$$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O \qquad E° = 1.00\ V$$

are nearly equal and well above that of the I_2/I^- system (0.54 V). Hence one must conclude that HNO_2 is a kinetically faster rather than a more powerful oxidizing agent than a dilute solution of HNO_3.

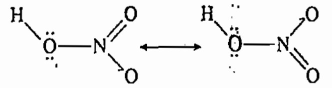
Red fuming nitric acid contains dissolved N_2O_4 and is a superior nitrating agent. A mixture of concentrated nitric and sulphuric acids is also used as a nitrating agent as it contains the nitronium ion, NO_2^+.

The gaseous HNO_3 molecule has the planar structure shown (microwave spectroscopy), 22-XXIV. The same general structure probably holds for the solid also.



22-XXIV

The N—O distances in the NO_2 group are equal. The third N—O distance is longer and corresponds to a single bond. The NO_2 group is tilted away from the H-atom by 2°. The structure is consistent with roughly sp^2 hybridization at the N-atom involving the VB structures :



The nitrate ion is symmetrical planar with all ONO bond angles equal to 180° and N—O distances equal to 1.22 Å°, consistent with a bond order of 1 and 1/3 (π-bond order 1/3; sp^2 hybridization).

Uses

The main consumption (≃ 80%) of nitric acid is in the manufacture of NH_4NO_3. It is chiefly used as a fertilizer, but is also used as an explosive in mining and quarrying.

Nitric acid is also used (5 - 10%) in making cyclohexanone and caprolactam as a route to nylon.

5 - 10% use of HNO_3 is confined to nitration reactions to produce nitroglycerine, nitrocellulose, trinitrotoluene (TNT) etc.

The acid is also used in pickling of metal surface, as oxidizer in rocket fuel and in the manufacture of various nitrates.

Nitrate salts are known for almost all metallic elements. They may be prepared, mostly hydrated, by reacting the metal or its oxide with nitric acid. Anhydrous metal nitrates may be prepared in liquid N_2O_4 (see before) or by the reaction of liquid N_2O_5 with an oxide or chloride of the metal :

$$TiCl_4 + 4N_2O_5 \longrightarrow Ti(NO_3)_4 + 2N_2O_4 + 2Cl_2.$$

The normal metal nitrates are all soluble in water. Basic nitrates of Bi and Hg are insoluble in water, but they dissolve in dilute HNO_3. Many anhydrous metal nitrates sublime without decomposition e.g., $Cu(NO_3)_2$ and the alkali metal nitrates (in vacuum at 350° - 500°C). These are also soluble in organic solvents.

Thermal stability of the nitrates varies with the basic character of the metal in the same fashion as is found with salts of other oxoacids. Thus the decomposition temperature (for $p_{O_2} = 1$ atm) increases slowly from $LiNO_3$ (4.74°C) to $CsNO_3$. The end-product may be nitrite, oxide or metal depending upon their relative stability.

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

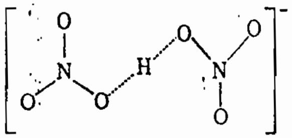
$$2KNO_3 \longrightarrow K_2O + N_2 + \tfrac{5}{2}O_2$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

NH_4NO_3 decomposes to N_2O (200° - 260°) or $N_2 + O_2$ (> 300°) depending upon the temperature.

A number of hydrogen dinitrates and dihydrogen trinitrates have been reported with hydrogen-bridged anions, e.g., the anion in $[AsPh_4]^+ [H(NO_3)_2]^-$ has the structure :



28-XXV

Fluorine nitrate, FNO_3 is formed by the action of F_2 on dilute HNO_3 or KNO_3. It is an explosive gas (b.p. −46°C) which reacts slowly with water as

$$2FONO_2 + 2H_2O \longrightarrow 2HNO_3 + 2HF + O_2$$

The reaction becomes rapid in presence of alkali. Its structure may be derived by replacing the hydrogen in HNO_3 by F.

The **orthonitrates** Na_3NO_4 and K_3NO_4 have been prepared as crystals by prolonged heating (300°C, 7 days) of $NaNO_3/KNO_3$ and Na_2O (K_2O) in a silver crucible. The compounds are very sensitive to moisture and CO_2 :

$$Na_3NO_4 + H_2O + CO_2 \longrightarrow NaNO_3 + NaHCO_3 + NaOH.$$

X-ray study shows that the anion has the tetrahedral structure with N—O distance 1.39 A°, consistent with a bond order of unity. Actually no π- bonding is possible in these ions as there are no energetically accessible orbitals on N suitable for such bonding. The slight shortness of the bonds may be associated with polar interactions in the N—O bonds.

[Sec. 22.3.5
Oxoacids]

The NO_3^- ion can function as a coordinating ligand, often in a symmetrical bidentate mode as in $Cu(NO_3)_2$, $Cu(NO_3)(PPh_3)_2$ and $Co(NO_3)_3$. When NO_3^- is coordinated, its effective symmetry is reduced; the coordinated NO_3 groups may then be distinguished by ir bands. Unsymmetrical bidentate coordination, unidentate coordination and bridging coordinations are also possible.

A convenient way of preparing nitrato-complexes involves reaction in liquid N_2O_4. In presence of tetraethyl ammonium nitrate (a base in N_2O_4), zinc and aluminium dissolves in liquid N_2O_4 to form 8-coordinate complexes :

$$Zn + 2Et_4NNO_3 + 2N_2O_4 \longrightarrow (Et_4N)_2\ [Zn(NO_3)_4] + 2NO$$

As mentioned before, organic donor molecules increase ionization of the solvent; copper, iron and zinc dissolve in presence of acetonitrile (CH_3CN) or ethyl acetate to form complexes NO [Cu $(NO_3)_3$], NO [Fe $(NO_3)_4$] and $(NO)_2$ [Zn $(NO_3)_4$] respectively.

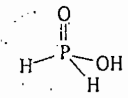
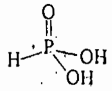
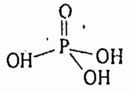
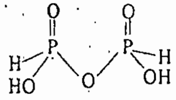
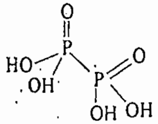
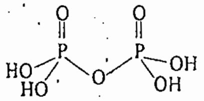
$$Cu + 3N_2O_4 \longrightarrow NO\,[Cu(NO_3)_3] + 2NO.$$

Oxo-acids of Phosphorus

Phosphorus forms a vast number of oxo-acids and anions some of which are very important in industry and in biological systems. We shall study the structural principle underlying this large domain followed by a brief survey of the chemistry of some representative species. The structural principles, summarized below, are illustrated in Table 22.13.

TABLE 22.13

Oxoacids of Phosphorus

H_3PO_2 (Hypophosphorus acid)		White P+ alkali. Monobasic, strongly reducing. (See text)
H_3PO_3 (Phosphorus acid)		P_4O_6 or $PCl_3 + H_2O$. Dibasic, reducing. (See text).
H_3PO_4 (Phosphoric acid)		P_4O_{10} or $PCl_5 + H_2O$. Tribasic. (See text).
$H_4P_2O_5$ (Pyrophosphorus acid)		Heating phosphite. Dibasic, reducing.
$H_4P_2O_6$ (Hypophosphoric acid)		Oxidation of red P or P_2I_4 in alkali. Tetrabasic, resistant to oxidation (see text).
$H_4P_2O_7$ (Pyrophosphoric acid)		Heating H_3PO_4

(i) In all oxoacids and anions, the P-atoms are 4-coordinate with at least one P = O unit.

(ii) All oxoacids have at least one P–OH group in which the hydrogen atom is ionizable. The number of P–OH groups thus effectively determine the ultimate basicity of an acid.

(iii) Some oxoacids (or ions) may have one or more P–H groups; such hydrogen atoms are not ionizable. In the phosphorus(V) acids, all four bonds from P are to oxygen. Replacement of one P—OH bond by a P—P bond lowers the oxidation state by 1, replacement by a P—H bond reduces the oxidation state by 2.

(iv) Catenation may occur by direct P—P bonds or P–O–P links. The linear and cyclic polyphosphoric acids contain P–O–P links through corner sharing of tetrahedral units.

Besides these, there are a large number of condensed phosphate systems. These will be discussed separately.

Hypophosphorus acid, H_3PO_2 ("Phosphinic acid")

The hypophosphite ion is produced in solution by boiling white phosphorus with strong aqueous alkali; phosphite and phosphine are also formed :

$$P_4 + 4OH^- + 4H_2O \longrightarrow 4H_2PO_2^- + 2H_2$$

$$P_4 + 4OH^- + 2H_2O \longrightarrow 2HPO_3^{2-} + 2PH_3.$$

The phosphite may be removed as insoluble $CaHPO_3$. H_3PO_2 is now generated in solution on acidification. Pure H_3PO_2 is obtained from this solution by continuous extraction into diethyl ether. Evaporation of ether gives white crystals, m.p. 26.5°C. The free acid can also be made by oxidation of phosphine with iodine in water.

$$PH_3 + 2I_2 + 2H_2O = H_3PO_2 + 4HI.$$

The pure acid cannot be isolated by evaporation of its aqueous solution as it is readily oxidized to phosphorous and phosphoric acids and also undergoes disproportionation to PH_3 and H_3PO_3. Its salts also disproportionate on heating.

$$3H_2P(O)OH = PH_3 + 2HP(O)(OH)_2$$

As evident from its structure, $H_2P(O)OH$ (Table 22.13), the acid is monobasic ($pK = 1.1$).

Hypophosphorus acid and hypophosphites are strongly reducing :

$$H_3PO_2 + 4AgNO_3 + 2H_2O = H_3PO_4 + 4Ag + 4HNO_3$$

$$3H_3PO_2 + 2CuSO_4 + 3H_2O = 3H_3PO_3 + 2CuH + 2H_2SO_4$$

Also, $H_3PO_2 + H_2O + Cu^{++}(aq) = H_3PO_3 + Cu^{\circ} + 2H^+(aq)$

$$E^{\circ} = (0.499 + 0.340)\ V = 0.839\ V$$

A solution of NaH_2PO_2, H_2O is used in deposition of Ni on both metals and nonmetals (**electrodeless plating**) — the material is dipped in a solution containing Ni(II) (10-30 g/l of $NiCl_2$ or $NiSO_4$) and NaH_2PO_2 (10-50 g/l). Acid solutions (pH 4-6; temp ~ 90°C) are used in plating other metals; plastics and other nonconducting materials are plated from an alkaline solution (pH 7-10; 25°-50°C). Though more expensive than electroplating, the process is useful when intricate shapes and non-conducting substances are to be plated.

As shown earlier, the acid and the hypophosphite ion are tetrahedral — involving sp^3 hybridization of the P-atom after unpairing the *s*-pair and promotion of an electron to one of the 3*d*-orbitals. This orbital then forms a *d*—*p* π-bond with the oxygen.

The systematic name of H_3PO_2, *phosphinic acid*, is hardly used. The compounds formed by replacement of H by R groups, i.e., $R_2P(O)OH$ are called phosphinous acids and the salts phosphinates.

Phosphorous acid, H_3PO_3 (phosphonic acid)

The acid is readily obtained by hydrolysis of PCl_3 or P_4O_6 in cold CCl_4 solution.

$$PCl_3 + 3H_2O \longrightarrow 3HCl + P(OH)_3 \longrightarrow HP(O)(OH)_2$$

The rearrangement involving replacement of a P—OH bond (P—O and O—H) by a P–H plus a P = O involves better utilization of the valence of P and is energetically favourable. [As $(OH)_3$ does not isomerize in this manner presumably due to weak bond energies); $P(OMe)_3$ also isomerizes to $MeP(O)(OMe)_2$ but some $P(OR)_3$ are stable (see later).

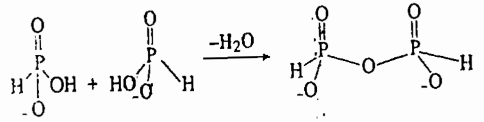
H_3PO_3 is also formed when PCl_3 is heated with oxalic acid :

$$PCl_3 + 3(COOH)_2 = H_3PO_3 + 3CO + 3CO_2 + 3HCl$$

The acid forms colourless deliquescent crystals (m.p. 70.1°C) with H-bonded network. The acid is dibasic ($pK_1 = 1.8, pK_2 = 6.7$) and disproportionates on heating :

$$4H_3PO_3 \longrightarrow PH_3 + 3H_3PO_4 \quad (200°C)$$

The acid phosphites on dehydration under reduced pressure produce *pyrophosphites* with P–O–P bridge: the free acid is unknown.

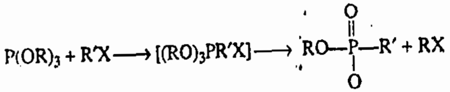


The acid is reducing in nature, reducing SO_2 (S), $CuSO_4$ (Cu), $AgNO_3$ (Ag) etc.

$$H_3PO_3 + 2AgNO_3 + H_2O = H_3PO_4 + 2Ag + 2HNO_3$$

The systematic name of H_3PO_3 (Phosphonic acid) is actually used when the P—H bond is replaced by P—R. $RP(O)(OH)_2$ are called phosphonic acids and their salts phosphonates.

Trimethyl phosphite $P(OMe)_3(PCl_3 + MeOH)$ spontaneously isomerizes to methyl dimethylphosphonate $MeP(O)(OMe)_2$. Other trialkyl phosphites react with alkyl halide to diesters of phosphonic acids (***Michaelis-Arbusov reaction***) :



$$P(OR)_3 + R'X \longrightarrow [(RO)_3PR'X] \longrightarrow RO\!-\!\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}\!-\!R' + RX$$

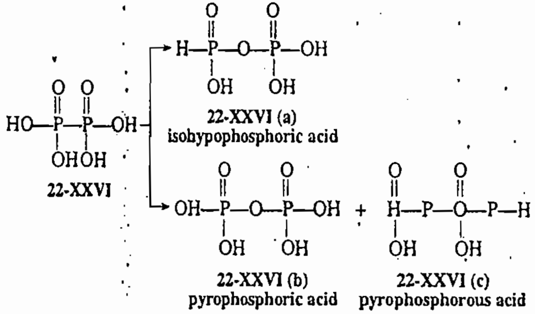
Hypophosphoric acid, $H_4P_2O_6$ (diphosphoric(IV) acid)

$Na_2H_2P_2O_6$, $6H_2O$ is obtained by controlled oxidation of red phosphorus with sodium chlorite solution (room temperature) followed by crystallization around pH 5 :

$$2P + 2NaClO_2 + 8H_2O \longrightarrow Na_2H_2P_2O_6, 6H_2O + 2HCl.$$

$Na_4P_2O_6$, $10H_2O$ crystallizes at pH 10. $H_4P_2O_6$, $2H_2O$ may be obtained from these salts by ion exchange. The anhydrous acid may be obtained by vacuum dehydration of the dihydrate (over P_4O_{10}). Or one may precipitate $Pb_2P_2O_6$ from a solution of the sodium salt and then carry out double decomposition with H_2S (– PbS).

Both the anhydrous acid and its dihydrate are stable in absence of moisture at 0°C. At higher temperature it undergoes slow decomposition and/or isomerization :



The acid melts (with decomposition) at 73°C. It is tetrabasic, successive *pK* values (25°C) are 2.2, 2.8, 7.3 and 10.0. It has no reducing action on metallic salts.

The acid is dimagnetic and has a P—P bond as shown in 22–XXVI. The structure of isohypophosphoric acid (22-XXVI) has been confirmed by ^{31}P nmr studies; the P—H bond is also supported by Raman spectroscopy. It may be prepared directly by hydrolyzing PCl_3 with stoichiometric quantities of H_3PO_4 and H_2O at 50°C. Dehydration of equimolar mixture of $Na_2HPO_4 . 12H_2O$ and $NaH_2PO_3 . 2.5H_2O$ at 180°C gives $Na_3 [HP_2O_6]$.

Phosphoric acid, H_3PO_4, (orthophosphoric acid)

It is the simplest oxoacid of phosphorus(V). Pure phosphoric acid is now prepared by burning phosphorus in a mixture of air and steam in a stainless steel chamber.

$$P_4 + 5O_2 \longrightarrow P_4O_{10} ; \quad P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4.$$

Usual commercial grades contain 80-85% H_3PO_4, but the method may be used to obtain anhydrous H_3PO_4.

The older process of digesting phosphate rock with sulphuric acid is also used to manufacture the acid for use in metallurgy, fertilizer etc.

$$3Ca_3(PO_4)_2 . CaF_2 + 10H_2SO_4 + 20H_2O \longrightarrow 6H_3PO_4 + 10CaSO_4 . 2H_2O + 2HF:$$

The gypsum formed and other insoluble matter like silica are filtered out; HF is separated as insoluble Na_2SiF_6. The acid containing 35-70% H_3PO_4 may be concentrated by evaporation. It contains many impurities e.g. combined Na, Mg, Ca, Al, Fe as well as sulphates and fluorides.

Pure H_3PO_4 forms colourless crystals (m.p. 42°C). The molten acid has appreciable electrical conductivity owing to self-ionization (autoprotolysis).

$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$$

Partial dehydration also occurs, though only slowly at room temperature :

$$2H_3PO_4 \longrightarrow H_2O + H_4P_2O_7$$

The acid is tribasic, successive *pK* values (25°C) being 2.1, 7.1 and 12.4 (approx). Titration of the acid has been discussed in Chapter 11 (section 11.4.2).

Phosphoric acid has ordinarily no oxidizing property, consistent with the stability of P(V). At elevated temperatures (350-400°C), H_3PO_4 is reduced by metals. Phosphoric acid and the phosphate group form complexes with several transistion metal ions — they may act as monodentate, chelating or bridging ligand.

[Sec. 22.3.5 *Salts of oxoacids*]

Crystalline phosphoric acid has a H-bonded layer structure of tetrahedral PO_4 units, P = O : 1.52 A°; P–O (H) : 1.57 A° : Concentrated solutions also contain extensive H-bonding, which gives rise to its syrupy nature. In dilute solutions, H-bonding with water molecules become more extensive.

Orthophosphates are formed by numerous metals and other cations. Different acid salts as well as hydrates are also known. Naturally occurring phosphates are all orthophosphates. The alkali metal and ammonium phosphates are soluble in water, while others are sparingly soluble. Phosphates of Ce(IV), Th(IV), Zr(IV), U(IV) etc. tetrapositive heavy metals are insoluble even in 4*M* HCl or HNO_3.

The sodium phosphates are prepared as follows :

Na_2HPO_4, $12H_2O$ is crystallized from a solution obtained by neutralizing H_3PO_4 with NaOH solution using phenolphthalein (solution turns pink). It is the *ordinary laboratory sodium phosphate.*

NaH_2PO_4, H_2O is made by adding calculated quantity of H_3PO_4 to a solution of the secondary phosphate, Na_2HPO_4, followed by crystallization.

Na_3PO_4, $12H_2O$ is made by dissolving Na_2HPO_4, $12H_2O$ in excess NaOH solution and crystallizing.

$NaNH_4HPO_4$, $4H_2O$ (*microcosmic salt*) deposits when concentrated solutions of NH_4Cl and Na_2HPO_4 are mixed hot and slowly cooled. On heating, it sets to a transparent glassy mass of sodium metaphosphate :

$$Na\,(NH_4)\,HPO_4 = NaPO_3 + H_2O + NH_3.$$

A bead may be formed in a platinum wire loop and heated with metal salts/oxides to characterize them from the colour of the bead :

$$NaPO_3 + CoO = NaCoPO_4 \text{ (blue)}$$

The sodium metaphosphate glass exhibits little tendency to combine with acidic oxides. Hence when a silicate is strongly heated in the bead, the liberated silica remains as a semi-translucent mass :

$$CaSiO_3 + NaPO_3 = NaCaPO_4 + SiO_2.$$

The appearence of the silica "skeleton" during and after fusion may be used as a test for silicates/silica. However, some silicates dissolve completely in the bead.

Interference of phosphates in group analysis

Except lithium phosphate, all alkali metal phosphates are soluble in water. Other common metallic phosphates are insoluble in water but soluble in dilute mineral acids.

When an acidic solution is subjected to systematic group analysis of cations, presence of phosphate salts gives rise to an additional problem : when the solution is made ammoniacal for the precipitation of Gr IIIA metal hydroxides (of Fe^{III}, Al^{III} and Cr^{III}), phosphates of Gr IIIA, IIIB and IV metals and of Mg^{2+}, if any, will be precipitated. So the normal group separation procedure will be hampered. The same is true for the presence of fluorides, borates and silicates. These are therefore called **interfering acid radicals.**

To run the systematic group analysis, it is necessary to remove the phosphate ion before entering Group III A. This can be achieved in three ways.

(a) **Ferric chloride method : $FePO_4$**, $AlPO_4$ and to a lesser extent $CrPO_4$ are insoluble in warm, dilute acetic acid-ammonium acetate buffer. Phosphates of Gr IIIB and IV metals and of Mg are soluble in such medium. The test solution after Gr II is first boiled to remove H_2S, oxidized by conc. HNO_3 and tested for iron. It is then made faintly ammoniacal; 2-3 ml dil (1 : 1) acetic acid and 10 ml of 3*N* ammonium acetate solutions are added, followed by enough $FeCl_3$ solution to impart red-brown colour. The solution is largely diluted and boiled for some time. The precipitte contains $FePO_4$, $AlPO_4$ (if Al is present), $CrPO_4$ (if Cr^{III} is present) together with basic acetates of Fe(III) (from excess $FeCl_3$).

$$FeCl_3 + 2Na_2HPO_4 = FePO_4 + 3NaCl + NaH_2PO_4$$

$$FeCl_3 + 3CH_3COONH_4 = Fe\,(CH_3COO)_3 + 3NH_4Cl$$

$$Fe\,(CH_3COO)_3 + 2H_2O \rightleftharpoons Fe\,(OH)_2\,(CH_3COO) + 2CH_3COOH$$

$$Fe\,(CH_3COO)_3 + 3H_2O \rightleftharpoons Fe\,(OH)_3 + 3CH_3COOH$$

Addition of filter paper pulp during boiling helps coagulation. The solution is *filtered hot*, because the reactions may reverse on cooling. Cr(III) acetate does not form a basic acetate in this condition but may be coprecipitated with the iron and aluminium. If large excess of Cr(III) is present, separation of phosphate will be incomplete.

(b) **Zirconyl nitrate method :** Zirconyl nitrate solution, $ZrO(NO_3)_2$, 10% in 1*N* HNO_3, forms a gelatinous precipitate of zirconyl phosphate in dil. HCl medium (≤ 1*N*) which is boiled and filtered. Only a slight excess of the reagent is added; otherwise a turbid supernatant liquid is obtained.

$$ZrO(NO_3)_2 + 2Na_2HPO_4 + 2HCl = ZrO\,(H_2PO_4)_2 + 2NaCl + 2NaNO_3$$

$$\text{or,}\quad ZrO(NO_3)_2 + Na_2HPO_4 = ZrO\,(HPO_4) + 2NaNO_3$$

(c) **Lead acetate method :** Lead phosphate is precipitated when lead acetate solution (20%) is added to a solution containing phosphate ion in faintly acetic acid medium (pH 2-3). The excess lead has to be removed by H_2S.

Phosphates are essential parts of the living system like bone, teeth and muscles. Their involvement in the structure of nucleic acids has been mentioned (Chapter 7).

Uses of phosphates

The most widely used ortho-phosphates are those of Na, K, NH_4 and Ca. Na_3PO_4 is used in scouring powders and grease saponifiers. Na_2HPO_4 is used as a buffer, emulsifier in cheese-manufacture, and other food-additives. Diammonium phosphate is a good fertilizer. It is also used in flame retardation of cotton fabrics. Urea phosphate is also widely used for the purpose as it is not removed by washing. On heating, these compounds produce H_3PO_4 which catalyzes the decomposition of cellulose to a slow burning char.

Calcium phosphates are used extensively as fertilizers. *Superphosphate* is made by digesting rock phosphate with calculated amount of H_2SO_4; it is a mixture of Ca $(H_2PO_4)_2$, H_3PO_4 and $CaSO_4$. ***Triple superphosphate***, made by treating rock phosphate with phosphoric acid, is mainly $Ca(H_2PO_4)_2$. It contains nearly 3 times the amount of soluble (available) P_4O_{10} than ordinary superphosphate — hence the name (45-50% by wt vs 18-20%). Mono and di-calcium phosphates are also used in baking powders, toothpastes, table salts etc. Tributyl phosphate ($POCl_3$ + n-BuOH) is an excellent solvent for extraction of metals from aqueous solution, usually as nitrates.

Condensed Phosphates

These contain more than one P atom and P—O—P bonds. The simplest member is pyrophosphoric (diphosphoric) acid $H_4P_2O_7$ (22-XXVII), obtained by heating H_3PO_4 between 213° and 416°C. Pyrophosphates are obtained on heating monohydrogen orthophosphates (240°C) or orthophosphates, e.g.,

$$2H_3PO_4 \xrightarrow{-H_2O} H_4P_2O_7$$

$$2HPO_4^{2-} \xrightarrow{-H_2O} P_2O_7^{4-}$$

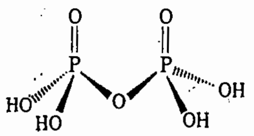
[Sec. 22.3.5 *Condensed phosphates*]

$$2H_3PO_4 + PbO_2 \longrightarrow PbP_2O_7 + 3H_2O$$

$$4Cr(PO_3)_3 \longrightarrow Cr_4(P_2O_7)_3 + 3/2\,P_4O_{10}$$

$$2Hg_3(PO_4)_2 \longrightarrow 2Hg_2P_2O_7 + 2Hg + O_2$$

$$2FePO_4 + H_2 \longrightarrow Fe_2P_2O_7 + H_2O.$$



22-XXVII

P–O (term) = 1.52 A°
P–O (bridge) = 1.61 A°
<P–O–P = 130°
(in $Na_4P_2O_7 \cdot 10H_2O$)
<P–O–P = 156°
(in α - $Mg_2P_2O_7$)

$H_4P_2O_7$ (m.p. 61°C) is a stronger acid than H_3PO_4 — *pK* values (25°C) are 0.8, 1.9, 6.5 and 9.6. Since $P_2O_7^{4-}$ ions are only slowly hydrolysed to PO_4^{3-} ions in aqueous solution, one can distinguish the former by simple chemical tests : $Ag_4P_2O_7$ (white) is sparingly soluble whereas Ag_3PO_4 is pale yellow.

A wide variety of condensed phosphates have been characterized in which some or all of the PO_4 tetrahedral units share two corner oxygens to give short chains, infinite chains or cyclic species. These may be of four main types :

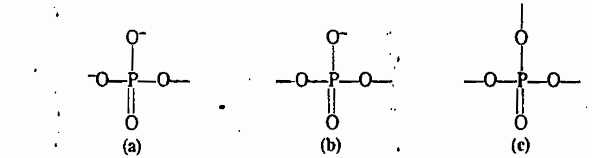
(i) short open chain species with general formula $(P_nO_{3n+1})^{(n+2)-}$, n=1 – 16. These are sometimes refered to as *polyphosphates*.

(ii) Infinite chain *metaphosphates* with the building unit $[(PO_3)_n]^{n-}$.

(iii) *Cyclic metaphosphates*, $[(PO_3)_n]^{n-}$, $n = 3 \rightarrow 10$, but commonly 3 or 4.

(iv) *Ultraphosphates* containing branching units (see below).

The main building units in all these condensed phosphates are the chain-terminating end unit (22-XXVIII a), middle unit (22-XXVIII b) and branching units or cross-linking groups (22-XXVIII c).



22-XXVIII

These units can be distinguished by either ^{31}P nmr spectroscopy or chemically. The chainlength in a polyphosphoric acid may be determined by titration with alkali. Each PO_4 unit has *one strongly acidic hydrogen* which is neutralised at pH 3.8 - 4.2. The other terminal hydrogens are only weakly acidic, and they are neutralised around pH 9. Hence the titre value at pH = 4 corresponds to one strongly acidic hydrogen per P-atom in the chain. The titre value at pH = 9 includes these as well as the two weakly acidic hydrogen at the two ends. The cross-linking units in polyphosphates are hydrolysed much faster than the others.

Complex mixtures of linear and cyclo-condensed phosphates are formed on heating hydrogen orthophosphates, e.g.,

$$NaH_2PO_4 \xrightarrow{>160^\circ C} Na_2[H_2P_2O_7] \xrightarrow{250^\circ C} cyclo\text{-}Na_3P_3O_9 \underset{300\text{-}500^\circ C}{\overset{625^\circ C}{\rightleftharpoons}} (NaPO_3)_n \text{ (chain)}$$

The actual nature of products depends largely on the conditions of heating. The cyclic tetrametaphosphate is formed when $Na_2H_2P_2O_7$ is dehydrated in an *open* system, allowing the water vapour to escape (see later). When $Na_2H_2P_2O_7$ is dehydrated in a *closed* system, different crystalline varieties of long chain polyphosphates are formed, for example the Maddrell's salts and the Kurroll salt. These consist of linear chains of PO_4 tetrahedra differening in the modes of orientation of the PO_4 units, the Kurroll salt having the units in the form of a helical chain. The inter relationship between the various forms of cyclic and chain metaphosphates are shown in Figure 22.12.

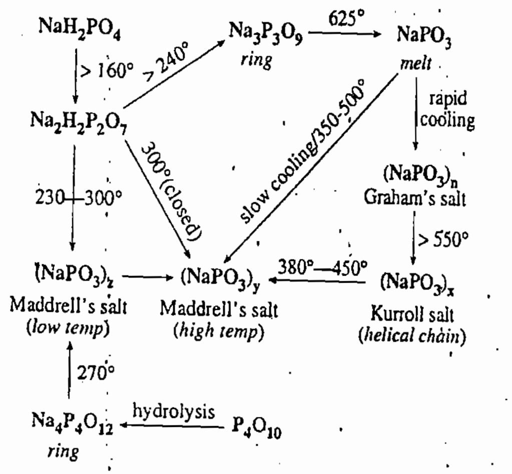


Fig. 22.12

The different metaphosphates (Temperatures in °C).

Apart from the various crystalline modifications, glassy forms of linear chain metaphosphates are also known. The most common example is the *Graham's salt* (first reported by Thomas Graham in 1833), a glassy mixture of different polymers obtained by quenching the melt of sodium cyclotrimetaphosphate $Na_3P_3O_9$ (m.p. 526°C) heated to 625°C. It has chains containing up to 200 PO_4 units together with a small portion of cyclometaphosphates. It is soluble in water and the solution can sequester Ca^{2+} and Mg^{2+} ions by forming soluble chelate complexes (similar to tripolyphosphate, see later). The substance is thus used widely in water-softening and removing scales from boilers and water-pipes. Commercially it is sold under the name *calgon*, once supposed to be sodium hexametaphosphate.

Uses

Linear sodium tripolyphosphate is now prepared in megatonne scales for synthetic detergents by heating a stoichiometric mixture of powdered Na_2HPO_4 and NaH_2PO_4 at 300 - 400°C.

$$2Na_2HPO_4 + NaH_2PO_4 \longrightarrow Na_5P_3O_{10} + 2H_2O.$$

It readily chelates and sequesters Ca^{2+} and Mg^{2+} ions in hard water, functioning as a water-softener. It also provides an optimum alkalinity suitable for washing and at the same time gets absorbed on the dirt particles building up a large negative charge on them., favouring peptization. $Na_5P_3O_{10}$ is also used as a dispersing agent in clay-suspensions required in the drilling of oil-wells. The large-scale use of tripolyphosphates in detergents and their disposal in sewage system causes depletion of oxygen in water and poses severe pollution problem (see below).

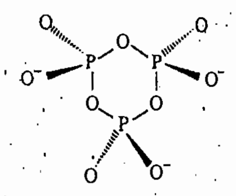
[Sec. 22.3.5. *Phosphate esters*]

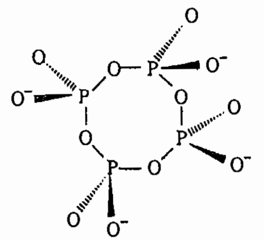
Cyclic polyphosphates are exemplified by the *cyclo*-trimetaphosphate $P_3O_9^{3-}$ [22-XXIX)] and *cyclo*-tetrametaphosphate $P_4O_{12}^{4-}$ ion [22-XXX]. *Cyclo*-$Na_3P_3O_9$ is formed by heating NaH_2PO_4 to 625°C and keeping the melt at 500°C to allow water vapour to escape. The anion may also be made effeciently by the reaction :

$$2\,(MeO)_3PO + (Me_2N)_3PO \longrightarrow [Me_4N]_3[P_3O_9]$$

In alkaline solution, the $P_3O_9^{3-}$ ion hydrolyses to the open chain tripolyphosphate $P_3O_{10}^{5-}$ ion. The $P_3O_9^{3-}$ ring has chair conformation.

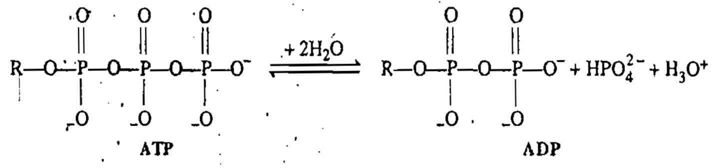
Sodium *cyclo*-tetrametaphosphate $Na_4P_4O_{12}$ (22-XXX) may be prepared by heating NaH_2PO_4 with H_3PO_4 (400°C) and cooling the melt slowly. It may also be obtained by dissolving P_4O_{10} in an ice-cold aqueous solution of NaOH and $NaHCO_3$. The $P_4O_{12}^{4-}$ ions are puckered and the conformation varies from compound to compound. The cyclic hexametaphosphate anion $P_6O_{18}^{6-}$ has all six P atoms in a plane.


22-XXIX


22-XXX

Ultraphosphates are cross-linked phosphates obtained by heating NaH_2PO_4 with P_4O_{10} above 350°C. The Na : P ratio in them appears to be less than unity. Some of them are glass-like but their detailed structures have not been investigated.

Phosphate esters play vital roles in several biological processes. For example, the reversible enzyme-catalysed hydrolysis of adenosine triphosphate (ATP) to the diphosphate (ADP) is associated with the energetics in biological systems :



$$\underset{\text{ATP}}{R-O-\overset{\overset{O}{\|}}{\underset{\underset{^-O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{^-O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{^-O}{|}}{P}}-O^-} \overset{+2H_2O}{\rightleftharpoons} \underset{\text{ADP}}{R-O-\overset{\overset{O}{\|}}{\underset{\underset{^-O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{^-O}{|}}{P}}-O^-} + HPO_4^{2-} + H_3O^+$$

where R ≡ Adenosine. The free energy change accompanying this proces depends on the pH, temperature, presence of metal ions etc. At pH = 7.4 and 298 K in presence of $[Mg^{2+}] = 10^{-4}$ *M*, the free energy *decreases* by 40.9 kJ mol^{-1}; the energy released may be utilized in doing work (say muscle contraction) or in maintaining other biochemical processes. The reverse reaction may be used to store energy (for example, from the oxidation of carbohydrates) in the form of ATP. Phosphate esters are vital in many other life processes like protein synthesis, genetic coding, photosynthesis, nitrogen fixation and several metabolic pathways. The involvement of phosphate esters in the H-bonded structure of DNA has been mentioned in chapter 7.

Pollution hazards

Environmentalists are worried by the escalating use of polyphosphates in detergents and in water softening — which is at least 6% of the annual world production, equivalent to about 70 million tonnes of H_3PO_4. These phosphates pass through sewage pipes into rivers and seas where they nourish bacteria and cause extensive growth of algae. These processes consume much of the dissolved oxygen in water endangering aquatic animals. Putrefaction of the water plants may also become hazardous to fishes and other aquatic animals.

Peroxophosphoric acids

H_3PO_5, peroxo monophosphoric acid, known in solution only, is formed by the action of dilute (3%) H_2O_2 on P_4O_{10} in acetonitrile solution at low temperature

$$P_4O_{10} + 4H_2O_2 + 2H_2O = 4H_3PO_5$$

It can oxidize Mn (II) to MnO_4^-. The molecule has one terminal peroxo group.

Peroxodiphosphoric acid $H_4P_2O_8$ may be made by adding H_2O_2 to pyrophosphoric acid ($H_4P_2O_7$). $K_4P_2O_8$ is prepared by electrolysis of K_2HPO_4 solution in presence of KF. The $P_2O_8^{4-}$ ion hydrolyses in acid solution to PO_5^{3-} (peroxomonophosphate) ion and finally to H_2O_2. It can oxidize aniline to nitrosobenzene and nitrobenzene.

Detection of Phosphates

(i) The most common test for the orthophosphate ion (other phosphates may be eventually hydrolysed to this form) is the formation of a canary-yellow precipitate of ammonium phosphomolybdate with ammonium molybdate solution in presence of nitric acid. Precipitation becomes rapid on gentle warming (60-65°C)

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = (NH_4)_3[PO_4.12MoO_3] + 2NaNO_3 + 21NH_4NO_3 + 12H_2O.$$

Ammonium molybdate must be in excess. Arsenates also give similar precipitate but only on boiling; phosphate alone gives the precipitate in presence of tartaric acid.

The test is based on the formation of the heteropolyacid anion by condensation of twelve MoO_6 octahedra around the PO_4 tetrahedron. This tendency is most prominent with tungsten and molybdenum. We shall discuss this in due course.

(ii) Ortho-, pyro-, and metaphosphates may be distinguished by means of the following reagents :

Reagent	Orthophosphate	Pyrophosphate	Metaphosphate
(i) $AgNO_3$ soln. (neutral)	Yellow ppt, sol. in dil NH_3/HNO_3	White ppt, sol. in dil NH_3/HNO_3	White gelatinous ppt, sol. in dil NH_3/HNO_3.
(ii) Albumin (dil acetic acid).	No coagulation	No coagulation	Coagulation
(iii) Magnesia mixture ($MgCl_2 + NH_4Cl$) ammoniacal solution.	White ppt on scratching, insoluble in excess reagent.	White ppt soluble in excess reagent but reappears on boiling.	No ppt, even on boiling.
(iv) $CdCl_2$ solution and dil acetic acid.	No ppt	White ppt	No ppt

Oxoacids and salts of As, Sb and Bi.

Oxoacids of As, Sb, Bi]

Arsenious acid, $As(OH)_3$, has never been isolated but it is the principal species in an aqueous acidic solution of As_4O_6. Basic solutions contain the additional ions AsO_3^{3-}, $[AsO_2(OH)]^{2-}$ and $[AsO(OH)_2]^-$. H_3AsO_3 is a very weak acid, $pK_1 = 9.2$ (See As_4O_6).

$As(OH)_3$ is pyramidal but it forms two isomeric methyl esters $As(OMe)_3$ and $MeAs(O)(OMe)_2$; these correspond to two forms of the acid, similar to phosphorus acid. The AsO_3^{3-} ion is present in the sparingly soluble yellow Ag_3AsO_3. Many solid arsenites are formulated meta-arsenities e.g., $NaAsO_2$. These contain polymeric chain of corner-linked pyramidal AsO_3 groups. They are highly soluble in water, but the arsenites of alkaline earth metals are only slightly soluble. Heavy metal aresenites are only sparingly soluble.

Redox-reactions of arsenites have been discussed under As_4O_6.

Detection

(i) A neutral solution of arsenite produces a *yellow* precipitate of silver arsenite (Ag_3AsO_3, an *orthoarsenite*), soluble in ammonia and in nitric acid; difference from arsenates).

(ii) A solution of an aresenite precipitates yellow As_2S_3 from HCl medium (insoluble in conc. HCl; see sulphides).

$$2Na_3AsO_3 + 6HCl + 3H_2S = As_2S_3 + 6NaCl + 6H_2O.$$

Sufficient free HCl must be present to prevent formation of soluble thio-salts (*no precipitation from neutral or alkaline solution*).

$$Na_3AsO_3 + 3H_2S \rightleftharpoons Na_3AsS_3 + 3H_2O.$$

(iii). Copper sulphate solution precipitates green copper arsenite $Cu_3(AsO_3)_2.xH_2O$ or $CuHAsO_3$ (*Scheele's green*) from neutral solutions of arsenites. The precipitate is soluble in acids and ammonia (blue solution). It also dissolves in alkali — the solution on boiling precipitates Cu_2O.

Paris green was formerly used as a green pigment. It is copper acetate arsenite $[Cu_2(CH_3COO)(AsO_3)]$ and is made by boiling basic copper acetate with As_4O_6 and acetic acid. It is also an insecticide.

Arsenic acid, H_3AsO_4 is formed by oxidation of As or As_4O_6 by concentrated HNO_3. It is also produced by catalytic oxidation of As_4O_6 with air and H_2O under pressure. The acid crystallizes from solution as $2H_3AsO_4.H_2O$ below 30°C; at 100°C, a ribbon-like polymeric form $(H_5As_3O_{10})_n$ separates. Both forms are H-bonded.

H_3AsO_4 is a tribasic acid, somewhat weaker than H_3PO_4; successive pK values at 298 K are 2.2, 6.9 and 11.5. Arsenates are easily formed by oxidation of arsenites in alkaline solution. Na_3AsO_4 is made by fusing sodium arsenite with sodium nitrate.

H_3AsO_4 and arsenates are strong oxidizing agents :

$$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O \qquad E^\circ = 0.56\ V$$

pH-dependence of the potential has already been discussed.

Condensed arsenic anions do not exist in aqueous solutions — they are kinetically much less stable with respect to hydrolysis than condensed phosphates. NaH_2AsO_4 dehydrates on heating

$$NaH_2AsO_4 \longrightarrow NaAsO_3 + H_2O.$$

It contains an infinite polymeric chain anion, $LiAsO_3$ and $KAsO_3$ also form chain ainons; $KAsO_3$ is also known to contain the cyclic trimeric anion $As_3O_9^{3-}$. Pyroarsenates may be prepared by heating monohydrogen ortho-arsenates.

MH_2AsO_4 (M = K, Rb, Cs, NH_4) are ferroelectric.

Detection

(i) Arsenates produce a chocolate red precipitate with silver nitrate solution from neutral medium:

$$Na_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3NaNO_3.$$

The precipitate is insoluble in acetic acid but soluble in other acids and ammonia (*distinction* from arsenite/phosphate which give yellow ppt).

Chromates, ferro-and ferri-cyamides also give coloured precipitates with $AgNO_3$ insoluble in acetic acid.

(ii) Magnesia mixture gives a white precipitate from neutral or ammoniacal solution (distinction from arsenite).

$$Na_2HAsO_4 + MgCl_2 + NH_3 = MgNH_4AsO_4 + 2NaCl.$$

When the precipitate is treated with silver nitrate solution containing acetic acid, Ag_3AsO_4 is precipitated (*distinction* from phosphate).

(iii) Arsenates give a yellow precipitate of ammonium arsenomolybdate on boiling with an excess of ammonium molybdate solution (see detection of phosphates).

Antimonious acid, H_3SbO_3 is not well characterized. Antimony(III) oxide dissolves in alkali to form antimonites like $NaSbO_2$. Polyantimonites are also known, e.g., $NaSb_3O_5.H_2O$ and $Na_2Sb_4O_7$.

Solutions containing the $[Sb(OH)_6]^-$ ion is obtained by adding dilute alkali to $SbCl_5$. Crystalline antimonates may be obtained from this solution, the sodium salt being the least soluble alkali metal salt. Other antimonates like $LiSbO_3$, Li_3SbO_4, $MgSb_2O_6$, $AlSbO_4$ have also been structurally characterized — they all contain only SbO_6 octahedra.

$$MSb(OH)_6 \longrightarrow MSbO_3 + 3H_2O \quad (M = \text{alkali metal}).$$

However, these are best considered as mixed oxides.

$Bi(OH)_3$ is distinctly basic. Only bismuth(V) shows some acidic character in forming "bismuthates" though the structures of the compounds in this unstable oxidation state of Bi are also not very certain.

Sodium bismuthate, $NaBiO_3$, may be obtained by fusing Bi_2O_3 with Na_2O_2 (or $NaOH + O_2$). It is also obtained by oxidizing $Bi(OH)_3$ in strongly alkaline solution with chlorine or other strong oxidizing agents;

$$Bi_2O_3 + 2NaOH + 2NaOCl = 2NaBiO_3 + 2NaCl + H_2O.$$

The brown solid is insoluble in water, but dissolves in 0.5 *M* $HClO_4$ solution. The solution is stable for several days in absence of light. The precise nature of the compound is not known. It shows strong oxidizing properties — the Bi(V)-Bi(III) potential is estimated to be + 2.03 V. comparable to ozone ($E° = 2.07$ V) and perdisulphate ($E° = 2.01$ V). Sodium bismuthate liberates chlorine from HCl and oxidizes a cold solution of Mn (II) in dilute H_2SO_4 or HNO_3 to pink permanganic acid - a reaction used in detection and estimation of Mn (in steel, for example):

$$2MnSO_4 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + NaNO_3 + 2Na_2SO_4 + 7H_2O.$$

22.3.6 Cationic Chemistry and Aqueous Solution Chemistry

Several aspects of cationic chemistry and aqueous solution chemistry have been considered in the previous sections. The principal cationic chemistry of nitrogen is covered by that of the ammonium (NH_4^+) and related quaternary ions. Similar quaternary cations R_4M^+ (R = H, alkyl, aryl, halogen, alkoxy etc) are also formed by phosphorous and to a somewhat less extent by arsenic. Only Ph_4Bi^+ is known for Bi (see organo compounds).

[Sec. 22.3.6 *Cation chemistry*]

The tetraalkyl and tetraaryl cations are readily obtained through reactions like

$$R_3M + RX \longrightarrow [R_4M]^+ X^-.$$

As mentioned earlier, phosphonium compounds are completely hydrolyzed by water, owing mainly to the low proton-affinity of PH_3. Tetra(hydroxymethyl) phosphonium chloride is obtained as a white crystalline water-soluble solid by the reaction

$$PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]^+ Cl^-$$

The arsonium cation, AsH_4^+, and its alkyl and aryl derivatives are important in making several organo-arsenic compounds (see organocompounds).

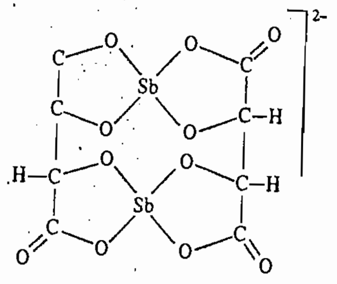
There is little evidence for P or As cationic species in aqueous media; As(III) is not sufficiently basic to form stable oxoacid salts such as sulphates, nitrates, perchlorates etc. Solutions of As_4O_6 in anhydrous H_2SO_4 may contain species like $As(OH)(HSO_4)_2$. The ability to form stable oxosalts increases remarkably at Sb and Bi. $Sb_2(SO_4)_3$, $Bi_2(SO_4)_3.nH_2O$ and $KBi(SO_4)_2$ may be isolated, but all are readily hydrolyzed to basic salts. The oxocation SbO^+ ("antimonyl") exists in dilute H_2SO_4 (~ 1.5 *M*), together with $[Sb(OH)_2]^+$. More concentrated acid contains $[SbOSO_4]^-$ and $[Sb(SO_4)_2]^-$ ions.

Tartar emetic is actually a binuclear tartrato complex of antimony(III), $K_2[Sb_2(d\text{-tart})_2].3H_2O$ where *d*-tart = *d*-tartaric acid anion, $C_4H_2O_6^{4-}$. Formerly it was considered potassium antimonyl tartrate. It is prepared by boiling a mixture of Sb_2O_3 and potassium hydrogen tartrate ("cream of tartar"):

$$2KHC_4H_4O_6 + Sb_2O_5 = K_2[Sb_2(C_4H_2O_6)_2].3H_2O.$$

The colourless crystals are soluble in water, but insoluble in alcohol.

The compound has long been used in medicine as an *emetic* (causing vomitting). It is used in the treatment of schistosomiasis and leishmaniasis, though with toxic side-effects. The ion has a pseudo tbp geometry around each Sb atom with a lone pair of electrons at one equatorial position (21-XXXI).



21-XXXI

The $Sb(C_2O_4)_3^{3-}$ ion has a pseudopentagonal bipyramid geometry around the Sb(III) with a lone pair of electrons at one axial position. Two oxalate ions act as bidentate and one oxalate ion acts as monodentate—the five oxygen atoms form the pentagonal base of a pyramid capped by Sb(III).

$Bi(NO_3)_3.5H_2O$ can be crystallized from a solution of Bi_2O_3 (or carbonate) in concentrated nitric acid. Similarly one can obtain crystals of $Bi(ClO_4)_3 . 5H_2O$ but the existence of simple Bi^{3+} ion in these crystals or their aqueous solutions has not been confirmed. Dilution of a solution of the nitrate in nitric acid precipitates the basic salt $BiO(NO_3)$ (bismuth subnitrate/*bismuthyl nitrate*). A very large excess of water gives the basic salt $Bi_2O_2(OH)(NO_3)$.

$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiO(NO_3) + 2HNO_3$$

$$2Bi(NO_3)_3 + 3H_2O \rightleftharpoons Bi_2O_2(OH)(NO_3)$$

The exact nature of the cationic species varies according to conditions but in most cases they contain clusters of Bi atoms with the nitrate ion functioning as a bidentate ligand. The first hydrolysis product appearing from bismuth nitrate solutions near pH 1.2 has the formula $[Bi_6O_4(OH)_4](NO_3)_6.4H_2O$. It has octahedral Bi_6 units with face-bridging M_3-oxo groups. Similarly, while Bi^{3+} ions may be present in highly acidic solutions of bismuth perchlorate, only a slight increase in pH makes $[Bi_6(OH)_{12}]^{6+}$ the dominant species. At higher pH $[Bi_6O_6(OH)_3]^{3+}$ is formed. In $[Bi_6(OH)_{12}]^{6+}$, six Bi atoms are arranged at the corners of an octahedron with hydroxo bridges between each pair of Bi atoms. Polycations having similar clusters of Bi are also present in a variety of crystalline basic salts.

Bismuth subnitrate is used in gilding porcelain and in cosmetic and medicines.

Sodium thiosulphate reacts with a solution of bismuth salt forming a soluble thiosulphato complex of bismuth :

$$Bi(NO_3)_3 + 3Na_2S_2O_3 = Na_3[Bi(S_2O_3)_3] + 3NaNO_3$$

The solution does not react with iodine. The corresponding potassium salt is much less soluble and separates as a yellow precipitate. The complex readily decomposes to black Bi_2S_3.

$$2Na_3[Bi(S_2O_3)_3] = Bi_2S_3 + 3Na_2S + 6H_2SO_4$$

Attempts have been made to obtain cations of antimony and bismuth stabilized by chelation with crown ethers. However, in the compounds isolated from reaction of $SbCl_3$ or $BiCl_3$ with crown ethers, the pyramidal MCl_3 molecules remain intact with their lone pair of electrons accommodated within the cavity of the crown ether.

22.3.7 Sulphur compounds

Since nitrogen is more electronegative than sulphur, the binary compounds of sulphur and nitrogen are conveniently treated as nitrides of sulphur in Group 16(VI).

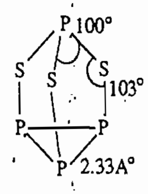
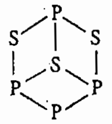
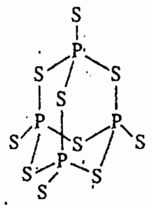
Sulphides of Phosphorus

Phosphorus forms a number of sulphides (Table 22.14) based on the P_4 tetrahedron but these do not necessarily correspond to the oxides. The phase diagram of phosphorus-sulphur system below 100° shows only solid solutions. Above 200°, P_4S_3, P_4S_7 and P_4S_{10} appear as definite compounds. P_4S_4, P_4S_5 and P_4S_9 have been prepared by careful control at low temperatures. P_4S_6 has not been isolated pure.

Preparation, properties and structures of the compounds are summarized in Table 22.14. Their structures may be considered as being derived from a P_4 tetrahedron through insertion of P–S–P bridges along the tetrahedron's edges and terminal P=S bonds.

TABLE 22.14

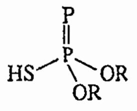
Main Sulphides of Phosphorus

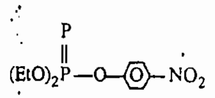
P_4S_3 	Red P + S in right proportion heated (> 180°C) in inert atmosphere. Recryst, from toluene.	Most stable sulphide of P. Yellow, m.p. 174°; b.p. 408° soluble in CS_2 (high), toluene. Adds I_2 across a P–P bond to give β-$P_4S_3I_2$. This slowly iomerizes to α-form. Used in match industry (See below).
P_4S_4  (α)	$P_4S_3I_2 + (Me_2Sn)_2S$ in CS_2 solution. Two forms (α, β) corresponding to $P_4S_3I_2$ taken.	Pale yellow, m.p. 230° (decomp). Soluble in CS_2.
P_4S_5	Irradiation of P_4S_3 + S in CS_2 (I_2 cat). Also, $5P_4S_3 + 12Br_2 \longrightarrow 3P_4S_5 + 8PBr_3$ $P_4S_7 + 2Ph_3P \longrightarrow P_4S_5 + 2Ph_3PS$	Bright yellow, m.p. 170-220 (dec). Disproportionates $2P_4S_5 = P_4S_3 + P_4S_7$. Slightly soluble in CS_2.
P_4S_7	Red P + S—heated in right proportion.	Second most stable. Pale yellow, m.p. 308°, b.p. 523°. Slightly soluble in CS_2.
P_4S_9	$P_4S_7 + P_4S_{10}$ heated.	Unstable.
P_4S_{10} 	(i) P_4 + S heated above 300°C. (ii) Fe_2P (ferrophosphorus, bye product in phosphorus preparation) heated with FeS_2 or S. (P_4S_{10} + FeS are formed).	Yellow, m.p. 288°, b.p. 514°. Hydrolyses : $P_4S_{10} + 16H_2O \longrightarrow 4H_3PO_4 + 10H_2S$ Alcohols (or phenols) form dialkyl (or diaryl) dithiophosphoric acids (22.XXXII) $P_4S_{10} + 8ROH \longrightarrow 4(RO)_2P(S)SH + 2H_2S$. Route to many organophosphorus compounds, they are very useful commercially.

P_4S_3 is used in "strike anywhere" matches. The match head contains a mixture of $KClO_3$ (~ 20%) and P_4S_3 (~ 9%) together with fillers like ground glass, Fe_2O_3, ZnO and glue. Friction of the match (e.g., on a ground glass paper on the side of the box) produces enough heat to set a violent reaction between $KClO_3$ and P_4S_3. The heat generated ignites the match stick.

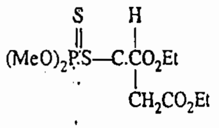
"Safety matches" contain mainly $KClO_3$ on the sticks; the side of the match-box is covered with a paste of red P (~ 50%), Sb_2S_3 (27%), Fe_2O_3 (1.2%) and gum.

P_4S_{10} is largely used to make dialkyl or diaryl dithiophosphoric acids (22-XXXII). Their zinc-salts are used as additives to high pressure lubricants like gearbox oil. Sodium and ammonium diethyl dithiophosphates are used in concentration of PbS and ZnS by oil floatation. Derivatives of these acids are also used as pesticides like parathion; methylparathion and malathion. These pesticides destroy the nervous system of insects by inhibiting acetylcholineesterase. But they are harmless to mammals as these will be fragmented during digestion.


22-XXXII


Parathion

22-XXXIII


Malathion

22-XXXIV

World production of P_4S_{10} exceeds 250, 000 tonnes p.a.

Sulphides of arsenic, antimony and bismuth

Arsenic forms several sulphides; some of them are structurally analogous to corresponding phosphorus sulphides. Naturally occurring *realgar* (red; As_4S_4) and *orpiment* (golden-yellow; As_2S_3) were used as pigments in old days. As_4S_3 also occurs in nature as orange-yellow *dimorphite*. Antimony forms only Sb_2S_3; the so called Sb_2S_5 is not a stoichiometric substance and contains only Sb(III) according to Mössbauer spectroscopy. Bismuth forms brown Bi_2S_3. At 1250°C and 50 kbar pressure, Bi reacts with S to form BiS_2 which may be $Bi^{3+}[BiS_4]^{3-}$. The gradual change to metallic character in bismuth is revealed by the increasing basic character of the sulphides. Arsenic and antimony sulphides dissolve in alkali and alkali metal sulphides (see reactions) but Bi_2S_3 does not.

As_2S_3 may be obtained by heating As_2O_3 with sulphur or by passing H_2S into an acidified solution of As_2O_3.

$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$

It is a yellow solid, m.p. 320°C, insoluble in water and concentrated HNO_3 with oxidation (H_3AsO_4). It is also readily soluble in solutions of alkali, ammonia and alkali metal sulphides, forming arsenites and thioarsenites. This is why sufficient free mineral acid must be present for complete precipitation of As_2S_3 by H_2S.

$$As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O.$$

$$As_2S_3 + 3Na_2S = 2Na_3AsS_3.$$

Acidification of the above solutions reprecipitates As_2S_3.

As_2S_3 dissolves readily in yellow ammonium sulphide solution — the excess sulphur oxidizes it to thioarsenate.

$$As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + (3x - 5)S$$

Acidification precipitates "As_2S_5", insoluble in conc. HCl, but soluble in alkali.

"As_2S_5" is also formed by passing H_2S rapidly into an ice-cold solution of arsenate in conc HCl. Slow passage of H_2S at room temperature causes reduction to arsenite and ultimate precipitation of As_2S_3. Yellow As_2S_5 decomposes in air above 95°C into As_2S_3 and S.

As_2S_3 has a layer structure similar to As_4O_6. Each As is bonded to three S atoms pyramidally, S—A—S angle = 99°. The structure of As_2S_5 has not been estabilished.

The sulphides As_4S_3 and As_4S_4 are structurally analogous to corresponding phosphorus sulphides, though different forms are known with different arrangement of moleular units. As_4S_3 may be prepared by heating As and S in required proportions. As_4S_4 results when As_2S_3 is boiled with sodium carbonate solution or As_4S_3 is heated with a solution of sulphur in CS_2. It is also formed by fusing As_2O_3 with sulphur or heating iron pyrites with arsenical pyrites. It dissociates reversibly above 550°C; at 1000°C, it is present as As_2S_2. It reacts violently on heating with KNO_3 and is used in pyrotechny. One form of As_4S_4 (present in the mineral realgar) has the cradle-like structure similar to S_4N_4 (Chapter 23) but with the S-atoms in place of N-atoms and As-atoms in place of S-atoms.

As_4S_5 is a minor side product in the formation of As_4S_4 from As_4S_3 + S. Its structure is different from that of P_4S_5 as it has no exocyclic As = S bond and has only one As-As bond.

Sb_2S_3 is precipitated from aqueous solution in a metastable red form, which changes into a black form on slow heating. This black form also occurs naturally as *stibnite*. It dissolves in alkali and alkali sulphide to give thiosalts. Sb_2S_5 (red) may be obtained similar to As_2S_5, but this is also not properly characterized. Sb_2S_3 has a ribbon-like polymeric structure involving interlocking SbS_3 and three SSb_3 pyramidal units. Sb_2S_3 is largely used in making safety matches, ammunitions, explosives, ruby glass, and as a flame retardant pigment in plastics and rubbers.

Bi_2S_3 (dark brown) is precipitated by H_2S from aqueous Bi(III). It is insoluble in alkali and alkalimetal sulphides or yellow ammonium sulphide but dissolves in dilute HNO_3. The solution gives a black precipitate of Bi in cold with sodium stannite solution.

$$2Bi\,(NO_3)_3 + 3Na_2\,[SnO_2] + 6NaOH = 2Bi + 3Na_2SnO_3 + 6NaNO_3 + 3H_2O.$$

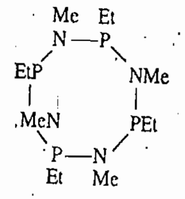
Like Sb_2S_3, Bi_2S_3 also has a complex double chain structure.

Other chalcogenides of As, Sb and Bi may be prepared by heating the elements in requisite quantities at 500-900°C. The compounds have complex ribbon or layer-lattice structures and are important as semiconductor materials. Selenides and telurides of Sb and Bi are used in solid-state refrigerators.

22.3.8 Phosphazenes (Phosphonitrilic halides)

A large number of compounds with phosphorus-nitrogen bonds are known :

(a) Compounds which are formally $P^{III} - N^{III}$ type, with nominally P—N single bonds, but having appreciable double bond character from N(*p*)—P(*d*) back bonding. Examples are the aminophosphanes $(R_2N)_nPX_{3-n}$ (monomeric) : aminoimino-phosphanes $R_2N - P = NR^1$ which may be monomers (bulky R and R^1), dimers; larger rings (22-XXXV) and polycyclic compounds (22-XXXVI).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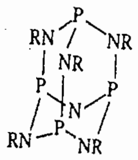

22-XXXVI

(b) Compounds containing P^V and N^{III}, the most important class being the phosphazenes — both linear and cyclic. Rings including other atoms (e.g., B or S) are also known.

Phosphazenes

Phosphazenes are formally "unsaturated" compounds with the grouping $>P = N -$. Monophosphazenes may be prepared through reactions like

$$PhN_3 + PR_3 \longrightarrow N_2 + R_3P = NPh \quad (R = Ar, NR_2, OR, Cl \text{ etc}).$$

$$Ph_3PCl_2 + PhNH_2 \longrightarrow HCl + Ph_3P = NPh \quad (\text{m.p. } 132°C).$$

The P—N distance is short, ~ 1.6A°; the angle at N lies around 120°.

Diphosphazenes may be prepared in chlorohydrocarbon solvents by reacting PCl_5 with NH_4Cl (see below). The P—N distances in these compounds are equal through delocalization of π-electrons.

The cyclic and linear polymers of phosphazene, particularly cyclic polymers of dichlorophosphazene $(PNCl_2)_n$ (also known as phosphonitrilic chlorides) are most important among the phosphazenes. These are discussed below.

Polyphos-phazenes

The polyphosphazenes are formal analogues of the silicones in which OSi in the R_2SiO units has been replaced by the isoectronic PN group forming chains and rings of R_2PN units. In 1834, Wöhler and Liebig prepared $(Cl_2PN)_n$ compounds by heating PCl_5 with NH_3, though (naturally, of course) without detailed structural elucidation. $(NPF_2)_n$ cmpounds were first made in 1956, $(NPBr_2)_n$ compounds in 1960.

$(NPCl_2)_n$ compounds are now prepared both in the laboratory and in industry by heating PCl_5 with NH_4Cl in solvents like chlorobenzene, *o*-dichlorobenzene, 1, 1, 2, 2 - tetrachloroethane (Schlenk and Römer, 1924) :

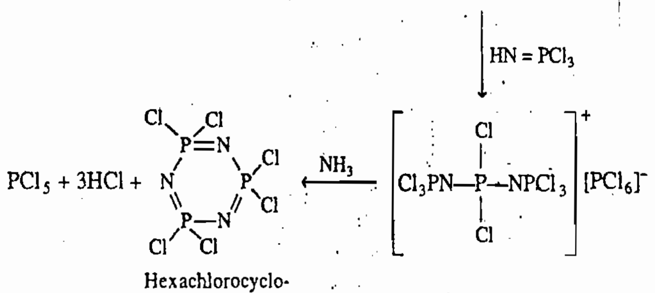
Preparation

$$n\,PCl_5 + nNH_4Cl \xrightarrow{120° - 150°C} (NPCl_2)_n + 4nHCl$$

A mixture of different polymers is usually formed — cyclic compounds with $n = 3$, 4, 5, ... as well as short linear chains. But the trimer and tetramer may be produced in high yield under controlled conditions. The products may be finally separated by fractional distillation.

It is believed that PCl_5 and NH_4Cl first forms $NH_4\,[PCl_6]$ which loses HCl to form unstable $HN = PCl_3$. This reacts with $PCl_5(s)$ in its ionic form to produce the trimer

$$[PCl_4]^+[PCl_6]^- + HN = PCl_3 \longrightarrow [Cl_3P = N = PCl_3]^+[PCl_6]^- + HCl$$



Hexachlorocyclo-triphosphazene

If PCl_5 is replaced by PBr_5 or Me_2PCl_3, the bromo or methyl derivatives are obtained respectively. Chlorine may be replaced by fluorine on heating the chloro derivative with (i) NaF suspended in nitrobenzene (or acetonitrile) or (ii) with KSO_2F.

$$[NPCl_2]_n + 2nNaF \longrightarrow (NPF_2)_n + 2nNaCl.$$

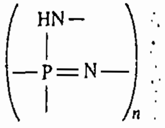
Water-repellant polymers may be obtained by replacing Cl with alkoxy group :

$$[NPCl_2]_3 + 6NaOR \longrightarrow [NP\,(OR)_2]_3 + 6NaCl.$$

Linear polymers may be obtained in larger amounts by using excess of PCl_5. Polymers with molecular mass 20,000 or more may be obtained by heating $(NPCl_2)_3$ to 250-350° C in CCl_4 in presence of oxygen. Certain catalysts like ethers, carboxylic acids, ketones, alcohols etc. afford polymerization at lower temperatures. Cross-linked polymers may also be obtained under suitable conditions.

Phospham is a highly cross-linked polyphosphazene (22-XXXVII); it is produced by the reaction

$$4NH_3\,(g) + 2P'(\text{red}) \xrightleftharpoons{500°C} 5H_2 + 2PN_2H\,(s).$$



22-XXXVII

Properties

The phosphazenes range from fluids and definite solids to polymeric elastomers. A wide range of physical properties may be achieved by suitable substituents and desired degree of polymerization — glasses, rubbers or tough, flexible solids. $(NPCl_2)_3$ and $(NPCl_2)_4$ are white solids with m.p. 113°C and 123°C respectively. The m.p. falls to 41° C at $(NPCl_2)_5$. It is a general feature of the cyclic polymers $(NPCl_2)_n$, the m.p. is higher when n is even.

The lower polymers are insoluble in water but soluble in organic solvents. The high molecular weight polymers are insoluble in organic solvents and resemble vulcanized rubber in mechanical properties; they are often called *inorganic rubber*.

The chloro-derivatives readily hydrolyze in moist air to polymetaphosphimic acids $[HN = P\,(O)\,(OH)]_n$. The amino, alkoxy, phenoxy and fluorinated compounds display greater stability.

Chlorine atoms in chlorophosphazenes are reactive and may be substituted by a variety of reagents, e.g.

$$(NPCl_2)_3 + 6CH_3MgI \longrightarrow [NP\,(CH_3)_2]_3 + 3MgCl_2 + 3MgI_2.$$

$$(NPCl_2)_3 + 6C_6H_5Li \longrightarrow [NP\,(C_6H_5)_2]_3 + 6LiCl.$$

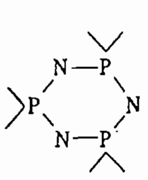
Substitution by $-NH_2$, $-NMe_2$, $-N_3$, $-OH$ may be achieved by treatment with liquid NH_3, Me_2HN, LiN_3 and H_2O respectively.

The N atom in the cyclopolyphosphazenes may also act as weak proton acceptors (Bronsted base) from strong acids like HF and $HClO_4$. Alkyl or NR_2 groups as substituents on P increase the basicity of the nitrogen - adducts may be formed with HCl also. Disruption of N–P π-bonding causes lengthening of the bonds adjancent to the site of protonation.

Cyclopolyphosphazenes may also act as N–donor ligands as in $TiCl_4\,(N_3P_3Me_6)$.

Structure

The cyclic trimers possess planar (or nearly planar) six-membered P_3N_3 ring structure (22-XXXVIII) of alternate N and P atoms; the bond angles are consistent with sp^2 hybridization at N and nearly sp^3 hybridization at P. The tetramers have different structures : only $(NPF_2)_4$ appears to be planar. $(NPCl_2)_4$ has two conformations : the metastable K-form (boat) and the stable T-form (chair) 22-XXXIX).



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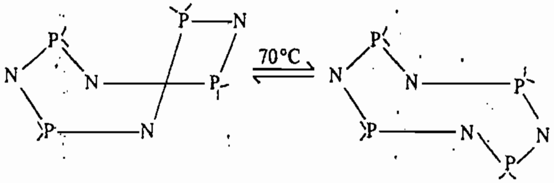


22-XXXIX

The P—N distances in a ring (or in a chain) are all equal — usually in the range 1.56 - 1.60 A°; this is considerably shorter than expected for a covalent single bond (1.77A°; in $Na^+ [H_3NPO_3]^-$). The N–P–N angles are usually around 120° (± 2°) but the P–N–P angles may vary widely — from 120° to about 148°.

Bonding

The equivalence of all N—P bond lengths in phosphazene cannot be adequately described by a system of alternate single and double bonds or by involving *p-p* π-bonding and delocalization similar to that in aromatic systems.

Two π-systems may be involved as follows. If we consider the *xy* plane to be the plane of the ring, the σ-bond system may be derived from sp^3 hybrid orbitals on P and sp^2 (sp_xp_y) hybrid orbitals on N. The p_z orbital on each N (with a lone pair of electrons) and the d_{xz} orbitals on P may now enter π-interaction in a plane perpendicular to that of the ring. From Fig. 22.13, we may appreciate that the π-delocalization cannot be as extensive as in benzene or even borazine (*p-p* π-bonding in both) because of the varying signs on the lobes of the *d*-orbitals.

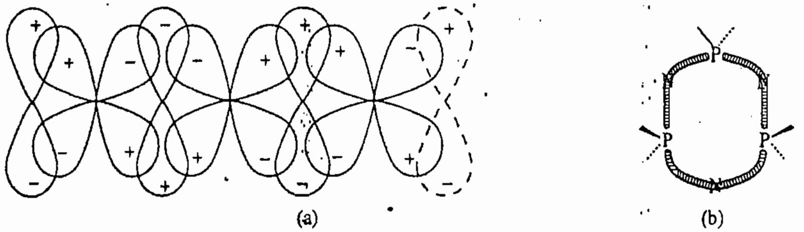


Fig. 22.13

(a) **Schematic π-overlap in $(PNCl_2)_3$.**
The P—N ring has been *split open* for clarity.
1, 3, 5 : *p*-orbitals on three N-atoms. 2, 4, 6 : *d*-orbitals on P-atom.

(b) **Islands of 3-center π-clouds above and below the ring plane in** $(NPX_2)_3$ (schematic).

Note the mismatch in signs of the lobes on 6 (P-atom) and 1 (N-atom) when *the ring closes*.

Alternatively, a π-system in the plane of the ring may be involved by placing the lone pair of electrons of the N atom in one of the sp^2 hybrid orbitals which can overlap with an empty $d_{x^2-y^2}$ orbital on P. The singly occupied p_z orbital on each N may form a three-center bond with d_{xz} and d_{yz} orbitals on adjacent P atoms. However, there may be many points for and against such *d*-orbital participation, particularly in view of the size and energy of the *d*-orbitals. In any case, extensive delocalization is not expected; the π-orbitals are separated into three 3-center islands segmented at each P atom (Fig. 22.13).

Participation of the nitrogen lone pair in π-bonding is expected to increase with more electronegative substituents on phosphorus. This should result in stronger and shorter P—N bonds. Indeed, the P—N bond lengths in $(PNF_2)_3$ are slightly smaller than those in $(PNCl_2)_3$ (156 pm vs 158 pm).

Uses

The polyphosphazenes form an extensive series of polymers, next only to carbon based polymers and silicone polymers. Substituted polyphosphzenes, especially the fluorinated compounds appear to be prospective materials for fuel hoses, gaskets etc. in extreme climates (e.g., in Arctic region) and in high-flying aircrafts. These may be used in conjunction with other substances for non-flammable insulating materials. Alkoxy substituted polyphosphazenes $[NP(OR)_2]_n$ are notable for their water-repelling properties. Highly inert products with $R = CH_2CF_3$ may be used for the construction of artificial blood vessels and organs. Biodegradable polymers derived from aminoacids $[NPR_2]_n$ where $R = NHCH_2CO_2Et$ for example, hydrolyze slowly to harmless products and are used in surgical applications like sutures. However, the cost of production of desirable polymers must come down before they can be put to wide use.

22.3.9 Complexes and clusters

Complexes

We have already mentioned several coordination compounds of As, Sb and Bi — particularly their complexes with halogens and oxo or hydroxo groups.

The elements of the nitrogen group also furnish a wide range of compounds as ligands. Ammonia, phosphine, arsine and their derivatives form complexes with several transition metals; the cyanide ion and nitric oxide are also very important as ligand. We shall cover these compounds in connection with transition metal chemistry.

Dinitrogen itself may act as a ligand, though much less extensively than isoelectronic CO. The complexes of dinitrogen and CO have linear M – N ≡ N and M – C ≡ O skeleton. The N – N distance in the complexes is only slightly increased (1.12 ± 0.02 A° compared to 1.10 A° in N_2), and the N – N stretching frequency also lies in the triple bond range 1990-2160 cm^{-1} compared to 2345 cm^{-1} in N_2. All these points suggest a parallelism between the bonding description of carbonyls and dinitrogen complexes, but with some basic differences in the extent. The highest filled m.o. in N_2 is at –15.57 eV, about 0.6 eV (58 kJ mol^{-1}) lower than the HOMO in CO (–14.01 eV). Thus the ligand to metal σ-donation is weaker in complexes of N_2 (the electrons are more tightly held). On the other hand, π-donation from filled metal orbitals to the LUMO of N_2 should be more favoured because of the lower energy of the π* m.o. than that in CO (–7 eV in N_2; –6 eV in CO), but this does not appear to balance the deficiency in σ-bonding. Similar conclusions are obtained by considering the polarization of the molecular orbitals in CO (Fig. 22.14) while the m.o.s in N_2 are symmetrically disposed.

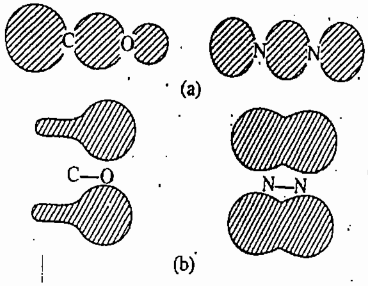


Fig. 22.14
Polarization of the m.o.-s in CO compared to those in N_2.
(a) filled σ-m.o. (b) filled π-m.o.

Bridging dinitrogen complexes differ from bridging carbonyls in having similar N–N bond lengths and stretching frequencies as in terminal complexes. Sideways coordination from $N \equiv N$ to metals is also known, but examples are rare.

Relatively stable dinitrogen complexes are formed in aqueous media by elements in the middle of the transition series, especially in d^6 configuration. These are commonly prepared by the action of strong reducing agents in presence of N_2 or replacement of labile ligands.

$$WCl_4\ (PR_3)_2 + Na\ (Hg) \xrightarrow{N_2} W\ (N_2)_2\ (PR_3)_4$$
$$[Ru\ (NH_3)_5H_2O]^{2+} + N_2 \rightleftharpoons [Ru\ (NH_3)_5\ (N_2)]^{2+} + H_2O.$$
$$CoH_3\ (PR_3)_3 + N_2 \rightleftharpoons CoH\ (N_2)\ (PR_3)_3 + H_2$$

But most of these complexes release unchanged N_2 in attempts to reduce them (to NH_3) under mild or moderate conditions. In a few cases, however, it is possible to convert the bound N_2 to NH_3 :

$$cis\ [W(N_2)_2(PMe_2Ph)_4] \xrightarrow{H_2SO_4} N_2 + NH_4^+ + W(VI)\text{ compounds.}$$

Certain molybdenum complexes, after reduction to Mo (0) with a strong reducing agent (e.g. a Grignard reagent), can promote reduction of nitrogen in acid media at room temperature, e.g., the dinitrogen complex formed with 1, 2 - bis (diphenylphosphino)-ethane (abbreviated dppe) :

$$MoCl_3\ (thf)_3 + 2N_2 + dppe\ (excess) \xrightarrow{+3e} [Mo\ (N_2)_2\ (dppe)_2] + 3Cl^- + 3thf$$
$$[Mo\ (N_2)_2\ (dppe)_2] + 6H^+ \longrightarrow 2NH_3 + N_2 + Mo\ (VI)\text{ products.}$$

Though the above reaction is not a catalytic one, similar works are likely to be of much help in modelling the role of the enzyme nitrogenase present in nitrogen-fixing bacteria.

There are two major proteins in nitrogenases (i) the smaller component (molar mass = 60 – 70 kg mol^{-1} i.e., 60,000 – 70,000 dalton) containing Fe_4S_4 clusters (ii) a larger nitrogen-binding one (molar mass 220 – 240 kg mol^{-1}) which contains 2 Mo atoms, about 30 Fe atoms and about 30 S atoms. Speculative structures of the active site involve Mo – N_2 coordination followed by reduction to NH_3 via an intermediate like $Mo = \underset{\alpha}{N} - \underset{\beta}{N}H_2$. The strong triple bond in N_2 is weakened by gradual build-up of multiple bond character between the α-N atom and the Mo; the β-N atom is protonated.

$$\sim\!\sim\!Mo{-}N_2 \longrightarrow MoNNH \longrightarrow Mo{=}N{-}NH_2 \longrightarrow Mo{\equiv}N \longrightarrow NH_3.$$

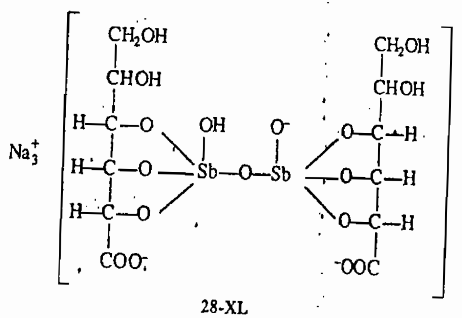
Phosphines and arsines function as important ligands to transition metals. PF_3 is a very ineffective ligand towards main group elements, owing to the high electronegativity of F and absence of filled d-orbitals on the main group elements. But PF_3 acts as strong ligand to transition metals. In spite of weak P – M σ-bonding, the complexes are stabilized by strong back bonding :

(i) F causes marked contraction of the otherwise diffuse $3d$ orbitals on P which can therefore hybridize better with the σ* orbitals than in other phosphines.

(ii) The energy of the P – F σ* orbitals is much lower in PF_3 than in similar orbitals in other phosphines. Thus they match better with the metal d-orbitals.

Phosphine complexes like Ni $(PF_3)_4$ were considered to be good examples of d_π—p_π bonding. Calculations have now revealed that the LUMO on a phosphine molecule is a pair of σ* m.o.-s with mainly phosphorus $3p$ character and has the proper symmetry to enter π-interaction with filled metal d-orbitals. The addition of a small amount of d-character to the σ* m.o.-s gives two hybrids which provide improved backbonding.

The oxalato, tartrato and similar hydroxy acid complexes form the main aqueous chemistry of Sb(III) (section 22.3.6). The structure of the $[Sb\ (ox)_3]^{3-}$ ion has already been discussed. Many complexes of Sb(III) are used in medicine, for example, sodium stibogluconate (28-XL).



28-XL

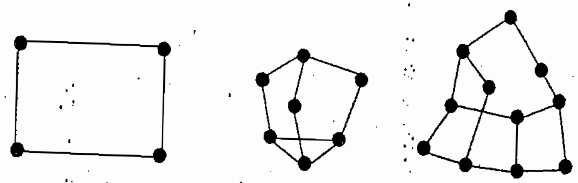
Clusters

Numerous polyatomic aggregates or clusters are formed by the heavier elements in Gr V(15). In addition to the few homonuclear clusters mentioned below, there are also a large number of heteronuclear clusters like

$$\left[As_{4-n}\left\{Co(CO)_3\right\}_n\right],\quad n = 0,1,2,4.$$

Alkaline earth phosphides $M_3^{II}P_{14}$ contain the P_7^{3-} cluster; this is isoelectronic and isostructural with P_4S_3. As_7^{3-} is present in Ba_3As_{14}, obtained as black monoclinic crystals by heating As with Ba at 800°C. Various other cluster ions have been prepared as crystalline solids by reacting alkali metal "alloys" of P, As, Sb and Bi with 2, 2, 2-crypt ligand in dry ethylenediamine. The crypt forms stable complexes with the alkali metal cations and thus prevents decomposition of the cluster anion by transfer of electrons to M^+ on removal of the solvent. Mixed tetrahedral clusters are obtained when ternary alloys like KSnBi are used :

$$K_5Bi_4 + crypt \longrightarrow [K\ (crypt)]_2^+\ Bi_4^{2-}$$
$$KAs_2 + crypt \longrightarrow [K\ (crypt)]_3^+\ As_{11}^{3-}$$
$$NaSb_3 + crypt \longrightarrow [Na\ (crypt)]_3^+\ Sb_7^{3-}$$
$$KSnBi + crypt \longrightarrow [K\ (crypt)]_2^+\ [Sn_2Bi_2]^{2-}$$



skeletons of As_4^{2-}, Sb_4^{2-}, Bi_4^{2-} As_7^{3-}, Sb_7^{3-} P_{11}^{3-}, As_{11}^{3-}

28-XLI

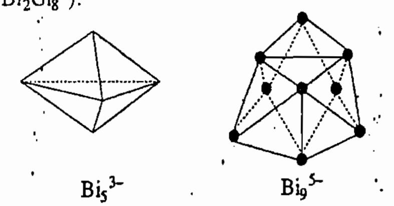
Several polyhedral cations containing clusters of Bi have been prepared by reduction of $BiCl_3$ with Bi or by oxidation of Bi with AsF_5 in liquid SO_2

$$BiCl_3 + 4Bi + 3AlCl_3 \longrightarrow Bi_5(AlCl_4)_3 \quad \text{(in fused } NaAlCl_4)$$

$$\text{do, excess Bi} \longrightarrow Bi_8(AlCl_4)_2$$

$$Bi + AsF_5 \xrightarrow{\text{liq } SO_2} 2Bi_5(AsF_6)_3, 2SO_2 + 3AsF_3.$$

Oxidation of Bi with $HfCl_4$ in presence of $BiCl_3$ produced $Bi_{10}Hf_3Cl_8$; X-ray studies established this as $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$. The cluster Bi_9^{5+} is also present in the black crystalline diamagnetic substance obtained by heating Bi + $BiCl_3$ to 325° and cooling slowly to 270°C. The gross composition $Bi_{24}Cl_{28}$ has been shown to consist of $(Bi_9^{5+})_2(BiCl_5^{2-})_4(Bi_2Cl_8^{2-})$.



28-XLII

22.3.10 Organic derivatives

The chemistry of organocompounds of the elements in this group is vast. We shall briefly mention a few important compounds only. The amines are elaborately discussed in organic chemistry texts. The organic esters of phosphate or thiophosphate (e.g., malathion, see before) are also not true organocompounds as they do not contain P—C bonds.

The organocompounds may be conveniently prepared by reacting the respective halides (or oxohalides) with excess Grignard reagents or lithium reagents, e.g.,

$$MCl_3 + 3RMgX \longrightarrow MR_3 + 3MgXCl.$$

$$MCl_3 + 3LiEt \longrightarrow MEt_3 + 3LiCl.$$

$$MX_5 + 5LiR \longrightarrow MR_5 + 5LiX.$$

$$OMX_3 + 3RMgX \longrightarrow OMR_3 + 3MgX_2.$$

Organo halides may be prepared by taking the halides in excess; these are useful in further synthesis.

$$PCl_3 + LiR \longrightarrow RPCl_2.$$

$$PCl_3 + 2LiR \longrightarrow R_2PCl \xrightarrow{Na} R_2P\text{–}PR_2$$

The trimethyl derivatives of P, As, Sb and Bi are attacked by air but the triaryl derivatives are stable. They are all pyramidal with a lone pair of electrons; the trialkyls of P and As possess strong donor properties and act as ligands toward transition metals. The empty d-orbital on P or As can act as acceptors of electrons from filled metal d-orbitals ($d\pi$-$d\pi$ back bonding).

The trialkylarsines also act as nucleophiles toward haloalkanes :

$$As(CH_3)_3 + CH_3Br \longrightarrow As(CH_3)_4Br.$$

[Sec. 22.3.10 *Organic derivatives*]

The resulting tetralkylarsonium slats contain As (V). Ph_3As being a much weaker nucleophile, does not give $AsPh_4Br$ by similar reactions.

Tetraphenyl arsonium salts are made through the reaction

$$O = AsPh_3 + PhMgBr \longrightarrow [AsPh_4]Br + MgO.$$

The $[AsPh_4]^+$ cation is used in several occasions as a bulky cation. It is also useful in the preparation of organo derivatives of As (V) e.g.,

$$AsPh_4Br + LiPh \longrightarrow AsPh_5 + LiBr.$$

This has a trigonal bipyramid structure, but $SbPh_5$ is square pyramidal.

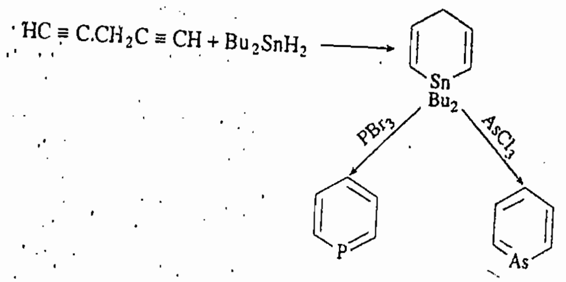
Dicacodyl, $(CH_3)_2As\,As(CH_3)_2$, (tetramethyldiarsine) is one of the oldest organometallics known (Cadet, 1760). It can be prepared by the reaction

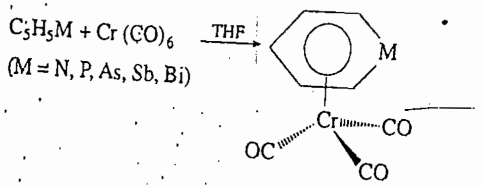
$$2(CH_3)_2AsI + 2Li \longrightarrow (CH_3)_2As\,As(CH_3)_2 + 2LiI \text{ (in THF)}.$$

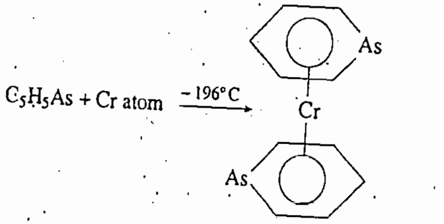
More extensive catenation is present in the cyclopolyarsanes :

$$6PhAsI_2 + 12Hg \longrightarrow (PhAs)_6 + 6Hg_2I_2.$$

Compounds containing π bond between P, As or Sb may be prepared by using bulky substituents. Analogues of pyridine and "sandwich" complexes similar to those of benzene have also been prepared :







SUMMARY

Introduction : The elements of group 15(VA) of the periodic table are collectively known as pnicogen (or pnictogen) or pnictides from the fact that nitrogen does not support respiration (from the Greek word for "to choke"/"strife"). However, nitrogen plays a vital role in living systems, for example as the amino acids. Phosphorus is an essential constitutent of bones.

General trend in properties : The general group trend follows the same pattern as observed in groups III and IV. Increased nuclear charge makes the elements more electronegative than the corresponding elements in group IV. The remarkable tendency of catenation observed in carbon practically disappears in nitrogen.

Nitrogen occurs mainly as the gaseous dinitrogen molecule ($N \equiv N$), whose stability and inertness may be assigned to the strong triple bond (a bond order of three) between the N atoms. Phosphorus, unable to establish such strong π-bond with its large 3*p*-orbitals, forms tetrameric P_4 units which are packed differently to give various allotropic modifications. Vapours of arsenic, antimony and bismuth also contain the tetramers. At room temperatures, the most stable forms of the elements are the lustrous metallic rhombohedral variety, comparable to rhombohedral black phosphorus.

From the electron configuration of the elemente we expect the following general trend in various properties in line with those expected in groups 13(IIIA) and 14(IVA) : (i) a gradual decrease in ionization energy and electronegativity; the effect will be less marked in As owing to poor shielding by the $3d^{10}$ core and also in Bi owing to poor shielding by $4f^{14}$ and $5d^{10}$ core of electrons. (ii) an increase in metallic character down the group (iii) appearance of inert pair effect in bismuth (iv) non existence of pentacovalent nitrogen owing to the lack of energetically accessible vacant orbital required for valence expansion (v) remarkable stability of 2*p*-2*p* π-bonds over 3*p*-3*p* π-bonds (vi) aptitude of nitrogen to form H-bonds (vii) the role of *d*-orbitals in the chemistry of phosphorus. The covalent bond energies of the elements support these expectations. N—H bonds are stronger than P—H bonds, but the trend is reversed with bonds formed with Cl or O. At the same time, stable phosphorus analogues of N_2, NO, NO_2, HCN, N_3^- etc. are absent, reflecting the importance of *p-p* π-bonding in nitrogen and *p-d* π-bonding in phosphorus.

The formation of M^{3-} ions by gain of three electrons or M^{5+} ions by loss of five electrons appear energetically unfavourable. Only a few ionic nitrides are known with strongly electropositive metals of high charge where the lattice energy of the resulting nitride compounds are sufficiently high. With increase in atomic number, we expect Sb^{3+} and Bi^{3+} ions to exist in crystalline salts like $Sb_2(SO_4)_3$ and $Bi(NO_3)_3 \cdot 5H_2O$. Most of the compounds of these elements are thus covalent with the elements in oxidation state of either + III or + V. Nitrogen covers a wide range of O.N. from –3 (in NH_3) to + 5 (in HNO_3).

The MR_3 type compouns are mostly pyramidal with a lone pair of electrons which are sterically active. The molecules undergo rapid inversion in which the M atom oscillates through the plane containing the three R-groups.

The MR_5 type compounds often have a trigonal bipyramid structure, e.g., PF_5 and PCl_5 (*g*). The solid halides PCl_5 and PBr_5 have ionic structures like $[PCl_4^+]$ $[PCl_6^-]$ and $[PBr_4^+]$ $[Br^-]$.

Principal Compounds

Hydrides : Hydrides of general formula MH_3 are formed by all the elements, though their stability decreases sharply as the M—H bond energy falls to heavier elements. M_2H_4 type hydrides are known for N, P, As and Sb, but only N_2H_4 (hydrazine) has any significant chemistry. Nitrogen alone forms N_3H (hydrazoic acid) and N_2H_2 (di-imide).

All the hydrides are good reducing agents. As expected, basic character also decreases from NH_3 to PH_3 onward. NH_3 and PH_3 can act as good ligands — NH_3 is a hard donor while PH_3 is a soft one.

Halides : The normal trihalides MX_3 are formed by all the elements in the group, though NBr_3 and NI_3 are extremely unstable. Pentahalides are known for the elements P to Bi, but the decreasing M—X bond energy as both M and X become larger becomes less able to stabilize the M(V) state; consequentyly fewer pentahalides are known with the lower members in the group and with heavier halogens. A few lower halides and mixed halides are also known. Bismuth alone in the group forms a subhalide $Bi_{24}Cl_{28}$ containing clusters of Bi atoms.

The pentahalides may be prepared by reacting the trihalides with excess halogen. The molecules are trigonal bipyramidal in the gaseous state, suggesting sp^3d hybridization of the central atom. However, the molecules are now described in terms of three usual 2-center-2-electron covalent bonds (in the equatorial plane) and two 3-center-4-electron bonds in the axial plane. The pentahalides are used as effecient chlorinating agent. AsF_5 and SbF_5 act as very powerful fluoride ion acceptor. Lewis acidity increases in the order $SbF_5 > BiF_5 > AsF_5 > PF_5$.

Oxides : The elements form oxides in their usual + III and + V states, though Bismuth (V) oxide is not well characterized. Nitrogen also forms N_2O, NO and NO_2 — all dominated by 2*p*-2*p* π-bonds and hence having no analogue among P or heavier members. High N≡N bond energy makes direct oxidation of nitrogen difficult.

Oxoacids : The oxo-acids of nitrogen are again dominated by nitrogen oxygen *p-p* π-bonding. There are no direct analogues of these acids among the heavier elements. Phosphorus has a rich chemistry of condensed phosphates.

Though H_3NO_4 (orthonitric acid) is not known, orthonitrates Na_3NO_4 (and K_3NO_4) have been prepared by heating $NaNO_3$ (KNO_3) and Na_2O in a silver crucible at 300°C for 7 days. The N—O bond length corresponds to a bond order of unity.

Phosphorus forms a vast number of oxoacids and anions e.g., hypophosphorus acid H_3PO_2, phosphorus acid H_3PO_3, phosphoric acid H_3PO_4 and various polyphosphoric acids. In all oxoacids and anions, the P atoms are 4-coordinate with at least one P = O unit and at least one P–OH group in which the hydrogen atom is ionizable. Hydrogen atoms in P—H bonds are not ionizable. Catenation may occur by direct P—P bonds or P–O–P links. H_3PO_2 (monobasic) and H_3PO_3 (dibasic) are reducing in nature.

In condensed phosphates, some or all of the PO_4 tetrahedral units share two corner oxygen atoms to give short chains (n = 1 – 16), very long chains and cyclic species. Linear polyphosphates are used in water softening and in detergents.

Cationic chemistry : The principal cationic chemistry of nitrogen is that of the NH_4^+ ion and related quaternary ions. Quaternary ions R_4M^+ (R = H, alkyl, aryl, halogen, alkoxy etc.) are also formed by P and to a somewhat less extent by As, Bi forms only Ph_4Bi^+. The ability to form aquocations increases to Sb and Bi. $Sb_2(SO_4)_3$, $Bi_2(SO_4)_3 \cdot nH_2O$ etc. may be isolated, but all are readily hydrolyzed to basic salts, forming oxocations like SbO^+ (antimonyl) and BiO^+ (bismuthyl). Bismuth salts are further hydrolyzed to form clusters of Bi atoms.

Sulphur compounds : Binary compounds of sulfur and nitrogen are treated as nitrides of sulfur in Gr 16(VI) - Phosphorus forms a number of sulphides based on the P_4 tetrahedron but these do not necessarily correspond to the oxides. P_4S_3 is used in "strike anywhere" matches. P_4S_{10} is used in the manufacture of dialkyl or diaryl dithiophosphoric acids; salts of these acids have various industrial uses including manufacture of pesticides. Arsenic forms both As_2S_3 and As_2S_5 but only Sb_2S_3 and Bi_2S_3 are known. Arsenic and antimony sulphides dissolve in alkali and alkali metal sulphides but Bi_2S_3 does not.

Phosphazenes are formally "unsaturated" compounds with the grouping ≡ P = N —. Among the line and cyclic polyphosphazenes, the phosphonitrilic halides are most important. Heating PCl_5 with NH_4Cl gives rise to $(PNCl_2)_n$ where *n* may be 3, 4, 5, ... for cyclic compounds as well as very large numbers for linear polymers. **A wide range of physical properties may be achieved by suitable substituents and desired degree of polymerization—glasses, rubbers or tough flexible solids. The high molecular weight polymers are insoluble in organic solvents and resemble vulcanized rubber in mechanical properties (inorganic rubber).**

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EXERCISE

1. (a) *Elemental nitrogen exists as the gaseous dinitrogen molecule while elemental phosphorus forms solid P_4 molecules — explain.*

   (b) *Single and multiple bonds of nitrogen and carbon are characterized by the following energy and length :*

	$-\ddot{N}=\ddot{N}-$	$-\ddot{N}-\ddot{N}-$	$-C=C-$	$-C-C-$
E, kJ mol^{-1}	418	155	606	334
d, nm	0.125	0.146	0.135	0.155

   Explain the great differences in stability of homochains of nitrogen and carbon.

2. *How do you expect the chemistry of nitrogen to differ from that of phosphorus? Give at least three examples from known chemical reactions.*

3. *Give balanced equations for reactions, if any, of conc. HNO_3 on the elements P, As, Sb and Bi.*

4. *How does white phosphorus react with (i) an excess of O_2, (ii) a deficiency of O_2, (iii) an excess of Cl_2 (ii) a deficiency of Cl_2 (v) S_8 (vi) solution of $Ba(OH)_2$.*

5. (a) *What happens when As_2S_3, Sb_2S_3 and Bi_2S_3 are separately treated with yellow ammonium sulfide?*

   (d) *How would you separate a mixture of As_2S_3, Sb_2S_3 and Bi_2S_3?*

6. *Give conditions and equations for the preparation of the following :*

   (a) *an aqueous solution of hydroxylamine hydrochloride; (b) anhydrous hydrazine; (c) solid sodium azide; (d) solid sodium hyponitrite.*

7. (a) *Compare and contrast the (i) structure and (ii) properties of hydrazine and hydrogen peroxide.*

   (b) *Write equations of thermal decomposition of NH_4Cl, $(NH_4)_2CO_3$, $NH_4H_2PO_4$ and $(NH_4)_2Cr_2O_7$. Compare them with the equations of decomposition of NH_4NO_2 and NH_4NO_3. How does the character of thermal decomposition depend on the nature of the anion?*

   [Hints : Oxidizing anions $\longrightarrow$ irreversible]

8. *Give examples to show that hydrazine and hydroxylamine possess oxidizing as well as reducing property.*

   Mention two important uses of hydrazine.

9. *Discuss the structure and bonding in hydrazoic acid and the azide ion in an ionic azide. Hence commnet on the different thermal stability of N_3H and N_3Na.*

10. *Give examples to show that nitrous acid can act both as an oxidizing and a reducing agent.*

    Draw the sturctures of (i) the oxides of phosphorus and (ii) the oxoacids of phosphorus containing one P atom per molecule.

    Comment on the relative acidities and redox properties of the acids.

11. *How would you titrate phosphoric acid as a tribasic acid?*

    50 ml of a solution of H_3PO_4 and HCl is titrated with 0.1 M NaOH solution . The first equivalence point appears at 30.0 ml using methyl orange as indicator. Titration is continued using bromothymol blue as indicator when a further 20 ml of the same acid is required to reach the second equivalence point.

    Calculate the concentration of HCl and H_3PO_4 in the solution.

[Hints : The first equivalence point shows the neutralization of HCl and first H$^+$ of H_3PO_4, total 30ml × 0.1 mol L^{-1} = 30 mmol (millimol).

The subsequent 20 ml alkali goes to neutralize the second H$^+$ of H_3PO_4, equal to 20 mmol.

Hence, 20 mmol alkali was required in the first stage to neutralize the first H$^+$ of H_3PO_4.

∴ H_3PO_4 present = 20 mmol.

$$\text{Concentration of } H_3PO_4 = \frac{20 \text{ mmol}}{50 \text{ mL}} = 0.4 \text{ mol L}^{-1}.$$

Concentration of HCl = 0.2 mol L^{-1}.

12. (a) *Arrange in order of increasing (i) bond length and (ii) bond angle :*

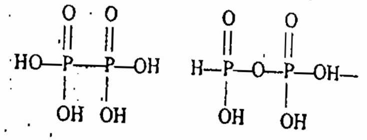
    NO_2^+, PF_3Cl_2, $PCl_5(g)$, $PCl_5\ (s)$

    (b) *Write the structures of*

    NF_4^+, PF_3Cl_2, $PCl_5\ (g)$, $PCl_5\ (s)$

    (c) *How does the use of polyphosphates in detergents affect our environment?*

    (d) *Indicate the oxidation number of each P-atom in the following compounds*



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH \qquad H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH-$$

    (e) *How would you chemically differentiate between a metallic azide and a metallic nitride?*

    (f) *Mention one use of sodium azide in chemical analysis.*

    (g) *How are P_4, P_4O_6 and P_4O_{10} related structurally?*

    (h) *Why is the phosphate radical considered "interfering' in qualitative analysis?*

    (i) *How would you establish that H_3PO_2 is a stronger reducing agent than H_3PO_3?*

    (j) *What are the similarities and differences between phosphates and arsenates?*

    (k) *What is Graham's salt? (not sodium hexametaphosphate).*

    (l) *Compare the main features in the chemistry of As(III) and As(V).*

    (m) *Suggest synthesis of $Na^{15}NH_2$ and $^{15}NOAlCl_4$ from $K^{15}NO_3$.*

    [Hints : (i) $^{15}NH_3$ from $K^{15}NO_3$. Then sodium metal. (ii) ^{15}NO by Hg and H_2SO_4 on $K^{15}NO_3$. Then $AlCl_3$ and Cl_2].

    (n) *What are the ions present in a solution of N_2O_5 in anhydrous H_2SO_4?*

13. *Give brief and most likely explanations for the following observations :*

    (i) *ΔT_f of H_2SO_4 by N_2O_5 is six times that calculated on the basis of the formula N_2O_5.*

    (ii) *PCl_3 and $SbCl_3$ behave differently with water.*

    (iii) *NF_3 has no donor properties at all, but PF_3 forms numerous complexes with transition metals.*

    (iv) *Compounds of the type R_3PO have lower dipole moments in comparison to R_3NO compounds, though the P—O bond has a greater electronegativity difference than the N—O bond.*

    (v) *NH_4F is a stable crystalline solid but PH_4F dissociates completely below 0°.*

    (vi) *Both NO and NO_2 are odd electron molecules but only NO_2 dimerizes readily.*

(vii) The common oxoanions of N(V) and phosphorus(V) are NO_3^- and PO_4^{3-} respectively.

(viii) Phosphorous acid is not $P(OH)_3$.

(ix) R_3PO is more stable than R_3NO.

(x) The base strengths of ammonia and the methylamines in aqueous solution follow the order

	NH_4^+	NH_3Me^+	$NH_2Me_2^+$	$NHMe_3^+$
pK_a	9.25	10.62	10.77	9.80

[**Hints :** The inductive effect of Me groups explain the base strength $NH_3 < NH_2Me < NHMe_2$. The lower base strength of $NHMe_3$ in aqueous solution is probably associated with solvation and hydrogen bonding. In $CHCl_3$, $NHMe_3$ is the strongest base in the series.

(xi) Base strength increases as

$$H_2NOH < H_2NNO_2 < H_2NNH_2 < NH_3.$$

14. *Consult the oxidation state reduction potential diagram for nitrogen (p. 347; section 22.2.2).*

(a) Calculate the reduction potentials (E°) for the reactions

(i) $NO_3^- + 8H^+ + 6e \longrightarrow NH_3OH^+ + 2H_2O$

(ii) $NO_3^- + 10H^+ + 8e \longrightarrow NH_4^+ + 3H_2O$

(b) Show that NH_3OH^+ cations have a strong tendency to give N_2 and $N_2H_5^+$ cations in acid solution.

[**Ans. :** (a) 0.73V; 0.89V; (b) $4NH_3OH^+ \longrightarrow N_2 + N_2H_5^+ + 4H_2O + 3H^+$; $E° = 3.28V$].

15. *Calculate E° for the following pairs using values given in the above diagram :*

(a) NO_3^-—NH_4^+ (b) NO_3^-—$N_2H_5^+$ (c) NO_3^-—NH_3OH^+ (d) NO_3^-—N_2O (e) NO_3^-—NO (f) NO_3^-—NNO_2.

[**Ans. :** (a) + 0.89V (b) + 0.83V (c) + 0.73V (d) + 1.12V (e) + 0.96V (f) + 0.94V].

16. *Use the same diagram and the results of question no. 16 to examine the feasibility of the following disproportionation reactions*

(i) $N_2O \longrightarrow N_2 + NO$; (ii) $NO \longrightarrow N_2O + HNO_2$ (iii) $NO_2 \longrightarrow HNO_2 + NO_3^-$

(iv) $N_2H_5^+ \longrightarrow N_2H_4^+ + N_2H_3^+$ (v) $NH_3OH^+ \longrightarrow N_2H_5^+ + NO_3^-$ (vi) $N_2O \longrightarrow N_2 + NO_3^+$

(vii) $NO \longrightarrow NO_3^+ + N_2O$ (viii) $HNO_2 \longrightarrow NO + NO_3^-$.

Complete and balance the above ionic equations and calculate E° for each.

[**Ans. :** (i) 0.18V (ii) 0.59V (iii) 0.27V (iv) $4H_2H_5^+ + 2H^+ + 3H_2O \longrightarrow 7NH_4^+ + NO_3^-$; 0.44V (v) $7NH_3OH^+ \longrightarrow 3N_2H_5^+ + 4H_2O + NO_3^- + 5H^+$; 0.73V (vi) 0.66V (vii) 0.63V (viii) 0.05V].

17. *Use E° values of the nitrogen-system to answer the following :*

(a) $E°(Cl_2–Cl^-) = 1.36V$. Do you expect chlorine to oxidize (i) NO_2 to NO_3^- (ii) N_2 to N_2O?

(b) Calculate E° for the reaction

$$2NH_3OH^+ \longrightarrow N_2 + H_2 + 2H_2O + 2H^+$$

Does the reaction proceed as written?

[**Ans. :** (a) (i) $2NO_2 + 2H_2O + Cl_2 \longrightarrow 2NO_3^- + 4H^+ + 2Cl^-$; $E° = 0.55V$. Feasible. (ii) $E° = -0.41V$.

(b) $2NH_3OH^+ \longrightarrow N_2 + 2H_2O + 4H^+ + 2e$; $H_2 \longrightarrow 2H^+ + 2e$.]

$E° = 1.87V$ for the given reaction. But it does not proceed as such. Hydroxylamine disproportionates as shown in Question 15(b).]

18. *The following information are given about hydrazine.*

(i) m. p. 2°C, b.p. 114°C.

(ii) $N_2H_4(aq) + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $K = 8 \times 10^{-7}$ (25°C)

(iii) $N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l)$ $\Delta H_f^0 = 50.2$ kJ mol^{-1}.

(iv) $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l)$ $\Delta H° = -623.4$ kJ mol^{-1}.

Comment on each, keeping in view the likely use of the compound.

[**Hints :** (i) a convenient liquid range (ii) a weak base (iii) decomposition into N_2 and H_2 would be strongly exothermic and may be explosive (iv) a high energy of combustion, leading to small molecules. Suitable for use as a rocket fuel.]

19. *Describe the following reactions with balanced equation :*

(a) Ag_2HPO_3 is warmed with water.

(b) A solution of hydroxylamine in sulfuric acid is boiled with an excess of iron(III) sulfate solution. The solution is next cooled and titrated with dilute aqueous $KMnO_4$ solution until a faint pink colour.

(c) Hydrogen peroxide is added to a mixture of hydrazine and hydroxylamine.

(d) Nitrogen pentoxide is added to anhydrous perchloric acid in nitromethane.

(e) Sodium hypophosphite is added to an aqueous solution of Ni(II).

(f) Phosphorus acid is added to an aqueous solution of mercuric chloride.

(g) $POCl_3$ is reacted with gaseous ammonia.

(h) $BiCl_3$ is treated with chlorine and hot concentrated KOH.

(i) Sodium bismuthate is added to a solution of manganese(II) sulfate in presence of dilute HNO_3.

(j) A solution of disodium hydrogen phosphate is added to a solution of magnesium chloride in presence of ammonia/ammonium chloride and the precipitate obtained is heated.

(k) Dry chlorine is passed over gently heated $AgNO_3$.

(l) Stannous chloride is added to a solution of As_2O_3 in conc. HCl and warmed.

(m) Excess of aqueous NaOH is added to a solution of $SnCl_2$ and the resulting solution is added to a solution of $Bi(NO_3)_3$.

(n) N_2O_5 is added to hydrogen peroxide (anhydrous).

[**Hints :** (a) $Ag + H_3PO_4$ (b) N_2O + Fe(II) (c) N_3H (d) $NO_2^+ClO_4^-$ (e) $Ni + H_2 + PO_4^{3-} + H^+$ (f) $Hg + H_3PO_4 + HCl$ (g) $PON + NH_4Cl$.

Phosphorus(V) oxynitride is an amorphous white solid stable below 750°C and insoluble in common solvents. (h) $KBiO_3$ (i) $MnO_4^- + Bi^{3+}$ (j) $MgNH_4PO_4$ (k) $AgCl + N_2O_5 + O_2$ (l) $As + SnCl_4$ (m) $Bi + Na_2SnO_3$ (n) $HNO_3 + HOONO_2$.]

20. *Explain the difference between the N—H stretching frequency in NH_3 with that in the ammine complexes :*

	NH_3	$[Co(NH_3)_6]^{3+}$	$[Cr(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
$\bar{\nu}$ cm^{-1}	3414	3320	3320	3397

[**Hint :** Transfer of electron density to the metal decreases the electron population in the N—H bond and reduces its rigidity. Transfer is influenced by the charge on the metal ion.]

21. *The products formed in the reactions*

$$2NO + Cl_2 = 2NOCl$$

$$6NO + 8BrF_3 = 6NO[BrF_4] + Br_2$$

have the following characteristics :

NOCl : gas, b.p. $-7°C$, $\bar{\nu}(N—O) = 1800\ cm^{-1}$.

NO[BrF₄] : crystalline, m.p. $255°C$, $\bar{\nu}(N—O) = 2300\ cm^{-1}$, *conductor in liquid state.*

In which of these compounds is the NO group bonded by a covalent bond and in which it is in the form of NO^+ *ion?*

22. *How are the condensed phosphates prepared? Show the characteristc features and the charges of the terminal, middle and branching units in their structure.*

Sodium hexametaphosphate is a misnomer — comment.

23. *A is a colourless liquid. Its aqueous solution produces a yellow precipitate **B** with* H_2S. *B is insoluble in dilute* HNO_3 *but dissolves in a solution of KOH + KHS forming solution C. Acidification of C reprecipitates B.*

B is also soluble in a mixture of KOH + H_2O_2 *forming solution **D** and a precipitate E. If D is treated with a mixture of* $Mg(NO_3)_2$ *and* NH_4NO_3, *a white precipitate **F** is formed.*

***F** dissolves in acetic acid and the solution gives a red precipitate **G** with silver nitrate.*

The precipitate E is insoluble in acids and bases but dissolves in CS_2.

When the aqueous solution of A is heated with HNO_3 *and* $AgNO_3$ *is added, a white precipitate H is obtained. H dissolves in aqueous* NH_3 *to solution I. I reprecipitates H on adding dilute* HNO_3.

*Identify **A—I** and give equations of the reactions involved.*

CHAPTER TWENTY THREE

ELEMENTS OF GROUP 16(VI A)

O, S, Se, Te(Po)

OBJECTIVES

23.1 Introduction
  Abundance and occurrence [23.1.1]
  Isolation [23.1.2]
  Use [23.1.3]

23.2 General Properties of the Elements
  Allotropic forms. [23.2.1]
  Atomic and Physical Properties [23.2.2]
  Chemical reactivity; Dioxygenyl compounds;
  The onium ions [23.2.3]
  Valence, oxidation state and redox potential diagram [23.2.4]

23.3 Principal Compounds
  Hydrides [23.3.1]
  Oxides, Sulphides, Selenides, Tellurides [23.3.2]
  Oxides of S, Se, Te [23.3.3]
  Oxoacids and their salts [23.3.4]
  Halides, oxo-halides, complex halides [23.3.5]
  Aqueous Solution Chemistry [23.3.6]
  Sulphur-nitrogen Compounds [23.3.7]
  Complexes and Clusters [23.3.8]
  Organo-derivatives [23.3.9]

23

ELEMENTS OF GROUP 16(VIA)

23.1 INTRODUCTION

The elements of this group are collectively called chalcogens (*kalkogens*) from Greek **chalcos** (= copper) as copper is usually found associated with sulphur and its congeners. Oxygen, the most abundant element in the earth's crust, is also vital to the living world. It reacts directly (sometimes under heating) with almost all other elements except halogens, noble gases and some of the platinum metals. We have already discussed a large portion of the chemistry of oxygen and sulphur in the discussion under oxides and sulphides in other periodic groups.

23.1.1 Abundance and occurrence

Oxygen, the most abundant element in the earth's crust (46% by weight), is the major constituent of silica, clay and various silicate minerals, together with some oxide, carbonate etc. minerals. It also contributes to about 89% (weight) of the water in the oceans. Uncombined oxygen is mainly present as O_2 in air (20.9% by vol.) and O_3 in the upper atmosphere (see later).

Sulphur, the sixteenth most abundant element, constitutes nearly 0.034% (wt) of the earth's crust. It is present as numerous sulphide minerals as well as in gypsum as sulphate. Native sulphur occurs in several places on the earth. Sulphur also occurs as H_2S in natural gas and petroleum and as organosulphur compounds in coal. S occurs in many organic compounds e.g., in hair, wool, egg albumen, garlic, onion and mustard.

Selenium and tellurium occupy sixtysixth and sixtyseventh position in order of crustal abundance (0.05 ppm and 0.02 ppm respectively). They occasionally occur native with S. Se forms selenide minerals with sulphides of Cu, Ag, Hg, Ni etc. Te is found as tellurides of Ag and Au. Both these elements are obtained as by-products in copper extraction and purification.

All 27 isotopes of polonium are radioactive. Only Po-210 occurs naturally in uranium ores (0.1 mg per tonne):

$$^{210}_{82}\text{Pb} \xrightarrow[22.3y]{\beta} {}^{210}_{83}\text{Bi} \xrightarrow[5d]{\beta} {}^{210}_{84}\text{Po} \ (\alpha\text{-active, } t_{1/2} = 138 \text{ d})$$

Oxygen has three stable iostopes; their relative atomic mass and abundance (atom %) are:

^{16}O : 15.994915; 99.763 ^{17}O : 16.999134; 0.037 ^{18}O : 17.999160, 0.200

The compositon of natural sources may slightly vary. ^{17}O and ^{18}O may be enriched by fractional distillation or electrolysis of water or by thermal diffusion of O_2. The ^{18}O isotope is used as tracer in kinetic and mechanistic studies. ^{17}O has a nuclear spin $\frac{5}{2}$ and can be used in nmr studies. Several radioactive isotopes of oxygen have also been prepared, ^{15}O is the longest-lived $\left(t_{1/2} = 122s: {}^{16}O\left({}^{2}_{3}He, \alpha\right){}^{15}O\right)$.

Sulphur has four stable isotopes (^{32}S 95.02%; ^{33}S 0.75%; ^{34}S 4.21% and ^{36}S 0.02%). Besides, there are six radioactive isotopes, of which ^{35}S has the longest half-life (87.1d). It is β-active and can be prepared by ^{35}Cl (n, p) reaction. It is widely used in mechanistic studies (see application of radio isotopes Ch. 13).

23.1.2 Isolation of the elements

Oxygen is obtained industrially by fractional distillation of liquid air. In the laboratory, oxygen may be prepared by (i) electrolysis of 30% KOH solution with Ni electrodes, (ii) catalytic decomposition of H_2O_2 over platinized Ni foil, (iii) thermal decomposition of certain compounds, e.g.,

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

The reaction occurs at 400°-500°C but can be made to occur at 150° by using MnO_2 as a catalyst. But this produces some ClO_2 also (up to about 3%). Thermal decomposition of pure $KMnO_4$ in vacuum gives very pure O_2

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2 \quad (215° - 235°C).$$

Sulphur is usually lifted from underground deposits by Frasch process. Three concentric pipes are sunk to the sulphur layer (150-750 m below surface); the sulphur is melted with superheated water and forced upward by compressed air.

India has no deposit of sulphur and has to depend on imported sulphur. Sulphur recovered from various other sources may partially meet this problem in the future.

Sulphur is now recovered on a large scale from sour natural gases which contain about 15-20% H_2S. The H_2S is absorbed in monoethanolamine followed by partial oxidation (about one-third). Sulphur is then produced by self-reduction between H_2S and SO_2 over Fe_2O_3/Al_2O_3 catalyst at 300°C.

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2.$$
$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$
$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

Sulphur may be recovered from crude petroleum oil in a similar manner. Millions of tonnes of S are already obtained in this manner in Japan and USA.

Sulphur in the form of SO_2 is obtained as a bye-product from roasting of sulphide minerals like iron pyrites, zinc blend etc.

Coal contains about 1-1.5% S, partly as pyrite and partly as organic compounds. Coal from Garo hills in Meghalaya contains as high as 3.6% sulphur (as organo compounds). This may be released as H_2S by dry distillation of the coal (coal gas preparation) or as SO_2 through combustion. Pyritic sulphur (e.g. in the coal from Rewa, M.P.) may be recovered by washing the coal.

Gypsum occurs extensively in Rajasthan. This may be converted to ammonium sulphate directly by NH_3 and CO_2.

Selenium and **tellurium** are usually recovered from the "anode mud" obtained in electrolytic refining of copper. The dried mud (contains about 3-28% Se and about 8% Te) is roasted with sodium carbonate in air (650°C). Sodium selenite and tellurite formed are leached with water. Neutralization with H_2SO_4 now leaves selenous acid in solution, precipitating $TeO_2.xH_2O$.

Selenium may be obtained from the solution by reduction with SO_2.

Tellurium is obtained by reduction of TeO_2 with carbon at red heat or electrolytic reduction.

$$Cu_2Se + Na_2CO_3 + 2O_2 \longrightarrow Na_2SeO_3 + 2CuO + CO_2$$
$$Cu_2Te + Na_2CO_3 + 2O_2 \longrightarrow Na_2TeO_3 + 2CuO + CO_2$$
$$H_2SeO_3 + 2SO_2 + H_2O \longrightarrow Se + 2H_2SO_4$$
$$Na_2TeO_3 + H_2O \longrightarrow Te + 2NaOH + O_2 \text{ (electrolytic reduction)}.$$

SeO_2 may also be volatilized by roasting the mud around 650-700°C.

Polonium -210 is obtained by neutron irradiation of ^{209}Bi in a nuclear reactor. The Bi-210 nuclide formed emits β-particles $(t_{1/2} = 5\text{days})$ and gets converted to Po-210.

23.1.3 Uses

Oxygen is the third chemical in order of use in industry (after H_2SO_4 and N_2), nearly 100 million tonnes being consumed annually throughout the world. It is largely used in metallurgy — in steel making, in blast furnaces and Bessemer converters. O_2 is also used in direct oxidation in many chemical processes, for example, in making synthesis gas, oxidizing ehylene to ethylene oxide etc. Liquid oxygen is also used as an oxidizer for the fuels in rocket propulsion.

Sulphur is largely (88% of total use) consumed in making H_2SO_4, which is the topmost chemical in industry. Other uses of sulphur include vulcanization of rubber, manufacture of CS_2 for use in making rayon, insecticides, fungicides etc. Sulphuric acid is largely used in making phosphate fertilizers and ammonium sulphate, in making detergents, paints, pigments, rayon, explosives and what not. SO_2 and sulphurous acid are essential bleaching agents in sugar and paper industry.

Selenium, in low percentage (0.01 kg/tonne), is used to decolorize glass. At higher concentration (1 kg/tonne) it gives a pink shade to glass. Cadmium sulphoselenide is used to make beautiful ruby red glasses. Xerography (Greek *xero* = dry; *graphy* = writing) or "photocopying" is based on the photoconducting property of Se.

Xerox copying : A thin film of Se on an Al support is used as a photoreceptor. The photoreceptor is sensitized electrostatically and an image focussed on to it. Areas exposed to light lose their electrostatic charge. The areas still charged are coated with a toner powder, which fuses on the hot paper. The photoreceptor is brushed clean and kept for recycling.

Selenium is also used in photo electric cells and as a rectifier in semiconductor devices. Ferroselenium is used in alloying with stainless steel. Selenium dithiocarbamate is used in processing natural and synthetic rubber.

Tellurium is mostly used in making steel and other non-ferrous alloys. Small amounts of TeO_2 are used in tinting glass.

23.2 PROPERTIES OF THE ELEMENTS

23.2.1 Elemental Forms

Oxygen

Oxygen occurs in two allotropic forms — dioxygen (O_2) and ozone (O_3). The colourless odourless O_2 molecule is paramagnetic with two unpaired electrons and its bonding is best described in terms of m.o. approach (Ch. 7). Liquid oxygen is pale blue, solid oxygen is blue in colour.

Singlet O_2. In the ground state, the highest occupied m.o. of O_2 has two electrons with parallel spin in the two π* m.o.-s. It is said to be in the triplet state : the total spin (s) of the two electrons is equal to $2 \times {}^1/_2 = 1$ and spin multiplicity = $2 \times 1 + 1 = 3$. The next higher state is one in which the electrons are spin-paired in one π* m.o., with resultant $S = \frac{1}{2} - \frac{1}{2} = 0$. So this is a singlet state $(2 \times 0 + 1)$. The next

higher state is also a singlet state with the electrons separate but having opposite spins. The electron distribution, term symbol and energy separation of the states are shown below :

	e-distribution in π*m.o.	State	Energy/kJ
Second excited state	↓ ↑	$^1\Sigma_g^+$	155
First excited state	↓↑ –	$^1\Delta_g$	92
Ground state	↓ ↓	$^3\Sigma_g^-$	0

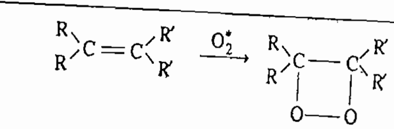
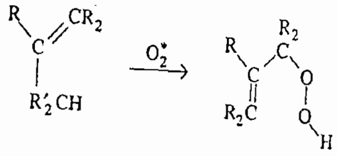
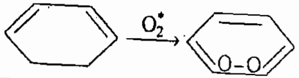
Normally a triplet to singlet transition is forbidden. This is why gaseous O_2 is colourless. But in liquid or solid oxygen, a single photon may simultaneously collide with two O_2 molecules (which are quite close) and excite both. Absorption of radiation in the red to green visible region imparts the observed blue colour.

Singlet oxygen has been prepared in several ways, e.g., (i) irradiation of O_2 in presence of a sensitizer like fluorescein, methylene blue etc or (ii) decomposition of ozonides or of H_2O_2

$$H_2O_2 + OCl^- \xrightarrow{EtOH} H_2O + Cl^- + O_2^*$$

$$H_2O_2 + Cl_2 \longrightarrow 2H^+ + 2Cl^- + O_2^*$$

O_2^* signifies singlet O_2 in the first excited state which has sufficiently long life-time to enter into chemical reactions. The involvement of singlet O_2 in various reactions, particularly in biological processes is now well established. It reacts as an electrophilic reagent, as for example in adding to an 1, 3 - diene to form an endo-peroxide (1, 4 addition); the singlet O_2 acts as a dienophile. Besides, singlet O_2 can also undergo 1, 2 and 1, 3 addition reactions (see below) :

1,2 addition	sterically hindered alkenes, alkynes, ketenes, allenes etc.	
1,3 addition	alkenes having at least one allylic hydrogen. The double bond shifts to an adjacent position in the resulting allylic hydroperoxide	
1,4 addition	cisoid 1, 3-diene	

Singlet O_2 is used as a selective oxidizing agent in many fine chemical industry.

Dioxygen is fairly soluble in water — about 3 cm³ (STP) per 100 cm³ at 20°C. It is also highly soluble in organic solvents like acetone and benzene, often with the formation of weak charge-transfer complexes.

Chemical properties of dioxygen have been discussed in section 23.2.3.

Ozone, O_3

Environmental aspects

Ozone is an important constituent of the upper atmosphere where it is formed by solar uv radiation of very high energy (< 242 nm):

$$O_2 + h\nu \longrightarrow O^{\cdot\cdot} + O^{\cdot\cdot} \quad \text{(free radicals)}$$

$$O_2 + O^{\cdot\cdot} + M \longrightarrow O_3 + M$$

M is a neutral body which shares some of the kinetic energy of the oxygen atoms and thus stabilizes the bond formation leading to O_3. The ozone molecules absorb moderately high energy uv radiation, i.e., at somewhat longer wavelength:

$$O_3 + h\nu \longrightarrow O_2 + O^{\cdot\cdot} \quad (220\text{-}320\ \text{nm}).$$

The process may be reversed in presence of suitable neutral body M to regenerate ozone or the O-atoms may recombine to form O_2. Actually, an equilibrium is established between the formation and destruction of ozone and a steady concentration is maintained (~ 27% by weight) between altitudes of 15-25 km in the atmosphere. The layer in effect protects the earth and its biosphere from the harmful ultraviolet radiations. Any significant decrease in this concentration may have severe adverse effects on the biosphere e.g. increased surface temperature, high incidence of skin cancer etc. Unfortunately, several human activities (in the name of civilization) are already at work for such damage. Nitrogen oxides from supersonic aircrafts and industries catalyze the conversion of O_3 to O_2. Similarly, chlorofluorocarbons (freons; used as foam-blowing agents, aerosol propellants and refrigerants, see Ch. 22) are photochemically decomposed to give Cl atoms which break the ozone molecules in chain processes:

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad CF_3Cl \xrightarrow{h\nu} Cl^{\cdot} + \dot{C}F_3 \quad (190\text{-}220\ \text{nm})$$

$$NO_2 + O^{\cdot\cdot} \longrightarrow NO + O_2 \qquad Cl^{\cdot} + O_3 \longrightarrow ClO^{\cdot} + O_2$$

$$NO_2 + O_3 \longrightarrow O_2 + NO_3 \qquad ClO^{\cdot} + O^{\cdot\cdot} \longrightarrow Cl^{\cdot} + O_2$$

$$NO_3 \longrightarrow O_2 + NO$$

It may be observed that the nitrogen oxides (NO_x) or chlorine atoms are continuously regenerated, causing permanent damage to the ozone balance. The actual role of each individual pollutant and the extent of damage caused by different human activity (e.g. from supersonic transport or SST) is still controversial but the situation has already reached an alarming stage. Present evidence indicates that the ClO_x cycle may be three times more active in destroying the ozone layer than the NO_x cycle. In fact, some scientists even suggest that NO_2 actually protects ozone by combining with the much more harmful ClO

$$ClO + NO_2 \longrightarrow ClONO_2.$$

In this connection it may be mentioned that the Nobel Prize in Chemistry in 1995 has been awarded to the scientists Paul Crutzen (Netherlands), Ms Marino Molina (Mexico) and F. Sherwood Rowland (Delaware, Ohio) for their contributions to the study of depletion of ozone in the atmosphere.

Preparation

Ozone may be prepared by the action of silent electric discharge on oxygen and streaming out the gas quickly to avoid reconversion to O_2.

$$^3/_2\,O_2 = O_3 \qquad \Delta H = +\,142\ \text{kJ mol}^{-1}$$

$$O_3 + O = 2O_2 \qquad \Delta H = -\,394\ \text{kJ mol}^{-1}$$

Elemental forms : Ozone]

Thus formation of ozone is a strongly endothermic process. Pure ozone may be obtained by fractional distillation of liquid O_3—O_2 mixture as a deep blue liquid (bp – 112°C). The gas also has a faint blue colour and a typical pungent smell (Greek *ozein* = to smell; Schonbein, 1840). Both the liquid and the gas are diamagnetic. The pure liquid is dangerously explosive.

Ozone is a powerful oxidizing agent:

$$O_3 + 2H^+ + 2e \rightleftharpoons O_2 + H_2O \qquad E^0 = 2.07\ \text{V at}\ [H^+] = 1$$

$$O_3 + H_2O + 2e \rightleftharpoons O_2 + 2OH^- \qquad E^0 = 1.24\ \text{V at pH} = 14$$

Properties

Thus ozone is much more stable in presence of high concentration of alkali — both thermodynamically and kinetically. In acid medium, the potential of ozone is exceeded only by a very few oxidizing agents like fluorine, perxenate, atomic O etc. Typical reactions are

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

$$3I^- + O_3 + 2H^+ \longrightarrow I_3^- + O_2 + H_2O.$$

$$2Co^{2+} + O_3 + 2H^+ \longrightarrow 2Co^{3+} + O_2 + H_2O.$$

Estimation

The concentration of ozone in gaseous O_2—O_3 mixtures can be determined by catalytic decomposition to O_2 and measuring the volume expansion. O_3 may also be estimated iodometrically by titrating the iodine liberated from a solution buffered with boric acid.

Ozonides

Ozone reacts with dry powdered alkali at – 10°C to form red-brown paramagnetic ozonides $M^IO_3/M^{II}(O_3)_2$ (M^I = Na, K, Rb, Cs; M^{II} = Ca, Sr, Ba)

$$5O_3 + 2KOH \longrightarrow 2KO_3 + 5O_2 + H_2O.$$

Stability decreases in the sequence of decreasing cation size (and increasing polarizing power) : Cs > Rb > K > Na and Ba > Sr > Ca. Lithium ozonide is known as an ammine $LiO_3.4NH_3$. The ozonides are hydrolytically unstable and decompose to superoxides above room temperature:

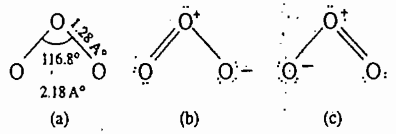
$$MO_3 \longrightarrow MO_2 + {}^1/_2\,O_2 \qquad MO_3 + H_2O \longrightarrow MOH + O_2 + OH$$

$$OH + OH \longrightarrow H_2O + {}^1/_2\,O_2.$$

"Ozonides" are also formed by the addition of ozone across π-bonds in alkenes and alkynes.

Structure and Bonding

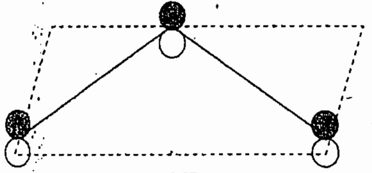
The molecule O_3 is bent with an OOO angle 117° and equal O—O distance of 1.28 A° [23.1 (a)]. In V.B. terminology this may be described by the canonical forms 23-I (b) and (c).



23-I

In M.O. description, each O forms a σ-bond to its neighbour using sp^2 type hybrid orbitals. The sigma-bonded system (23-II) has one *p*-orbital on each O in a perpendicular plane. These may form three π-M.O.s, one bonding, one nonbonding and one antibonding. Regarding electron count, we recall that there are a total of 6 × 3 = 18 valence electrons of which 4 are used in forming two σ-bonds. The central O has one lone pair and the end O atoms have two lone pairs each. So the system has 4 electrons to fit the π-bonding system. 4 electrons fill the bonding and nonbonding m.o. s, imparting a π-bond order of $^1/_2$ between each pair of atoms.

SO_2 has the same number of valence electrons and a similar bonding scheme is applicable. The much greater stability of the molecule may be partly ascribed to the effect of the *d*-orbitals available on the central S-atom. The filled non-bonding orbitals in oxygen may then contribute to bonding in SO_2.



23-II

The 3-center 4-electron π-bond system in O_3.

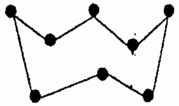
Sulphur

Sulphur forms a large number of allotropes which contain puckered rings (of 6-20 S atoms) or long chains of sulphur atoms. The S-S distance (2.06 A°) and SSS bond angles (102°-108°) in these forms are nearly all equal, suggesting similarity in bonding. The allotropes practically differ in different ways of packing the units and the varying repulsion between lone pairs of electrons on neighbour atoms.

Solid sulphur contains either (a) cyclic species or (b) chains.

(a) **Cyclic species.** These contain non-planar (puckered) rings of 6-20 S atoms and are named as **cyclo-hexasulphur** (*cyclo*-S_6), cyclo-octasulphur (*cyclo*-S_8) etc.

The most stable form of sulphur is the orthorhombic sulphur (S_α) which contains S_8 ring in crown conformation (23-III). At 95.5°C, it undergoes slow transition into the monoclinic form (S_β) which also contains S_8 rings but in a different packing. It may be prepared by crystallization of molten sulphur at about 100°C followed by rapid cooling to room temperature. The crystals (m.p. 119.6°C) are stable for weeks.



23-III

The crown of S_8.

The enthalpy of transition for $S\alpha$—$S\beta$ is very low (0.4 kJ per g-atom at 95.5°C); the transformation occurs so slowly that sulfur may be melted at 112.8°C by rapid heating.

A third crystalline variety, γ-monoclinic sulphur is obtained by chilling hot concentrated solutions of sulphur in CS_2 (or ethanol) or by slowly cooling molten sulphur from 150°C. It is best obtained by reacting pyridine with Cu(I)-ethyl xanthate, CuSSCOEt. The pale yellow crystals are stable between 95° to 115°C but transforms slowly to α-S_8 at room temperature. It has a relatively higher density (2.19 g cm^{-3}), indicating more efficient packing.

[Sec. 23.2.1 *Elemental forms : sulphur*]

Solutions of S_8 in polar solvents like methanol or acetonitrile contain a small percentage of S_6 (0.8%) and S_7 (0.3%). The *cyclo*-S_6 species, also called ε-sulphur or *Engel's sulphur*, was prepared by Engel in 1891 by adding conc HCl to a saturated solution of sodium thiosulphate at 0°. It is now prepared from hydrogen polysulphide by reaction in dry ether :

$$S_2Cl_2 + H_2S_4 \longrightarrow S_6 + 2HCl.$$

The orange red crystals, decomposing above 50°C, have puckered rings of S_6 units in chair conformation.

Other cyclic species (S_9, S_{10} etc. upto S_{20}) are mostly obtained by reacting sulphur chlorides with hydrogen

$$H_2S_x + S_yCl_2 \longrightarrow S_{x+y} + 2HCl \text{ ...... (for } S_6, S_{10}, S_{12}, S_{18}, S_{20})$$

$$S_xCl_2 + [Ti(\eta^5\text{-}C_5H_5)_2(S_5)] \longrightarrow S_{x+5} + [Ti(\eta^5\text{-}C_5H_5)_2Cl_2] \text{ ....(for } S_7, S_9, S_{10}, S_{11})$$

All the crystalline cyclo-forms are soluble in CS_2. Density and melting point of the main cyclo forms and of chain catena-S are shown in Table 23.1.

TABLE 23.1

Density and Melting Point of some Sulphur-allotropes

	density (g cm^{-3})	m.p. (°C)
cyclo-S_6	2.21	dec > 50°
cyclo-S_7	2.18 (at – 110°)	dec > 39°
cyclo-S_8 (α)	2.07	112.8
(β)	1.94-2.01	119.6
(γ)	2.19	106.8
cyclo-S_9	—	dec > room temp
cyclo-S_{10}	2.10 (at – 110°)	dec > 0
cyclo-S_{11}	—	—
cyclo-S_{12}	2.04	148[*]
cyclo-S_{18}	2.09	128 (dec)
cyclo-S_{20}	2.02	124 (dec)
catena-S (S_∞)	2.04	104 (dec)

(b) **Chain Species.** These are collectively known as **catena**-sulphur (S_∞) and are available in various metastable forms like rubbery, plastic, laminar, fibrous etc. A fibrous form insoluble in CS_2 is obtained by pouring molten sulphur into ice-water. Long fibres may be obtained by heating S_8 in N_2 at 300° and quenching a thin stream in ice-water. The stretched fibres contain helical chains of S-atoms. In the lamellar form, these chains are partly criss-crossed. All the forms revert to the *cyclo*-S_8 (α) form at room temperature.

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[*] **cyclo-S_{12}** contains S-atoms in three parallel planes and has the highest m.p. among all S-allotropes—about 35° higher than rhombic sulphur. This, as well as other cyclo forms differ in the mode of packing of the S-atoms.

Liquid sulphur

Liquid sulphur near its melting point (115°C) consists almost entirely of S_8 molecules. The viscosity of the transparent yellow liquid first decreases with increasing temperature (at par with other liquids) but after 159°C, the viscosity rises steeply (Fig. 23.1); it reaches maximum around 170°C and thereafter falls smoothly to the boiling point (444°C). The increase in viscosity is also accompanied by a darkening of the colour to intense red. These changes occur due to breaking of S_8 rings to diradicals with unpaired electrons on both terminal S atoms. The diradicals may form larger rings or polymerise to form chains containing up to 10^6 S-atoms. At 200°C, the mass percent of S_8 is about 60% while that of the linear polymer (S) is nearly 30% (determined by high pressure liquid chromatography HPLC). The polymer has its greatest average length (5 to 8 × 10^5 S atoms) at the region of highest viscosity. The dark red colour is ascribed mainly to S_3 and S_4.

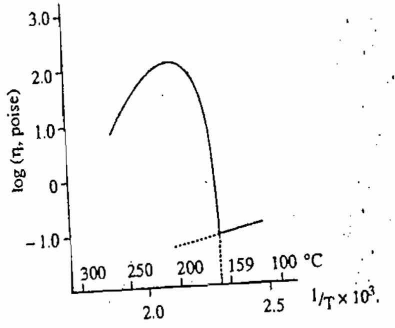

Fig. 23.1

Nature of variation of log η vs 1/T for liquid sulphur.

Gaseous sulphur. Sulphur vapour near its boiling point (444°C) consists mainly of S_7 (40%), S_6 (30%) and S_8 (20%) together with small amounts of S_2, S_4 and S_5. Paramagnetic blue S_2 becomes the principal species above 600°C. Only above 2200°C, dissociation occurs to atoms.

Selenium and Tellurium

Grey selenium and silvery white tellurium are the only important allotropes of these elements. Both have infinite spiral chains of the atoms. Weak metallic interaction within the neighbouring atoms in different chains is also present. The viscosity of molten selenium (m.p. 220°C) decreases rapidly with temperature as the long chains gradually split into smaller ones. Crystallization from solution in CS_2 yields two metastable red crystalline varieties containing rings. A highly polymeric form is also obtained by pouring molten Se into cold water. No molecular form of tellurium is known.

The vapour of selenium at the boiling point (685°C) consists mainly of Se_2 and Se_6 molecules, together with other Se_n species (n = 2–10)

Unlike sulphur which is an insulator, selenium and tellurium are semiconductors (band gap = 1·7 and 0·35 eV respectively). Illumination causes ready promotion of electron across the band gap in Se; the conductivity may be increased as much as a thousand fold. This forms the basis of using selenium in photocells.

23.2.2 Atomic and Physical Properties

Some of the important atomic and physical properties of the elements are shown in Table 23.2

TABLE 23.2

Some properties of the elements of Gr VI (16)

Element (At. No.)	O (8)	S (16)	Se (34)	Te (52)	Po (84)
Electron configuration	[He]$2s^22p^4$	[Ne]$3s^23p^4$	[Ar]$3d^{10}4s^24p^4$	[Kr]$4d^{10}5s^25p^4$	[Xe]$4f^{14}5d^{10}6s^26p^4$
ΔH° (atomization) (kJ mol⁻¹)	247	278	207	192	145
M.P. (°C)	−229	115	217	452	254
B. P. (°C)	−183	444	685	990	962
r (cov)/pm (2-coordinate)	73	104	119	142	168 (6-coord; metallic)
r (X^{2-})/pm	140	185	198	221	—
Electronegativity (P)	3.44	2.6	2.55	2.10	2.0
I.E. (first) kJ mol⁻¹	1314	999	941	869	813

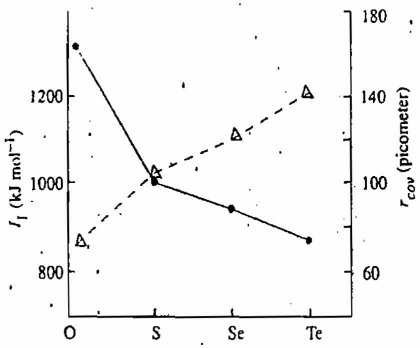

Fig. 23.2 (a)

Variation of I_1 (—) and r_{cov} (- - -) among Gr 16(VI) elements.

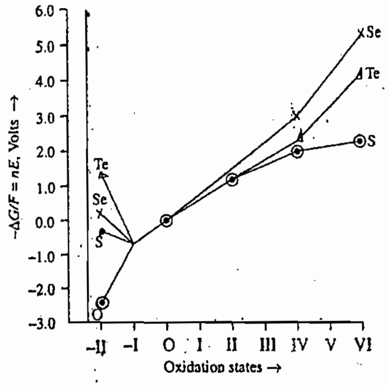

Fig. 23.2 (b)

Oxidation state free energy diagram of the chalcogen elements.

The trends observed in the group parallel those observed in previous groups. Thus oxygen exists as the diatomic gaseous O_2 molecule due to strong p-p π-bonds while

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sulphur is a solid with S—S single bonds. The elements develop increasing metallic character with increasing atomic number as evident from their decreasing electrical resistivity (sec. 23.2.1) and band gap. The trends in ionization energy, electronegativity and related properties are also understandable from the electron configurations with the help of discussions made in previous groups. Some of the properties of the elements are plotted in Fig. 23.2 (a) and 23.2 (b).

There is a steady decrease in ionization energies and increase in covalent radius down the group (Fig. 23.1 a). Changes in slopes after sulfur show that both the decrease in ionization energy and increase in covalent radii are somewhat arrested at selenium and tellurium owing to poor shielding effects of the d^{10} (and f^{14}) inner shells. The high ionization energies required to produce M^{6+} and M^{4+} ions make their existence most unlikely in the compounds in this group and the elements attain a rare gas electron configuration in other ways (see later).

The high electronegativity of oxygen, exceeded only by fluorine, is already known to give rise to many specialities in the compounds of oxygen. To mention a few, we have a large number of oxides with ionic structures and a dominance of hydrogen bonding in compounds containing —OH groups.

As noted for carbon and nitrogen groups, oxygen also differs significantly from other members in its group by forming strong *p-p* π-bonds to itself, carbon and nitrogen. In fact, there are no analogues of O_2, O_3, CO, NO etc. π-bond dominated molecules among other members in the family. As elements, sulfur, selenium an tellurium form only rings and chains containing single bonds, while polonium forms a metallic lattice. However, carbon-sulfur multiple bonds of the $d_\pi - p_\pi$ type are apparently present in some compounds of hypervalent carbon and sulfur with particularly short C—S distances :

$$F_5SCH_2Br + C_4H_9Li \xrightarrow{-70°C} F_5SCH_2Li \xrightarrow{-LiF} F_4S = CH_2 : (155.4 \text{ pm})$$

$$F_3CCH = SF_4 \xrightarrow[70°C]{\text{solid KOH}} F_3CC \equiv SF_3 : (139.5 \text{ pm; dimerizes above} - 30°C).$$

Catenation among the Group 16 elements

In the previous section, we have already noted the tendency of elementl sulfur, selenium and tellurium to form chains and rings. With oxygen, tendency for catenation is limited to O_3 and the highly unstable O_4F_2, strong repulsion between nonbonded pairs of electrons on adjacent atoms being one of the principal reasons. Elemental sulfur shows a wide variety of allotropic forms involving different chains and rings. As already noted, S_n rings with *n* upto 23 have been isolated using HPLC from rapidly chilled molten sulfur, and still higher members (up to $n = 36$) are also known to exist. It is interesting to note that many sulfur rings have been prepared by substituting one or two sulfur atoms in S_8 by the $\eta^5 - Cp_2Ti$ unit (Cp = cyclopentadienyl group) :

$$2NH_3 + H_2S + \tfrac{1}{2} S_8 \longrightarrow (NH_4)_2S_5 \xrightarrow{Cp_2TiCl_2} Cp_2TiS_5$$

The Cp_2TiS_5 anion has been used to prepare many other sulfur rings, for example,

$$Cp_2TiS_5 + SCl_2 \longrightarrow S_6 + Cp_2TiCl_2$$

Mixed sulfur-selenium rings have also been made from Cp_2TiS_5 (see below).

Selenium also forms five-, six-, seven- and eight-membered rings, but these are readily converted to the more stable chains. Infinitely long chains are present in some forms of solid selenium and tellurium and these break on melting into smaller chains and rings. Unlike sulfur, these chains and rings do not increase in size on heating the melts.

Several mixed rings containing sulfur and selenium, $S_{8-n}Se_n$, have been characterized from molten mixtures of S and Se. Mixed six- and seven-membered rings are also obtained from Cp_2TiS_5 and Cp_2TiSe_5 rings :

$$Cp_2TiS_5 + Se_2Cl_2 \longrightarrow S_5Se_2 + Cp_2TiCl_2$$

$$Cp_2TiSe_5 + SCl_2 \longrightarrow SSe_5 + Cp_2TiCl_2$$

$$Cp_2TiSe_5 + S_2Cl_2 \longrightarrow S_2Se_5 + Cp_2TiCl_2.$$

Catenation is also extensive in the group 16 elements in the form of cationic clusters (section 23.3.8) and in several compounds, particularly those of sulfur, for example, the polysulfanes HS—S_n—SH (n = 0—6); poly chlorosulfanes ClS—S_n—SCl (n = 0-100 probable) and the polythionates $[O_3S—S_n—SO_3]^{2-}$ (n = 1-22 isolated). Some of these compounds have been discussed under appropriate sections.

The physical properties of the elements have already been discussed in connection with their allotropes.

23.2.3 Chemical reactivity of the elements

Dioxygen.

Dioxygen is a powerful oxidizing agent; as discussed in chapter 9, the potential for the system

$$\tfrac{1}{2} O_2 + 2H^+ + 2e \rightleftharpoons H_2O \qquad E° = + 1.23 \text{ V at } [H^+] = 1.$$

is comparable to that of acidfied dichromate solution. However, its reactions are often sluggish under ordinary conditions. Thus, a solution of Fe(II) is only slowly oxidized by air at room temperature even though the process is thermodynamically favourable. This may be attributed to the high energy of activation involved in this and similar cases. Several factors may be held responsible.

1. Transfer of a single electron to O_2 (to its π* m.o.) is thermodynamically unfavourable, though marginally :

$$O_2\,(g) + H^+\,(aq) + e \longrightarrow HO_2\,(g) \qquad E° = -0.13 \text{ V at pH} = 0.$$

$$O_2(g) + e \longrightarrow O_2^-\,(aq) \qquad E° = -0.33 \text{ V at pH} = 14.$$

Hence one-electron reducing agents like Fe^{2+} must exceed these potentials before any appreciable reaction rate may be attained.

2. The ground state of O_2 has both π* m.o. -s singly occupied. Hence O_2 is neither a good Lewis acid nor a good Lewis base and is reluctant to combine with p-block electrophiles or nucleophiles.

3. The bond dissociation energy of O_2 is high (496 kJ mol^{-1}). So reactions involving such dissociation require high energy of activation.

Some of these activation barriers may be overcome through radical chain mechanisms, particularly in high temperature combustion processes.

> **Q. 23.1** *Do you expect* I^- *and* Cr^{2+} *to be stable in neutral water saturated with* O_2*?* $E°\,(Cr^{3+} - Cr^{2+}) = -0.41$ V.
>
> **Hint :** At $[H^+] = 10^{-7}M$, $E°$ + 0.81 V for $O_2 - H_2O$ half-cell. Hence both I^- and Cr(II) should be readily oxidized.

The rates of oxidation by oxygen may be sometimes increased remarkably by transition metal ions acting as catalysts. Thus I^- is only slowly oxidized in solution by air but the rate is appreciable in presence of Cu^{2+} or Fe^{3+} ions.

Formation of the oxide ion in the gas phase is endothermic (from electron affinity values):

$$\tfrac{1}{2}O_2(g) \longrightarrow O(g) \qquad \Delta H = 248 \text{ kJ mol}^{-1}$$

$$O(g) + 2e \longrightarrow O^{2-}(g) \qquad \Delta H = 752 \text{ kJ mol}^{-1}$$

This is compensated by the high lattice energy of many metal oxides. Peroxides and superoxides are also known for a few metals (see later). Besides, oxygen forms a large number of covalent oxides.

Dioxygenyl compounds

The first ionization energy of O_2 is 1168 kJ mol^{-1}. O_2 may be oxidized to O_2^+ (the dioxygenyl cation) by strong oxidizing agents like PtF_6, to give the orange salt $O_2^+PtF_6^-$. Other salts $O_2^+[EF_6]^-$ are known where E is As, Sb, Bi, Nb, Au, Ru etc. They may be prepared by heating a mixture of O_2, F_2 and powder of the corresponding metal in an autoclave for 10-20 hours at temperatures between 150-500°C or otherwise.

$$O_2 + Pt + 3F_2 \xrightarrow{280°C} O_2^+[PtF_6]^-$$

$$O_2 + SbF_5 + F_2 \xrightarrow{h\nu} O_2^+[SbF_6]^-$$

$$O_2 + BF_3 + \tfrac{1}{2}F_2 \xrightarrow{h\nu;\,-78°C} O_2^+[BF_4]^-$$

$$2O_2 + 2GeF_4 + F_2 \xrightarrow{h\nu} 2O_2^+[GeF_5]^-$$

$$O_2F_2 + PF_5 \longrightarrow O_2^+[PF_6]^- + \tfrac{1}{2}F_2$$

O_2PtF_6 decomposes with melting at 219°C. Some of the others are quite volatile, e.g., O_2RhF_6 sublimes at room temperature. As expected, they are all readily hydrolyzed by water.

The O–O stretching frequency in O_2^+ (1905 cm^{-1}) does not change in the compounds, indicating the presence of the cation as such in the salts.

The O_2^+ ion is paramagnetic; the O–O distance is 1.12 A° (1.21 A° in O_2; see Ch. 7).

Oxygenation

In addition to its strong and versatile oxidizing action, dioxygen may also function as a ligand to various transition metals. In such dioxygen complexes, the oxygen is not reduced and the O_2 molecule retains its identity. Such oxygen addition processes without oxidation have been termed *oxygenation*. Reversible oxygenation occurs at every moment of our life process during respiration; deoxyhaemoglobin, a complex containing Fe(II) and heme, carries the oxygen to different parts of our body. Complexes of dioxygen have been discussed in section 23.3.8.

Sulfur, Selenium, Tellurium

The elements S–Po react on heating with oxygen (air), halogen, most metals and nonmetals. Hot oxidizing acids oxidize them. Sulphur reacts with hot aqueous alkali to give a complex mixture of polysulphides and polythionates.

$$S_8 + 12\,KOH = 4K_2S + 2K_2S_2O_3 + 6H_2O. \; (K_2S + \tfrac{1}{8}S_8 = K_2S_2 \text{ etc.})$$

Se and Te are attacked by hot concentrated or fused alkali only:

$$3Se + 6NaOH = 2Na_2Se + Na_2SeO_3 + 3H_2O \text{ (also for Te).}$$

S, Se and Te dissolve in oleum to form intensely coloured solutions containing cations like S_4^{2+}, S_8^{2+} etc. (also for Se, Te; section 23.3.8).

Many nucleophilic reagents attack sulphur by opening the ring:

$$S_8 + CN^- \longrightarrow S_7 - SCN^-; \quad S_7 - SCN^- + CN^- \longrightarrow S_6 - SCN^- + SCN^- \ldots\ldots$$

Summarily, $S_8 + 8CN^- \longrightarrow 8SCN^-$

Na_2SO_3, Ph_3P react similarly.

Natural and synthetic rubbers add sulphur to their double bonds. The reaction is taken advantage of in the vulcanization of rubber.

The onium ions

We have already discussed the oxonium ion H_3O^+ (sec. 17.3.1); the pyramidal ion is isoelectronic with NH_4^+ and has been characterized in many crystalline hydrates of strong acids. Strong hydrogen bonding with further water molecules leads to the formation of other cations like $H_5O_2^+$ and $H_7O_3^+$. Similarly, the peroxonium ion $H_3O_2^+$ is also known. All of them are formed in liquid HF media by the action of AsF_5 (SbF_5) on H_2O/H_2O_2:

$$H_2O + AsF_5 + HF \longrightarrow H_3O^+AsF_6^-$$

$$H_2O_2 + AsF_5 + HF \longrightarrow H_3O_2^+AsF_6^-$$

The H_3S^+ cation may also be formed in the same manner.

$$H_2S + SbF_5 + HF \longrightarrow H_3S^+SbF_6^-$$

Organo substituted onium salts may be prepared readily as:

$$Me_2Se + MeI \longrightarrow Me_3Se^+I^-$$

$$Me_3Se^+I^- + AgOH \longrightarrow Me_3Se^+OH^- + AgI$$

$$Me_3Te^+OH^- + HF \longrightarrow Me_3Te^+F^- + H_2O$$

Most of the onium salts can be isolated as crystals by evaporating the solvent. O-17 NMR spectrum of $H_3O^+SbF_6^-$ (in an approximately 1:1:1 mixture of H_2O^{17}, HF and SbF_5 dissolved in liquid SO_2 at −15°C) indicates three equivalent H-atoms bound to the oxygen.

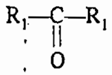
Onium ions substituted by three different organic groups are optically active at par with expectations for a pyramidal species. However, the oxonium species undergo rapid inversion and cannot be resolved. Other onium ions have been resolved into their respective isomers.

The triphenyloxonium cation, Ph_3O^+, is virtually planar owing to steric crowding around the small oxygen atom. The phenyl rings are twisted at such an angle that π-bonding between the 2*p* orbital of O and the empty π* orbitals of the aromatic ring is indeed very small.

23.2.4 Valence and Oxidation states

[Sec. 23.2.4 *Valence*]

Oxygen, with $2s^22p^4$ configuration in the valence shell may attain the neon configuration by gaining two electrons. But this is an endothermic process (see before) and is compensated only by high lattice energy of some ionic oxides. The larger sulphide ion also has a large positive enthalpy of formation (gas phase : +330 kJ mol^{-1}) and a still less lattice energy is expected in ionic sulphides. Since this ion is easily polarizable and reducing in character, sulphides corresponding to high oxidation state oxides are not known (e.g., MnO_2 abd PbO_2). High ionization enthalpy rules out the possibility of M^{6+} ion formation; even the M^{4+} ion with ns^2 configuration is not definitely established except in one form of PoO_2. The elements may attain inert gas configuration in various ways as shown below (E is a lone pair of electrons) :

(i)	Two single covalent bonds, two lone pairs of electrons (X_2OE_2 type, E = lone pair).	H_2O, R_2S
(ii)	One double bond, two lone pairs (X = OE_2 type) :	 $R_1-\underset{\underset{O}{\|}}{C}-R_1$ $Cl_4Re{=}O$
(iii)	One single bond together with an electron gain (XME_3 system).	OH^-, RO^-, HS^-
(iv)	Three covalent bonds, one lone pair (X_3ME^+ system; "onium" salts or their derivatives).	H_3O^+, R_3S^+ Me_3Se^+, Me_3Te^+
(v)	Four covalent bonds (rarely formed by O).	$Be_4O(CH_3COO)_6$ * SF_4 etc.

The coordinating ability of dioxygen has been mentioned earlier. Several hypervalent compounds MR_4 and MR_6 are formed by all the elements except oxygen.

The major differences between O and the remaining elements in the group follow the same general trend as observed in previous groups. As expected, these arise mainly due to the increasing size and decreasing electronegativity of the elements. Some of the major differences are :

	Difference in S–Po	Consequences
(1)	*p-p* π-bonding becomes much less important.	No sulphur analogues of O_3, O_2, CO and NO.
(2)	*d-p* π-bonding emerges.	Short S–O distances in SO_4^{2-} (oxygen 2*p*-sulphur 3*d*).
(3)	Electronegativity decreases sharply.	(i) Very feeble H-bonding, e.g., S...H–S. (ii) The compounds have less ionic character.
(4)	Involvement of *d*-orbitals in bonding is likely.	Valence expansion beyond octet, e.g., SF_6 and $Te(OH)_6$.
(5)	Reduced repulsion between non-bonding pairs of electrons.	(i) S—S or Se—Se bond energy higher than O—O (Table 23.3). Similarly $E_{S-F} > E_{O-F}$.
(6)	Only sulphur shows stong tendency for catenation (see below).	Polysulphides S_n^{2-} ; Poly-thionates $(O_3S-S_n-SO_3)^{2-}$ XS_nX, X = Cl, CN, H, NR_2.

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* See Chapter 19

Q. 23.2 *The highest fluoride of oxygen is OF_2 whereas sulphur forms SF_6. Comment.*

Q. 23.3 *Consult Table 23.3. Bond energies for O—O and O—F are much lower than those for S—S and S—F. But S—H and S—C bonds are weaker than O—H and O—C bonds. Comment.*

Hint : Stronger repulsion between non-bonding electrons in case of O—O and O—F.

TABLE 23.3

Some mean covalent bond enthalpy values (kJ mol^{-1}) for O, S, Se, Te

O—O	146	S—S	267	Se—Se	172	Te—Te	138
O—H	467	S—H	338	Se—H	276	Te—H	238
O—C	360	S—C	260	Se—C	242	—	
O—F	190	S—F	496	Se—F	285	Te—F	335
O—Cl	205	S—Cl	250	Se—Cl	242	—	
O=O	497	S=S	430				
O=C	743	S=C	477				

Parallel to groups 14(IV) and 15(V), in this group also one observes

(i) the gradual emergence of metallic character in Te and Po.

(ii) decreasing stability of the hydrides.

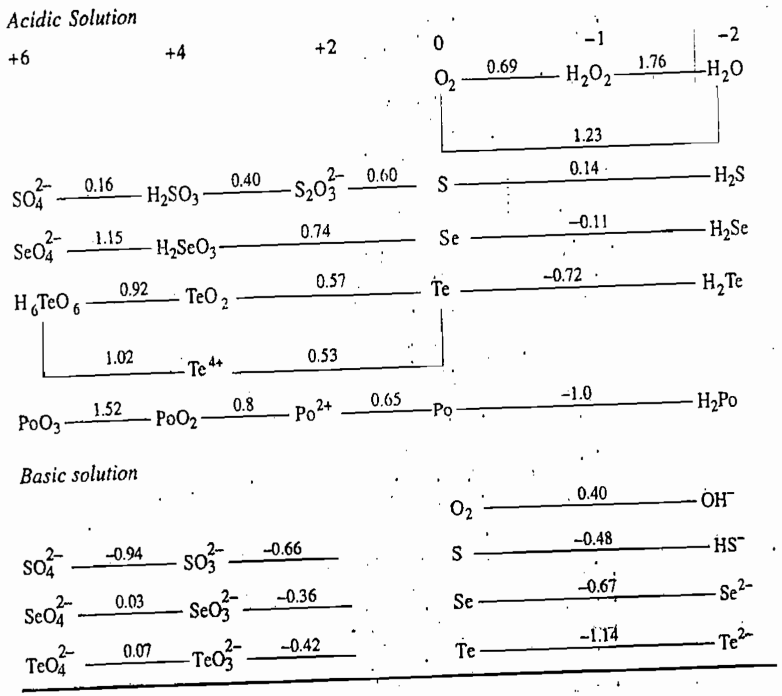
(iii) increasing tendency to form complexes e.g., $SeBr_6^{2-}$.

The elements also form a number of cationic clusters, e.g., O_2^+, S_4^{2+}, S_8^{2+}, Se_{10}^{2+}, Te_4^{2+} etc. These have been discussed separately (sec. 23.3.8).

Oxidation states

The common oxidation states of the elements are –2, +4 and +6. Oxygen, second to fluorine in electronegativity, attains the +2 oxidation state only with fluorine (OF_2). Its common oxidation state is therefore –2. Lower oxidation states are known only in peroxides (−1), superoxides ($-\frac{1}{2}$) and ozonides ($-\frac{1}{3}$). Sulphur may be assigned a variety of gross oxidation numbers in several oxoanions e.g. $S_2O_3^=$ (+2), $S_4O_6^=$ = (+ 2.5), $S_2O_6^=$ = (+5) etc; however, these species contain S–S bonds and the assignment of oxidation number is neither clearcut nor very significant. Po exhibits a clean +2 oxidation state in Po^{2+}. The +4 and +6 states are shown by all the elements except O in their oxides, halides and oxoanions. As expected, the higher oxidation state becomes increasingly oxidizing from Se(VI)—Te(VI)—Po(VI). The standard reduction potential values for the elements are shown in Table 23.4.

TABLE 23.4
Standard reduction potential (volt)



23.3 PRINCIPAL COMPOUNDS

23.3.1 Hydrides

The hydrides MH_2 may be formed by direct combination of the elements (M = O – Te) with hydrogen. H_2S, H_2Se or H_2Te are better prepared by treating the respective metal chalcogenide with aqueous acid or water :

$$Al_2Te_3 + 6H_2O = 3H_2Te + 2Al(OH)_3.$$

Water is a liquid due to extensive hydrogen bonding while others are colourless volatile foul-smelling gases (Table 23.5).

TABLE 23.5
Some physical properties of MH_2 compounds (M = O, S, Se, Te)

	H_2O	H_2S	H_2Se	H_2Te
M.P., °C	0	−86	−65.7	−51
B.P., °C	100	−60	−41.3	−4
Dielectric constant	78.4	8.99 (−78°)	—	—
K_{diss} (aq) 1st :	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}
2nd :	—	$\sim 10^{-14}$	10^{-11}	1.6×10^{-11}
ΔH_f^0/kJ mol^{-1}	−286	+ 20.1 (g)	+ 73	+ 99.6
∠H–M–H (g)	104.5°	92.1°	91°	90°
M–H dist, A°	0.96	1.34	1.46	1.69

We observe that all the hydrides except H_2O are endothermic. H_2Te decomposes in light even at room temperature. As M becomes large, poorer overlap (with the small 1s orbital of H) makes the M—H bond weaker and the MH_2 species a stronger acid. This is also reflected in the dissociation constant values and increasing reducing character of the compounds. H_2Se and H_2Te are unstable and very good reducing agents. Their solutions in water are oxidized by air. All the gases burn in air with pale blue flames to dioxides.

$$2MH_2 + 3O_2 = 2H_2O + 2MO_2$$

All the three gases (and their aqueous solutions) precipitate metal chalcogenides from aqueous solution of their salts. Precipitation with H_2S is a common practice in routine laboratory analysis (see Ch. 11). Precipitation of selenides and tellurides is accompanied by simultaneous formation of Se/Te from oxidation of H_2Se or H_2Te.

Water

Several aspects of water have been discussed earlier, e.g., hydration of ions and solubility of salts (Ch. 6); ionic equilibrium, pH scales, acid-base reactions (Ch. 11); redox stability in water (Ch. 9); structure of ice and water; hydrates and clathrates (Ch. 17). Heavy water has also been discussed in chapter 17.

Availability of hygienically safe water for public use has become a recent concern for the environmentalists all over the world. Sewage disposal, industrial wastes, fertilizers, insecticides and detergents seem to be the major pollutants for water. The case of arsenic contamination in several places in West Bengal has been mentioned in the last chapter. Fluoride contamination, leading to the crippling disease fluorosis, is even more widespread (Ch. 24). Of late, several action plans have been initiated to identify and reduce such disasters but the overall situation is still disappointing.

The World Health Organization standard for a few dissolved inorganic chemicals in drinking water are as follows :

Nature of contamination		**Maximum permissible (max. desirable) concentration (mg L^{-1})**
Total dissolved solids	...	1500 (500)
Mg	...	150 (30)
Ca	...	200 (75)
Chlorides	....	60 (20)
Sulphates	...	400 (200)

Sinking of underground water layers owing to deforestation etc. causes an increase in the concentration of salts in water. The problem of obtaining hygienically safe water is a big problem all over the world.

Small quantities of water for domestic use may be purified by sedimentation followed by chlorination or treatment with ozone. The specifications for industrial water are often more stringent than those for domestic water. For example, high-pressure boiler feed water should contain less than 2 ppm of dissolved solids. Industrial water is mainly purified through ion-exchange resins, typical representative reactions being :

Cation exchange : $R–SO_3H + Na^+ \text{———} RSO_3Na + H^+$

$R–SO_3H + Ca^{2+}/2 \text{———} RSO_3Ca^{2+}/2 + H^+$

Anion exchange : $R–\overset{+}{N}Me_4OH^- + Cl^- \text{———} R–\overset{+}{N}Me_4 Cl^- + OH^-$

The de-ionized water so obtained may still contain some soluble silicates and CO_2. The exhausted resinbed may be regenerated by dilute H_2SO_4 (cation exchanger) or Na_2CO_3 solution (anion exchanger).

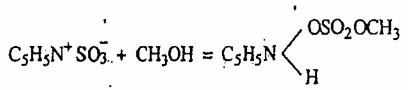
"Polywater" reported around 1966-1973 to have an unusual density of 1.4 g cm^{-3}, has been found to be a colloidal mixture of silicates and Na^+, Ca^{2+}, BO_3^{3-}, NO_3^- etc. ions dissolved out from the glass capillary in which it was made.

Estimation of water

Small amounts of water (e.g. in organic solvents) may be determined by **Karl Fischer titration**.

The reagent consists of a mixture of I_2 and SO_2 in anhydrous pyridine and methanol. Water reacts with the reagent :

$$H_2O + SO_2 + I_2 + 3C_5H_5N = 2C_5H_5NH^+I^- + C_5H_5\overset{+}{N}SO_3^-$$



$$C_5H_5N^+SO_3^- + CH_3OH = C_5H_5N\begin{cases}OSO_2OCH_3\\H\end{cases}$$

Since the reaction has to be carried out in anhydrous medium, the titration is best carried out electrometrically in an air-tight vessel fitted with a pair of platinum electrodes connected to a microammeter. Usually a slight excess of the reagent is added to the sample (in anhydrous methanol) so that all the water in it may react. The excess reagent is then back-titrated with a standard solution of water in methanol. The current in the electrode circuit suddenly increases at the first appearance of unused I_2 in the solution.

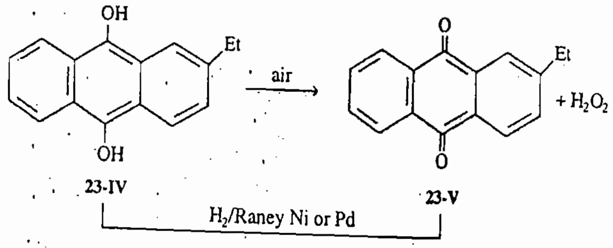
Alternatively, the titration may be carried out coulometrically by replacing the iodine with iodide; the iodine is generated on a platinum anode. Each molecule of H_2O consumes one molecule of I_2, which requires two electrons for generation.

Hydrogen peroxide

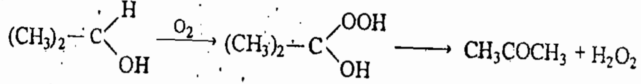
H_2O_2 may be prepared in the laboratory by reacting dilute H_2SO_4 with a paste of barium peroxide ($BaO + O_2$; heat). D_2O_2 may be prepared from potassium peroxodisulphate and D_2O.

Industrially, more than half a million tonnes of H_2O_2 are produced annually all over the world, mainly through aerial oxidation of 2-ethylanthraquinol in a mixed solvent system : alcohol or ester (solvents for quinol) and alkylbenzenes (solvents for quinone). The H_2O_2 formed (≃ 1%) is extracted time to time by shaking with water; the quinone is reduced back to the quinol by catalytic (Pd) hydrogenation. The aqueous solution of H_2O_2 may be concentrated upto 85-90% by distillation under reduced pressure.

[Sec. 23.3.1 *Hydrogen peroxide*]



Hydrogen peroxide is now also manufactured by the oxidation of isopropanol (vapour or liquid) under high pressure (15–20 atm) at about 100°C.



$$(CH_3)_2\text{—}C\begin{cases}H\\OH\end{cases} \xrightarrow{O_2} (CH_3)_2\text{—}C\begin{cases}OOH\\OH\end{cases} \longrightarrow CH_3COCH_3 + H_2O_2$$

Some secondary reactions may also occur. The H_2O_2 is separated by fractional distillation.

Hydrogen peroxide is used mainly (≃ 30%) as a bleaching agent for textiles, paper pulp, leather, oils etc. A large quantity is also used (≃ 33%) in the manufacture of peroxoborates (Ch. 20), epoxides, propylene oxide and other organic chemicals and pharmaceuticals. H_2O_2 is gradually finding greater use (≃ 20%) in pollution control for treatment of sewage water and wastes.

Pure H_2O_2 is an extremely pale blue liquid, m.p. – 0.43°C, b.p. 150°C, $\rho = 1.4$ g cm^{-3} (liquid). The heat of formation of liquid H_2O_2 is –187.8 kJ mol^{-1} but it is thermodynamically unstable with respect to decomposition to water and oxygen :

$$H_2O_2\,(l) \longrightarrow H_2O\,(l) + \tfrac{1}{2}O_2 \qquad \Delta H = -98.3 \text{ kJ mol}^{-1}$$

However, decomposition is very slow at ordinary temperature in absence of catalysts like Ag, Pt, charcoal or MnO_2. Decomposition is rapid at higher temperatures (may be explosive) and in basic solutions. Traces of alkali dissolved from glass or dust articles may initiate decomposition and hence H_2O_2 is preferably kept in polythene containers with stabilizers like urea or phosphoric acid. Traces of transition metal ions also catalyze the decomposition, e.g. Fe^{2+} (see Fenton's reagent).

Decomposition of H_2O_2 is a disproportionation process and is usually catalyzed by redox systems having reduction potentials between the limits for (i) reduction of H_2O_2 to H_2O i.e., + 1.76 V and (ii) reduction of O_2 to H_2O_2, i.e., + 0.70 V. The oxidized form of the redox couple in the catalyst may then oxidize H_2O_2 to O_2 while the reduced species can be oxidized by H_2O_2. The catalyst thus alternately oxidizes and reduces H_2O_2 through a shuttle-cock role. Fe^{3+}–Fe^{2+} ($E° = 0.77$ V), Br_2–Br^- ($E° = 1.1$ V) etc. are thus good catalysts for the decomposition of H_2O_2.

H_2O_2 has a high dielectric constant (89 at 0°C) and undergoes little self-ionization :

$$2H_2O_2 \rightleftharpoons H_3O_2^+ + HO_2^-; \qquad [H_3O_2^+]\,[HO_2^-] = 1.5 \times 10^{-12}$$

It is a slightly stronger acid than water :

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + OOH^- \qquad pK_a\ (20°C) = 11.75$$

Hydroperoxides of alkali metals and ammonia are known.

No exchange of ^{18}O is observed between H_2O_2 and $H_2{}^{18}O$ in liquid phase, even in the presence of strong acids.

H_2O_2 is a much weaker base than water and hence cannot be protonated in aqueous solution. But salts of $H_3O_2^+$ have been prepared from strongly acidic solvent systems e.g.,

$$H_2O_2 + HF + 2SbF_5 \longrightarrow [H_3O_2]^+ [Sb_2F_{11}]^-$$

The $H_3O_2^+$ ion is isoelectronic with NH_2OH.

Peroxohydrates containing H_2O_2 of crystallization are known, e.g., $K_2CO_3.3H_2O_2$ and $(NH_4)_2CO_3.H_2O_2$. "Sodium perborate" or "perborax" was once thought to be a peroxohydrate. It is now known to be a peroxo compound of boron (Ch-20).

Redox behaviour of H_2O_2 in aqueous solution may be summarized by the potentials :

$$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \qquad E° = 1.77\ V$$
$$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2 \qquad E° = 0.68\ V$$
$$HO_2^- + H_2O + 2e \rightleftharpoons 3OH^- \qquad E° = 0.87\ V$$

Thus, it acts as a strong oxidizing agent in both acidic and basic medium. It shows reducing behaviour only to strong oxidizing agents like permanganate.

Oxidizing

Acid : $H_2O_2 + 2H^+ + 2e = 2H_2O.$

$2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O.$

$(Fe^{2+} \rightarrow Fe^{3+};\ SO_3^{2-} \longrightarrow SO_4^{2-})$

Alkaline : $Mn^{2+} + H_2O_2 + 2OH^- \longrightarrow MnO_2 + 2H_2O.$

Reducing

Acid : $H_2O_2 = 2H^+ + O_2 + 2e$

$2Ce^{4+} + H_2O_2 \longrightarrow 2Ce^{3+} + 2H^+ + O_2$

Alkaline : $H_2O_2 + 2OH^- = 2H_2O + O_2 + 2e$

$KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$

$2[Fe(CN)_6]^{3-} + H_2O_2 + 2OH^- \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

$2Fe^{3+} + H_2O_2 + 2OH^- \longrightarrow 2Fe^{2+} + 2H_2O + O_2$

$Cl_2 + H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 2H_2O + O_2$

The oxygen evolved in the last reaction (or in acid medium with HOCl) is in a singlet state; its return to the triplet ground state is accompanied by a red chemiluminescence.

Study with labelled H_2O_2 shows that in the oxidation of H_2O_2 (by Cl_2, MnO_4^- etc.) as well as its catalytic decomposition (I_2, MnO_2 etc.), the O_2 comes exclusively from the H_2O_2. The O–O bond thus remains intact, the oxidizing agent simply removing the electrons. A mechanism of the following kind has been suggested for the oxidation by Cl_2

$$Cl_2 + H{-}\overset{18}{O}{-}\overset{18}{O}{-}H \longrightarrow H^+ + Cl^- + H{-}\overset{18}{O}{-}\overset{18}{O}{-}Cl$$

$$H{-}\overset{18}{O}{-}\overset{18}{O}{-}Cl \longrightarrow H^+ + Cl^- + \overset{18}{O}{-}\overset{18}{O}.$$

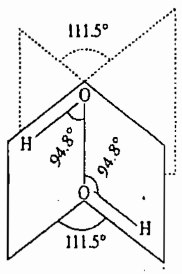
Free radicals, mainly HO_2 and OH, are also involved in many reactions of H_2O_2, for example, its decomposition catalyzed by metal ions. The HO_2 (hydroperoxo) radical has been detected in reactions of H_2O_2 with Ti^{3+}, Ce^{4+} or Fe^{2+}. A mixture of Fe^{2+} with H_2O_2 is used in organic chemistry under the name **Fenton's reagent**. It oxidizes or dehydrogenates organic substances via the formation of $\dot{O}H$ radical

$$Fe^{2+}(aq) + H_2O_2 \longrightarrow [Fe^{III}(OH)]^{2+}(aq) + \dot{O}H$$

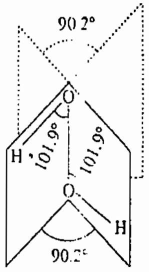
However, such reactions do not occur in dry MeCN. The $Fe^{IV}O^{2+}$ ion ("ferryl" ion) may be formed intially, which subsequently generates singlet O_2

$$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O$$
$$FeO^{2+} + H_2O_2 \longrightarrow Fe^{2+} + O_2(^1\Delta_g) + H_2O.$$

H_2O_2 has a gauche structure as shown in 23-VI (a) and (b). The structure in the solid is slightly modified by H-bonding.



23-VI (a)
Structure of H_2O_2 (*gas*)



23.VI (b)
Structure of H_2O_2 (*solid*)

Higher chalcogenides

Unbranched chains containing upto 6 chalcogen atoms are known in X_n^{2-} anions (X = S, Se, Te). The compounds H_2S_2 to H_2S_6 are generally called **sulphanes**, which may be obtained through reactions like

$$2H_2S\,(l) + S_nCl_2 = 2HCl\,(g) + H_2S_{n+2}\,(l)$$

Various salts containing these anions may be prepared e.g.,

$Cs_2S + 4S \longrightarrow Cs_2S_5$ (*aqueous solution*).

$Na + Te \longrightarrow Na_2Te_2 + Na_2Te_3$ (*liq NH_3*)

$K + Te + (2, 2, 2\text{-crypt}) \longrightarrow [K(crypt)]_2\,Te_3$

$Na_2S_5 + 2Me_4NCl \longrightarrow (Me_4N)_2\,S_6$ (*aqueous solution*).

S_4^{2-} and S_5^{2-} ions are also known to function as bidentate chelating ligands (Section 23.3.8).

23.3.2 Oxides, Sulphides, Selenides, Tellurides.

Alkali metal compounds containing all four $X_?^{2-}$ ions where X = O, S, Se and Te are known. As pointed out earlier, formation of the X^{2-} ion is highly endothermic even when X = O :

$$\tfrac{1}{2}O_2\,(g) = O\,(g) \qquad \Delta H = 248\ kJ\ mol^{-1}$$
$$O\,(g) + 2e = O^{2-}\,(g) \qquad \Delta H = 752\ kJ\ mol^{-1}$$

As such, ionic oxides are formed only when they are stabilized by high lattice energy.

Formation of S^{2-} (g) is much less endothermic due to larger size and consequent less repulsion between electrons in the valence shell :

$$S(g) + 2e \longrightarrow S^{2-}(g) \quad \Delta H = 332 \text{ kJ mol}^{-1}.$$

However, true ionic sulphides are not large in number owing to easy polarizability of the sulphide ion. Owing to increase in metallic character down the group, the stability of the X^{2-} ion decreases gradually. Treatment of soluble oxides and sulphides with water produces hydroxides and hydrogen sulphides, but selenides and tellurides are decomposed to H_2Se or H_2Te. The HS^- ion is also much less stable than the OH^- ion - aqueous solutions of hydrosulphides evolve H_2S on boiling.

Oxides may be classified in a number of ways, for example in terms of their acid-base character or according to their structure.

Acid-base character based on oxide ion transfer is the basis of the Lux concept of acids and bases. Acidic character increases from left to right along a period in the periodic table, while basic character increases downward along any group.

Types of oxides

Structurally, oxides cover a wide range :

(i) molecular (CO, CO_2, OsO_4, P_4O_{10} etc.); these are dominated by π-bonds to oxygen.

(ii) chain (HgO, SeO_2, CrO_3 etc.); these have a moderate degree of π-bonding.

(iii) layer (SnO, As_2O_3, MoO_3 etc.) and

(iv) three-dimensional (majority of metal oxides, SiO_2 etc.).

The six-coordinate radius of the oxide ion is 1.40 A°. This is comparable to those of K^+ (1.38 A°) and Ba^{2+} (1.35 A°). Rb^+, Cs^+, Tl^+ etc. ions have large radii, but most other metal ions are smaller than the oxide ion. So, their oxides usually consist of the metal ions held in the interstices of a close-packed lattice of oxide ions. The common metal oxides may be conveniently classified into the following formula types :

(i) **M_2O** [M = univalent metal e.g., alkali metal and Tl(I)]. They usually adopt the anti-fluorite structure (8:4 coordination) i.e., O^{2-} ions in place of Ca^{2+} ions and M^+ ions in place F^- ions in the fluorite lattice (See 23-VII).

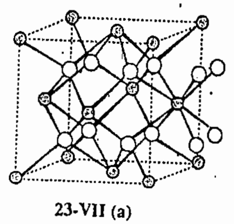
(ii) **MO :** Be(II) and Zn(II) adopt the wurtzite structure (4 : 4 coordination). Larger Group II elements (Mg, Ca–Ba) and Cd, V, Mn, Co, Ni form NaCl type lattice (6 : 6 coordination). Monoxides of early d-block metals (left of Fe) are strong reducing agents. MnO is very effective in removing oxygen from inert gases.

(iii) **M_2O_3 :** Trivalent metals form oxides of this stoichiometry. The corundum structure (Al_2O_3) is typical — the metal is octahedrally coordinated by O^{2-} ions and each O^{2-} ion is tetrahedrally surrounded by M^{3+} ions.

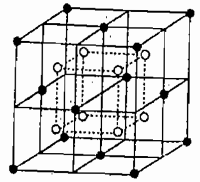
(iv) **MO_2 :** SiO_2 occurs in many forms, most of which posses macromolecular structure built up of SiO_4 tetrahedra sharing O atoms (section 21.3.5). GeO_2 exists in quartz structure and also in rutile structure (TiO_2) with 6 : 3 coordination. SnO_2 and PbO_2 also adopt the rutile structure. Larger cations (from Zr, Hf, Po, Ce, Pr, Tb, Th, U etc.) adopt the fluorite structure.

(v) **M_3O_4** or **$M_1M_2O_4$** (usually M_1 = bivalent metal ion from Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn; M_2 = a trivalent metal ion from Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni, Rh). In M_3O_4 oxides, the metal is present in two oxidation states e.g. $Fe^{II}Fe_2^{III}O_4$, $Pb^{IV}Pb_2^{II}O_4$. $M_1M_2O_4$ oxides are typified by the mineral spinel $MgAl_2O_4$. The unit cell contains 32 O atoms in cubic close packing (i.e., $Mg_8Al_{16}O_{32}$). 8 Mg ions (or other M^{II} ions) occupy tetrahedral sites and 16 Al^{3+} ions (or M^{III} ions) occupy octahedral sites.

The thermochemistry of oxides and the Ellingham diagram have been discussed in Chapter 15. 23-VII shows the common structural types in oxides.



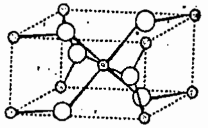
23-VII (a)



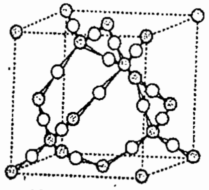
23-VII (b)

23-VII (a) and (b) : The Fluorite (also antifluorite) structure. In Fluorite, the Ca^{2+} ions (small circles, dark) lie in an expanded face centered cubic (fcc) array and the F-ions (large white circles) occupy all the tetrahedral holes. The structure is related to that of CsCl (Fig. b) : If half of the cation in the CsCl lattice are removed and such cubes are arranged as in Figure (b), we get the fcc array of cations. Now there are a total of eight F-ions, and a total of four Ca^{2+} ions. ($\frac{1}{8} \times 8$ corner ions + $\frac{1}{2} \times 6$ face center ions). The coordination description is 8 : 4.

In the antifluorite structure, the anions form the fcc array (black circle) and the cations occupy the tetrahedral holes. The anion site is surrounded by a cubic array of cations. The coordination is 4 : 8. (in K_2O, for example, there are twice as many K^+ ions than O^{2-} ions).



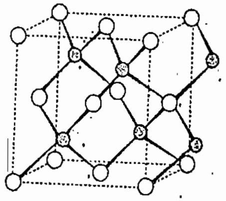
23-VII (c)



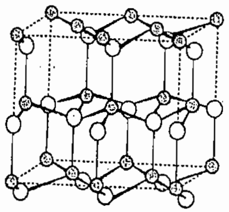
23-VII (d)

23-VII (c) : The Rutile structure : Rutile is a mineral form of TiO_2, titanium dioxide. Each Ti is surrounded by six O ions and each O is surrounded by three Ti — 6 : 3 coordination. The structure is derived from hexagonal close packing (hcp) of anions, cations occupying only half the octahedral holes. Cassiterite, SnO_2, also has the rutile structure.

23-VII (d) : β-cristobalite (one form of SiO_2) : SiO_2 makes a giant covalent lattice with coordinations 4 (tetrahedral) and 2 (linear) for Si and O respectively. Si—dark circles.



23-VII (e)



23-VII (f)

23-VII (e) : The zinc blende structure (Sphalerite) : It is also based on an extended fcc array of sulphide anions (white circles). Cations occupy half the tetrahedral holes. Each ion is surrounded by four neighbours - 4 : 4 coordination.

23-VII (f) : The Wurtzite structure : Wurtzite is another polymorph of zinc sulphide. The sulphurs (large circles) are now in hexagonal close-packed array with zinc atoms (black) occupying half of the tetrahedral holes (4 : 4 coordination). In wurtzite and sphalerite, the local symmetries of the cations and anions are identical toward their nearest neighbours but differ at the second-nearest neighbours.

Sulphur and the remaining elements in the group are much less electronegative than oxygen and show greater affinity for the softer metals (class-b) in the later part of the transition series. Sulphides, selenides etc. of less electropositive metals are mostly insoluble in water - a reflection of greater covalence in their bonding and soft nature of the anions. Many class-b metals occur naturally as sulphides etc. (chalcophilic elements). Their insolubility is also taken advantage of in separation/estimation of the elements in routine analytical procedure (Ch. 11 for precipitation of sulphides). Thus Al^{3+} (*aq*) or Sc^{3+} (*aq*) are unaffected by H_2S while Pb^{2+}, Cu^{2+}, Hg^{2+} etc. are readily precipitated from their aqueous solutions. The catenating tendency of sulphur is shown by the formation of polysulphides containing S_n^{2-} ions, e.g. Na_2S_2 and Na_2S_7.

The blue paramagnetic S_2^- ion corresponding to the superoxide ion has been reported in solutions of alkali metal polysulphides in acetone or DMSO. Simple salts of the ion are not known. The blue minerals lapis lazuli and ultramarine owe their colour primarily to the presence of the S_3^- radical ion which absorbs at 610 nm. Green ultramarine contains some S_2^- (400 nm).

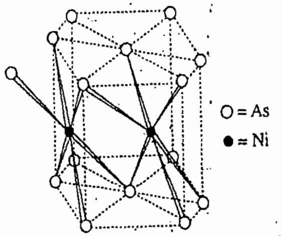
Sulphides, selenides and tellurides may also exhibit acidic or basic character, though certainly much less pronounced than the oxides. For example,

Basic $K_2Se + H_2O \rightleftharpoons KSeH + KOH$

Acidic $CSe_2 + 3H_2O \rightleftharpoons 2H_2Se + H_2CO_3$

Structure of sulphides, selenides etc.

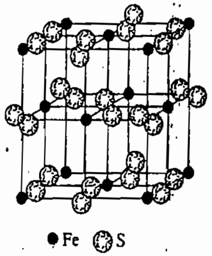
Sulphides, selenides and tellurides of alkali metals (M_2S) also have the antifluorite structure. Sulphides and selenides of Mg, Ca, Sr, Ba, Cd, V etc. +2 ions (MS type) are also similar to the MO type oxides in having the NaCl structure. The more covalent sulphides of softer metals adopt the nickel arsenide structure with shorter metal-metal separations (23-VIII).



23-VIII

Structure of disulphides

The disulphides MS_2 of transition metals do not necessarily contain M(IV) and S^{2-} ions. The S^{2-} ion is fairly reducing in nature and can co-exist only with a stable high oxidation state of a metal. Thus MoS_2 may be expected to contain Mo(IV) and S^{2-} ion, though with a fair degree of covalence. FeS_2, on the other hand, is not expected to contain the unusual Fe(IV) and is likely to contain Fe(II) and S_2^{2-}. Compounds with S_2^{2-} ion are more common than peroxides with O_2^{2-} ion — the loss of lattice energy in *not* forming the oxide is much greater in the latter case. Disulphides with S_2^{2-} units usually adopt the pyrite (mineral name of FeS_2) structure (23-IX). Other disulphides commonly have a layered structure containing alternate metal and sulphide layers. The sulphide-metal-sulphide layers are stacked over one another to provide 6 S atoms around each metal atom — sometimes in octahedral (PtS_2) and sometimes in trigonal prismatic (MoS_2) coordination. In MoS_2 ($MoO_3 + H_2S$; heat) there is evidence for weak S—S bonds between successive S-Mo-S slabs; these may easily slide over one another, making MoS_2 a very effective lubricant for use in engine oils (Molyslip).



23-IX

Non-stoichiometry

Non-stoichiometry is a common feature among the chalcogenides. The loss of oxygen by the lattice of zinc oxide on heating and turning yellow has already been mentioned (Ch. 6);

$$(1 + x)\,ZnO \longrightarrow Zn_{1+x}O + x/2O_2$$

"FeO" is always poor in iron, its highest composition being $Fe_{0.93}O$ (570°C). Some Fe^{3+} ions present in the lattice maintain electrical neutrality. Titanium monoxide can be prepared with the stoichiometry TiO, but the lattice actually contains about 15 percent vacancies in both Ti^{2+} and O^{2-} ions. The compound shows metallic conductivity arising from overlap of the diffuse *d*-orbitals on neighbouring Ti^{2+} ions — this type of overlap is not unusual for the early *d*-block elements in view of their low effective nuclear charge.

Uses

The chalcogenides cover a wide range of physical properties — they may be insulators, semiconductors or even metallic or superconductors. Many of these compounds have potentialities as solid-state optical, electrical and thermoelectric devices. A storage battery system with *molten* sodium and *molten* sulphur electrodes and a *solid* electrolyte of sodium-β-alumina has several advantages over the conventional lead-acid battery (much lighter, also longer life); these have the potentiality to be used in battery-driven cars. The cell reaction can be written formally as

$$2\,Na\,(l) + n/8\,S_8\;(l) \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Na_2S_n\,(l)$$

Suboxides, Peroxides, Superoxides

We have come across carbon suboxides in chapter 22. Suboxides with the elements in subnormal oxidation state are also formed by rubidium and cesium when they are heated in a limited supply of oxygen (chapter 18). The highly reactive, dark crystalline compounds may have a wide range of compositions, e.g., Cs_3O, Cs_4O, Cs_7O and Rb_6O. The compounds are good metallic conductors. A metallic network evidently runs through the crystal. In Cs_3O, for example, each O atom is surrounded octahedrally by six Cs atoms — the octahedra are linked to one another by sharing faces. Columns of Cs atoms running through the crystal provide metallic conduction.

Superoxides containing the O_2^- ion are formed by the alkali metals except Li (Chapter 18). Alkaline earth, zinc and cadmium superoxides are also formed with their peroxides which remain as solid solutions.

Solid ionic peroxides containing the $[O\text{–}O]^{2-}$ ion are formed by the alkali and alkaline earth metals (Chapters 18 and 19). The O-O distance in the ion, 1.49 A°, is typical for a single bond. Hydroperoxides M^+OOH^- are also formed by the alkali metals; these correspond to the hydroxides in water system. The peroxides and hydroperoxides liberate H_2O_2 on treatment with cold dilute acids or water. Barium oxide rapidly absorbs oxygen from the atmosphere at about 500°C to form barium peroxide; this decomposes at 700°C to give back the oxygen. The reaction may be used to prepare pure oxygen.

$$2\,BaO_2\,(s) \underset{500°C}{\overset{700°C}{\rightleftharpoons}} 2BaO\,(s) + O_2.$$

As expected, these peroxides are all strong oxidizing agents. Even at moderate temperatures, they oxidize most organic compounds to carbonates. Sodium peroxide is often used in many oxidizing fusions, for example chromium(III) and Mn(II) compounds are oxidized to chromates (Cr^{VI}) and manganate (Mn^{VI}) respectively. Iron is violently oxidized to ferrate, FeO_4^{2-}.

However, with strongly oxidizing substances like MnO_4^-, peroxides may also behave as reducing agents.

Peroxides of Mg and the lanthanides possess a fair degree of covalence. Covalent peroxides are formed by soft metals like zinc, cadmium and mercury.

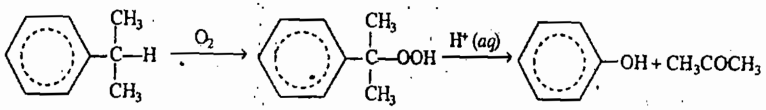
Stable hydrates may be formed by many ionic peroxides through hydrogen bonding of water molecules to the O_2^{2-} ions e.g., $Na_2O_2.8H_2O$; $M^{II}O_2.8H_2O$. (M^{II}= alkaline earth metals).

Many organic compounds containing the peroxo and hydroperoxo groups are also termed peroxide and hydro peroxide, e.g. benzoyl peroxide and cumene hydroperoxide :

$$2C_6H_5COCl + 2NaOH + H_2O_2 \xrightarrow{\text{cold solution}} (C_6H_5CO)_2\,O_2 + 2NaCl + 2H_2O.$$

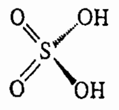
m.p. 104°C

It gives perbenzoic acid, $C_6H_5.CO.OOH$ with sodium methoxide, CH_3ONa. **Cumene hydroperoxide** is readily formed by auto-oxidation of cumene (isopropyl benzene); it is used in the synthesis of phenol :

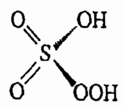


Similar autooxidation is also known for ethers, alkenes and the like. These proceed by a free radical chain mechanism initiated by traces of metals like Cu, Co or Fe. Distillaion of such oxidized solvents may lead to explosion. The peroxides may be removed by washing with acidified $FeSO_4$ solution or by passing through a bed of activated alumina (for ethers and hydrocarbons). The absence of peroxides is indicated when no red colour is produced with $FeSO_4 + NH_4SCN$ solutions.

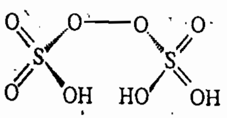
A large number of peroxoacids and their salts are known in which O—O—groups substitute —O— bridges in pyro oxo-acids and —OOH substitutes —OH groups in ortho oxo-acids.



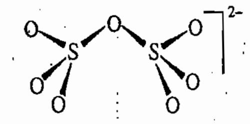
23-X (a) H_2SO_4



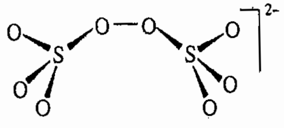
23-X (b) H_2SO_5



23-X (c) $H_2S_2O_8$



23-X (d) $S_2O_7^{2-}$



23-X (e) $S_2O_8^{2-}$

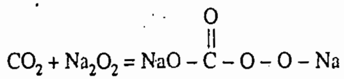
The peroxoacids or their salts may be prepared by the action of H_2O_2 or peroxides on suitable reagents or by anodic oxidation.

$$P_4O_{10} + 2H_2O_2 + H_2O = 4H_3PO_5$$

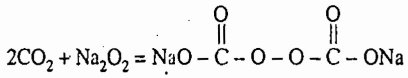
$$N_2O_5 + H_2O_2 = HNO_3 + HNO_4$$

$$HO.SO_2.Cl + H_2O_2 = HO.\ SO_2.OOH + HCl$$

$$HO.SO_2.Cl + H_2O_2 + Cl.SO_2.OH = HO.SO_2 - O - O - SO_2.OH$$

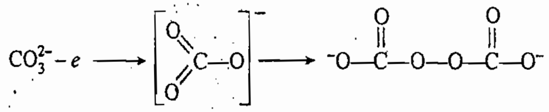


$$CO_2 + Na_2O_2 = NaO - \overset{\overset{\displaystyle O}{\|}}{C} - O - O - Na$$



$$2CO_2 + Na_2O_2 = NaO - \overset{\overset{\displaystyle O}{\|}}{C} - O - O - \overset{\overset{\displaystyle O}{\|}}{C} - ONa$$

Electrolytic oxidation of a cold concentrated solution of an acid or its salt using a high anode current density (sometimes in presence of a fluoride) is a useful method for the preparation of many peroxo acids/salts; for example, the formation of peroxodicarbonate may proceed via the possible intermediate radical ion :



Peroxoborates have been discussed in chapter 20. Peroxosulphuric acids will be discussed in connection with oxoacids of sulphur. Peroxocompounds of transition metals (Ti, Cr etc.) will be discussed in connection with the metals.

Peroxo compounds containing fluorine groups may be prepared by fluorination of oxygen compounds, e.g.,

$$SO_3 + F_2 \xrightarrow[160°C]{AgF_2} (FSO_2)\ OO\ (SO_2F) \text{ (Peroxodisulfonyl difluoride)}$$

$$COF_2 + ClF_3 \xrightarrow[250°C]{KF} CF_3OOCF_3 \text{ Bis(perfluoromethyl) peroxide}$$

Peroxo-hydrates

Many of these compounds are quite stable.

While true peroxocompounds contain an –O–O– group, there are some salts which **crystallize** with hydrogen peroxide of crystallization, e.g. $2Na_2CO_3.3H_2O_2$. They are called peroxohydrates (or perhydrates). They readily liberate H_2O_2 in contact with water which may be extracted with ether. Peroxocompounds liberate H_2O_2 only slowly. Peroxohydrates also do not immediately oxidize a 3% KI solution buffered to pH 7.5-8 by sodium bicarbonate (*Riesenfeld reaction*).

23.3.3 Oxides of S, Se, Te (Po)

The main oxides fall into two groups — dioxides MO_2 (M = S, Se, Te, Po) and trioxides MO_3 (M = S, Se, Te). MO oxides are known as transient species in gas phase for S, Se and Te, but PoO is a stable black solid. Besides, there are several oxides of sulphur, including the homocylic species S_nO ($5<n\leq10$). These have been mentioned briefly at the end of this section.

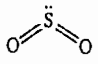
Dioxides

Values of ΔH_f^0 for the gaseous dioxides are (kJ mol^{-1}) :

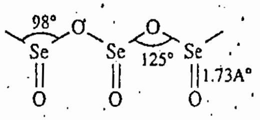
SO_2	SeO_2	TeO_2
–297	–230	–325

These may be prepared by heating the elements in air (or oxygen). The oxides are soluble in water, SO_2 and SeO_2 giving distinctly acidic solutions of sulphurous acid and selenious acid respectively. TeO_2 is amphoteric and much less soluble.

The decreasing M—O π-bond strength and increasing metallic character from S to Po are also reflected in the structures of the oxides. SO_2 contains discrete bent molecules in both gaseous and solid state; SeO_2 solid contains infinite Se–O–Se chains (23-XI/XII); TeO_2 and PoO_2 are essentially ionic solids with rutile and f-c-c structures respectively. Some degree of pi-bonding is inferred in gaseous SeO_2 monomers with a short Se—O distance of 1.61 A°; the Se—O—Se bond angle is 125°.



23-XI



23-XII

Since sulphur can be easily oxidized to the + VI state and reduced to 0 oxidation state, SO_2 can act both as an oxidizing and reducing agent. The + VI state for Se is attained only with difficulty and so SeO_2 behaves primarily as an oxidizing agent.

Preparation

Though the dioxides are prepared by directly heating the elements in air, roasting of sulphide minerals and burning of sulphur containing fuels (oil, coal) also produce sulphur dioxide which is a major pollutant of the atmosphere (see later).

SO_2 is also obtained as a bye-product in the manufacture of cement by heating gypsum with clay, sand and coke in a rotary kiln at 1200°C.

$$2CaSO_4 + C + (xSiO_2 + yAl_2O_3) = 2SO_2 + CO_2 + (2\ CaO.xSiO_2.yAl_2O_3)$$

Selenium and tellurium dioxides may also be obtained by oxidizing the elements with hot conc. HNO_3 to H_2SeO_3 or $2\ TeO_2.HNO_3$ respectively, followed by heating.

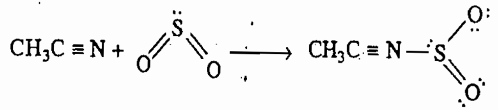
Properties

SO_2 is a colourless heavy gas with a choking smell which can be easily liquefied by cooling in a freezing mixture (b.p. –10°C; m.p. –75°C). It can also be liquefied by pressure e.g., 2.5 atm at 15°C (critical temp. 157.5°C). Liquid sulphur dioxide is a nonaqueous solvent suitable for super acid systems. It has a low dielectric constant (≅ 15) and undergoes little self-ionization (Ch. 12). Some reactions in liquid SO_2 have been discussed in Chapter 12.

SO_2 is highly soluble in water (= 40 volumes in one volume of water at ordinary conditions). The aqueous solution contains the unstable sulphurous acid H_2SO_3, though the bulk of dissolved SO_2 is present as hydrate $SO_2.nH_2O$. Crystalline clathrate hydrate of approximate composition $SO_2.7H_2O$ may be isolated by cooling the solution to 0°C.

As an acidic oxide, SO_2 reacts with alkalis to form sulphites and bisulphites. The acid-base and redox behaviour of SO_2 is versatile in the sense that it can function in all *four* capacities :

(i) *Lewis acid*

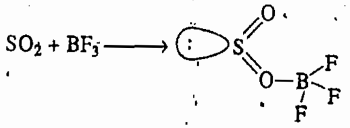


$$Me_3N + SO_2 \longrightarrow Me_3NSO_2$$

$$SO_2 + SbF_5 \longrightarrow SbF_5.SO_2 \text{ (O-bound; Fig. 23.3a)}$$

The dimensions of the SO_2 molecule do not change significantly in Me_3NSO_2. Crystalline 1 : 1 charge-transfer complexes are formed (with other amines also) in which electon density is transferred from nitrogen to the antibonding LUMO of SO_2 which are localized near S.

(ii) *Lewis base*



(iii) *Oxidizing agent* $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$

(iv) *Reducing agent* $Cl_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

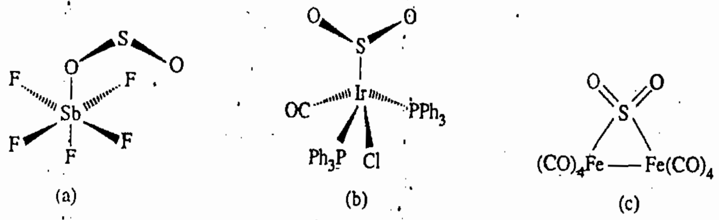


Fig. 23.3. Co-ordination by SO_2 : (a) through O (b) through S (c) bridge.

Some more reactions of SO_2 are :

(i) $2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(ii) $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(iii) $2\ KIO_3 + 5SO_2 + 4H_2O = 2KHSO_4 + 3H_2SO_4 + I_2$

excess $(I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4)$

(iv) $2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + 2HCl + H_2SO_4$

(v) $4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S$ (strong HCl)

(vi) $6SnCl_2 + 2SO_2 + 8HCl = 5SnCl_4 + 4H_2O + SnS_2$ (strong HCl)

SO_2 can coordinate to metals through S (see Fig. 23.3b) or sometimes through O e.g., Pt $(PPh_3)_2(SO_2)_2$ (pyramidal); Ni $(PPh_3)_2(SO_2)_2$ (planar); $[\{Fe(C_5H_5)(CO)_2\}_2SO_2]$ (bridging); Mn $(OPPh_3)_4(OSO)_2]$ (O-bound).

SO_2 may also be inserted between M—C and M—M bonds e.g.

$$Me_4Sn + SO_2 \longrightarrow Me_3\,Sn\,SO_2.Me$$

$$C_2H_5MgBr + SO_2 \longrightarrow C_2H_5S(O)OH \quad \text{(sulphinic acid)}$$

$$RCH_2HgOAc + SO_2 \longrightarrow RCH_2\,SO_2\,Hg\,OAc.$$

The angular structure of SO_2 (23-XI) is consistent with sp^2 hybridization on S atom, with two unpaired electrons in one *p* and one *d* orbital. The hybrid orbitals account for two S—O σ-bonds and a lone pair on the sulphur, while the remaining electrons can form π-bonds with the oxygen atoms. Dipole moment of $SO_2 = 1.6$ D.

Sulphurous acid and sulphites have been discussed in the next section (oxoacids).

Selenium dioxide forms colourless sublimable crystals which melt under pressure at 340°C. It is highly soluble in water — the solution on evaporation forms colourless hexagonal crystals of selenious acid, H_2SeO_3.

Less stable than SO_2, SeO_2 is easily reduced to Se by S, SO_2, HI etc.

$$SeO_2 + S = SO_2 + Se$$

$$SeO_2 + 4HI = Se + 2I_2 + 2H_2O$$

It is largely used in organic chemistry as an oxidizing agent, e.g.

$$CH_3CHO + SeO_2 \longrightarrow Se + CHO.CHO + H_2O.$$

Solid SeO_2 has a polymeric chain structure (23-XII). The gaseous molecule is symmetrically bent like SO_2.

Tellurium dioxide prepared in the laboratory is colourless (α-form), but another yellow mineral variety (β) is also known. It is much less volatile than SeO_2 and melts at 733°C (red melt). It is soluble in water giving acidic solution.

TeO_2 is amphoteric; it dissolves in both acids and alkalis. Basic salts like $2TeO_2.HNO_3$ are also known.

The structure of TeO_2 is predomimantly ionic — the β-form is orthorhombic with a layer structure; the α-form has a rutile like structure. The coordination number of Te in both cases is four.

PoO_2 is more basic and insoluble in aqueous alkali. It has a fluorite structure.

Trioxides

Sulphur trioxide is produced in large quantities (for the preparation of sulphuric acid) by aerial oxidation of SO_2 in presence of V_2O_5 catalyst around 450°C. In the laboratory, SO_3 may be prepared by distilling conc. H_2SO_4 over P_4O_{10} or by heating oleum.

$$2H_2SO_4 + P_4O_{10} = 4HPO_3 + 2SO_3$$

The standard heats of formation of the trioxides show that selenium can be oxidized to the +6 state with difficulty :

	SO_3	SeO_3	TeO_3
ΔH_f^0	− 432	−184	− 348 kJ mol^{-1}

SeO_3 is also thermodynamically unstable with respect to dissociation into SeO_2 and O_2 :

$$SeO_3 \longrightarrow SeO_2 + \tfrac{1}{2}O_2\,(g) \qquad \Delta H^0 = -46 \text{ kJ mol}^{-1}$$

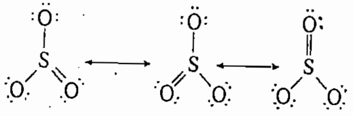
Thus SeO_3 can be made only with difficulty by dehydration of H_2SeO_4 with P_4O_{10} (150-160°C). TeO_3 is made by dehydration of $Te(OH)_6$ at 300-360°.

SO_3 is a colourless liquid (m.p. 17°C, b.p. 44.6°C) which reacts vigorously with water to form H_2SO_4. But since this gives rise to a thick mist, the gas is absorbed in conc. H_2SO_4 to obtain oleum which is suitably diluted with water to 98% H_2SO_4.

SO_3 is a strongly acidic oxide, forming sulphates with many metal oxides. It reacts with HCl (and other HX) to form chlorosulphuric acid $HO.SO_2.Cl$. Solutions containing SbF_5, HSO_3F and SO_3 make superacid systems. It also acts as a strong Lewis acid, forming adducts like $Ph_3P.SO_3$. Ammonia gives NH_2SO_2OH (amidosulphuric acid) and $HN(SO_3H)_2$ etc.

SO_3 may also act as an electron pair donor to strong acceptors like AsF_3, SbF_3 or $SbCl_3$.

The monomer SO_3 has a symmetrical planar structure in the gas phase (23-XIII) with short S—O bonds (1.43 A° vs 1.60 A° for single bond lengths). The *p*π-*p*π bonding is probably augmented by *p*π-*d*π bonding from filled oxygen 2*p* orbitls to empty sulphur 3*d* orbitals. This exists in equilibrium with a cyclic trimer in both gaseous and liquid phases.

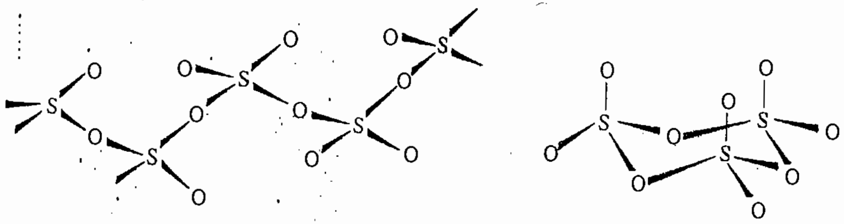


23-XIII

Canonical forms of SO_3 (*g*) molecule

Liquid SO_3 is also a mixture of the monomer and trimer, though it readily polymerizes in the pure state by traces of water. The liquid may be stabilized by boric acid.

In solid SO_3, the π-bonds are partly sacrificed in favour of σ-bonding via formation of S—O—S bridges either in helical chains or cyclic trimers. Three distinct forms are known — the most stable α-SO_3 has helical chains of linked SO_4 tetrahedra cross-linked into layers; it has an asbestos-like appearance. The β-form is also asbestos-like and contains similar chains (23-XIV a). The γ-form, obtained by condensation of SO_3 (*g*) at 80°C or below, contains the puckered cyclic trimer.



β-SO_3

(a)

γ-SO_3

(b)

23-XIV

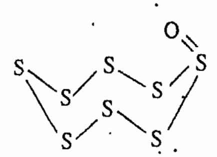
SeO_3 consists of a Se—O—Se bridged cyclic tetramer in the solid. TeO_3 has a three-dimensional structure with octahedral TeO_6 units sharing oxygen atoms.

Lower oxides

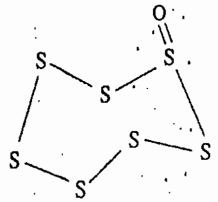
S_2O is formed by passing a slow stream of thionyl chloride ($SOCl_2$) vapour over heated Ag_2S (160°C) at pressures below 1 mm Hg. It is also formed by burning S_8 in O_2 at very low pressure. The gas readily decomposes to SO_2 and S at room temperature. It has a bent S = S = O structure (angle 113°; S—O = 1.46 A°; S—S = 2.02 A°).

SO and S_2O_2 are extremely unstable.

Cyclo sulphur oxides are obtained by oxidizing cyclo $-S_{10}$, $-S_9$, and $-S_8$ (in CS_2 solution) by trifluoroperacetic acid ($CF_3C.O.OOH$) below −10°C. Oxides of cyclo S_7 and S_6 forms are also formed from CH_2Cl_2 solution. S_8O may also be made by reacting $OSCl_2$ and H_2S_7 in CS_2 at −40°. It is appreiably stable — melts with decomposition at 78°C. All these compounds are orange or dark yellow in colour and decompose to SO_2 and S on heating to room temperature or above.



S_8O
23-XV (a)



S_7O
23-XV (a)

SO_4 has been isolated in inert gas matrix at very low temperatures (15-78 K) by photolysis of SO_3-ozone mixture. SO_3 may also be oxidized by atomic oxygen to SO_4; which is unstable and decomposes far below room temperature.

SeO and TeO have transient existence in flames. PoO is obtained as a black solid which is rapidly oxidized.

Air Pollution and SO_2

Sulphur dioxide is a major pollutant of our environment. SO_2 released by burning of oil and coal, together with that discharged by industries, causes severe damage to the plant and animal life, particularly the respiratory organ. About 200 million tonnes of the gas are released annually over the world, and nearly an equal amount is released by natural processes. Coal-based power plants make the largest contribution to SO_2 pollution; localities near sulphuric acid plants also often contain a higher level of SO_2 in the air. The pollution is thus severe in highly populated urban areas — often exceeding 2-5 ppm while the recommended limit is only 0.5 ppm. SO_2 is partially oxidized to SO_3 in air by photolytic and catalytic processes initiated by ozone, hydrocarbon, nitrogen oxides and soot or dust. The SO_3 gives rise to H_2SO_4 with water particles, causing *"acid rain"*. In addition to general plant and aquatic life, buildings, specially archaeological specimens are severely damaged by such acid rains.

Small amounts of SO_2 in the atmosphere (down to 1 in 10^9) may be estimated by reducing the gas in H_2/air flame and flame photometry of S_2 vapour at 394 nm. Pulsed fluorescent analysers are also available commercially. Chemically, the gas may be absorbed in H_2O_2 and the H_2SO_4 formed may be titrated in the usual way or conductimetrically. Colorimetric determination is possible by absorbing the gas in Na_2HgCl_4:

$$Na_2[HgCl_4] + 2SO_2 + 2H_2O \longrightarrow Na_2[Hg(SO_3)_2] + 4HCl.$$

The disulphitomercurate formed is determined by adding acidic pararosaniline and formaldehyde.

There are several methods for reducing SO_2 content of effluent gases, e.g. scrubbing with milk of lime or absorption with suitable solvents like ethanolamine (from H_2SO_4 plants). SO_2 may also be reduced partially to H_2S by CH_4 in natural gas, naphtha or coal; the H_2S then catalytically reduces the remaining SO_2 into S (in presence of activated Al_2O_3). But since the technical and economic involvements are large, these are not fully utilized in practice in many cases, not only in developing countries, but in several so called advanced countries too.

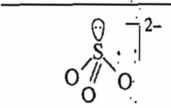
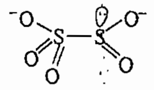
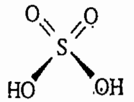
23.3.4 Oxoacids and their salts

The principal oxoacids and anions of the Group 16(VI) elements in +IV and VI oxidation states are shown in Table 23.6. As expected, species containing sulphur(IV) are strongly reducing in character; reducing property decreases to Se(IV) which is predominantly oxidizing. No acid containing Te(IV) is formed though its anions are known. Sulphur and selenium show coordination numbers upto 4, the most common geometry being tetrahedral. Tellurium is six-coordinate to oxygen.

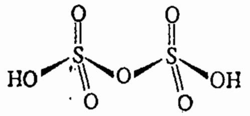
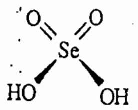
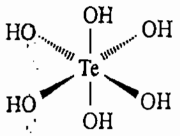
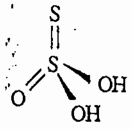
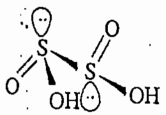
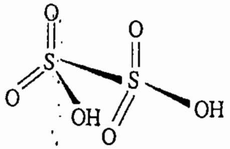
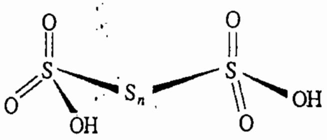
Sulphur forms several oxoacids in lower oxidation states — they commonly possess S—S bonds (H_2SO_4 is exception). The Se—Se bond is much weaker and is not observed in oxoacids. The peroxo acids H_2SO_5 and $H_2S_2O_8$, corresponding to sulphuric acid and pyrosulphuric acids, have been mentioned earlier (23-X).

The principal oxoacids are summarized below. Details follow.

TABLE 23.6
Principal Oxoacids of S, Se, Te

A. IV State		
(i) **Sulphurous acid** H_2SO_3 HSO_3^-, SO_3^{2-}		$SO_2 + H_2O$; but existence of free acid doubtful. Weak, reducing, dibasic. Pyramidal with l.p. on S. Heating, solid bisulphite or passing SO_2 into HSO_3^- (*aq*)
$S_2O_5^{2-}$ (disulphite) (free acid not known)	 S—S bonded $^-O—SO_2.SO.O^-$	
(ii) **Selenous acid** H_2SeO_3 $HSeO_3^-$, SeO_3^{2-} $Se_2O_5^{2-}$ (diselenite)	$[O_2Se—O—SeO_2]^{2-}$	$SeO_2 + H_2O$; Se + dil HNO_3. Less reducing than H_2SO_3. Stronger oxidizing agent. Pyramidal structure; H_2SeO_3 (*s*) has an orthorhombic layer lattice.
(iii) **Tellurous acid** H_2TeO_3 $HTeO_3^-$, TeO_3^{2-}		Hydrolysis of TeX_4. Free acid not very stable. Structure unknown. Tellurites are made by fusion of TeO_2 with metal oxides.
+VI State		
(i) **Sulphuric acid** H_2SO_4 HSO_4^- SO_4^{2-}		$SO_3 + H_2O$ Stable strong acid, strongly oxidizing.

Contd. next page

$H_2S_2O_7$ $HS_2O_7^{-}$ $S_2O_7^{2-}$ (also $S_3O_{10}^{2-}$, $S_5O_{16}^{2-}$)		$SO_3 + H_2SO_4$ (conc.) Loses SO_3 on heating. Sulphonating agent.
Selenic acid H_2SeO_4 $HSeO_4^-$, SeO_4^{2-} $H_2Se_2O_7$ $Se_2O_7^{2-}$		Oxidation of H_2SeO_3 by O_3, $KMnO_4$ etc; or of Se by Cl_2. Strong, dibasic acid. Strongly oxidizing; dissolves Ag, Au, Pd. $H_2SeO_4 + SeO_3$
Telluric acid H_6TeO_6 $[TeO(OH)_5]^-$ $[TeO_2(OH)_4]^{2-}$ $(H_2TeO_4)_n$ (Polymetatelluric acid; n ≈ 10).		Oxidation of Te or TeO_2 with strong oxidizing agents. Very weak dibasic acid. Most tellurates contain TeO_6 octahedra. Partial dehydration of H_6TeO_6 in air at 160°C.
Other oxoacids of sulphur		
Thiosulphuric acid $(H_2S_2O_3)$ $S_2O_3^{=}$		$S + SO_3^{2-}$ in alkaline media. Decomposes to give S in acid media. Mild reducing agent.
Dithionous acid $H_2S_2O_4$ $S_2O_4^{2-}$		Reduction of H_2SO_3 or sulphites by zinc. Salts stable in solid or alkaline media. Powerful reducing agent.
Dithionic acid $(H_2S_2O_6)$ $S_2O_6^{2-}$		Oxidation of sulphites (MnO_2) Acid stable in dilute solution only. Strong, dibasic acid. Dithionates are stable, solution may be boiled without decomposition.
Polythionic acids $(H_2S_nO_6)$ $(n = 3-6)$ $S_nO_6^{2-}$ chains with upto 22 S atoms known.	 $(n = 1-4)$	Various anions formed by reaction of SO_2 and H_2S or arsenites. Unstable, reducing. Readily lose S.

Sulphurous acid

The free acid has not been isolated but is known to be stable in the gas phase as $(HO)_2S = O$. It may be slightly formed in aqueous solutions of SO_2 where the principal species is $SO_2.xH_2O$. The dissociation constants of "sulphurous acid" relate to the equilibria (K values at 25°C)

$$SO_2.xH_2O \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq) \qquad 1.6 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq) \qquad 1 \times 10^{-7}$$

Salts of the sulphite (SO_3^{2-}) and bisulphite (HSO_3^-) ions are well known. Sulphites except those of alkali metals and ammonium are usually insoluble. Solid bisulphites can be isolated only with large cations like Rb^+, Cs^+ and NR_4^+. With smaller ions, evaporation of a solution containing HSO_3^- leaves disulphite, e.g.,

$$2NaHSO_3 = Na_2S_2O_5 + H_2O.$$

Disulphites are also called pyrosulphite or metabisulphite. However, the name pyrosulphite suggests the presence of an S—O—S bridge in $S_2O_5^{2-}$ and should be discouraged. The $S_2O_5^{2-}$ ion contains a direct S—S bond (see Table 23-6).

The sulfites and disulfites are moderate reducing agents :

$$SO_4^{2-} + 4H^+ + (x-2)\,H_2O + 2e \rightleftharpoons SO_2.xH_2O \qquad E° = 0.17\text{ V}$$

$$SO_4^{2-} + H_2O + 2e \rightleftharpoons SO_3^{2-} + 2\,OH^- \qquad E° = -0.93\text{ V}$$

In ice cold solution, MnO_2 oxidizes "H_2SO_3" to dithionate (see later). Anodic oxidation of a neutral or alkaline solution of sodium sulphite also produces dithionate :

$$2SO_3^{=} = S_2O_6^{=} + 2e$$

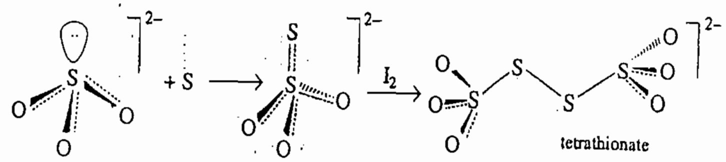
Sodium amalgam reduces sulfites to dithionites; formates give thiosulphates :

$$2SO_3^{2-} + 2H_2O + 2Na.Hg \longrightarrow S_2O_4^{2-} + 4OH^- + 2Na^+$$

$$2SO_3^{2-} + 4HCOO^- \longrightarrow S_2O_3^{2-} + 2C_2O_4^{2-} + 2OH^- + H_2O.$$

Thiosulphates are also formed by boiling sulfites with elemental sulphur

$$Na_2SO_3 + \tfrac{1}{8}S_8 \longrightarrow Na_2S_2O_3.$$



Action of H_2S on an aqueous solution of SO_2 produces "Wackenroder's solution" which contains a number of polythionic acids (see later).

The SO_3^{2-} ion can coordinate to a metal through the S atom, e.g., $[Pt(NH_3)_2(SO_3)_2]^{2-}$, *cis* and *trans*.

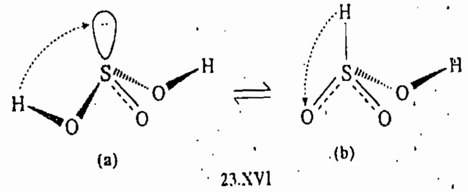
The solution chemistry of the disulphite ion $S_2O_5^{2-}$ is similar to that of the HSO_3^- ion into which it decomposes on acidification, liberating SO_2.

The sulphite ion is pyramidal with a lone pair of electrons on the S-atom. In valence bond description, this corresponds to sp^3 hybridization of the sulphur valence orbitals, an electron promoted to the 3d orbital (and excluded from hybridization) forming π-bond with O-atom. In the structure (Table 23.6), ∠O—S—O = 106°; S—O = 1.5 A°.

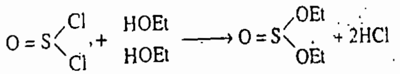
In the disulphite ion ($S_2O_5^{2-}$), the S—O distances are nearly equal. The S—S distance is rather long, equal to 2.17 A°.

Tautomeric forms of the sulphite ion

There is some evidence for another tautomeric form of the sulphite ion (extrapolated to sulphurous acid) in which a hydrogen is attached directly to the S : H—SO_2—O^-. The corresponding diethyl sulphite (b.p. 213°), Et—SO_2—OEt, is obtained by digesting sodium sulphite with ethyl iodide. Only one ethyl group of the ester (bound via O) may be split by hydrolysis. The isomeric diethyl sulphite O=S(OEt)$_2$ is obtained by reacting $SOCl_2$ with ethanol; it has a different boiling point, 161°C.



23.XVI



$$O=S\langle^{Cl}_{Cl} + {HOEt \atop HOEt} \longrightarrow O=S\langle^{OEt}_{OEt} + 2HCl$$ (suggests structure in 23·XVIa for H_2SO_3)

b.p. 161°C

$$Na_2SO_3 + EtI \longrightarrow \underset{b.p.\ 213°C}{Et.SO_2.OEt} + 2NaI$$ (suggests structure in 23·XVIb for H_2SO_3)

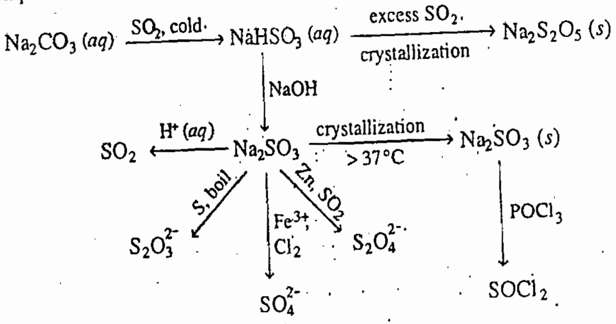
The bisulphite ion also exists in aqueous solution in two tautomeric forms in equilibrium

$$H\text{-}SO_3^- \rightleftharpoons H\text{-}OSO_2^- \qquad [SO_2(OH)^-]/[HSO_3^-] \simeq 5 \text{ at } 20°C \text{ from } ^{17}O \text{ NMR.}$$

In solid $RbHSO_3$ and $CsHSO_3$, the H-atoms are attached to S.

Uses

Sodium sulphite is extensively used in industry — e.g., in bleaching paper pulp, removing O_2 from boiler water and as a reducing agent in photography. World production is more than 1 million ton per year. It is prepared by passing SO_2 into aqueous Na_2CO_3 solution. Crystallization at the $NaHSO_3$ stage with excess SO_2 produces $Na_2S_2O_5$ (disulphite). Crystallization of Na_2SO_3 solution below 37°C gives hydrated $Na_2SO_3 \cdot 7H_2O$; the industrial demand is mostly for the anhydrous salt which is obtained by crystallization at higher temperature.



Scheme 23-1 : Preparation of sulphites.

Selenous acid

Selenous acid crystallizes from an aqueous solution of SeO_2. It is also formed by oxidizing powdered Se with dil. HNO_3 :

$$3Se + 4HNO_3 + H_2O = 3H_2SeO_3 + 4NO.$$

It is a moderately weak acid, $K_1 = 3.5 \times 10^{-3}$; $K_2 = 5 \times 10^{-8}$.

Both acid salts and normal salts are known. The acid readily dehydrates to SeO_2 at 70°C.

Selenous acid and selenites are feeble reducing agents — they are oxidized to selenates by ozone. On the other hand, they oxidize H_2S, SO_2, S, HI etc. and get reduced to selenium (red powdered form) :

$$H_2SeO_3 + 4H^+ + 4e = Se + 3H_2O \qquad E° = 0.7\text{ V}$$

$$H_2SeO_3 + 2H_2S = Se + 2S + 3H_2O.$$

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4.$$

$$H_2SeO_3 + 4HI = Se + 2I_2 + 3H_2O.$$

Alkali metal diselenites contain the oxygen bridged anion $\mathbf{O_2Se - O - SeO_2^{2-}}$.

Unlike the bisulphite ion, which can exist in two **tautomeric** forms, the diselenite ion is thought to exist only as the H—$OSeO_2^-$ **isomer**.

Tellurous acid

Tellurous acid may be made by hydrolysis of $TeCl_4$:

$$TeCl_4 + 3H_2O = H_2TeO_3 + 4HCl.$$

Tellurites may be prepared by heating TeO_2 with metal oxides. H_2TeO_3 is a weak acid : $K_1 = 3 \times 10^{-3}$; $K_2 = 2 \times 10^{-8}$ (approx). The acid may be easily dehydrated to TeO_2. Its structure is unknown. Cs_2TeO_3 contains pyramidal TeO_3^{2-} ion. Tellurous acid and tellurites are oxidized to telluric acid/tellurates by strong oxidizing agents like Cl_2 or $KMnO_4$. Reduction to Te may be achieved by SO_2 or zinc-acid.

Sulphuric acid

The importance of sulphuric acid in chemical industry needs little mention. It is now manufactured by the contact process (see below). The anhydrous acid is a colourless, heavy, viscous liquid with a high dielectric constant :

M.P.(°C)	*B.P.(°C)*	*ρ (g cm⁻³)*	*η (25°C; centipoise)*	*ε*
10.4	~ 300 (dec)	1.83	24.5	100

The molecules are strongly hydrogen bonded in both the liquid and the solid. The liquid is highly conducting, κ (25°C) = 1.04 × 10^{-2} ohm^{-1} cm^{-1}.
Several ionization equilibria are simultaneously present, e.g.

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad K\,(10°C) = 1.7 \times 10^{-4} \text{ mol}^2\text{ kg}^{-2}$$

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \qquad = 3.5 \times 10^{-5} \text{ mol}^2\text{ kg}^{-2}$$

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \qquad = 7 \times 10^{-2} \text{ mol}^2\text{ kg}^{-2}$$

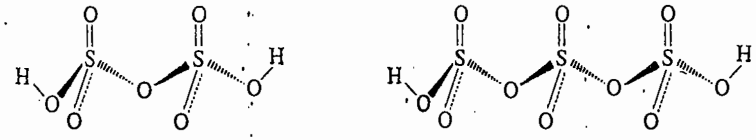
Hydration of H_2SO_4 liberates large amount of heat (= 880 kJ mol^{-1} for infinite dilution). This is why the acid is always diluted by slowly pouring *into* water with stirring — the reverse addition may cause explosive spurting of the acid mixture by the steam formed. Several crystalline hydrates are formed at low temperatures.

Solvent properties of anhydrous H_2SO_4 have been discussed in chapter 12. Oleum or fuming sulphuric acid is obtained by dissolving SO_3 into concentrated H_2SO_4 and may contain disulphuric (pyrosulphuric) acid $H_2S_2O_7$ together with $H_2S_3O_{10}$ and $H_2S_4O_{13}$ and other $H_2SO_4.nSO_3$. These contain joined tetrahedral SO_4 units.

The aqueous solution of H_2SO_4 is a strong dibasic acid, $K_1 = 10^3$, $K_2 = 1.2 \times 10^{-2}$. Two series of salts — the sulphates and bisulphates are well established. These may be prepared by desired neutralization of the acid. Anhydrous sulphates are obtained by the action of SO_3 in nonaqueous media e.g. in liquid SO_2 :

$$CuCl_2 + 2SO_3 = CuSO_4 + SO_2Cl_2.$$

Concentrated sulphuric acid is an effective dehydrating agent; sometimes charring takes place with many organic compounds. The hot concentrated acid possesses oxidizing power also.



(a) $H_2S_2O_7$

(b) $H_2S_3O_{10}$

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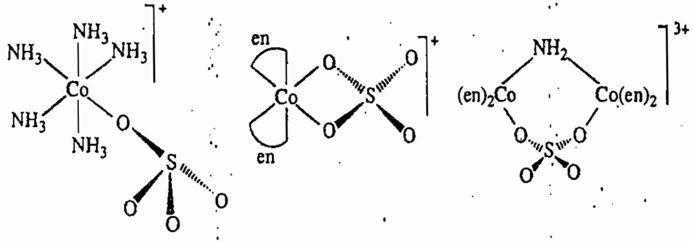
Q. 23.4 *The S—OH and S—O distances in the tetrahedral species are as follows :*

	S—OH (A°)	S—O (A°)
H_2SO_4 (*g*)	1.54	1.42
HSO_4^-	1.56	1.47
$SO_4^=$	—	1.49

Comment on the increase in S—O bond length.

Hint : Draw valence bond structures. As the π-bonding is distributed over a larger number of atoms, bond order decreases resulting in an increase in bond length.

The sulphate ion can act as a monodentate, bidentate or a bridging ligand :



(a) (b) (c)

Fig. 23.4

SO_4^{2-} ion as ligand : (a) monodentate (b) bidentate (c) bridge.

Manufacture of sulphuric acid

The contact process is based on the oxidation of SO_2 to SO_3 on vanadium pentoxide catalyst promoted by potassium sulphate. The exothermic reaction

$$SO_2 + {}^1/_2\,O_2 \rightleftharpoons SO_3 \qquad \Delta H^\circ = -98 \text{ kJ mol}^{-1}$$

gives higher equilibrium conversion at low temperature and high pressure but at low temperature the rate of the reaction becomes very slow. Also the V_2O_5 catalyst is inactive below 400°C and disintegrates above 620°C. The conversion is actually effected in 4 stages working around 450°C - 550°C and the SO_3 produced is absorbed in 98% H_2SO_4 to get oleum. This is subsequently diluted with water to 98% H_2SO_4.

The success of the process rests on efficient utilization of the sulphur burnt — the sulphur emitted to the atmosphere should be below 0.5% of the total sulphur used. Even within this limit, the total annual production of the whole world leaves a large amount of SO_2 into air : 150 million ton of H_2SO_4 ≡ 50 million ton of S; 0.5% of 50 × 10^6 ton = 250000 ton of S per year or 685 ton per day.

In terms of SO_2, the figures will be just doubled. Inefficient plant handling (as it frequently occurs here) releases more than this amount of SO_2.

The largest use of sulphuric acid is in the manufacture of fertilizers. Manufacture of paints, pigments, dyestuffs, fibres, detergents and other chemicals also consume huge quantities of the acid.

Selenic acid

Selenic acid is formed by oxidation of selenium or selenium(IV) compounds :

$$H_2SeO_3 + H_2O_2 \longrightarrow H_2SeO_4 + H_2O$$

$$8H_2SeO_3 + 2KMnO_4 \longrightarrow 5H_2SeO_4 + K_2SeO_3 + 2MnSeO_3 + 3H_2O$$

$$Se + 3Cl_2 + 4H_2O \longrightarrow H_2SeO_4 + 6HCl$$

$$Ag_2SeO_3 + Br_2 + H_2O \longrightarrow H_2SeO_4 + 2AgBr.$$

Selenic acid forms white deliquescent crystals, m.p. 62°C which readily lose water on heating. The acid decomposes above 200°C, evolving oxygen. Hydrated crystals $H_2SeO_4.H_2O$, $H_2SeO_4.2H_2O$ and $H_2SeO_4.4H_2O$ are known.

Like H_2SO_4, H_2SeO_4 takes up water and chars organic compounds. Its aqueous solution is a strong acid; $K_1 = 10^3$; $K_2 = 10^{-2}$. The hot concentrated acid dissolves Cu, Ag, Au and Pd. Iron is rendered passive. Platinum dissolves in presence of Cl^-.

$$2Au + 6H_2SeO_4 \longrightarrow Au_2(SeO_4)_3 + 3H_2SeO_3 + 3H_2O.$$

The dilute acid liberates hydrogen with zinc.

Selenic acid is a stronger oxidizing agent than sulphuric acid, but often kinetically slow.

$$SeO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SeO_3 + H_2O; \qquad E^\circ = 1.15 \text{ V}.$$

The dilute acid oxidizes HI quantitatively. The concentrated acid liberates chlorine from HCl :

$$H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2.$$

The acid is quantitatively reduced to selenium by concentrated HCl saturated with SO_2 — the selenium may be filtered, dried and weighed to estimate selenates (distinction from tellurates).

Sulphates and selenates are isomorphous — the ionic radii of the two tetrahedral ions are similar : 2.44 A° ($SO_4^=$) and 2.35 A° ($SeO_4^=$). Alums are also formed by the selenates. The selenates are more soluble in water than corresponding sulphates — $BaSeO_4$: ~ 0.08 g/l vs $BaSO_4$: ~ 0.002 g/l at 25°C. Selenates are readily formed by oxidation of selenites or even alkali fusion of selenides with an oxidizing agent, e.g.

$$K_2Se + 4NaNO_3 \xrightarrow{\text{fused}} K_2SeO_4 + 4NaNO_2$$

Telluric acid

Telluric acid corresponding to the formulae H_2SO_4 and H_2SeO_4 is not common (see later). The most common oxoacid of Te(VI) is orthotelluric acid H_6TeO_6, rather $Te(OH)_6$ — consistent with the trend observed in the period to attain a coordination number 6 among the isoelectronic species : $[Sn(OH)_6]^{2-}$, $[Sb(OH)_6]^-$ and $O = I(OH)_5$.

H_6TeO_6 may be prepared by oxidation of Te or TeO_2 by various oxidizing agents like chloric acid, $KMnO_4$, CrO_3 - HNO_3 or H_2O_2 (30%) :

$$5TeO_2 + 2KMnO_4 + 6HNO_3 + 12H_2O \longrightarrow 5H_6TeO_6 + 2KNO_3 + 2Mn(NO_3)_2.$$

Since the acid is sparingly soluble in cold water but easily soluble in hot water, it can be crystallized from aqueous solution. Below 10°C, the hydrate H_6TeO_6, $4H_2O$ separates.

Orthotelluric acid is a white crystalline solid, m.p. 136°C, though above 120° it gradually loses water to form condensed systems (see below). It is a weak acid, $K_1 \simeq 10^{-8}$, $K_2 \simeq 10^{-11}$, $K_3 \simeq 10^{-15}$. When titrated with alkali using phenolphthalein, telluric acid behaves only as a monobasic acid giving salts like $M^ITeO(OH)_5$. However, other salts may also be prepared, e.g., Ag_6TeO_6 or $Li_2TeO_2(OH)_4$.

H_6TeO_6 is a fairly strong oxidant :

$$H_6TeO_6 + 3SO_2 \longrightarrow Te + 3H_2SO_4$$

$$H_6TeO_6 + 2HCl \longrightarrow H_2TeO_3 + 3H_2O + Cl_2$$

Regular octahedral $Te(OH)_6$ units (Table 23.6) have been confirmed in crystals (X-ray) and solutions (Raman spectra). The hexamethyl ester $Te(OMe)_6$ may be prepared by reacting diazomethane.

Polymetatelluric acid, $(H_2TeO_4)_n$ is formed in equilibrium on heating an aqueous solution of H_6TeO_6.

$$nH_6TeO_6 \rightleftharpoons (H_2TeO_4)_n + 2nH_2O$$

The sparingly soluble product may be separated by rapid cooling. It may also be obtained as a white amorphous powder by partial dehydration of H_6TeO_6 at 160° in air. The value of n is around 10.

Allotelluric acid is a syrupy liquid formed when orthotelluric acid is heated in a sealed tube at 300°C. Its composition approximates $(H_2TeO_4)_3(H_2O)_4$. It reverts to H_6TeO_6 at room temperature; on heating in air $(H_2TeO_4)_n$ is obtained.

Metatellurates may be prepared by oxidizing tellurites; e.g. fusion of K_2TeO_3 with nitre or passing chlorine through its aqueous solution. K_2TeO_4 forms the pentahydrate K_2TeO_4, $5H_2O$. Barium tellurate is fairly soluble in water.

Other Oxo-acids of Sulphur

Dithionous Acid, $H_2S_2O_4$ is not known to exist under any condition but salts containing the $S_2O_4^{=}$ ion (dithionite) are stable under anhydrous conditions, though they disproportionate readily in aqueous solution.

$$2S_2O_4^{=} + H_2O \longrightarrow S_2O_3^{=} + 2HSO_3^-.$$

The process is slow at pH ≥ 7, but extremely rapid in acid solution.

Dithionites are prepared by reduction of aqueous sulfite solutions containing an excess of SO_2 by zinc dust, sodium-amalgam or electrolytically. Reduction of SO_3 by formate in aqueous methanol also produces $S_2O_4^{=}$.

Sodium dithionite may be prepared by reducing a cold solution of $NaHSO_3$ containing excess SO_2 with zinc dust.

$$2NaHSO_3 + SO_2 + Zn = Na_2S_2O_4 + ZnSO_3 + H_2O.$$

$ZnSO_3$ is precipitated by milk of lime [as $Zn(OH)_2$] and the filtrate is saturated with NaCl when $Na_2S_2O_4.2H_2O$ crystallizes out. These are washed with acetone and dried over conc: H_2SO_4 in a desiccator to obtain anhydrous $Na_2S_2O_4$ which is fairly stable in air.

Technically, SO_2 is passed into a cold suspension of zinc dust in water to form ZnS_2O_4; this gives $Na_2S_2O_4$ by double decomposition with soda ash :

$$Zn + 2SO_2 = ZnS_2O_4; \quad ZnS_2O_4 + Na_2CO_3 = Na_2S_2O_4 + ZnCO_3.$$

On saturation with common salt, the dihydrate separates as fine needle shaped crystals. The suspension is now rapidly heated to 60°C when anhydrous $Na_2S_2O_4$ separates. These are filtered, washed with alcohol and dried. The process is carried out in absence of air/oxygen.

$NaHSO_3$ may also be reduced by $NaBH_4$.

Sodium dithionite is a white crystalline solid. The anhydrous compound is fairly stable in air but the hydrate is rapidly oxidized. $Na_2S_2O_4$ also decomposes on heating - rapidly above 150°C.

$$2Na_2S_2O_4 \longrightarrow Na_2S_2O_3 + Na_2SO_3 + SO_2$$

The aqueous solution gives esr signals corresponding to the $SO_2^{-\cdot}$ ion radical :

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{-\cdot}$$

Dithionites are powerful reducing agents :

$$2SO_3^{2-} + 2H_2O + 2e = S_2O_4^{2-} + 4OH^- \quad E^\circ = -1.12 \text{ V}.$$

They reduce solutions containing Cu(II), Ag(I), Hg(II), Pb(II) etc. heavy metal ions to the metals. Cr(VI) is reduced to Cr(III), I_2 to I^- and $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$.

$$S_2O_4^{2-} + 2Ag^+ + 2NH_3 + H_2O \longrightarrow S_2O_5^{2-} + 2Ag + 2NH_4^+ \ (\textit{ammoniacal } AgNO_3)$$

$$S_2O_4^{2-} + 3I_2 + 4H_2O \longrightarrow 2SO_4^{2-} + 6I^- + 8H^+ \ (\textit{acetic acid}).$$

Vat dyes : Sodium dithionite is extensively used as a powerful reducing and bleaching agent in dyeing. Some dyes like indigo are insoluble in water but when their pastes are agitated with alkaline sodium dithionite in large vats, the indigo is reduced to a colourless soluble form. The fabric is soaked in the solution and then exposed to air when the original blue dye is formed on the cloth. Such dyes are called "vat dyes".

Rongalite is a relatively more stable product used in this process. It is an adduct of formaldehyde with sodium sulphoxylate, Na_2SO_2 and is prepared by reducing formaldehyde-bisulphite adduct with zinc/acetic acid.

Sodium dithionite also reacts with formaldehyde to give rongalite :

$$[Na_2S_2O_4 + H_2O = NaHSO_2 + NaHSO_3]$$

$$Na_2S_2O_4 + 2HCHO + H_2O = CH_2(OH)SO_3Na + CH_2(OH)SO_2Na \text{ (rongalite)}$$

Q. 23.5 *A solution of sodium dithionite consumes 3 moles of I_2 per mole. When the solution is first treated with formaldehyde and then titrated, only two moles of I_2 are required per mole. Comment.*

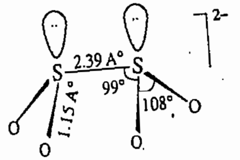
Hint : 1st Case : $S_2O_4^{=} + 3I_2 + 4H_2O = 2SO_4^{=} + 8H^+ + 6I^-$

2nd Case : Dithionite reacts with formaldehyde to give rongalite and a bisulphite-adduct (see above). *Only rongalite* now reacts with I_2.

$$CH_2(OH)SO_2Na + 2I_2 + 2H_2O = HCHO + NaHSO_4 + 4HI.$$

Solutions of sodium dithionite are widely used in removing O_2 from gases - often catalyzed by 2-anthraquinonesulfonate (*Fieser's solution*).

The structure of the dithionite ion (23-XVIII) has a rather long S—S bond and an eclipsed configuration



23-XVIII

The bonding is formally consistent with sp^3 hybridization at both the S-atoms but the long S-S distance is believed to be due to repulsion between lone pairs of electrons of S-atoms resulting from *dp* hybridized bonding.

Sulphoxylic acid H_2SO_2 is not known but derivatives corresponding to HS(O)OH and $S(OH)_2$ are known :

$$\underset{\underset{O}{\|}}{H.S}.OH \longrightarrow \underset{\underset{O}{\|}}{H.S}.ONa \quad \text{(known as formaldehyde adduct)}$$

$$S(OH)_2 \longrightarrow S(OC_2H_5)_2 \quad \text{diethyl sulphoxylate}$$

Cobalt sulphoxylate is obtained by the action of ammonia on cobalt dithionite :

$$Co^{2+} \xrightarrow{S_2O_4^{2-}} CoS_2O_4 \xrightarrow{NH_3(aq)} CoSO_2 + (NH_4)_2SO_3$$

Dithionic acid $H_2S_2O_6$ also cannot be obtained pure. A concentrated aqueous solution may be prepared by double decomposition of the barium salt with dilute H_2SO_4.

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + H_2S_2O_6.$$

The filtrate may be concentrated on a water bath and then in vacuum over conc. H_2SO_4. Above a specific gravity ~ 1.34, it decomposes rapidly to H_2SO_4 and SO_2 :

$$H_2S_2O_6 = H_2SO_4 + SO_2$$

Barium dithionate is prepared via the manganous salt. SO_2 is slowly passed into a suspension of powdered MnO_2 in ice-cold water :

$$2MnO_2 + 3SO_2 = MnSO_4 + MnS_2O_6.$$

[**Sec. 23.3.4** *Polythionic acids*]

Addition of $Ba(OH)_2$ solution (baryta) precipitates $Mn(OH)_2$ and $BaSO_4$. Excess baryta may be removed by passing CO_2. The filtrate is evaporated to obtain colourless crystals of BaS_2O_6, $2H_2O$. The oxidation of SO_2 may also be done with hydrated ferric oxide or electrolytically.

$H_2S_2O_6$ is a moderately stable strong acid stable in dilute solutions.

Dithionates form water soluble crystals which decompose on heating; the solutions may be boiled without decomposition :

$$K_2S_2O_6 = K_2SO_4 + SO_2 \quad (> 258°C)$$

The ion is relatively stable towards oxidation (probably kinetically slow). Only strong oxidizing agents like halogens, dichromate and permanganate oxidize it to sulphate. Strong reducing agents like sodium-amalgam reduce dithionate to dithionite and sulphite.

Diamagnetism and conductivity study of the sodium salt indicate the dimeric formula of the acid $H_2S_2O_6$. The dithionate ion has two approximately tetrahedral SO_3 units linked by an S—S bond :

$$S—S = 2.15\ A°,\ S–O = 1.43\ A°,\ \angle SSO = 103°.$$

The structure has been confirmed by X-ray studies.

Q. 23.6. *Dithionic acid is not considered a member of the polythionic acid group having the general formula $H_2S_nO_6$. Comment.*

Hint : Structurally, the polythionic acids have anions of the type $[O_3S - S_n - SO_3]^{=}$, with at least one S-atom ($n = 1$) which is linked only to other S-atoms. In the dithionate ion $[O_3S - SO_3]^{=}$, there is no such S-atom.

Chemically, (i) the polythionates are decomposed by alkali sulphides and sulphites (see later) but dithionates are not. The polythionates are also relatively easily oxidized in solution.

Polythionic acids $H_2S_nO_6$

The free acids are unstable. Polythionate ions, $S_nO_6^{2-}$ may be separated chromatographically upto $n = 22$ or higher. The lower members ($n = 3 - 6$) were studied earlier, mainly in a solution obtained by passing H_2S into aqueous SO_2 (*Wackenroder's solution*).

The polythionic acids may be looked upon as polysulphane disulphonic acids, $HO_3S.S_n.SO_3H$. Thus $S_4O_6^{2-}$ would be disulphane disulphonate though it is commonly called tetrathionate. The anions of the acid salts $HS_nO_6^-$ are also unstable.

Polythionates are best prepared by selective reactions e.g.,

Trithionate : $2S_2O_3^{2-} + 4H_2O_2 \longrightarrow S_3O_6^{2-} + SO_4^{2-} + 4H_2O.$

[Cold saturated solution of sodium thiosulphate is used].

Tetrathionate : $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-.$

[This reaction is widely used in volumetric estimations involving iodine.]

Also, $2S_2O_3^{2-} + 2Fe^{3+} = S_4O_6^{2-} + 2Fe^{2+}$

[Oxidation may also be carried out by Cu(II) or electrolytically.]

Higher polythionates may be prepared by reactions of the type

$$Na_2S_2O_3 + S_7Cl_2 \longrightarrow Na_2S_xO_6 + 2NaCl \ (x = 4 - 18)$$

$$K_2S_2O_3 + S_2Cl_2 \xrightarrow{\text{Conc. HCl}} K_2S_yO_6 + 2KCl \ (y = 3 - 22).$$

The salts may be separated by crystallization and by chromatography. The free acids are generated by double decomposition of the potassium salts with perchloric or tartaric acids (or of the barium salt with dilute H_2SO_4). The tetra and pentathionic acids may be concentrated to some extent. The acids decompose by adding or leaving S-atoms and ultimately change to H_2SO_4, SO_2 and S :

$$H_2S_4O_6 + S = H_2S_5O_6 ; H_2S_6O_6 = H_2S_5O_6 + S$$

$$H_2S_nO_6 = H_2SO_4 + SO_2 + (n-2) S.$$

Most polythionates, except those of Ag(I) and Hg(II), are soluble in water. The alkali metal salts are fairly stable but those of the heavier metals are less stable. Polythionates decompose on heating to sulphate, SO_2 and S.

$$K_2S_nO_6 = K_2SO_4 + SO_2 + (n-2) S.$$

Polythionates react rapidly with alkali cyanides, hydroxides, sulphides and sulphites :

$$S_3O_6^= + 3CN^- + H_2O = SO_4^= + SO_3^= + CNS^- + 2HCN$$

$$S_4O_6^= + 3CN^- + H_2O = SO_4^= + S_2O_3^= + CNS^- + 2HCN$$

$$2\,S_3O_6^= + 6OH^- = S_2O_3^= + 4SO_3^= + 3H_2O$$

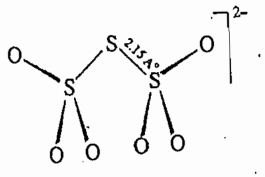
$$2S_4O_6^= + 6OH^- = 3S_2O_3^= + 2SO_3^= + 3H_2O$$

$$S_4O_6^= + S^= = 2S_2O_3^= + S; S_5O_6^= + S^= = 2S_2O_3^= + 2S$$

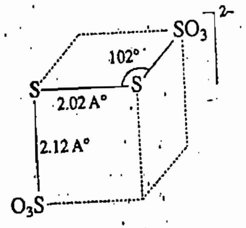
$$S_4O_6^= + SO_3^= = S_3O_6^= + S_2O_3^=$$

$$S_4O_6^= + SO_3^= = S_4O_6^= + S_2O_3^=$$

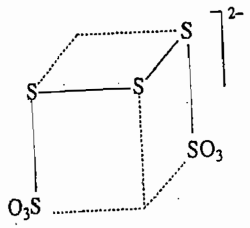
The structures of some polythionates are shown below :



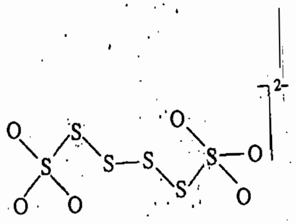
(a) trithionate



(b) tetrathionate



(c) pentathionate (cis form)



(d) hexathionate (cis-cis)

Thiosulphuric acid, $H_2S_2O_3$

The formula of thiosulphuric acid may be derived by replacing an oxygen atom in H_2SO_4 by an atom of sulphur. The free acid is again unstable.

Sodium thiosulphate is formed by boiling powdered sulphur with sodium sulphite solution. The solution is filtered, cooled and evaporated to obtain colourless crystals of $Na_2S_2O_3 . 5H_2O$ ("hypo"). The crystals are highly soluble in water.

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The sodium sulphite may be formed by starting with sodium carbonate and SO_2 :

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2$$

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2$$

Sodium thiosulphate is formed in many other reactions e.g.

$$Na_2SO_3 + Na_2S + I_2 = Na_2S_2O_3 + 2NaI ; \ 2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S;$$

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2 ; \ 4S + 6NaOH = Na_2S_2O_3 + 2Na_2S + 2H_2O.$$

On adding dilute acid to a solution of sodium thiosulphate, the free thiosulphuric acid immediately decomposes to SO_2 and S and the solution becomes turbid :

$$H_2S_2O_3 = H_2O + SO_2 + S .$$

The anhydrous acid may be prepared at low temperatures :

$$H_2S + SO_3 \longrightarrow H_2S_2O_3 \cdot nEt_2O \ [\text{in } Et_2O \text{ at } -78°C]$$

$$Na_2S_2O_3 + 2HCl \longrightarrow H_2S_2O_3 \cdot 2Et_2O + 2NaCl \quad [\text{in } Et_2O \text{ at } -78°C)$$

$$HSO_3Cl + H_2S \longrightarrow H_2S_2O_3 + HCl \quad [\text{low temp.}]$$

Sodium thiosulphate crystals, m.p. 48°C, lose water at 215°C and decompose above 223°C.

$$2Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$$

Thiosulphates are moderately reducing :

$$S_4O_6^= + 2e \rightleftharpoons 2S_2O_3^= ; \quad E° = 0.17 \text{ V}$$

Sodium thiosulfate is used as a secondary standard reducing agent in volumetric estimation. Its aqueous solution slowly turns turbid owing to slow decomposition by carbondioxide present in ordinary distilled water

$$S_2O_3^{2-} + H^+ = HSO_3^- + S.$$

Bacteria (e.g. ***thiobacillus thioparus***) and light facilitate decomposition. A few drops of chloroform or a little sodium carbonate (< 0.1 g L^{-1}) improve the keeping quality.

I_2 and very dilute bromine solution oxidize thiosulfate to tetrathionate in neutral or faintly acid solution :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \quad (\text{similarly with } Br_2).$$

But iodine in alkali (OI^- ion) and other strong oxidizing agents give *sulphates* :

$$Na_2S_2O_3 + 4\,NaOI + 2\,NaOH = 2\,Na_2SO_4 + 4NaI + H_2O.$$

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + 8HCl + H_2SO_4 \quad (\text{similarly with } Br_2)$$

The reaction with bromine-water is interesting. In concentrated solutions, 4 mol Br_2 reacts with 1 mol thiosulphate; the thio acts as an 8-electron reducing agent and gets oxidized to SO_4^{2-}. But in very dilute solutions (say 0.01 N), 1 mol thio will reduce $\frac{1}{2}$ mol Br_2, when $S_2O_3^=$ acts as an 1-electron reducing agent and gets oxidized to $S_4O_6^{2-}$.

Silver nitrate first gives a white precipitate of silver thiosulphate which undergoes rapid hydrolysis, the colour changing to yellow, brown and finally black.

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

When an excess of thiosulphate is added, the silver thiosulphate dissolves to form a colourless thiosulphato complex :

$$Ag_2S_2O_3 + 3Na_2S_2O_3 = 2Na_3\,[Ag\,(S_2O_3)_2].$$

Similar soluble complexes are formed with many metal ions. Sulphides of Ag, Pb(II), Hg(II) etc. are precipitated on heating the solution. Cu(II) is first reduced to Cu(I), which precipitates black Cu_2S on boiling :

$$2CuSO_4 + 2\,Na_2S_2O_3 = Cu_2SO_4 + Na_2SO_4 + Na_2S_4O_6.$$

$$Cu_2SO_4 + Na_2S_2O_3 = Cu_2S_2O_3 + Na_2SO_4$$

$$3Cu_2S_2O_3 + 2\,Na_2S_2O_3 = Na_4\,[Cu_6\,(S_2O_3)_5]$$

Ferric chloride solution first gives an intense purple thiosulphate complex but the colour readily disappears due to reduction to Fe(II).

$$2Na_2S_2O_3 + FeCl_3 = Na[Fe(S_2O_3)_2] + 3NaCl$$

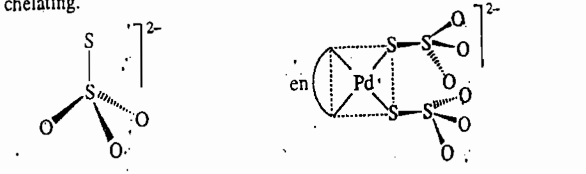
$$2Na_2S_2O_3 + 2FeCl_3 = Na_2S_4O_6 + 2FeCl_2 + 2NaCl$$

Silver halides also dissolve in sodium thiosulphate solution :

$$AgBr + 3Na_2S_2O_3 \longrightarrow Na_5\,[Ag\,(S_2O_3)_3] + NaBr$$

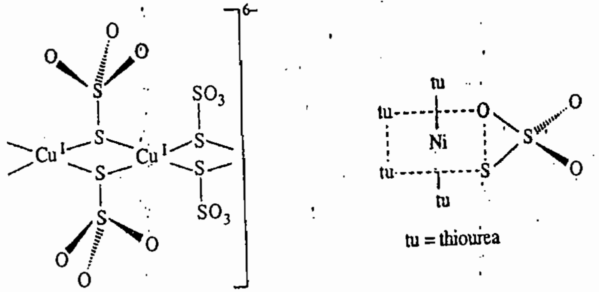
The reaction is used in photography to dissolve out excess AgBr (unphotolyzed) from exposed photofilms — hence the use of hypo as a fixer.

The thiosulphate ion can act as a ligand in various modes - monodentate, bidentate, bridging and chelating.



(a) thiosulphate ion.

(b) S_2O_3 as monodentate ligand (η^1-S).



tu = thiourea

(c) bridging (monohapto : μ, η^1-S)

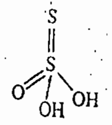
(d) chelating (η^2-S, O).

23-XX

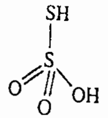
The thiosulphate ion is tetrahedral (23-XX), consistent with sp^3 hybridization of the central S-atom. The difference in the environment of two S-atoms is shown by radioactive tracer studies using ^{35}S. (S^*; see ch. 14) :

$$SO_3^{=} + S^* \rightleftharpoons S^*\,SO_3^{=} \rightleftharpoons S^* + SO_3^{=}$$

The entire radioactivity is found associated with the sulphur precipitated.



23-XXI (a)



23-XXI (b)

Thiosulphuric acid may have two tautomeric forms as shown in 23-XXI (a) and (b). Structure (a) is supported by the ready decomposition of "thiosulphuric acid" in solution to sulphurous acid (sulphite ion) and sulphur.

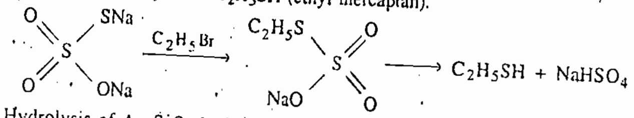
Structure (b) is supported by

(i) formation of sodium thiosulphate from sodium sulphite and sodium sulphide by the action of I_2 (**Spring's. reaction**)

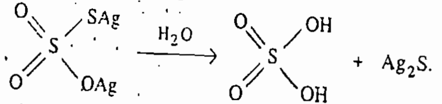
$$Na_2SO_3 + Na_2S + I_2 = 2NaI + Na_2S_2O_3$$

The thiosulphate may be reduced to Na_2SO_3 by sodium amalgam.

(ii) Ethyl bromide acts on sodium thiosulphate to give sodium ethyl sulphonate. This compound may be hydrolyzed to C_2H_5SH (ethyl mercaptan).



(iii) Hydrolysis of $Ag_2S_2O_3$ by boiling water.

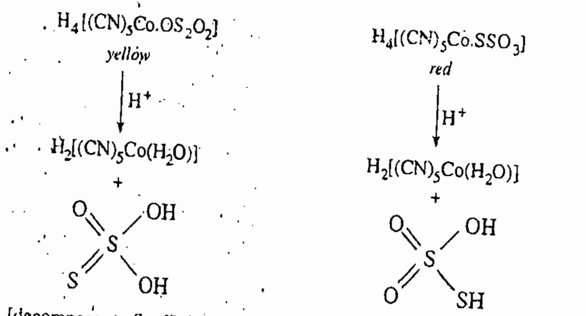


However, thiosulphuric acid ordinarily does not decompose to give H_2S, rather it forms H_2SO_3 and S, supporting structure (a).

Complex compounds corresponding to both forms were subsequently prepared and characterized (P. Ray).

(i) yellow salts of the anion $[Co(CN)_5S_2O_3]^{4-}$ produce on hydrolysis thiosulphuric acid which decomposes to S and H_2SO_3.

(ii) red salts of the anion $[Co(CN)_5S_2O_3]^{4-}$ give thiosulphuric acid which gives H_2S and H_2SO_4.



[decomposes to S + H_2SO_3]

[decomposes to $H_2S + H_2SO_4$]

Sodium thiosulphate is largely used in photography and as an antichlor (to destroy excess chlorine from bleached fibres). It is also used in the extraction of gold and silver.

Peroxo acids of sulphur : H_2SO_5 and $H_2S_2O_8$

Peroxomonosulphuric acid : Replacement of one —OH group in H_2SO_4 by —O—O—H group results in the formula of peroxomonosulphuric acid H_2SO_5 i.e., $HO.SO_2.OOH$ [Caro's acid; 23-XXII (a)].

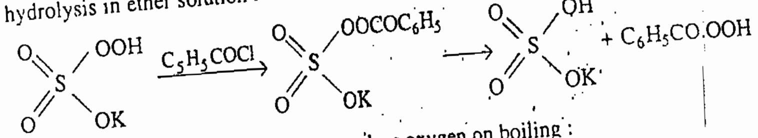
H_2SO_5 can be prepared by the action of concentrated H_2O_2 on sulphuric acid or chlorosulphuric acid :

$$H_2O_2 + H_2SO_4 \longrightarrow HO.SO_2.OOH + H_2O$$

$$H_2O_2 + HO.SO_2.Cl \longrightarrow HO.SO_2.OOH + HCl$$

Salts $KHSO_5$ and $K_5(HSO_5)_2(HSO_4)(SO_4)$ have also been prepared.

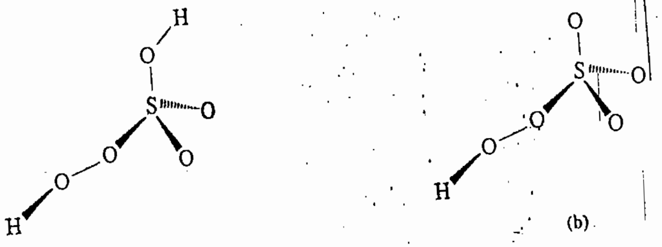
H_2SO_5 is a colourless, crystalline solid, m.p. 45°C. The acid has specific oxidizing properties, e.g., it oxidizes aniline to nitrosobenzene and rapidly liberates iodine from KI solution (difference from $H_2S_2O_8$). The hydroperoxide group (OOH) is too weakly acidic to form salts. The benzoyl derivative gives *benzoyl peroxide* on acid hydrolysis in ether solution :



An aqueous solution of $KHSO_5$ evolves oxygen on boiling :

$$2KHSO_5 = 2KHSO_4 + O_2$$

The HSO_5^- ion (23-XXII b) has three shorter S—O distances = 1.44 A°; the S—O distance to –OOH is longer, 1.63 A°.



23-XXII

Peroxodisulphuric acid (Marshall's acid) **:** It is prepared by anodic oxidation in the electrolysis of ice-cold 50% sulphuric acid with bright platinum electrodes and a high current density (protected cathode).

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Anode : $2HSO_4^- - 2e = H_2S_2O_8$ *Cathode* : $2H^+ + 2e = H_2$

[Sec.23.3.4 *Peroxoacids of sulfur*]

Electolysis of cold concentrated aqeuous solutions of $KHSO_4$ or NH_4HSO_4 produces $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ respectively. The perdisulphuric acid formed at the anode reacts with excess salt when the less soluble perdisulphate crystallizes out :

$$H_2S_2O_8 + 2KHSO_4 = K_2S_2O_8 + 2H_2SO_4.$$

$H_2S_2O_8$ is a colourless solid, m.p. 65°. The acid and its salts are powerful oxidizing agents :

$$S_2O_8^{2-} + 2e = 2SO_4^{2-} \qquad E^\circ = 2.01 \text{ V}$$

However, uncatalyzed reactions are often slow, e.g. the liberation of I_2 from KI. Ag^+ ion is a commonly used catalyst in such oxidation reactions, which probably operates via a Ag(II) intermediate. Thus, Mn(II) and Cr(III) are quantitatively oxidized to MnO_4^- and $Cr_2O_7^=$ respectively under boiling conditions in presence of $AgNO_3$:

$$2Mn^{2+} + 5S_2O_8^= + 8H_2O = 2MnO_4^- + 16H^+ + 10SO_4^=.$$

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O = Cr_2O_7^{2-} + 6HSO_4^- + 8H^+$$

The excess persulfate is destroyed by boiling the solution. Thus the reactions may be used to estimate Mn(II) or Cr(III).

$AgNO_3$ is oxidized to black AgO by $K_2S_2O_8$:

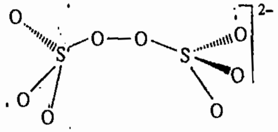
$$K_2S_2O_8 + 2AgNO_3 + 2H_2O = 2AgO + 2KHSO_4 + 2HNO_3.$$

In many reactions, there is evidence for the formation of the radical ion SO_4^- by one electron reduction :

$$S_2O_8^= + e = SO_4^= + SO_4^{-\cdot}$$

Cu, Zn etc. few metals dissolve in persulphate solution :

$$Cu + K_2S_2O_8 = K_2SO_4 + CuSO_4.$$



23-XXIII

The structure of the $S_2O_8^{2-}$ ion (23-XXIII) has been confirmed by X-ray studies of caesium and ammonium salts. The O—O and S—O distances are 1.31 and 1.50 A° respectively.

Peroxodisulphates are widely used as oxidizing and bleaching agents. They are also used to initiate polymerization of vinyl chloride to PVC and styrenebutadiene copolymer rubber.

Summary of the aqueous chemistry of some oxoanions of sulphur

With the exception of Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} and Hg^{2+}, most common metal ions form soluble sulphates (and selenates). The sulphate (and also the selenate) ion is a very stable one, both kinetically and thermodynamically. As such, it has no significant aqueous chemistry except the formation of insoluble precipitates with the cations listed above. Selenates are similar, but they are more oxidizing — e.g. liberating chlorine from HCl on boiling.

The response of sulphite (SO_3^{2-}), thiosulphate ($S_2O_3^{2-}$) and peroxodisulphate ($S_2O_8^{2-}$) ions to some common reagents are summarized in the next page.

TABLE 23.7

Some Reactions of SO_3^{2-}, $S_2O_3^{2-}$ and $S_2O_8^{2-}$

	SO_3^{2-}	$S_2O_3^{2-}$	$S_2O_8^{2-}$
1. *Boiling*	Oxidation (by air) to SO_4^{2-}	No change	Dec. to $SO_4^{2-} + O_2$ $(+ O_3)$
2. *Dilute HCl*	SO_2	S precipitated	$SO_3^{2-} + Cl_2$
3. *Dilute Alkali*	No action	No action	No action
4. *$BaCl_2$*	$BaSO_3$ (white) precipitated.	BaS_2O_3 (white) precipitated.	No reaction. $BaSO_4$ on boiling.
5. *KI*	No reaction	No reaction	I_2
6. *I_2 in KI*	Reduced to I^- (SO_4 formed)	Reduced to I^- ($S_4O_6^{=}$ formed)	No decolorization
7. *$KMnO_4$*	SO_4^{2-} (decolorization)	SO_4^{2-} (decolorization)	No reaction
8. *Cr^{3+} ion*	No reaction	No reaction	Slow oxidation to Cr_2O_7 (rapid with Ag^+ catalyst).
9. *Lead acetate*	$PbSO_3$ (white) precipitated, soluble in dil HNO_3. White $PbSO_4$ on boiling.	PbS_2O_3 (white) precipitated, soluble in excess. Black PbS on boiling.	Precipitation of $PbSO_4$ only on boiling.

Halogen substituted oxo acids

Fluorosulfurous acid HSO_2F is not known, but KSO_2F is used as a fluorinating agent. The salt is obtained by reacting SO_2 with KF :

$$KF + SO_2 \rightleftharpoons KSO_2F.$$

The salt dissociates appreciably at room temperature. It is a mild fluorinating agent :

$$(PNCl_2)_3 + 6KSO_2F = (PNF_2)_3 + 6KCl + 6SO_2$$

Fluorosulphuric acid FSO_3H is obtained by the reaction

$$SO_3 + HF = FSO_3H$$

It also results by the action of oleum on KHF_2 or CaF_2 at 250°C.

Reaction of KF gives the salt KSO_3F.

FSO_3H is a colourless mobile liquid which is one of the strongest pure liquid acids. The self-ionization

$$2\,FSO_3H \rightleftharpoons FSO_3H_2^+ + FSO_3^-.$$

is much lower than for H_2SO_4 but increases dramatically in presence of SbF_5 forming a superacid system (section 10.2.7). The acid is slowly and incompletely hydrolyzed by water to HF and H_2SO_4 :

$$F.SO_2.OH + H_2O = HF + HO.SO_2.OH$$

Fluorosulphuric acid is a convenient fluorinating agent even at room temperature—converting, for example, K_2CrO_4 to CrO_2F_2 and $KClO_4$ to ClO_3F.

Chlorosulphuric acid $ClSO_3H$ is formed by treating SO_3 with HCl or by the action of PCl_5 on concentrated H_2SO_4. It is a colourless fuming liquid, b.p. 151°C. It gets explosively hydrolyzed by water :

$$Cl.SO_2.OH + H_2O = HO.SO_2.OH + HCl$$

[Sec. 23.3.4

The acid is an important sulphonating agent in organic chemistry

$$C_6H_6 + ClSO_3H = C_6H_5SO_3H + HCl.$$

Bromosulphuric acid, $BrSO_3H$ (HBr + SO_3 in liquid SO_2 at −35°C) decomposes at 8°C (its melting point) into Br_2, SO_2, and H_2SO_4.

Amides of sulphuric acid]

Amides of sulphuric acid

Sulphamic acid

Replacement of an OH group by an NH_2 group in H_2SO_4 gives rise to sulphamic acid (amidosulphuric acid) $H_2N.SO_2.OH$. When both OH groups are substituted, we get sulphamide. Sulphamic acid may be prepared through reactions like

(i) $F.SO_2.OH + NH_3\,(aq) = H_2N.SO_2.OH + HF$

(ii) $NH_2OH + SO_2 = H_2NSO_2.OH + H_2SO_4$

(iii) $O = C(NH_2)_2 + 2H_2SO_4 = CO_2 + H_2NSO_3H + NH_4HSO_4$

Anhydrous H_2SO_4 or dilute oleum is used. The method is used in large scale manufacture.

Sulphamic acid is insoluble in sulphuric acid and separates as a white mass on cooling; it may be crystallized from hot water.

It is a white crystalline, non-hygroscopic solid, m.p. 205°C, but it begins to decompose near and above 205°C. The acid is moderately soluble in water and alcohol.

Sulphamic acid is a strong monobasic acid, $K_1 = 1 \times 10^{-1}$ at 298 K. It is thus suitable as a standard for acidimetry. The dilute aqueous solution is quite stable at room temperature though at higher temperature hydrolysis to NH_4HSO_4 becomes rapid.

It is oxidized to N_2 by several oxidizing agents like Cl_2, Br_2, HNO_2 etc.

$$KClO_3 + 2NH_2SO_3H = N_2 + KCl + 2H_2SO_4 + H_2O$$

$$HNO_2 + NH_2SO_3H = N_2 + H_2SO_4 + H_2O.$$

Concentrated HNO_3 gives N_2O. The reaction with HNO_2 (or $NaNO_2$ + acid) is quantitative and is used in volumetric analysis to remove HNO_2.

Hypochlorous acid reacts with sulphamic acid to give N-chlorosulphamic acid. This reaction is used to stabilize chlorinated water :

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

$$HOCl + NH_2SO_3H \rightleftharpoons HN(Cl)SO_3H + H_2O$$

Sulphamic acid is strongly H-bonded in solid, the zwitterion unit $^+H_3NSO_3^-$ being probably present.

In liquid NH_3, the acid is dibasic. Sodium forms $NaNH.SO_3Na$ from such solution.

Sulphamide, $SO_2(NH_2)_2$ is prepared by the action of NH_3 (*g*) on SO_2Cl_2 in benzene or chloroform.

$$SO_2Cl_2 + 4NH_3 = SO_2(NH_2)_2 + 2\,NH_4Cl$$

It is a colourless crystalline solid, m.p. 93° which dissolves in water to give a neutral solution. On boiling, decomposition to ammonia and H_2SO_4 takes place. It acts as a dibasic acid in liquid ammonia.

Sulphamic acid is used in industry in a large scale in scale removers, detergents, stabilizers for chlorine waters and several other uses. The salts are used in flame proofing fabrics, as a selective weed-killer and in dye industry to remove excess nitrous acid after diazotization.

Q. 23.7 *The action of conc. H_2SO_4 on urea produces a white crystalline solid X, H_3NO_3S. It is a monobasic acid. On treatment with $NaNO_2$ + dil HCl (0°C), X liberates one mole of N_2 per mole of X; on addition of aqueous $BaCl_2$ to the resulting solution, one mole of $BaSO_4$ is obtained per mole of X. Deduce the structure of X.*

Hint : See reactions of sulphamic acid.

23.3.5 Halides, oxo-halides, complex halides

The main chalcogen halides are listed in Table 23.8. Owing to higher electronegativity of oxygen, its binary compounds with chlorine, bromine and iodine are more appreciately-classed as oxides rather than halides (Ch. 24).

TABLE 23.8

Halides of chalcogens

	Fluoride	Chloride	Bromide	Iodide
Oxygen	O_2F_2			
	O_4F_2	Oxygen compounds of these elements are discussed under oxides of halogens (Ch. 24).		
	OF_2			
Sulphur	FSSF	S_2Cl_2	S_2Br_2	S_2I_2
	SSF_2			—
	SF_2	S_nCl_2 $(n = 3 – 8)$	S_nBr_2 $(n = 3 – 8)$	—
	SF_4			—
	SF_6	SCl_2	—	—
	S_2F_{10}	SCl_4	—	
Selenium		Se_2Cl_2	Se_2Br_2	
	SeF_4	$(SeCl_4)_4$	$(SeBr_4)_4$	
	SeF_6			
Tellurium		$TeCl_2$	$TeBr_2$	
	$(TeF_4)_x$	$(TeCl_4)_4$	$(TeBr_4)_4$	$(TeI_4)_4$
	TeF_6			
	Te_2F_{10}			

The fluorides of oxygen and sulphur are rather different from the other halides and are discussed separately. A remarkable difference is observed among the halides in this group — the lowest oxidation state (+ 2) becomes gradually *less* stable with increase in atomic number, i.e., from S to Se to Te. Thus the lowest fluorides of Se and Te are SeF_4 and TeF_4; $TeCl_4$ is the only tetrachloride which is stable in the gaseous state. Similarly, the iodides become stable only at Te (and Po). Sulphur iodides exist only at very low temperatures.

The halides are essentially covalent. Some of the tetrahalides are associated in the solid state : TeF_4 forms polymeric chains; tetrameric units occur in the tetrachlorides and tetrabromides of Se and Te and also in TeI_4.

Fluorides of Oxygen

Oxygen fluorides]

Oxygen difluoride, OF_2, is formed when fluorine is passed rapidly through 2% sodium hydroxide solution.

$$2F_2 + 2NaOH = OF_2 + 2NaF + H_2O$$

It is also formed by electrolysis of KHF_2 in 80% HF - H_2O.

It is a pale yellow poisonous gas (b.p. –145°C) which does not react with H_2, CH_4 or CO on mixing but explodes on sparking. Cl_2, Br_2 or I_2 react explosively with OF_2 even at room temperature. Thermally the gas is stable to 200°C when pure but above this decomposition occurs to $F_2 + O_2$. It reacts slowly with water, explosively with steam. Bases cause ready hydrolysis :

$$OF_2 + H_2O = O_2 + 2HF$$

$$OF_2 + 2OH^- = O_2 + 2F^- + H_2O$$

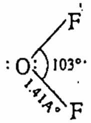
Though OF_2 is the formal anhydride of hypofluorous acid HOF (c.f. Cl_2O - HOCl), it does not produce HOF with water (or hypofluorites with base). HOF has been prepared by other routes (Chapter 24).

OF_2 is a strong fluorinating and oxidizing agent e.g., it liberates other halogens from halides :

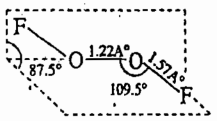
$$OF_2 + 4HX = 2X_2 + 2HF + H_2O.$$

Many metals are oxidized by OF_2 to oxides and fluorides, as also are several nonmetals like P (giving $PF_5 + POF_3$) and S (giving $SO_2 + SF_4$). Even xenon gives a mixture of fluoride and oxofluorides under electric discharge.

The OF_2 molecule is angular (23-XXIV). ∠FOF is slightly smaller than that in H_2O (104.5°); the bond pairs, at a larger separation, exert less repulsion (Chapter 7).



23-XXIV



23-XXV

O—F = 1.57 A° (in OF_2 : O–F = 1.41 A°)
O—O = 1.22 A° (in H_2O_2 : O–O = 1.48 A°)

Dioxygen difluoride, O_2F_2 is formed by subjecting liquid $O_2 – F_2$ mixture to high voltage electric discharge at low temperature and pressure (–196°C, 10 – 20 mm Hg). The yellow-orange solid (m.p. –154°C) decomposes rapidly above –100°C. It is a strong oxidizing and fluorinating agent even at such low temperatures. It oxidizes ClF to ClF_3, BrF_3 to BrF_5 or even H_2S to SF_6 :

$$H_2S + 4O_2F_2 = SF_6 + 2HF + 4O_2.$$

Dioxygenyl salts are formed by transferring a F^- ion to a suitable acceptor.

$$BF_3 + O_2F_2 \longrightarrow O_2^+BF_4^- + {}^1/_2\,F_2$$

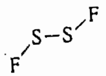
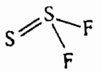
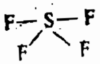
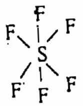
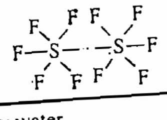
The structure of O_2F_2 is comparable to that of H_2O_2. The O—O distance is remarkably smaller and stronger (dissociation energy = 435 kJ mol^{-1}) than in H_2O_2 and close to that in O_2 gas. Conversely, the O—F distance is somewhat longer compared to OF_2 (1.41 A°). The bonding has been rationalized by molecular orbital theory. Roughly, one might also consider interaction between the two singly occupied π^* m.o. of O_2 with singly occupied σ a.o. on two F-atoms resulting in two 3c—2e O—O—F bonds in approximately perpendicular directions. The O—O bond thus retains nearly the same double bond character as in O_2, while the O—F bonds become weaker than normal 2-electron bonds. Also, the high electronegativity of F allows little electron density to be transferred to the π* m.o. of O_2, hence the O—O bond is not substantially weakened. Repulsion between lone pairs of electrons naturally contributes to the weakness of the O—F bond.

Other reported oxygen fluorides are highly unstable.

Fluorides of Sulphur

The fluorides of sulphur are summarized below; individual discussion follows:

TABLE 23.9
Fluorides of sulphur

	compound		Prep. Principle	structure	comment
(i)	**FSSF**		S + AgF		Readily isomerizes to SSF_2
	m.p.	−133° C	(125°C; perfectly dry)		
	b.p.	15° C			
(ii)	$S = SF_2$		From (i) or $S_2Cl_2 + KF/SO_2$		Rapidly disproportionates $(S + SF_4)$
	m.p.	**−165° C**			
	b.p.	**−10.6° C**			
(iii)	**SF_4**		**$SCl_2 + NaF$**		**Amphoteric Lewis** acid-base. Highly reactive.
	m.p.	**−121° C**	**(CH_3CN/75°C)**		
	b.p.	−38° C			
(iv)	**SF_6**		$S + 3F_2$		Highly stable and inert.
	m.p.	−50.5° C			
	b.p.	−64 (sub)			
(v)	**S_2F_{10}**		$SClF_5 + H_2$ (hν)		Disproportionates at 150°. Less reactive than SF_4.
	m.p.	−53° C			
	b.p.	+30° C			

Except the last two, all are rapidly hydrolyzed by water.

S_2F_2 represents two compounds — FSSF and SSF_2.

Disulphur difluoride, FSSF is first formed when molten sulphur is fluorinated with silver fluoride. It readily isomerizes to thiothionyl fluoride SSF_2. The latter compound is also obtained by fluorinating S_2Cl_2 with KF – SO_2. It is thermodynamically unstable and disproportionates to S_8 and SF_4 in presence of acid catalysts like HF or BF_3. Both FSSF and SSF_2 are rapidly hydrolyzed to sulphur, HF and polythionic acids

$$S_2F_2 + H_2O \longrightarrow S_8 + HF + H_2S_nO_6 \; (n = 4 - 6)$$

FSSF has a structure resembling H_2O_2. The S – S distance 1.89 A° is shorter than in S_8. SSF_2 is pyramidal, the S – S distance being still shorter, 1.86 A°.

SF_2 Sulphur difluoride is formed in small amount when SCl_2 is fluorinated by KF – SO_2 at 150°. It may be separated from others by fractionation and is known as a dilute gas. It rapidly dimerizes to $FSSF_3$.

SF_4 Sulphur tetrafluoride is obtained by fluorinating SCl_2 with HF-pyridine or with NaF at 75°C in acetonitrile solution

$$3SCl_2 + 4NaF = S_2Cl_2 + SF_4 + 4NaCl$$

[**Sec. 23.3.5**
Sulfur fluorides]

It is a highly reactive gas and gets hydrolyzed rapidly:

$$SF_4 + H_2O \longrightarrow [SOF_2 + 2HF] \longrightarrow SO_2 + HF.$$

It forms stable adducts with both Lewis acids and bases:

Lewis bases: Py.SF_4 (sq. pyramid); SF_5^- (e.g., $CsSF_5$ and Me_4NSF_5).

Lewis acids: $SF_4.BF_3$ $(SF_3^+ BF_4^-)$

SF_4 is a selective fluorinating agent; it converts $\rangle C = O$ to $\rangle CF_2$, P = O to PF_2 groups without disturbing unsaturation or other functional groups, e.g.

$$C_6H_5CHO + SF_4 \longrightarrow C_6H_5CHF_2 + SOF_2$$

A few more reactions of SF_4 are

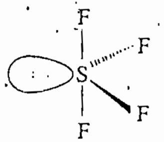
$SF_4 + F_2 = SF_6$; $\quad SF_4 + CsF + Cl_2 = SF_5Cl + CsCl$
$SF_4 + ClF = SF_5Cl$; $\quad 5SF_4 + I_2O_5 = 2IF_5 + 5OSF_2$

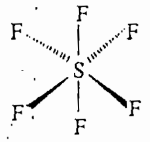
The structure of sulphur tetrafluoride is based on a trigonal bipyramid, one equatorial position occupied by a lone pair of electrons (23-XXVI). As expected, the axial bonds (1.64 A°) are longer than the equatorial bonds (1.54 A°). Repulsion by the lone pair squeezes the equatorial FSF angle to 102° and the axial FSF angle is bent at 173°.

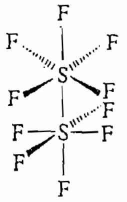
Structure and Bonding

The bonding in SF_4 is formally consistent with sp^3d hybridization of the valence orbitals of sulphur and the VSEPR approach based on 4 bond pairs and 1 lone pair. However, d-orbital participation via sp^2 $(s + p_x + p_y)$ plus pd $(p_z + d_{z^2})$ scheme implies rather high contribution from the d-orbitals. This is unlikely in view of the high energy of the d-orbitals, even after admitting contraction caused by the F-atoms. In fact, recent calculations show that d-orbital participation may be only around 12%.

The alternative bonding scheme (compare PCl_5) describes the equatorial bonds by $sp^2(sp_xp_y)$ hybrid orbitals of sulphur. The p_z orbital, with two electrons and two F-atoms (one electron each) now establish two axial 3-center-4-electron S–F bonds.


SF_4
23-XXVI


SF_6
23-XXVII


S_2F_{10}
23-XXVIII

SF_6 Sulphur hexafluoride is made by burning sulphur in fluorine. A little S_2F_{10} formed breaks to SF_4 and SF_6 at 400° C. SF_4 may be removed by absorption in dilute alkali.

It is a colourless, odourless, nontoxic gas (b.p. 64°C) which is chemically very inert. It does not react with water or even steam at 500°C or molten alkalis or hot concentrated HCl. It can be heated to 500°C without deomposition and is not attacked by most metals and nonmetals like P, As etc. on heating.

SF_6 is attacked by boiling sodium metal giving Na_2S and NaF. Sodium in liq. NH_3 and $LiAlH_4$ (in ether) also reduce it. Sodium in ethyleneglycoldimethylether containing bipheyl reacts with SF_6 *at room temperature* rapidly and quantitatively:

$$SF_6 + 8Na \longrightarrow 6NaF + Na_2S$$

SF_6 undergoes electrophilic attack by Lewis acids. SO_3 gives SO_2F_2 slowly at 250°C. Al_2Cl_6 at 200°C gives AlF_3, Cl_2 and sulphur chlorides. Reactivity of SF_6 increases with increase in temperature and pressure.

The stability and inertness of SF_6 are not thermodynamic as suggested by the negative free energy change for the gas phase reaction :

$$SF_6\,(g) + 3H_2O\,(g) = SO_3\,(g) + 6\,HF\,(g) \qquad \Delta G° = -200\ \text{kJ mol}^{-1}.$$

Also, the average bond energy in SF_6 is slightly less than that in SF_4 (326 kJ mol^{-1}). Hence the lack of reactivity must be kinetic sluggishness. Several factors may be responsible :

(i) High S—F bond strength

(ii) S is coordinately saturated as well as sterically shielded by the F atoms

(iii) The molecule lacks polarity

Structure and Bonding

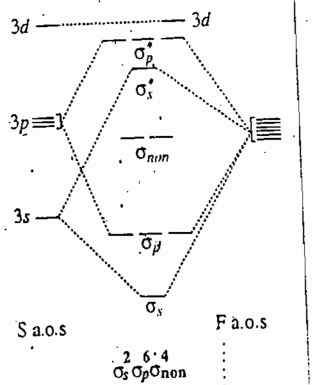
SF_6 has a regular octahedral structure with S—F bond lengths 1.56 A° (23-XXVII). The bonding formally agrees with V.B. description involving sp^3d^2 hybridization of the valence orbitals of sulphur. The electronegative F atoms develop a net positive charge on the S-atom; this contracts the *d*-orbitals, making their energy low and favourable for hybridization. Additional *p*–*d*.π-bonding is possible, since the bond lengths are smaller than expected single bond lengths. Alternatively all the F-atoms may be supposed to involve 3-centre-4electron bonds; the whole molecule has 3 sets of such bonds (each set holding two diagonally opposite F-atoms).

Q. 23.8 *Although S—F ans S—H bonds have similar energies, SH_4 and SH_6 are non-existent. Comment.*

Hint : The high electronegativity of F is primarily responsible for the stability of SF_4 and SF_6. Also, the bond energy of F_2 is less than that for H_2, which favours dissociation of SH_4 and SH_6 into $H_2S + H_2$. In fact, detailed m.o. calculations show that the compounds are capable of existence, but are unstable with respect to such decomposition.

If we consider a simplified m.o. description involving only the m.o.-s arising from the overlap of *s*-and *p*-a.o.-s on S with the σ a.o.-s on the six terminal F atoms, we get a total of 10 m.o.-s : 4 bonding, 4 antibonding and 2 non-bonding. Out of the total 12 valence electrons, 8 electrons occupy the four bonding m.o.-s, while 4 electrons are accommodated in the non-bonding m.o.-s, localized near the F atoms. There are thus effectively 8 electrons in the bonding m.o.-s meeting all 6 bonds, i.e., leading to a σ-bond order of 2/3.

In SH_6, low electronegativity of hydrogen places the non-bonding m.o.-s comparatively higher; the non-bonding electrons are thus considerably destabilized.



Sulphur hexafluoride is extensively used as an insulating gas for high voltage generators and switch gears.

Various substitution products of sulphur hexafluoride are now developing a new area of study. Many of them are made photochemically via SF_5Cl.

$$ClF + SF_4 \longrightarrow SF_5Cl; \quad Cl_2 + CsF + SF_4 \xrightarrow{110°} SF_5Cl + CsCl$$

SF_5Cl is a colourless gas (b.p. −15° C) inert to acids but readily attacked by OH^- and other nucleophiles. It is more reactive than SF_6 and a powerful oxidizing agent consistent with the charge distribution $\overset{\delta-}{F_5S} - \overset{\delta-}{Cl}$:

[Sec. 23.3.5 *Fluorides of Se, Te*]

$$SF_5Cl + C_2H_2 \longrightarrow ClCH = CHSF_5$$

A compound with C=S double bond has been prepared :

$$SF_5Cl + CH_2 = C = O \longrightarrow SF_5CH_2COCl \xrightarrow{H_2O/Ag^+} SF_5CH_2COOAg$$

$$SF_5CH_2COOAg \xrightarrow{Br_2} SF_5CH_2Br \xrightarrow{BuLi} F_4S{=}CH_2$$

S_2F_{10} **Disulphur decafluoride** (b.p. 29°C) is obtained by photolytic reduction of SF_5Cl :

$$2\,SF_5Cl + H_2 \xrightarrow{h\nu} S_2F_{10} + 2\,HCl$$

The compound is extremely poisonous and intermediate in reactivity between SF_4 and SF_6. It is not hydrolyzed by water or dilute acids or alkalis and does not show significant reactivity at ordinary temperature. It oxidizes KI in acetone solution at room temperature. It is a powerful oxidizing and fluorinating agent at high temperature. Itself it disproportionates on heating to 150°C :

$$S_2F_{10} \longrightarrow SF_4 + SF_6$$

Each S atom in S_2F_{10} has an octahedral environment (23-XXVIII)—two SF_6 octahedra share one apex; the SF_5 groups are "staggered". The S—S bond is (2.21 A°) slightly longer than that in elemental sulphur while the S—F bonds are again slightly shorter (by ~ 0.2 A°) than expected for a single bond.

Fluorides of Selenium and Tellurium

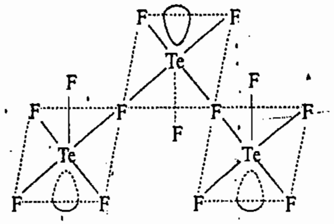
FSeSeF, Se=SeF_2 and SeF_2 have been prepared in traces by trapping at low temperatures but no significant chemistry has yet developed around them. The tetra-and hexa fluorides are well established.

SeF_4 and TeF_4 : These may be prepared by controlled fluorination of the elements with F_2 or F_2/N_2 at 0° or by reactions such as

$$SeO_2 + 2SF_4 = SeF_4 + 2SOF_2 \quad (> 100°)$$

$$TeO_2 + 2SeF_4 = TeF_4 + 2SeOF_2 \quad (80°)$$

SeF_4 is a colourless liquid (b.p. 106° C, m.p. −39°C) resembling SF_4 in many of its properties like ready hydrolysis, fluorinating capacity etc. TeF_4 is a colourless crystalline solid (m.p. 130°C) which decomposes above 190° forming TeF_6. It is much more reactive than SeF_4 — it reacts with SiO_2 and metals like Cu, Ag, Au and Ni on heating. The solid consists of chains of square-pyramidal TeF_5 groups sharing corner F atoms (23-XXIX).



23-XXIX

SeF$_6$ and TeF$_6$ may be prepared by direct fluorination of the elements or by reacting respective dioxides with BrF$_3$. Both the compounds are colourless gases : SeF$_6$ m.p. –35° (2 atm), sublimes at –47°; TeF$_6$ m.p. –38°, sublimes at –39°. SeF$_6$ does not react with water but TeF$_6$ undergoes slow hydrolysis to Te (OH)$_6$ (larger size, ease of valence expansion). TeF$_6$ combines with CsF to form Cs$_2$ [TeF$_8$].

TeF$_5$Cl and TeF$_5$Br are made by subjecting TeCl$_4$ or TeBr$_4$ to F$_2$–N$_2$ at 25°C. Te$_2$F$_{10}$ is also known.

Other halides of S, Se and Te

Steady decrease in bond energies to the halogens makes other halides in this group increasingly unstable. The S-halogen bond energies (kJ mol^{-1}) clearly reveal the trend.

S—F	S—Cl	S—Br	S—I (extrapolated)
327	271	218	~170

Comparison with S—S (225 kJ mol^{-1}) and I-I (150 kJ mol^{-1}) suggests that sulphur iodides are least likely to be formed.

Chlorides of sulphur

The chlorides of sulphur are summarized below :

TABLE 23.10
Chlorides of sulphur

Compound		Prep. note	Comment
S$_2$Cl$_2$		Molten S + Cl$_2$	Golden yellow, foul smelling toxic liquid.
m.p.	~–80°		Rapid hydrolysis.
b.p.	138°		(Structure same as S$_2$F$_2$ (H$_2$O$_2$ - like).
SCl$_2$		S$_2$Cl$_2$ + Cl$_2$	Cherry-red liquid. Foul smelling, toxic, rapid hydrolysis.
m.p.	–78°	(FeCl$_3$ etc. catalyst)	Bent molecule
b.p.	59°		
SCl$_4$		SCl$_2$ + liq Cl$_2$	Unstable;
dec.	–31°	(–78°C)	Powdery off white solid; decomposes above –30°C. May be $SCl_3^+Cl^-$.
S$_n$Cl$_2$		H$_2$S$_n$ + S$_2$Cl$_2$ (or SCl$_2$);	Yellow to orange yellow viscous liquid. Unstable.
n = 1 – 8		–80°	

S$_2$Cl$_2$ Disulphur dichloride is produced in large quantities by chlorination of molten sulphur followed by fractionation. The golden yellow liquid undergoes ready hydrolysis to H$_2$S, SO$_2$, H$_2$SO$_3$, H$_2$SO$_4$ and polythionic acids. It reacts with NH$_3$ in warm CCl$_4$ or benzene solution to form tetrasulphur tetranitride, S$_4$N$_4$. Heating with NH$_4$Cl gives the same product.

$$6S_2Cl_2 + 16NH_3 = S_4N_4 + 8S + 12NH_4Cl.$$

$$6S_2Cl_2 + 4NH_4Cl = S_4N_4 + 8S + 16HCl.$$

The molecule has a structure like that of S$_2$F$_2$ or H$_2$O$_2$; S—S = 1.95 A°, S—Cl = 2.06 A°, ∠Cl—S—S = 107.7°.

S$_2$Cl$_2$ is largely used (ton quantities) in vapour-phase vulcanization of rubbers, as chlorinating agent (in the preparation of chlorohydrins) and also in metallurgical processes.

SCl$_2$ Disulphur dichloride results from further chlorination of S$_2$Cl$_2$ in presence of trace FeCl$_3$ as catalyst. The foul-smelling toxic liquid decomposes into S$_2$Cl$_2$ and Cl$_2$. Decomposition may be retarded by a little PCl$_5$ (0.01%). It undergoes rapid hydrolysis. Fluorination results in SF$_4$ and S$_2$Cl$_2$.

$$3SCl_2 + 5NaF \longrightarrow SF_4 + S_2Cl_2 + 4NaCl.$$

SCl$_2$ adds across ethylenic double bonds, e.g. *Mustard gas* is formed with ethylene.

$$SCl_2 + 2H_2C = CH_2 \longrightarrow S\ (CH_2CH_2Cl)_2$$

SCl$_2$ may be oxidized to SOCl$_2$ (thionyl chloride) and SO$_2$Cl$_2$ (sulphuryl chloride).

SCl$_2$ forms a bent molecule, ∠ClSCl = 103°.

SCl$_4$, sulphur tetrachloride, is produced by reacting SCl$_2$ with liquid chlorine at –80°C. The light yellow solid decomposes above –31° into SCl$_2$ + Cl$_2$. Its formulation as $SCl_3^+ + Cl^-$ is not well confirmed, but adducts $SCl_3^+AlCl_4^-$ and $SCl_3^+ICl_4^-$ are known with pyramidal SCl_3^+ cation (Cl—S—Cl 101°, S—Cl 1.98 A°).

Higher chlorosulphanes

Dichlorosulphanes of general formula S$_n$Cl$_2$ are known up to S$_{100}$Cl$_2$; those up to n = 8 have been prepared pure. They may be prepared by chlorinating polysulphanes with SCl$_2$ or S$_2$Cl$_2$:

$$H_2S_x + 2SCl_2 \longrightarrow S_{x+2}Cl_2 + 2HCl\ (-80°C).$$

These are yellow viscous liquids having densities around 1.6–1.8 g cm^{-3} (or higher) and pungent odours. They are thermally unstable and undergo ready hydrolysis.

The formation of such wide range of dichlorosulphanes is naturally related to the ability of sulphur to form long chains with terminal S—Cl bonds. The lower electronegativity of Cl compared to F and the lower S—Cl bond energy favours retention of the sulphur chain.

Bromides and Iodides of sulphur are poorly characterized. Only S$_2$Br$_2$ may be prepared by heating S with Br$_2$ at 100°C. It is a red-brown viscous liquid : m.p. –46°, b.p. 54° (0.18 mm Hg), d 2.63 g cm^{-3}. It tends to dissociate into S and Br$_2$ even at room temperature. Its structure is similar to that of S$_2$Cl$_2$: S—S 1.98 A°, ∠Br—S—S 105°.

Unstable SBr$_2$ and dibromosulphanes S$_n$Br$_2$ (n = 2 – 8) have also been reported.

The existence of sulphur iodides is controversial. S$_2$I$_2$ has been prepared at –90°C by reacting S$_2$Cl$_2$ (in pentane) with HI–N$_2$. The red-brown solid decomposes above –30°C. Definite S—I bonds are present in the S_7—I$^+$ cation formed by reacting iodine and sulphur in SbF$_5$ solution.

$$I_2 + S_8 + SbF_5 \longrightarrow [S_7X^+]\ [SbF_6^-]$$

In presence of AsF$_3$, the AsF$_3$-adduct of the iodo-bridged species $[(S_7I)_2I^{3+}]\ [SbF_6^-]_3$ have been obtained.

The iodocycloheptasulphur cation has a puckered S$_7$ ring with a pendant X atom; the conformation of the ring is same as that in elemental S$_7$ — species.

The $S_2I_4^{2+}$ cation in [S$_2$I$_4$] [AsF$_6$]$_2$ has weak interaction from I$_2$ molecules coordinating to S_2^{2+} cations. The cation is formed by reacting sulphur and I$_2$ with AsF$_5$ in presence of SO$_2$.

Chlorides, Bromides and Iodides of Se and Te

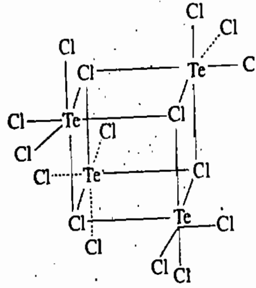
Se_2Cl_2 and Se_2Br_2 may be prepared by reacting the halogens with a suspension of powdered selenium in CS_2. The dark coloured heavy liquids as well as the vapours decompose into Se and SeX_4.

$SeCl_2$ and $SeBr_2$ are more unstable and may be present in the vapour above $SeCl_4/SeBr_4$.

$SeCl_4$ is much more stable than SCl_4 and may be prepared by direct synthesis. The colourless crystalline solid (m.p. 309°) sublimes at 196°C. The solid consists of tetrametric Se_4Cl_{16} units. $SeBr_4$ is similar - the orange-red solid (m.p. 123°) occurs in two different tetrameric forms. Both the halides are hydrolysed by water. In presence of concentrated HCl, alkali metal chlorides give yellow complexes like $K_2[SeCl_6]$. Salts of SeX_3^+ cation are also known in fused state in presence of strong halide ion acceptors, e.g., $[SeCl_3^+][GaCl_4^-]$ and $[SeBr_3^+][AlBr_4^-]$.

"$TeCl_2$" and "$TeBr_2$" may be formed by reacting fused Te with Cl_2F_2 or $CBrF_3$.

$TeCl_4$ is the only stable chloride of tellurium and may be prepared by (i) heating Cl_2 + Te or (ii) by the action of $SeCl_2$ on Te or TeO_2. The pale yellow solid (m.p. 228°, b.p. 390°) melts to a maroon coloured conducting liquid which may be $[TeCl_3^+]Cl^-$. The solid consists of tetrameric Te_4Cl_{16} units : 4Te and 4Cl atoms occur at alternate corners of a cube (23-XXX).



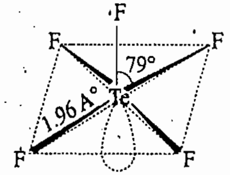
23-XXX

Molecules in the vapour have a pseudo trigonal bipyramid arrangement. Like $SeCl_4$, $TeCl_4$ is also hydrolyzed by water and forms complexes like K_2TeCl_6.

The $TeCl_6^{2-}$ ion is regular octahedral and does not readily conform to our expectation from the VSEPR model for 7 valence shell electron pairs. One may assume an electron configuration $5s^2\,5p^6\,5d^4\,6s^2$ for the central atom and invoke hybridization involving 5p, 5d and 6s orbitals only (the 5s is thus excluded). On the other hand, one may also consider the mo-s formed by the three 5p orbitals and the Cl-orbitals. Two p-orbitals from two Cl^- ions and a 5p-orbital of Te give rise to a set of 3-center 4-electron m.o. - the 4 electrons occupy the bonding and nonbonding m.o.-s. There will be three such sets - providing 6 bonding electrons for the whole ion; this imparts a bond order of 0.5 for each Te—Cl bond. Summarily we find that the geometry is dominated by inter-ligand repulsion of the large ligand ions.

Halide complexes

We have already come across some of the halide complexes. Pentafluoroselenates (IV) are formed when alkali metal or thallium fluoride are dissolved in SeF_4. The $MSeF_5$ compounds are unstable white solids. The $MTeF_5$ compounds are white crystalline solids formed by dissolving the metal fluoride and TeO_2 in aqueous HF or SeF_4.



23-XXXI

The TeF_5^- ion is a distorted square pyramid—repulsion of the lone pair of electrons lifts the basal F atoms slightly above the Te atom. The F (apex) - Te - F (base) angles are correspondingly reduced to 79°.

Hexahalo complexes M_2SeX_6 and M_2TeX_6 are known for X = Cl, Br and I. Crystalline compounds are obtained by direct combination of MX with SeX_4/TeX_4 or solution of SeO_2/TeO_2 in aqueous HX. The structure of $TeCl_6^{2-}$ has already been discussed.

Oxohalides

Sulphur and selenium form two main series of oxohalides : OMX_2 and O_2MX_2 (M = S, Se). The SOX_2 compounds are commonly known as thionyl halides and SO_2X_2 compound as sulfuryl halides.

Thionyl (and selenyl) halides

These are prepared by reactions like

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

$$SO_3 + SCl_2 = SOCl_2 + SO_2 \; (\textit{Industrial})$$

$$SOCl_2 + 2HF = SOF_2 + 2HCl$$

$$SOCl_2 + 2HBr = SOBr_2 + 2HCl \; (0°C)$$

$$SeO_2 + SeCl_4 = 2SeOCl_2 \; (\text{in } CCl_4).$$

The dihalides are stable at room temperature but decompose on heating. The m.p., b.p., and some structural parameters of the thionyl dihalides are given below :

TABLE 23.11

Some characteristics of $O{=}SX_2$ (X = F, Cl, Br)

	m.p., °C	b.p., °C	d(O—S), A°	d(S—X) A°	∠X—S—X
$O{=}SF_2$	−110	−44	1.41	1.58	93°
$O{=}SCl_2$	−101	76	1.45	2.07	—
$O{=}SBr_2$	−50	140	—	2.27	96°

The thionyl (and selenyl) halides are mostly liquids — the fluorides and chlorides are colourless and more volatile. $SOBr_2$ and $SeOBr_2$ are orange-coloured; $SeOBr_2$ is a solid (mp 42°C).

The compounds undergo rapid hydrolysis (fume in moist air) :

$$SOCl_2 + H_2O = 2HCl + SO_2$$

$SOCl_2$ is often used in preparing anhydrous metal halides from hydrated salts or hydroxides : SO_2 and HCl are removed as gases.

$$AlCl_3, 6H_2O + 6SOCl_2 = AlCl_3 + 6SO_2 + 12\,HCl$$

$$Mg(OH)_2 + 2SOCl_2 = MgCl_2 + 2SO_2 + 2HCl$$

As thionyl chloride readily decomposes above its bp (76°C) into SO_2, Cl_2 and S_2Cl_2, it is much used in organic chemistry as an oxidizing and chlorinating agent.

$SOCl_2$ can function both as a weak Lewis acid (vacant *d*-orbital on S) and as a weak Lewis base (lone pair on O).

Q. 23.9 *Suggest a structure for the adduct $SeOCl_2Py_2$ (py = pyridine).*

Hint : A square pyramid with the O-atom at the apex. A lone pair of electrons below the $SeCl_2py_2$ plane.

Thionyl chloride (and related compounds) has a pyramidal structure; the sulphur atom may be considered to involve sp^3 hybrid orbitals with one lone pair (AB_3E type). A *d*-orbital with an unpaired electron forms a π-bond to O.

Q. 23.10 *The bond order of the S—O bond increases in the order $OSBr_2 < OSCl_2 < OSF_2$. Comment.*

Hint : O—S π-bonding is facilitated by the electronegative halogen atoms.

Sulphuryl halides

SO_2F_2, SO_2Cl_2 and the mixed halides SO_2FCl, SO_2FBr are known.

Preparation

SO_2F_2 may be prepared by (i) reacting SO_2 with F_2 (ii) fluorination of SO_2Cl_2 or (iii) by heating barium fluorosulphonate (500°C).

$$Ba\,(SO_3F)_2 = BaSO_4 + SO_2F_2.$$

SO_2Cl_2 is prepared on a large scale by chlorination of SO_2 in presence of $FeCl_3$ as catalyst.

$$SO_2 + Cl_2 = SO_2Cl_2$$

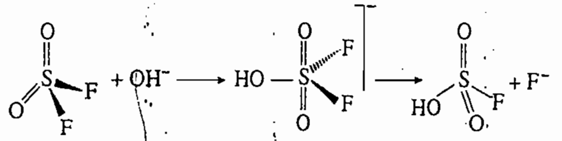
It is also formed in the reaction of SO_3 with the otherwise inert compound SF_6 ($\Delta G^c = -202$ kJ mol^{-1}).

$$SF_6 + 2\,SO_3 = 3\,SO_2F_2 \text{ (250°, 24 hr; 20\% conversion).}$$

The mixed halides may be obtained by reacting together SO_2F_2 with SO_2Cl_2 or SO_2Br_2.

Properties

SO_2F_2 is a colourless gas (bp −55°C) while SO_2Cl_2 is a fuming liquid (bp 69°C). SO_2F_2 dissolves in water without hydrolysis. But it reacts with bases and other nucleophiles (attacking S) with displacement of F^-.



Ammonolysis gives $SO_2(NH_2)_2$. SO_2Cl_2 dissociates into SO_2 and Cl_2 above 300°C and is rapidly hydrolyzed by water. A solution in benzene gives $SO_2(NH_2)_2$ with ammonia.

$$SO_2Cl_2 + 4\,NH_3 = SO_2\,(NH_2)_2 + 2NH_4Cl$$

SO_2Cl_2 is used as a chlorinating agent, e.g., in the direct chlorination of hydrocarbons

$$RH + SO_2Cl_2 = RCl + SO_2 + HCl \quad \text{(sunlight, organic peroxide)}$$

It acts also as a sulphonating agent

$$C_6H_6 + SO_2Cl_2 = C_6H_5SO_2Cl + HCl \quad \text{(in presence of } AlCl_3).$$

[Sec. 23.3.6 *Aqueous chemistry*]

Acetyl chloride may be prepared by the reaction

$$CH_3COONa + SO_2Cl_2 = CH_3COCl + SO_3 + NaCl$$

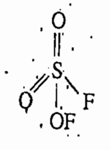
The molecules are tetrahedral (distorted) - consistent with sp^3 hybridization at S with S—O π-bonds.

Some data on these compounds are given below :

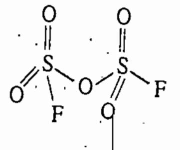
	m.p.	b.p.	d(O—S)	d(S—F)	<OSO	<XSX
SO_2F_2	−120	−55	1.41 A°	1.53A°	124°	96°
SO_2Cl_2	−54	69	1.43A°	1.99A°	120°	111°

For Se and Te, only SeO_2F_2 is known. The colourless gas (b.p. −8°C) may be prepared by reacting SeO_3 with SeF_4 or KBF_4 (70°). It is readily hydrolyzed.

Some other complex oxofluorides are formed by S, Se and Te, e.g.,



23-XXXII



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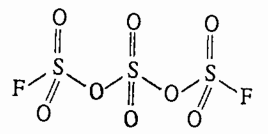


23-XXXIV

Tellurium also forms a number of oxofluorides derived from successive replacement of F in TeF_6 octahedron by $OTeF_5$ groups, e.g., $F_4Te(OTeF_5)_2$, $F_2Te(OTeF_5)_4$, $FTe(OTeF_5)_5$ and $Te(OTeF_5)_6$.

The $OTeF_5$ (and $OSeF_5$) group may also bond to other atoms, e.g., Xe $(OTeF_5)_n$ (*n* = 2, 4 and 6); B $(OTeF_5)_3$; I $(OSeF_5)_5$ and V $(OTeF_5)_6$. The last compound has an octahedral VO_6 unit with V—O—Te angle 170° suggesting appreciable V—O—Te π-bonding. Ionic species like $Na^+\,(OSeF_5)^-$ are also known. The $OSeF_5$ and $OTeF_5$ groups thus behave like F.

23.3.6 Aqueous Solution Chemistry

The elements in this group have no cation chemistry in aqueous medium.

The redox and acid-base behaviour of water have been discussed earlier. We have also mentioned the aqueous solution chemistry of H_2S and various oxoanions of sulphur. The overall behaviour may be summarized with reference to the reduction potential values. A few selected values (at $[H^+] = 1$) are repeated here for −II, + IV and + VI oxidation states.

$$SO_4^{2-} \xrightarrow{+0.16} H_2SO_3 \xrightarrow{+0.50} S \xrightarrow{+0.14} H_2S$$
$$SeO_4^{2-} \xrightarrow{+1.15} H_2SeO_3 \xrightarrow{+0.74} Se \xrightarrow{-0.11} H_2Se$$
$$H_6TeO_6 \xrightarrow{0.92} TeO_2 \xrightarrow{+0.57} Te \xrightarrow{-0.72} H_2Te$$

We observe that (i) H_2Se and H_2Te are unstable. (ii) sulphates are feebly oxidizing but oxidizing power is much higher for selenates and tellurates. (iii) E° values of sulphites, selenites and tellurite differ very little from one another, particularly in view of the large difference between the + VI oxo-anions.

We have also mentioned the tautomeric nature of sulphite and thiosulphate ions.

23.3.7 Sulphur-nitrogen Compounds

There are no binary sulphur-nitrogen compounds corresponding to the nitrogen oxides. But a large number of sulphur-nitrogen compounds are now known with interesting properties. They mostly contain sulphur-nitrogen π-bonds and many of them are cyclic and polymeric.

The occurrence of a vast number of sulphur-nitrogen compounds is consistent with the diagonal position of these elements in the periodic table. They have similar electronegativities (N 3.0 and S 2.5) and the difference is further reduced when sulfur is bonded to strong electron withdrawing groups. This leads us to expect extensive π-bonding in addition to σ-bonds. The most important compound is tetrasulphur tetranitride S_4N_4 which is also the source of other S—N compounds.

Tetrasulphur tetranitride, S_4N_4

It was first prepared in 1835 (Gregory) in an impure form by reacting S_2Cl_2 with aqueous ammonia. Its structure was established after 1944.

Preparation

S_4N_4 is now prepared by passing ammonia gas into a solution of S_2Cl_2 or SCl_2 in dry CCl_4 (50°C).

$$6S_2Cl_2 + 16NH_3 = S_4N_4 + 12NH_4Cl + S_8.$$

$$6SCl_2 + 16NH_3 = S_4N_4 + \frac{1}{4}S_8 + 12NH_4Cl.$$

It is also formed by

(i) heating solid ammonium chloride with S_2Cl_2 (160°C)

$$6S_2Cl_2 + 4NH_4Cl = S_4N_4 + S_8 + 16HCl$$

(ii) reaction of sulphur powder with anhydrous liquid ammonia in presence of AgI

$$4NH_3 + 10\,S \rightleftharpoons S_4N_4 + 6H_2S.$$

AgI removes H_2S by precipitation of Ag_2S and drives the equilibrium to right.

Properties

Tetrasulphur tetranitride is endothermic with respect to the elements (ΔH_f^0 = 460 kJ mol^{-1}) but is kinetically stable at ordinary temperature in air. It may detonate if struck or ground or heated rapidly — on slow heating it melts at 178°C. The solid is orange yellow at room temperaure but is thermochromic in nature, i.e. it changes colour with temperature. It is almost colourless at very low temperature (–190°C) but colour gradually deepens on heating and becomes red above 100°C.

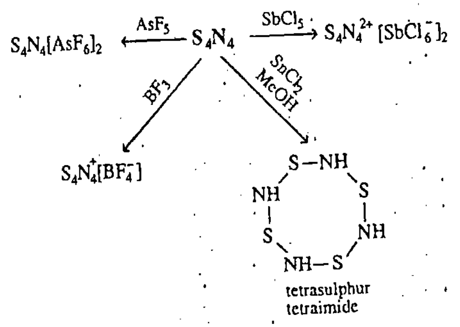
S_4N_4 is insoluble in water and practically unreactive to it (very slow hydrolysis may occur). It is readily hydrolyzed by alkali.

Dilute : $2S_4N_4 + 6OH^- + 9H_2O \longrightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$

Concentrated : $S_4N_4 + 6OH^- + 3H_2O \longrightarrow S_2O_3^{2-} + 2SO_3^{2-} + 4NH_3$

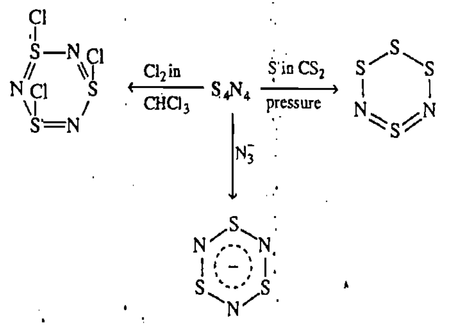
The compound has a ring structure (see later) and may undergo two main types of reactions :

(a) reactions in which the heterocyclic ring is retained



(b) reactions in which the ring is cleaved :

(i) Rings of other size (usually smaller) may be formed, as in the reactions of N_3^- or Cl_2 or S :



(ii) non-cyclic S — N groups may be formed :

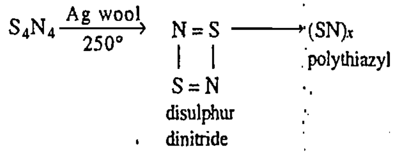
$$S_4N_4 \xrightarrow[CCl_4]{HgF_2} N \equiv SF \text{ (thiazyl fluoride)}$$

Sometimes the cyclic compounds formed initially may undergo further fragmentation, e.g.,

$$\underset{\text{trithiazyl trichloride}}{S_3N_3Cl_3} \underset{110°}{\overset{25°}{\rightleftharpoons}} NSCl \xrightarrow{S_2Cl_2} [S_3N_2Cl^+]\,Cl^-$$

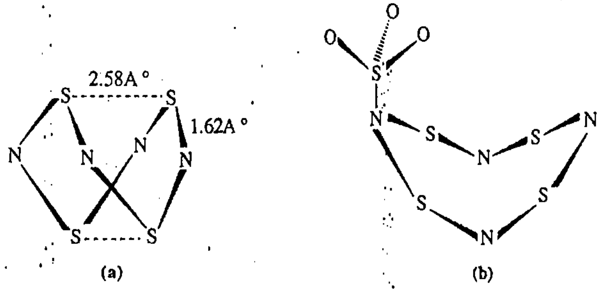
$$\underset{\text{tetrathiazyl tetrafluoride}}{(SF)_4N_4} \longrightarrow \underset{\text{thiazyl trifluoride}}{N \equiv SF_3}$$

Another important reaction of S_4N_4 is :



$$S_4N_4 \xrightarrow[250°]{\text{Ag wool}} \underset{\text{disulphur dinitride}}{\begin{array}{ccc} N & = & S \\ | & & | \\ S & = & N \end{array}} \longrightarrow \underset{\text{polythiazyl}}{(SN)_x}$$

Some of the compounds appearing as products will be discussed later. Besides, S_4N_4 may act as a donor through one of the N-atoms as in $BF_3.S_4N_4$, $SO_3.S_4N_4$ etc.



(a) (b)

Fig. 23.5

Structure of (a) S_4N_4 and (b) $S_4N_4.SO_3$.

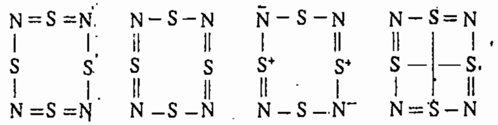
Structure

S_4N_4 has an 8-membered heterocyclic structure resembling that of a cradle [23.7 (a)]. The S—N distances (1.62 A°) are all equal and shorter than the sum of covalent radii (1.78 A°). The four N-atoms are coplanar. In the adducts $S_4N_4.BF_3$, $S_4N_4.SbCl_5$ and $S_4N_4.SO_3$ however, the four S-atoms become coplanar due to a rearrangement of the structure.

The S—S distances shown in the figure (2.58 A°) are well less than the nonbonding van der waals distance (3.3 A°) — suggesting significant (though weak) bonding interaction.

Bonding

No single valence bond structure appears to fit the bonding requirements of S_4N_4. Numerous resonance hybrids may be considered, e.g.,



M.O. calculations have been made to obtain a better understanding of the bonding as well as electron charge density on individual atoms.

Disulphur dinitride S_2N_2 is formed as an extremely unstable cyclic dimer when the vapour of S_4N_4 is passed over heated silver wool (300°C) at low pressure (0.1 – 1.0 mm Hg). The compound explodes when struck or warmed to about 30°C. The solid also undergoes slow but spontaneous polymerization at ordinary temperature. The polymer $(SN)_x$ has certain remarkable properties (see below).

Polythiazyl, $(SN)_x$ is a bronze coloured solid with metallic lustre. It is produced by room-temperature polymerization of S_2N_2 (S_4N_4 + heated silver wool, 300°C). A better method involves reaction of $SiMe_3N_3$ with trithiazyl trichloride ($S_3N_3Cl_3$, see before) in CH_3CN at –15°C. The compound can be sublimed in vacuum at 135°C. It decomposes with explosion at 240°C.

Polythiazyl is remarkable for its metallic electrical conductivity down to liquid helium temperature; it becomes superconductor below 0.26 K. It's conductance is much higher in one direction than in the perpendicular direction. It consists of zig-zag nearly planar chains of S—N—S — over which π-electrons are extensively delocalized.

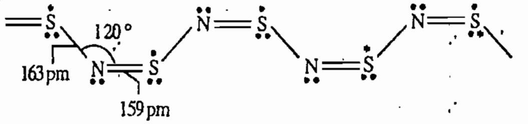


Fig. 23.6
Structure of $(SN)_x$ chain.

There are two S—N distances 1.59 A° and 1.63 A° — the structure may be looked upon as a conjugated system in which unpaired electrons on the sulphur atoms half-fill a conduction band formed by overlapping π* orbitals. This conduction band lies only along the direction of the S—N—S chain, making it a "one-dimensional metal". Partial bromination of $(SN)_x$ with bromine vapour produces blue-black $(SNBr_{0.4})_x$, which is an even better conductor.

Several other sulphur-nitrogen compounds as well as ions are known for example, S_4N_2 (see reactions of S_4N_4), S_5N_6, $S_{11}N_2$ and $(S_7N)_2S_x$ (x = 1,2,3,5). The red, orange or yellow crystalline solids are stable at room temperature in an inert atmosphere.

23.3.8 Complexes and Clusters

We have already come across several complexes formed by the elements in this group. Firstly, there are complexes in which the elements themselves act as ligands, e.g., those of dioxygen or sulphur clusters. Secondly there are complexes in which Se, and particularly Te, serve as the central atom.

Complexes of dioxygen

Weak charge-transfer associates

Electronic spectra reveal that the dioxygen molecule enters into weak charge-transfer type interactions with solvents like alcohols, ethers, benzene and even saturated hydrocarbons. However, these interactions occur at van der Waals distances between the molecules and there is no true complex formation. The heats of formation of these charge transfer associates are also negligible. Such charge-transfer interactions are often reversible, as in the case of *N, N*-dimethyl aniline which turns yellow in presence of air/O_2, but becomes colourless when the oxygen is removed. It is likely that such charge-transfer interactions are the first stage in photooxidation; they also increase the intensity of certain electronic transitions in molecules.

Coordination compounds

Several transition metal complexes containing O_2 as one of the ligands are now well established. Research in these compounds were first stimulated in 1963 following Vaska's observation on reversible oxygen take up in the equilibrium

$$trans\text{-}[Ir^{I}(CO)Cl(PPh_3)_2] + O_2 \rightleftharpoons [Ir^{III}(CO)Cl(O_2)(PPh_3)_2] \quad \text{(in benzene)}$$

A large number of dioxygen-metal complexes have since been isolated. These are generally prepared by reaction of gaseous dioxygen with solutions of the metal complexes :

$$[Pt(PPh_3)_4] + 2O_2 \longrightarrow [Pt(\eta^2-O_2)(PPh_3)_2] + 2Ph_3PO$$

$$[Co(3\text{-BuSalen}^*)_2] + O_2 + py \longrightarrow [Co(3\text{-BuSalen})_2(\eta^1-O_2)py]$$

Dinuclear complexes with bridging peroxogroups are also formed in this manner :

$$2CoCl_2 + 2\,pydien^{**} + 4NaI + O_2 \xrightarrow{EtOH} [\{Co(pydien)\}_2(\mu-O_2)]^{4+}I_4 + 4NaCl$$

$$2[RhCl(PPh_3)_3] + O_2 \xrightarrow{CH_2Cl_2} [(Ph_3P)_2RhCl(\mu-O_2)]_2$$

Hydrogen peroxide may also be used to prepare many dioxygen complexes :

$$CrO_4^{2-} + H_2O_2 + OH^-(aq) \longrightarrow [Cr^{V}(O_2)_4]^{3-} \quad \text{red; } \mu = 1.8\text{ B.M.}$$

$$Cr_2O_7^{2-} + H_2O_2 + H^+(aq) + py \xrightarrow{ether} [Cr(O)(O_2)_2py] \quad \text{blue; TIP} = 0.5\text{ B.M.}$$

$$(NH_4)_2Cr_2O_7 + NH_3(aq) + H_2O_2 \longrightarrow [Cr^{IV}(NH_3)_3(O_2)_2] \quad \text{brown; } \mu = 2.8\text{ B.M.}$$

Measurement of O—O distance in these complexes indicate that the complexes are mainly of two types — those containing peroxo groups (O_2^{2-}) or those containing superoxo group (O_2^-). Typical values of O—O distances in these complexes are given below; values of d (O—O) in O_2, KO_2 and Na_2O_2 together with O—O stretching frequencies (ν_{O-O}) are also given for comparison.

	d_{O-O} (pm)
(i) $[Co(CN)_5O_2]^{3-}$	124
(ii) $[Co(3\text{-Busalen}^*)_2\,py\,O_2]$	126
(iii) $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$	147
(iv) $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$	124

	d_{O-O} (pm)	ν_{O-O}
O_2	121	1556
KO_2	128	1145
Na_2O_2	149	738

---

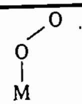
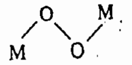
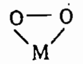
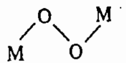
* 3-BuSalen = N,N'-ethylenebis (3-*tert*-butylsalicylideniminate) anion.
** pydien = 1, 9-bis (2-pyridyl)-2, 5, 8-triazanonane

Comparison with O—O distances in representative cases (see box) suggests that in (i) the O—O distance is intermediate between the values for O_2 and KO_2. However, the complex is ultimately classed as a superoxo complex. In (ii), the O—O distance is closer to that in the superoxide KO_2, suggesting coordination via the superoxide ion O_2^-; (iii), the O—O distance is closer to that in sodium peroxide, suggesting a peroxo bridging group, O_2^{2-}. But the complex in (iv) may be expected to contain a bridging superoxo group.

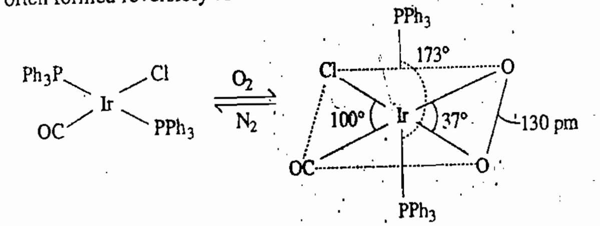
The common types of dioxygen-metal complexes are summarized in Table 23.12.

TABLE 23.12

The common types of dioxygen-metal complexes

M : O_2	Type	Structure	O—O distance (pm)	O—O str. frequency, cm^{-1}
(a) 1 : 1	Superoxo		125–135	1130–1195
(b) 2 : 1	Superoxo (bridging)		126–136	1075–1122
(c) 1 : 1	peroxo		130–155	800–932
(d) 2 : 1	peroxo		144–149	790–884

Type (a) complexes (superoxo; M : O_2 = 1 : 1) are known for Fe, Co, Rh and a few other transition metals. Haemoglobin and myoglobin are complexes of this type. Peroxocomplexes of formula type MO_2 (type c in Table 23.12) are more common and are formed by almost all transition metals except Cr, Mn, Fe, Cu and the Sc group. They are often formed reversibly as in the case of *Vaska's compound* (23-XXXV) :



(yellow)
23-XXXV

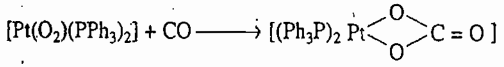
(orange)
23-XXXVI

The bonding in the dioxygen-metal complexes may be explained satisfactorily by MO treatment involving the pi mos of dioxygen. Thus the three membered peroxo complexes (type c, Table 23.12) may be supposed to involve (i) a σ-bond formed by O_2 (π) → M ($d\pi$) bonding and (ii) a back bonding of the type M ($d\pi$) → O_2 (π^*). In the bridge complexes, electron density is delocalized over both the metal atoms. The O—O distance of 1.30 A° in the oxygenated product of Vaska's compound is close to 1.28A° for the superoxide ion, O_2^-. But since the compound is diamagnetic, it cannot consist of Ir (II) and O_2^-. The particular case of oxygenation is best described as an oxidative addition : the oxygenated product (23-XXXVI) has Ir(III) with the peroxide ion, O_2^{2-}.

The dioxygen complexes produce H_2O_2 with aqueous acids. The coordinated dioxygen in these complexes show enhanced reactivity—many species which do not react readily with molecular oxygen are easily oxidized by these complexes, e.g., CO_2, SO_2, NO_2, RCHO, PPh_3 etc.

$$[Ir(CO)Cl(O_2)(PPh_3)_2] + SO_2 \longrightarrow [Ir(CO)Cl(PPh_3)_2SO_4]$$

$$[Ir(CO)Cl(O_2)(PPh_3)_2] + 2NO_2 \longrightarrow [Ir(CO)Cl(PPh_3)_2(NO_3)_2]$$



$$[Pt(O_2)(PPh_3)_2] + CO \longrightarrow [(Ph_3P)_2\,Pt\langle^{O}_{O}\rangle C = O\,]$$

Such enhanced reactivity of coordinated dioxygen may lead to use of such complexes as potential catalysts in many synthetic reactions. These complexes are also important to throw light on the mechanism of oxygen transfer in biological systems.

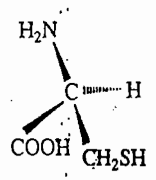
Q.. 23.11 *If the Cl is Vaska's compound is replaced by I, the resulting compound adds O_2 irreversibly; also, the O—O distance in the oxygenated product is 1.51 A° compared to 1.30A° in 23-XXVI. Comment.*

Hint : Lower electronegativity of I confers a higher electron density on the metal. This facilitates Ir ⟶ O_2 π-back bonding and stabilizes the oxygenated species.

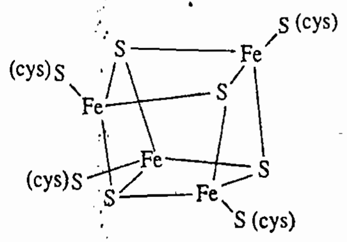
Back donation increases electron density in the antibonding π* m.o.-s of O_2, and hence the O—O distances increases.

Complexes of Sulfur

Sulphur behaves as an effective Lewis base towards many transition metals — either as the free sulphide ion or when covalently bound, as in the amino acids cysteine and methionine :



23-XXXVII
Cystein



23-XXXVIII
Distorted Fe_4S_4 cube in the protein chain of Ferredoxin : bond to 4 cysteine sulphur atoms.

A wide variety of metallo-enzymes contain Fe, Cu, Zn or Mo coordinated by cystein sulphur atoms. Several iron-sulphur proteins have important biological functions e.g. in the oxidation of carbohydrates and fats occurring in the mitochondria of cells; the iron porteins are integral parts of the inner membrane of the mitochondria. Iron sulphur proteins are also involved in the nitrogen fixation enzyme nitrogenase and in photosynthesis.

A cage of four Fe and four S atoms appears to be more stable thermodynamically than other combinations and a model compound containing the Fe_4S_4 moiety may be prepared in absence of air in methanol solution :

$$4FeCl_3 + 4HS^- + 6RS^- + 4CH_3O^- \longrightarrow [Fe_4S_4(SR)_4]^{2-} + RS - SR + 4CH_3OH + 12Cl^-.$$

The Fe_4S_4 cluster has a cubic arrangement with Fe and S atoms at alternate corners; the thiolate ($S\bar{R}$) groups occupy terminal positions on Fe atoms, one electron reduction to $[Fe_4S_4(SR)_4]^{3-}$ leaves the cluster intact. Redox reactions of the enzyme ferredoxin are supposed to involve similar clusters.

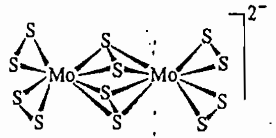
The tetrathiomolybdate ion MoS_4^{2-}, obtained as

$$MoO_4^{2-}(aq) + 4H_2S = MoS_4^{2-} + 4H_2O$$

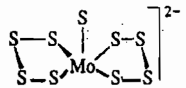
may coordinate to a number of metals in + II oxidation state e.g. Co^{2+} and Fe^{2+} :

$$Co^{2+} + 2MoS_4^{2-} \longrightarrow [S_2MoS_2CoS_2MoS_2]^{2-}$$

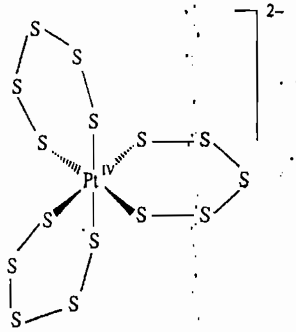
Polysulphide anions S_2^{2-}, S_3^{2-} etc. may also act as **ligands (23-XXXIX-XL).**



23-XXXIX (a) $[Mo_2(S_2)_6]^{2-}$



23-XXXIX (b) $[MoS(S_4)_2]^{2-}$



23-XL

The complex $[Pt^{IV}(S_5)_3]^{2-}$ is chiral and may be resolved into enantiomorphs.

Other Complexes

Complexes of tetravalent chalcogens are interesting for the steric properties of the lone pair electrons. These are strongly directional, as seen in their equatorial position in the trigonal bipyramid geometry of halides like SF_4, SeF_4 etc. The R_3M^+ cations are also pyramidal with a lone pair taking up the fourth position of a tetrahedron around M (M is an element of Gr 16), as in $[TeMe_3]^+[B\,Ph_4]^-$.

However, the hexa-halo anions e.g., those in K_2TeBr_6, Rb_2SeCl_6 etc. as also *trans*-$SeCl_4py_2$ and *trans*- $TeCl_4(mtu)_2$ (mtu = tetramethyl thiourea $SC(NMe_2)_2$) have undistorted octahedral structure, suggesting that the lone pair on M occupies an *s*-orbital. The last compound is easily prepared as :

$$TeO_2 + HCl\ (conc.) + S{=}C(NMe_2)_2 \longrightarrow TeCl_4[SC(NMe_2)_2]_2$$

Tellurium has a tendency to attain higher coordination number, as in $MTeF_7$, M_2TeF_8 (M = alkali metal) or TeF_6, $2R_3N$.

Cationic Clusters

It was mentioned earlier (section 23.2.3) that sulfur, selenium and telurium dissolve in oleum to form M_4^{2+} and other cations. The elements also form a large number of other cationic chain and ring clusters. These are usually formed by oxidation of the elements by oleum, AsF_5 or SbF_5 :

$$S_8 + 3AsF_5 = [S_8]^{2+}(AsF_6^-)_2 + AsF_3$$

$$10Se + 3AsF_5 = Se_{10}^{2+}(AsF_6^-)_2 + AsF_3$$

$$4Te + 3AsF_5 \longrightarrow Te_4^{2+}(AsF_6^-)_2 + AsF_3$$

$$S_8 + 3SbF_5 \longrightarrow S_8^{2+} + 2SbF_6^- + SbF_3 \qquad \text{(in liq. HF)}$$

$$7Te + TeCl_4 + 4AlCl_3 \longrightarrow 2Te_4^{2+} + 4AlCl_4^- \qquad \text{(in molten } AlCl_3)$$

Such cations are oxidizing agents and strong Lewis acids and as such, are formed in strongly acidic medium, as in fluorosulphuric acid HSO_3F. Oxidation by peroxocompounds is also useful.

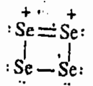
$$Te + oleum \longrightarrow Te_6^{4+}$$

$$4Se + FO_2SOOSO_2F = [Se_4][SO_3F]_2 \qquad \text{(in } HSO_3F)$$

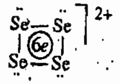
The cations form intensely coloured solutions in oleum — yellow (S_4^{2+}), deep blue (S_8^{2+}), red (S_{19}^{2+}) and intermediates depending on the strength of oleum and reaction time. Some crystalline salts of these cations have been studied by X-rays, e.g., $S_8^{2+}[AsF_6^-]_2$ and $S_4^{2+}[SbF_6^-]_2$.

The M_4^{2+} species are square planar with bond lengths slightly shorter than M—M single bond lengths : 198 pm vs 204 pm for S_4^{2+}. They may be represented as a resonance hybrid of structures like 23-XLI (a) or may be looked upon as a quasiaromatic system with six π-electrons (23-XLI (b)). The S_8^{2+} and Se_8^{2+} ions have puckered ring structures (23-XLII). In S_8^{2+}, the mean S—S distance lies between 204—206 pm. The two S-atoms joined by dashed line may have a weak interaction at 283 pm.

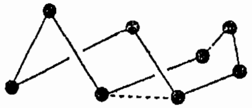
Mixed cationic species like $Te_2Se_8^{2+}$ and $Te_3S_3^{2+}$ are obtained by oxidizing mixture of chalocogens with AsF_5 or SbF_5 in liquid SO_2.



23-XLI (a)



23-XLI (b)



23-XLII

23.3.9 Organo-derivatives

Except polonium, all elements in this group form R_2M derivatives (M = O, S, Se, Te). The chemistry of ethers (R_2O) is largely covered in organic chemistry. Other R_2M compounds are commonly prepared by reacting a halide with the Grignard or lithium reagent containing the alkyl group; an ether is commonly used as the solvent :

$$MCl_2 + 2LiR \longrightarrow MR_2 + 2LiCl \quad (M = S, Se, Te)$$

Some other reactions are :

$$RI + S \xrightarrow[\text{tube}]{\text{sealed}} R_2S + RS{-}SR + RS{-}S{-}SR \quad (R = CF_3, C_6F_5)$$

$$R_2Se + X_2 \longrightarrow R_2SeX_2 \xrightarrow{HgR_2} R_3SeX \quad (X = Cl, Br)$$

$$R_2M + RX \longrightarrow R_3MX \quad (X = I)$$

Thioethers are relatively weak donors but macrocyclic thioethers and thioanalogues of crown ethers have remarkable complexing ability. The organic chemistry of selenium Se/Te form alkyl and aryl selenium (tellurium) halides (see above for preparation). Me_2SeX_2 and Me_2TeX_2 have trigonal bipyramidal distribution of valence orbitals around Se/Te, the lone pair of electrons being in an equatorial position. Me_2TeI_2 also exists as $Me_3Te^+[TeMeI_4]^-$; the cation is pyramidal and the anion square pyramidal.

SUMMARY

Introduction : The elements of group 16 are collectively called chalcogen from their natural association with copper (chalcos). Oxygen has two allotropic forms, O_2 (dioxygen) and O_3 (ozone). Ozone is formed in the upper atmosphere by the action of solar uv radiation on O_2. The ozone layer protects the earth from harmful uv radiations coming from the sun. Nitrogen oxides and chlorofluorocarbons destroy the ozone layer. Sulfur forms a large number of allotropes containing puckered rings of 6-20 S atoms or long chains.

Common rhombic sulfur and liquid sulfur near its melting point (115°C) consist entirely of S_8 rings.

The trend in various properties among the group members parallels those observed in previous groups. The first member oxygen is distinguished by its tendency to form strong p-p π-bonds and strong H-bonds. It is also a strong and versatile oxidizing agent. Besides molecular oxygen (O_2) can act as a ligand to various transition metals with out undergoing reduction ; such processes are termed *oxygenation*.

Dioxygen also forms a few compounds of the dioxygenyl cation O_2^+, e.g. $O_2^+MF_6^-$ where M = Pt, As, Sb, Bi etc. These may be prepared by heating a mixture of O_2, F_2 and powder of the element M.

Oxides : Dioxides MO_2 and trioxides MO_3 are formed by all the elements S, Se, Te and Po. The dioxides may be prepared by heating the elements in air. They are soluble in water; SO_2 and SeO_2 giving distinctly acidic solutions of "sulfurous acid" (H_2SO_3) and selenous acid (H_2SeO_3) respectively. TeO_2 is amphoteric and much less soluble.

The trioxides MO_3 may be prepared by dehydrating the corresponding acids with P_4O_{10}. SO_3 is prepared industrially by catalytic oxidation of SO_2 (V_2O_5, 450°C) as the main step in the manufacture of H_2SO_4.

SO_2 is a major pollutant of our environment — it is released in air by burning of oil and coal and as an industrial discharge.

Oxoacids : The principal oxoacids of the elements fall into two categories — the "ous" acids (oxidation state IV) and the "ic" acid (oxidation state VI). Besides, sulfur forms a large number of oxoacids, for example dithionous acid ($H_2S_2O_4$); dithionic acid ($H_2S_2O_6$) and the polythionic acids ($H_2S_nO_6$; n = 3—6); and thiosulfuric acid ($H_2S_2O_3$).

Sulfuric, selenic and telluric acids (H_2SO_4, H_2SeO_4 and H_6TeO_6) are all strongly oxidizing in nature. Selenic acid can singly dissolve gold, platinum etc. noble metals. Both selenic and telluric acids liberate chlorine from concentrated HCl.

Peroxoacids of sulfur : Peroxomonosulfuric acid (H_2SO_5, *Caro's acid*) can be prepared by the action of H_2O_2 on H_2SO_4 or chlorosulphuric acid. It is a colourless crystalline solid with specific oxidizing properties — e.g. it oxidizes aniline to nitrosobenzene and liberates I_2 from KI instantaneously.

Peroxodisulfuric acid ($H_2S_2O_8$, ***Marshall's acid***) is prepared by electrolysis of ice-cold 50% H_2SO_4. It is a colourless solid and a powerful oxidizing agent but uncatalyzed reactions are often slow, e.g. the oxidation of KI to I_2. Ag(I) is a common catalyst in its reactions.

Halides : All the elements form a large number of binary halogen compounds. Oxygen forms oxygen fluorides OF_2 and O_2F_2 with fluorine and oxides with other halogens. Sulfur, selenium and tellurium form fluorides and chlorides in +II and +IV states as well as several mixed valences. A remarkable difference is observed among the halides in this group — the lowest oxidation state (II) becomes gradually *less* stable from S to Te. Thus the lowest fluorides of Se and Te are SeF_4 and TeF_4; $TeCl_4$ is the only tetrachloride which is stable in the gaseous state. Similarly, the iodides become stable only at Te (and Po). Sulfur iodides exist only at very low temperatures.

The halides are essentially covalent. Some of them are associated in the solid e.g. $(TeF_4)_n$ (polymeric chains); $(MX_4)_4$ (X = Cl, Br, I for M = Te and X = Cl, Br for M = Se).

Sulfur-nitrogen compounds : There are no binary S—N compounds corresponding to the nitrogen oxides. But a large number of compounds containing S—N π bonds are known — many of them cyclic and polymeric. S_4N_4 is the most important compound — it is prepared by passing NH_3 (gas) into a solution of S_2Cl_2 or SCl_2 in CCl_4 at 50°C. It is a orange yellow solid at room temperature — insoluble in water and undergoes only very slow hydrolysis. It has an 8-membered heterocyclic structure with alternate S and N atoms in a cradle-like arrangement. The S—N distances (162 pm) are all equal and shorter than the sum of covalent radii (178 pm). When S_4N_4 is heated with silver wool (250°C), the bronze coloured solid *polythiazyl* is formed. It consists of zig-zag chains of S—N—S over which π-electrons are extensively delocalized giving rise to metallic electrical conductance down to liquid helium temperature.

EXERCISE

1. *What is the importance of the atmospheric ozone layer to life on earth?*

   What are the reasons for depletion of the ozone layer?

2. *Briefly summarize the observation on gradual heating of rhombic sulfur from room temperature to its boiling point.*

3. *Point out the main similarities and differences among sulfuric, selenic and telluric acids.*

4. *Give equations to show how you will obtain thiosulfate, dithionite, dithionate and tetrathionate starting with an aqueous solution of sulfite.*

5. *The following standard heats of formation (kJ mole^{-1}) are given :*

$B_2H_6(g)$	$B_2O_3(s)$	$CH_4(g)$	$CO_2(g)$	$SiH_4(g)$	$SiO_2(s)$
29.3	−1280.3	−75	−393.3	−62.8	−857.7

   The standard heat of formation of H_2O at 25°C is −242.7 kJ mol^{-1}. Arrange the hydrides in the increasing order of effeciency as fuel in terms of heat produced (a) per gram of fuel (b) per gram of fuel + oxygen mixture. Assume ΔH_f^0 independent of temperature.

   [Hint : Write balanced equation for the combustion of each hydride and calculate heat of combustion.]

   Ans : (a) $SiH_4 < CH_4 < B_2H_6$; (b) $CH_4 < SiH_4 < B_2H_6$.

6. *Describe the shapes of the following isolated molecules and the probable hybridization of the central atoms*

   (a) SO_2 (b) SO_3 (c) $SOCl_2$ (d) SO_2Cl_2 (e) SF_4 (f) $TeCl_4$.

7. *Draw Lewis structures for the following molecules/ions and state the probable geometry and hybridization at each sulfur atom*

   (a) $H_2S_2O_8$ (b) $S_2O_3^{2-}$ (c) $S_2O_4^{2-}$ (d) $S_2O_6^{2-}$ (e) $S_4O_6^{2-}$.

8. *What happens when*

   (a) *An aqueous solution of Mn(II) is boiled with potassium perdisulfate.*

   (b) *Potassium perdisulfate is added to an acidified solution of barium permanganate.*

   (c) *Sulfur dioxide is passed into an aqueous suspension of pyrolusite.*

   (d) *Ferric nitrate is added to anhydrous sulfuric acid.*

   (e) *Sodium thiosulfate solution is slowly added to silver nitrate solution.*

   (f) *Ferric chloride solution is gradually added to sodium thiosulfate solution.*

   (g) *A solution of sodium dithionite is added to a solution of iodine in acetic acid medium.*

   (h) *The above reaction is repeated in presence of formalin.*

(i) *Urea is heated with anhydrous sulfuric acid.*

(j) *Sodium sulfite is added to a solution of I_2 decolorized with thiosulfate.*

(k) *SCl_2 is reacted with NaF.*

(l) *Silver nitrate is added to a concentrated solution of ammonium persulfate.*

(m) *A solution of sodium thiosulfate is boiled with KCN and NaOH; the resulting solution is cooled, acidified with HCl and to it a few drops of $FeCl_3$ solution are added.*

[**Hint :** (b) Perdisulfate hydrolyzes to H_2SO and $SO_4^{=}$ (d) solvolysis; $Fe_2(SO_4)_3$ is precipitated; (f) $S_4O_6^{=} + SO_3^{=} \longrightarrow$ (l) Black ppt. $Ag_2O_2 + NH_4HSO_4 + HNO_3$ (m) $Na_2S_2O_3 + KCN \longrightarrow KSCN + Na_2SO_3$.]

9. *Explain :*

(a) *Bond orders of the S—O bond among the oxohalides follow the order*

$$SOF_2 > SOCl_2 > SOBr_2$$

(b) *SF_6 is a stable compound but SH_6 or even SH_4 are not known.*

(c) *The O—O bond in O_2F_2 is much shorter than that in H_2O_2.*

(d) *Dithionic acid is given the dimeric formula $H_2S_2O_6$.*

(e) *The two sulfur atoms in thiosulfate are not identical.*

(f) *There are two isomeric diethyl sulfites $(C_2H_5)_2SO_3$ with different boiling points.*

(g) *Dithionic acid, $H_2S_2O_6$, is not considered a member of the series of polythionic acids, common formula $H_2S_nO_6$.*

(h) *SF_4 has two S—F bonds 164 pm long and two other S—F bonds 154 pm long.*

(i) *SF_6 is unreactive towards water but TeF_6 is readily hydrolyzed.*

(j) *H_2O, H_2S and H_2Se can be made by direct reaction of the elements but H_2Te cannot be made in this way.*

(k) *SF_4 is readily hydrolyzed but SF_6 is not.*

(l) *SO_3 is planar but $SO_3^{=}$ is pyramidal.*

10. *The energies of O—O and S—S single bonds are 138 and 213 kJ mol^{-1} respectively.*

Explain the difference between the energies of the bonds and the tendency of sulfur for catenation.

11. *Give examples of sulfides which fit the following categories*

(a) soluble in water; (b) insoluble in water but soluble in dilute acids; (c) insoluble in acids; (d) insoluble in water or acids but soluble in solutions of basic sulfides; (e) unstable in water (completely hydrolyzing).

12. *The O—H and S—H stretching frequencies in solid, liquid and gaseous H_2O/H_2S are as follows :*

	H_2O (g)	H_2O (l)	H_2O (c)	H_2S (g)	H_2S (s)
$\bar{\nu}$, cm^{-1}	3655	3219	3400	2615	2532

The value changes significantly in case of H_2O with physical states, but not in case of H_2S. Comment.

[**Hint :** H-bonding]

13. *Give short answers :*

(a) *Give an example of analytical use of $K_2S_2O_8$.*

(b) *Give a reaction of thiosulfate as a ligand as well as reductant.*

(c) *How will you detect sulfite in presence of thiosulfate.*

[**Hint :** See Table 23.7)

(d) *What is polythiazyl?*

(e) *Show by a chemical reaction that selenic acid is a more powerful oxidizing agent than H_2SO_4.*

(f) *How will you show that the —O—O— bond does not open during oxidation of H_2O_2 by $KMnO_4$ (acid)?*

(g) *Write electron dot structures of $S_2O_3^{=}$, $S_2O_4^{=}$, $S_2O_6^{=}$ and $S_2O_8^{=}$.*

(h) *How will you show that sodium dithionite is not $NaSO_2$?*

(i) *How and where is ozone formed in nature?*

(j) *What do you mean by singlet O_2?*

(k) *What type of species are formed on dissolving S, Se and Te in oleum?*

(l) *Give one example where oxygen forms four covalent bonds,*

14. *The selenium present in a 10.0 g sample of soil is distilled as the tetrabromide which is collected in aqueous solution. The selenium hydrolyzes to SeO_3^{2-} which is determined iodometrically, requiring 4.2 mL of a standard thiosulfate solution.*

If the thiosulfate solution contains 2 milliequivalent per liter, what is the concentration of selenium in the soil in ppm?

[**Hint :** $SeO_3^{2-} + 4I^- + 6H^+ \rightleftharpoons Se + 2I_2 + 3H_2O$]

15. *A saturated solution of sodium sulfite is added to a concentrated solution of H_2SeO_3 and heated. A red-brown amorphous precipitate is obtained. Explain with equation.*

CHAPTER TWENTY FOUR

ELEMENTS OF GROUP 17(VII A)

Halogens : F, Cl, Br, I (At)

OBJECTIVES

24

ELEMENTS OF GROUP 17(VII A)

24.1 INTRODUCTION

The use of salt is associated with very early days of our civilization. Scientific interest in various uses of salts also developed since the period of ancient civilization. Fluorine and chlorine were familiar to seventeenth century chemists, though chlorine was systematically prepared and used in the eighteenth century. The beginning of chemical industry was marked by N. Leblanc when he devised a process for obtaining NaOH from NaCl (1787). Bleaching powder was prepared in 1788 and the process patented in 1798. In 1810, Davy established chlorine as an element and also suggested the name. The term ***halogen*** was given by J. S. C. Sch weigger to chlorine for its ability to form salts with metals. The term has later been extended to all members of the family which bear close resemblance to one another — a feature not common in any other group in the periodic table except Gr. I.

24.1.1 Abundance and occurrence

None of the elements occurs free in nature owing to their high reactivity.

Fluorine Fluorine occurs in the earth's crust to the extent of 0.065% (544 ppm; thirteenth in abundance)-which is higher than that of chlorine (0.055%, 126 ppm, twentieth). Minerals found with concentrated deposits are *fluorite* or *fluorspar* (CaF_2), *cryolite* (Na_3AlF_6) and ***fluorapatite*** ($3Ca_3(PO_4)_2, CaF_2$).

^{19}F is the only isotope found in nature. ^{18}F (half-life ≃ 09.7 m) may be prepared and used as a tracer with difficulty.

In India, fluorite occurs in (i) Madhya Pradesh in the districts of Durg, Raipur and Jabalpur; (ii) **Rajasthan** in Jaipur, Alwar, Ajmer and Kishangarh. A vast deposit exceeding 2 million tonnes has also been reported from Dengarpur District. Veins of fluorite also occur in the rocks of some other parts of the Peninsula and the Himalayas.

Chlorine Chlorine occurs mainly as sodium chloride deposited by evaporation of lakes. NaCl also occurs in large concentration in sea water. Natural chlorine consists of the isotopes ^{35}Cl (75%) and ^{37}Cl (24.5%).

Bromine Bromine is much less abundant in crustal rocks, only to the extent of 2.5 ppm (46th in order). The largest natural source is the oceans (~ 65 mg/L of ocean water). Some salt lakes and seas have a much greater concentration of bromide ion, e.g. Searle's lake in California : ~850 mg/L and Dead Sea : 4 g/L.

Like chlorine, bromine also has two stable isotopes—^{79}Br (50.7%) and ^{81}Br (49.3%).

Iodine is still less abundant, only 0.46 ppm (60th order). $NaIO_3$ and $Ca(IO_3)_2$ are found in certain minerals. Brines contain iodide ion up to the extent of 100 ppm. Ocean water contains iodine in very small concentration (0.05 ppm) but certain marine life can concentrate it, e.g. the sea weeds *Laminaria* and *Fucus* can concentrate iodine up to 0.45% of their dry weight.

Iodine has only one stable isotope, ^{127}I.

Astatine Astatine has only transient existence in the decay series of uranium and thorium. In the U-235 series, nearly 1.2% ^{227}Ac undergoes α-decay to Fr-223 (the main decay occurs by β-emission; see Ch. 13). The Fr-223 is β-active, but a very small fraction (0.004%) undergoes α-decay to ^{219}At. It has a half-life of only 54s. The element was obtained in cyclotron by the reaction $^{209}Bi\ (\alpha, 2n)\ ^{211}At$ for study of its properties. Of the nearly 20 isotopes known, At-211 and At-210 have relatively longer half-lives, 8.3 and 7.2 hours respectively.

Some isotopes of the halogens are useful in nmr and mass spectrometric studies. The only natural isotope of fluorine, ^{19}F, having a nuclear spin 1/2 is very suitable for nmr studies. The ^{19}F reasonance can be studied conveniently with high receptivity at a frequency close to that for ^{1}H. For other halogens, the charge-distribution in the nucleus is not strictly spherical and gives rise to some nuclear quadrupole moment. Very high field nmr sprectrometers can now resolve the proton spectrum of say CH_3Cl corresponding to $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$; at 500 MHz. two peaks with relative intensities 3 : 1 (approx) is consistent with the relative abundance of the ^{35}Cl and ^{37}Cl isotopes.

Mass spectrometric studies of the halogen compounds are also interesting — CH_3Cl, for example, gives four peaks for the ion cluster CH_3Cl^+ : $^{12}CH_3{}^{35}Cl$, $^{13}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$ and $^{13}CH_3{}^{37}Cl$.

Some radioactive isotopes of the elements are also useful in the study of isotope exchange reactions. Some of them are

Nuclide	Production	Half-life	Mode of decay
^{18}F	$^{19}F\ (n, 2n)$	110 min	β^+
^{36}Cl	$^{35}Cl\ (n, \gamma)$	3×10^5 y	β^-
^{38}Cl	$^{37}Cl\ (n, \gamma)$	37 min	β^-
^{82}Br	$^{81}Br\ (n, \gamma)$	35 hours	β^-
^{129}I	U-fission	1.6×10^7y	β^-
^{128}I	$^{127}I\ (n, \gamma)$	25 min	β^-
^{131}I	$^{130}Te\ (n, \gamma)$ or Pu-fussion	8 days	β^-

24.1.2 Isolation of the elements

Fluorine

History : Fluorine derived its name from the mineral fluorspar (CaF_2) — it was suggested by Ampere in a letter to Davy(1812). Fluorspar was so called because of its role as a flux to promote fusion of metals and minerals (*fluor* - flowing). Light emission by fluorspar on heating was also termed fluorescence (1852).

The corrosive nature of HF was observed in the seventeenth and eighteenth century by many chemists, including Scheele. But it could not be prepared owing to several difficulties :

(i) anhydrous HF is a nonconductor of electricity while an aqueous solution of it produces ozonised oxygen on electrolysis.

(ii) No chemical oxidizing agent was able to oxidize a fluoride or HF. E^0 of F_2–F^- system is + 2.85 v.

(iii) High volatility of HF and its severe corrosive nature.

(iv) Decomposition of fluorine compounds to give fluorine is highly unlikely from a thermodynamic point of view since the compounds have high lattice energy/bond energy.

Finally, Moissan succeeded (1886) in preparing fluorine by electrolysing KF dissolved in anhydrous HF in a U-tube of Pt with Pt-Ir electrodes. The volatility of HF was tackled by using a bath of boiling ethyl chloride at –24°C.

Fluorine is now prepared by electrolysing molten KF-HF mixtures having compositions around KF.HF (m.p. 240°C) to KF.2-3 HF (m.p. 70-100°C). These have much lower vapour pressures of HF than the original composition used by Moissan : KF.13HF). The electrolyte is taken in a mild-steel cell acting as cathode. The anode is a central rod of nongraphitic carbon (see precaution) separated from the cathode by a porous diaphragm. The temperature of the cell is carefully monitored by heating and cooling coils around the cell which produces much heat while in operation. F_2 evolves at the anode while H_2 comes out from the cathode in the typical overall cell reaction

$$HF \rightleftharpoons H^+ + F^-;\ H^+ + e = H;\ \ H + H = H_2$$

$$F^- - e = F;\ \ F + F = F_2$$

Precaution

1. The electrolyte is highly corrosive and must be handled carefully.

2. F_2 is highly reactive — it will combine explosively with the H_2 if not completely separated.

3. Grease and other oxidizable substances must be thoroughly removed; otherwise these may catch fire and lead to puncture of the protective fluoride coating.

4. Any graphite in the anode material is likely to form explosive graphite-fluoride. Ungraphitized carbon anode is made from powdered coke compacted with copper.

With due precaution, fluorine is now routinely produced in different countries for various industrial uses. The medium temperature cell (70-100°C) is preferred over the high temperature cells (230-250°C) owing to lower corrosion problem and longer life of the anode.

Chemical preparation of fluorine has been achieved recently (K. O. Christe, 1986) through the reaction

$$2SbF_5 + K_2MnF_6 \longrightarrow 2KSbF_6 + MnF_3 + \tfrac{1}{2}F_2 \quad (150°C)$$

SbF_5, the stronger Lewis acid, displaces the weaker MnF_4 which itself is unstable and decomposes to MnF_3 and F_2. The starting materials may be obtained by using HF, without necessitating fluorine itself.

Chlorine

Chlorine may be readily prepared in the laboratory by oxidation of HCl by MnO_2 (gentle heat) or $KMnO_4$. On a technical scale, the gas is obtained by the electrolysis of sodium chloride, either molten or in aqueous solution, metallic sodium and caustic soda being the by-products respectively. The latter procedure, using mercury cathode, is being gradually discouraged owing to alarming mercury pollution through effluent water. The possibility of replacing the traditional diaphragms (separating the anodes and cathodes) by membranes is now being explored. A porous membrane of *Nafion* — a copolymer of tetrafluoroethylene and a perfluorosulphonylethoxy ether, reinforced with a teflon mesh, has good prospect.

The old Deacon process of oxidation of HCl by air ($CuCl_2$ catalyst; 450°C) is being tried again. The equilibrium may be shifted to right by converting the Cl_2 to dichloroethane (to produce vinyl chloride).

Bromine is prepared by chlorinating concentrated solutions from brine around pH 3.5; the bromine liberated is swept by air, condensed and purified.

Iodine is prepared in a variety of processes depending upon the source.

(i) Natural brines containing iodides may be chlorinated to evolve I_2; this is swept by air, condensed and resublimed.

(ii) In another method, the iodide is precipitated by silver nitrate solution. The precipitated AgI is treated with scrap iron to set free the silver which is recycled by dissolving in nitric acid. The solution of ferrous iodide is oxidized by Cl_2.

I_2 set free in very small concentration may be adsorbed on activated charcoal or on an ion-exchange resin (in the form of a polyiodide). The iodine is then collected with NaOH solution and regenerated by acidification.

(iii) Chile saltpetre ($NaNO_3$), commonly called caliche, contains about 0.2 per cent $NaIO_3$. The mother liquor after crystallization of $NaNO_3$ is concentrated to about 6 g. per litre. One part of it is reduced by calculated amount of sodium bisulphite to iodide and mixed with unconverted iodate to liberate I_2.

$$5IO_3^- + 15HSO_3^- \longrightarrow 5I^- + 15SO_4^{2-} + 15H^+$$

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O.$$

24.1.3 Uses of the elements

Fluorine

At least 10,000 tonnes of F_2 are now produced annually over the world.

1. The largest consumption of F_2 is in the manufacture of UF_6 in nuclear power stations.

2. F_2 is largely used in making SF_6 for dielectrics, and the fluorinating agents ClF_3, BrF_3 etc.

3. W and Re are fluorinated to volatile WF_6/ReF_6 required in vapour deposition of the metals on machine components.

4. Hydrogen fluoride, chlorofluorocarbons, BF_3, synthetic cryolite are some of the industrially important compounds of fluorine. Fluorspar is an important flux in metallurgy.

Chlorine

About 25 million tonnes of chlorine are produced annually in the world by most of the industrially developed countries. Its main uses are

1. As a bleaching agent in paper, pulp and textile industries.
2. As a disinfectant in water supply and in sewage water treatment.
3. Manufacture of hydrochloric acid and other inorganic compounds e.g. $NaClO_3$, NaOCl, Al_2Cl_6, $SOCl_2$ etc.

4. Production of chlorinated organo compounds of industrial importance e.g. ethylene dichloride and vinyl chloride. Nearly 70% of the total chlorine produced is used under this category.

Bromine

World production of bromine is much less than that for chlorine — nearly 0.4 million tonnes per year.

1. Bromine is largely consumed to prepare 1,2-dibromoethane (ethylene dibromide); this was added to petrol to remove the lead from lead tetraethyl. But this use has now declined in view of lead pollution from automobile exhausts.

Ethylene dibromide is still produced in large quantities for use in pesticides.

2. Bromine is also used in the production of several bromocompounds which are effective as pesticide and flame retardant in fabrics. Tris-(dibromopropyl) phosphate $(Br_2C_3H_5O)_3PO$ has remarkable flame retarding property.

3. Bromine is used in making various inorganic chemicals like HBr, AgBr (in making photo films) and bromides and bromates. Organic bromo-compounds are also used in high density drilling fluids and dyes.

Iodine

World production of I_2 lies around 16,000 tonnes per annum, Japan alone producing nearly half this amount.

1. Iodine is largely used in the manufacture of various organic compounds like iodoform (CHI_3, antiseptic) and methyl iodide (CH_3I).

2. Silver iodide is used in high speed photographic films.

3. I_2 as such and several inorganic chemicals containing iodine are used in the laboratory, as catalyst in rubber industry, in dye-stuffs and many other purposes.

4. NaI (and $NaIO_3$) is added to table salt (~ 10 ppm) to supplement iodine deficiency in our body which may hamper the production of thyroxine (a growth regulating hormone) and cause goitre and other diseases. KI is added to animal and poultry feeds.

24.2 GENERAL PROPERTIES

24.2.1 The Elements

Both fluorine and chlorine are gases at ordinary temperature—fluorine faint greenish yellow, chlorine greenish yellow. Bromine is a dark red liquid of high density—its vapour is brown. Iodine is a black solid with metallic lustre.

In the vapour state, the halogens normally exist as diatomic molecules. The dimers are held by weak van der Waals attraction. The m.o. description of F_2 is KK $\sigma_{2s}^2\, \sigma^{*2}_{2s}\, \sigma_{2p}^2\, \pi_{2p}^4\, \pi^{*4}_{2p}$. The energy difference between the 2*s* and 2*p* a.o.-s is quite large (~ 2500 kJ mol^{-1}); the amount of mixing between the σ_{2s} and σ_{2p} in F_2 is negligible for all practical purposes and is not sufficient to repel the σ_{2p} m.o. above the π_{2p} level. The *ns-np* separations in other halogen atoms are less than half that of fluorine; their diatomic molecules should then have the m.o. description for their valence shell as $\sigma_{ns}^2\, \sigma^{*2}_{ns}\, \pi_{np}^4\, \sigma_{np}^2\, \pi^{*4}_{np}$. In all cases, the highest occupied m.o. (HOMO) is the antibonding π^* (*np*) level which is completely filled. The lowest unoccupied m.o. (LUMO) is the σ^* (*np*). Theoretical calculations on FCl require inclusion of some back bonding from chlorine *d*-orbitals to obtain accurate F-Cl bond distance. This suggests that some *p-d* π-bonding may also be present in Cl_2, Br_2 and I_2.

Solid iodine forms a layer lattice, the distance between non-bonded I atoms (3.56 A°) in a layer is considerably shorter than twice the van der Walls radius of I (2.15 A°) suggesting some sort of weak interaction between the molecules. Solid iodine is a semiconductor with band gap ~1.3 eV and the conductivity at room temperature is only ~10^{-12} ohm^{-1} cm^{-1}. At 350 kbar pressure, the conductivity becomes ~10^4 ohm^{-1} cm^{-1} and has a negative temperature coefficient.

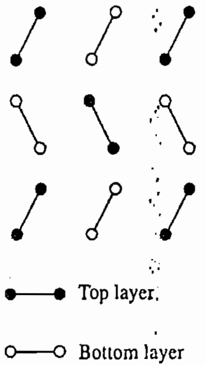


Fig. 24.1
The crystal structure of iodine.
Alternate planes of I_2 molecules are staggered. Distance between the layers is ~427 pm.

Fluorine, chlorine and bromine also form similar layer lattice in the solid state. Some X_4 species have been detected with bromine and iodine in the gas phase and in certain solvents; I_4 is present by about 1.4 mol per cent at 240°C and 2.5 atm pressure.

F_2 is about 1% dissociated into atoms at 765°C and 1 atm pressure. Cl_2 shows 1% dissociation at 975°C. Corresponding temperatures for Br_2 and I_2 are 775°C and 57.5°C respectively. The values are consistent with the respective bond dissociation enthalpies (see later) since entropy effects are practically same.

Some physical properties of the X_2 molecules are given in Table 24.1.

TABLE 24.1
Some physical properties of X_2 molecules

	F_2	Cl_2	Br_2	I_2
M.P., °C	−219	−101	−7.3	113.6*
B.P., °C	−188	−34	59.5	183*
Dissociation enthalpy (kJ mol^{-1})	159	243	193	151

*Vapour pressure 90.5 Torr at 113.6°C.

Colours of the halogens

Gases In the gas phase, colours of the halogens vary remarkably : fluorine, pale yellow; chlorine, pale greenish-yellow; bromine, deep red-brown; iodine, deep violet. All these colours may be assigned to transition of an electron from the highest occupied π^* m.o. to the lowest unoccupied σ^* m.o. This transition between two states with different spin multiplicity (singlet - triplet) is formally forbidden. As one moves from F_2 to I_2, the difference between the two energy levels decreases and the probability of this transition also increases at the same time. Hence the absorption maximum gradually shifts from the near ultra violet to the red region of the visible specturm; the intensity of absorption also increases side by side. Hence we observe the *complementary colour* with increasing intensity.

Solutions Chlorine, bromine and iodine also dissolve unchanged in many organic solvents like saturated hydrocarbons, CCl_4 etc. Thus iodine dissolves in CCl_4 to give a violet solution. But donor solvent molecules may share one of their electron pairs with the empty σ^* m.o. of the halogen molecule forming weak charge-transfer complexes which vary in colour. As shown in Fig. 24.2, the separation between the HOMO and LUMO is effectively increased in the X_2-solvent complex and the absorption band moves

towards the blue end. Thus iodine gives a brown solution in alcohol and ethers; in poor donor solvents like benzene, the colour is intermediate between brown and violet. There occurs another intense band located in the uv region which is due to the transfer of electronic charge from the bonding m.o. localized near the donor orbitals (B) to the antibonding m.o. (A) localized near the halogen orbital. Such transition, called a *charge transfer transition*, gives rise to intense colours. (See Ch. 27)

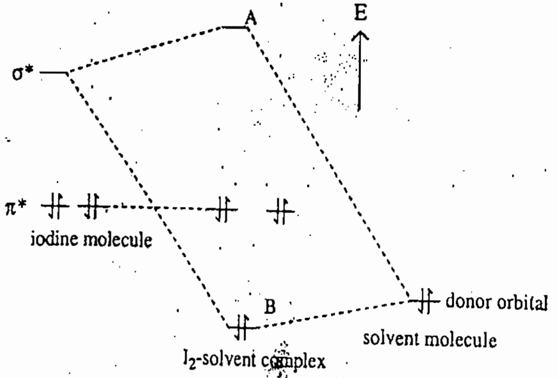


Fig. 24.2
Interaction of I_2 with a donor solvent.

The absorption maximum for violet solutions lies in the range 520-540 nm and shifts to about 460-480 nm in a typical brown solution (Fig. 24.3). The amines, ethers and alcohols interact with iodine through lone pair of electrons on N/O, aromatics and alkenes do so through their π m.o.-s. It has been possible to isolate some of the complexes and determine their structures by X-ray crystallography. The X–X distance in the halogens is larger than in the uncoordinated X_2 molecule, since coordination increases electron density in the antibonding orbital. There is a parallel decrease in the Br-Br or I-I stretching frequency. Thus, even in the weak complex $C_6H_6.I_2$ ($\Delta H = -5$ kJ mol^{-1}), the I-I frequency is 204 cm^{-1} as against 215 cm^{-1} in I_2.

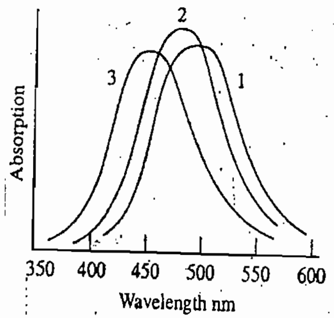
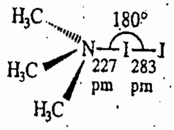
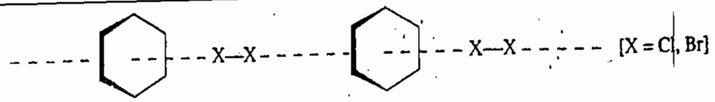


Fig. 24.3
Spectrum of iodine in various solvents.
1—in CCl_4; 2—in C_6H_6; 3—in $(C_2H_5)_2O$.



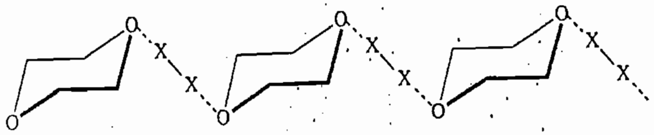
[I—I in I_2 = 267 pm]

24-I (a)
Complex of trimethylamine and iodine.



24-I (b)

Benzene X_2 complex



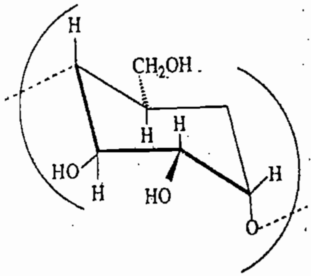
24-I (c)

1, 4-dioxan—X_2 complex (X = Cl, Br, I).

Many of these complexes dissociate on heating and the brown solutions of I_2 may revert to their original violet colour.

Q. 24.1 *Iodine dissolves in cyclohexane forming a violet solution. When benzene, dioxan or pyridine are added to such solution, the colour changes to purple, brown and yellow respectively and the apparent dipole moment of the iodine in solution rises. The moments of the dipolar species formed in the above three cases are 1.8, 3.0 and 4.5 D respectively with cyclohexane solution as reference zero. Comment.*

Hint : Donor strength increases from benzene to pyridine. Greater interaction implies increased electron transfer, hence higher dipole moment.



24-II.

Amylose, a component of starch, has a helically coiled structure derived from 1, 4-linked α-D (+) glucopyranose units. There are six glucose residues per turn of helix (diameter ~ 13A°)

Iodine produces an intense blue black colouration with starch in presence of iodide ions. Raman spectroscopy and ^{129}I Mössbauer spectroscopy has confirmed that I_5^- ions $(I_2 + I_3^-)$ are trapped in the helical coils of amylose (24-II), a component of starch. The I_5^- amylose complex has its absorption maximum at about 600 nm. The amylopectin fraction of starch does not form any complex with iodine.

Hydrates

Chlorine, bromine and iodine are only sparingly soluble in water, during which they disproportionate into HX and HOX (see later). Solid hydrates of chlorine and bromine may be obtained by freezing such solutions. These hydrates, approximating the composition $X_2.8H_2O$, actually contain the halogen molecules trapped in the H-bonded network of water molecules found in ice. These are examples of *clathrate* (cage) *compounds*.

Chemical Reactivity

Fluorine is the most electronegative and most chemically reactive of all the elements. It combines directly with metals and almost all nonmetals, exceptions being oxygen, nitrogen and the noble gases except xenon and krypton. The reactions with many elements are vigorous and sometimes explosive. Some metals like Fe, Cu, Ni and Al (in massive form) get a protective layer of fluoride which prevents further reaction. Powdered metals react vigorously. Reactivity decreases to chlorine to bromine to iodine.I_2 reacts with hydrogen only when heated in presence of a catalyst like Pt.

The exceptionally high reactivity of fluorine may be assigned primarily to the low F-F bond dissociation energy. The X-X dissociation energies are as follows :

F–F	Cl–Cl	Br–Br	I–I	
159	243	193	151	kJ mol^{-1}

The gradual decrease in bond energy from Cl_2 to I_2 is consistent with poorer overlap with increasing size of the overlapping orbitals. The reverse trend in F_2 is mainly assigned to (i) large internuclear repulsion, since the F–F distance is quite small, 1.48 A° (ii) large inter-electron repulsion between the lone pairs of electrons on the two F atoms which have high charge density. In addition, it has been suggested (Mulliken) that the bonds in Cl_2, Br_2 and I_2 may acquire slight multiple bond chracter via *pd* hybridization, thereby gaining some extra stability. Fluorine has no such scope as its valence shell is limited only to *s* and *p* orbitals ($n = 2$).

The factors responsible for the great reactivity of fluorine have been summarized in section 24.2.3. Because of its high electronegativity, small size, low bond dissociation energy and high strength of bonds formed in compounds, fluorine shows some marked deviation from the remaining halogens. It is sometimes termed a "superhalogen".

A few important chemical properties of the halogens are summarized in Table 24.2 :

TABLE 24.2

Some chemical reactions of the halogens

Reaction with	F_2	Cl_2, Br, I_2
(i) H_2	$H_2 + F_2 = 2HF$ explosive even at –252°C	$H_2 + X_2 = 2HX$ X = Cl, Br : *sunlight* (Cl>Br) X = I : Pt cat.; *heat*
(ii) H_2O	(a) $2F_2 + 2H_2O = 4HF + O_2$ (b) $3F_2 + 3H_2O = 6HF + O_3$	(c) $X_2 + H_2O \rightleftharpoons HX + HOX$ (Cl>Br>I) (b) $2X_2 + 2H_2O \rightleftharpoons 4HX + O_2$ (X = Cl, Br; *slow*) (c) $4HI + O_2 \rightleftharpoons 2I_2 + 2H_2O$
(iii) ***aqueous alkali***	(a) *dil* : $2F_2 + 2NaOH = F_2O + 2NaF + H_2O$ (b) *conc* : $2F_2 + 4NaOH = 4NaF + 2H_2O + O_2$	(a) *cold, dil* : $X_2 + 2OH^- = X^- + OX^- + H_2O$ (b) *hot, conc* : $3X_2 + 6OH^- = 5X^- + XO_3^- + 3H_2O$

Reaction with	F_2	Cl_2, Br, I_2
(iv) **non-metals**	O_2, N_2, He—Ar : no direct reaction. C, S, Br, I etc. burn spontaneously	C, O_2, N_2, He—Ar : no direct reaction. S, P etc. combine with decreasing vigour from Cl—I. $2S + Cl_2 = S_2Cl_2$ (also Br) $S + 2Cl_2 = SCl_4$ $P_4 + 6Cl_2 = 4PCl_3$ (also Br, I) $2As + 3Cl_2 = 2AsCl_3$ (also Br, I)
(v) **metals**	Most metals form fluorides, Na, K etc. catch fire. $Ag + F_2 = AgF_2$	Many metals form halides, though less energetically. $2Ag + Cl_2 = 2AgCl.$

Fluorine is often very agressive in its attack on different compounds as it can form stronger bonds with the consitituent atoms of these compounds, Thus fluorination of benzene in the vapour phase in the presence of a metallic catalyst gives a complex mixture of aliphatic and alicyclic fluoro-compounds like CF_4, C_2F_6, C_6F_{12} etc.

Fluorine is an extremely strong oxidizing agent, as shown by the standard reduction potential :

$$\frac{1}{2}F_2 + e \rightleftharpoons F^- \qquad E^\circ = +2.65 \text{ V}.$$

It oxidizes potassium chlorate to potassium perchlorate and potassium sulphate to persulphate.

Chlorine, bromine and iodine are slightly soluble in water; the aqueous solution contains mostly hydrated X_2 molecules together with HOX produced on disproportionation. Disproportionation is negligible with I_2.

TABLE 24.3

Solubility of halogens in water (25°C)

	Solubility, mol dm^{-3}	Conc. of X_2 (*aq*) mol dm^{-3}	Conc. of HOX mol dm^{-3}
Cl_2	0.09	0.06	0.03
Br_2	0.21	0.21	1.1×10^{-3}
I_2	0.0013	0.0013	6.4×10^{-6}

As seen in Table 24.3, oxidation of water by chlorine is extremely slow though the reaction is thermodynamically feasible. With I_2, the reverse process, that is oxidation of iodide by oxygen, takes place spontaneously

$$2H^+ + 2I^- + \frac{1}{2}O_2 \longrightarrow I_2 + H_2O \qquad \Delta G^\circ = -105 \text{ kJ mol}^{-1}.$$

This is why the blue colour of starch-iodine returns soon to a solution after titration of iodine with thiosulphate. The end point of such titrations are taken at a stage when the starch-iodine colour disappears for at least thirty seconds.

Chlorine and bromine readily add to ethylenic double bonds and oxidize H_2S to sulphur, arsenites to arsenates and sulphites to sulphates. Iodine also gives these reactions, but it oxidizes thiosulphate to tetrathionate, while chlorine and bromine oxidize thiosulphate to sulphate in concentrated solutions (Ch. 23).

Iodine is oxidized by concentrated nitric acid to iodic acid :

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Chemistry of Astatine

All 21 isotopes of astatine are highly radioactive with short half-lives. The relatively stable isotopes have half-lives of the order of a few hours :

$$^{209}\text{At} : 5.5 \text{ h}; \qquad ^{210}\text{At} : 8.3 \text{ h}; \qquad ^{211}\text{At} : 7.2 \text{ h}$$

Bombardment of Bi—209 with α-particles having energy greater than 21 MeV (to overcome nuclear repulsion) produces all the above three isotopes of astatine. These are removed from the bismuth target by heating. The isotopes undergo decay through K-electron capture followed by gamma radiation.

Like iodine, astatine is readily extracted into CCl_4 from aqueous solutions but the presence of At_2 molecules has not been confirmed. Reduction of At(0) by zinc dust or SO_2 produces the astatide ion, At^-. This is coprecipitated with AgI as AgAt.

$$2At + SO_2 + 2H_2O \longrightarrow 2At^- + 3H^+ + HSO_4^-$$

Iodine oxidizes At(0) to AtI; this is soluble in CCl_4 and $CHCl_3$ and gives C_6H_5At with C_6H_5I.

Oxidation of astatine by dichromate produces At(I) and At(III); peroxodisulphate and Ce(IV) probably give AtO_3^- which may be coprecipitated with $Ba(IO_3)_2$. The formation of AtO_3^- has not been absolutely confirmed but migration in an electric field confirms the negative charge.

$$At^- + 6Ce^{4+} + 3H_2O \longrightarrow AtO_3^- + 6Ce^{3+} + 6H^+$$

Astatine differs from iodine in two respects : (i) it does not form a compound with + VII oxidation state, resembling Tl, Pb and Bi in the same period. (ii) it does not form the At^+ cation.

AtBr and AtI are the two interhalogens known for astatine; there is also some evidence for polyhalide ions containing At.

A large number of organic compounds containing astatine are known—RAt, $RAtO_2$, R_2AtCl and $RAtCl_2$. The R-groups may be widely varied, including biologically important molecules.

24.2.2 Atomic and Physical Properties

Some atomic and physical properties of the elements are summarized in Table 24.4 Melting and boiling points of the elements and some other data for the molecules have been given earlier.

TABLE 24.4

Atomic and Physical properties of the halogens

	F	Cl	Br	I
Atomic No.	9	17	35	53
Electronic configuration	[He] $2s^22p^5$	[Ne] $3s^23p^5$	[Ar] $3d^{10}4s^24p^5$	[Kr] $4d^{10}5s^25p^5$
I.E./kJ mol^{-1}	1680	1256	1143	1009
Electron attachment enthalpy/kJ mol^{-1} (E.A.)	−333	−349	−325	−296
Electronegativity (Pauling)	4.0	3.2	3.0	2.7
X—X distance	143	199	228	266
Covalent radius pm	64	99	114	133
Ionic radius (6 – coord, pm)	133	181	196	220
Dissociation enthalpy of X_2 (g)/kJ mol^{-1}	159	243	193	151
$E°$ (volt) for $\frac{1}{2}X_2 + e \rightleftharpoons X^-(aq)$	+ 2.9	+ 1.36	+ 1.07	+ 0.54

The trends observed in first ionization energy, electronegativity and size are consistent with the electron configuration of the elements and the expected change in effective nuclear charge. The electron affinity of fluorine is however less than that of chlorine (the electron attachment enthalpy is less negative) due to increased repulsion on the incoming electron by the dense population of non-bonding electrons on the small fluorine atom. The influence of repulsion between non bonding electrons in F is also reflected in the F—F distance which is substantially longer than twice the covalent radius; for other halogens, the X—X distances are almost twice their covalent radii.

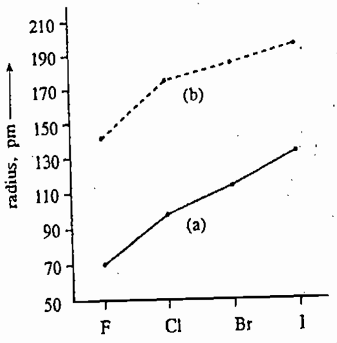


Fig. 24.4 (a)

Variation of atomic radii (——)
Variation of V–W radii (----)
The radii of the anions are nearly identical with the corresponding V–W radii.

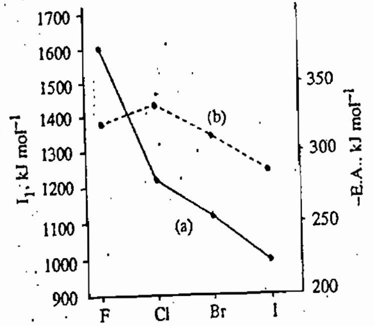


Fig. 24.4 (b)

Variation of first I. E (kJ mol^{-1}) (——)
Variation of EA (scale on right, in kJ mol^{-1}) (----)

24.2.3 General Group Trend

The elements in this group resemble one another in chemical properties more than those in any other group except the alkali metals.

The general group trend in the chemistry of halogens follows the same general pattern as found in earlier groups. The general trend observed among the halogens are briefly summarized below. Compounds in individual category have been discussed in section 24.3.

Valence and Oxidation States

The elements are just one electron short of the next noble gas configuration and the ready formation of halide ion is indicated by the large negative electron attachment enthalpy (–E.A.). The stabilization of the halide ions in the crystal lattice of an ionic compound may be readily understood with reference to the Born-Haber cycle illustrated for NaCl (Ch. 6). the solubility of the halides follow our expectation from hydration energy of the constituent ions; for a fixed cation, hydration energy decreases from F^- to I^-; the consequences of this have also been discussed (Ch. 6 and Ch. 18). Degree of covalence increases with increasing polarizability of the anion.

Where the formation of an ionic lattice is not energetically favourable, covalent halides are formed. As seen in periodic groups III(13) to VI(16), these may be molecular, bridged or three-dimensional polymeric compounds.

In all cases, fluorine shows a higher valence and higher coordination number of the element with which it combines, e.g. IF_7, SF_6, OsF_8 etc.

Besides being able to form a single bond by pairing the sole unpaired electron in its valence shell, chlorine, bromine or iodine may also donate one or more lone pairs of electrons and also enter π-bonding using *d*-orbitals. The oxoacid ions like ClO_3^-, ClO_4^- etc. and the polyhalide ions like ICl_4^- exemplify such cases. However, as we have mentioned in connection with phosphorus and sulphur, *d*-orbital participation may be actually very small and the bonding can be described by three center m.o.-s without involving the *d*-orbitals.

The important oxidation states and coordination numbers of the halogens are given in Table 24.5.

TABLE 24.5

Oxidation states and coordination numbers of halogens

Element	Oxidation States	Coordination Numbers
F	–I	1, (2)
Cl	–I, I, III, (IV), (V), (VI), (VIII)	1, 2, 3, 4
Br	–I, I, III, (IV), (V), (VI), (VII)	1, 2, 3, 5
I	–I, I, III, V, (VII)	1, 2, 3, 4, 5, 6, 7
At	–I, I, (III)?, V	—

Except fluorine, halogens exhibit several positive oxidation states in their oxides, oxoacids and inter halogen compounds. Polyatomic cations X_2^+ and X_3^+ are known for X = Cl, Br and I, those of iodine being most stable. None of the halogens form a stable

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monatomic cation though the ionization energy of all halogens except fluorine are less than that of hydrogen(130 kJ mol⁻). This is probably due to the fact that the large X^+ cation is unlikely to find necessary stabilization through lattice formation or solvation. A few compounds of strongly solvated or coordinated Br^+ and I^+ have been reported, e.g. $[Ipy_2]^+$, $[Br\,py_2]^+$, both linear and $[I\ (cryptand)^+]$.

Other polyatomic cations like I_3^+, I_4^{2+}, Br_2^+, Br_3^+ have also been prepared in superacid systems. The Cl_3^+ cation has been isolated as $Cl_3^+\ AsF_6^-$. In Br_2^+ ion, the Br–Br distance is 213 pm against 227 pm in Br_2, consistent with the removal of an electron from the antibonding HOMO.

The effect of increasing size among the halogens is again shown by the tendency to attain higher covalency and coordination number by iodine : it alone forms IF_7 while chlorine and bromine does not go beyond ClF_3 or BrF_5 respectively. Similarly, solid periodic acid is not HIO_4 but $OI\,(OH)_5$ or H_5IO_6.

Bond Energies

Bond enthalpies for single covalent bonds with the halogens have been mentioned in every group. Some important values are quoted again for ready reference (in kJ mol⁻¹).

TABLE 24.6

Some bond enthalpies of halogens

H—F	566	H—Cl	431	H—Br	366	H—I	299
C—F	485	C—Cl	327	C—Br	285	C—I	213
Si—F	582	Si—Cl	391	Si—Br	310	Si—I	234
N—F	272	N—Cl	193		—		—
P—F	490	P—Cl	319	P—Br	264	P—I	184
O—F	190	O—Cl	205		—	O—I	201
S—F	326	S—Cl	255	S—Br	213		—

We observe that

(i) Bonds with fluorine are much stronger than bonds with other halogens. The O–F bond is however weaker than the O–Cl bond.

(ii) Bonds to C, N and O are weaker than bonds to the corresponding element in the next row i.e., Si, P or S as the case may be.

These and similar other observations may be related to (among other things) strong repulsion between non-bonded electron pairs on smaller atoms.

Redox behaviour

Oxidation state-free energy diagram for the elements is shown in Fig. 24.4. Like earlier groups, the stability of the only negative oxidation state (–I) decreases from F to I (and to At). It appears that the positive oxidation states are all fairly stable — the V and VII states are least stable for bromine. There is a reversal in stability between V and VII states among chlorine and iodine. Cl(V) is less stable than I(V) but Cl(VII) is more stable than I(VII). In other words, I(V) is more stable with respect to I(VII) than is Cl(V) relative to Cl(VII).

[Sec. 24.2.3 *Redox behaviour*]

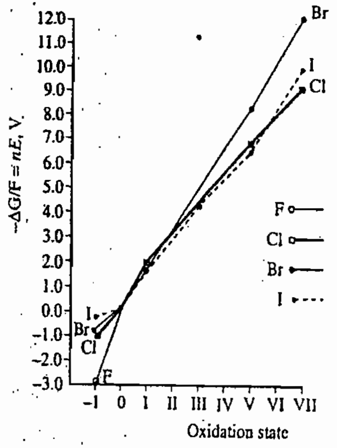
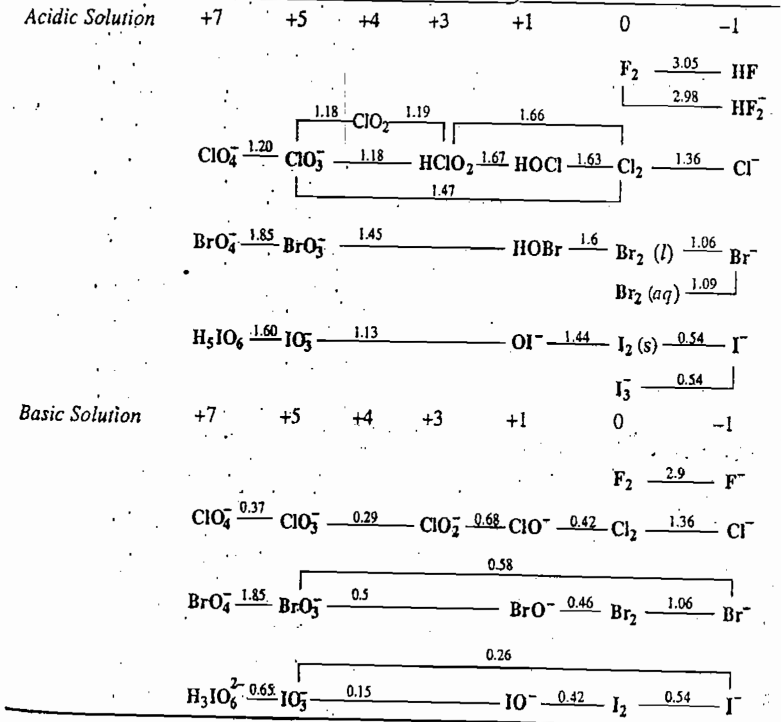


Fig. 24.5
Oxidation state-free energy diagram of the halogens.

The decreasing oxidizing power of the halogens from fluorine to iodine has already been mentioned in the last section. Redox behaviour of other oxidation states may be compared from the following aqueous reduction potentials.

TABLE 24.7

Standard aqueous reduction potentials (volt) of the halogens



Acidic Solution +7 +5 +4 +3 +1 0 –1

$$F_2 \xrightarrow{3.05} HF \qquad F_2 \xrightarrow{2.98} HF_2^-$$

$$ClO_4^- \xrightarrow{1.20} ClO_3^- \xrightarrow{1.18} HClO_2 \xrightarrow{1.67} HOCl \xrightarrow{1.63} Cl_2 \xrightarrow{1.36} Cl^-$$

$$ClO_3^- \xrightarrow{1.18} ClO_2 \xrightarrow{1.19} HClO_2 \qquad HClO_2 \xrightarrow{1.66} Cl_2 \qquad ClO_3^- \xrightarrow{1.47} Cl_2$$

$$BrO_4^- \xrightarrow{1.85} BrO_3^- \xrightarrow{1.45} HOBr \xrightarrow{1.6} Br_2\,(l) \xrightarrow{1.06} Br^- \qquad Br_2\,(aq) \xrightarrow{1.09} Br^-$$

$$H_5IO_6 \xrightarrow{1.60} IO_3^- \xrightarrow{1.13} OI^- \xrightarrow{1.44} I_2\,(s) \xrightarrow{0.54} I^- \qquad I_3^- \xrightarrow{0.54} I^-$$

Basic Solution +7 +5 +4 +3 +1 0 –1

$$F_2 \xrightarrow{2.9} F^-$$

$$ClO_4^- \xrightarrow{0.37} ClO_3^- \xrightarrow{0.29} ClO_2^- \xrightarrow{0.68} ClO^- \xrightarrow{0.42} Cl_2 \xrightarrow{1.36} Cl^-$$

$$BrO_4^- \xrightarrow{1.85} BrO_3^- \xrightarrow{0.5} BrO^- \xrightarrow{0.46} Br_2 \xrightarrow{1.06} Br^- \qquad BrO_3^- \xrightarrow{0.58} Br^-$$

$$H_3IO_6^{2-} \xrightarrow{0.65} IO_3^- \xrightarrow{0.15} IO^- \xrightarrow{0.42} I_2 \xrightarrow{0.54} I^- \qquad IO_3^- \xrightarrow{0.26} I^-$$

As discussed in Fig. 9.6, a species may be expected to be unstable with respect to disproprotionation (to two neighbouring oxidation states) when it lies (in the Frost diagram) above the line joining two neighbouring oxidation states. It appears from Fig. 24.4 that many halogen containing species are susceptible to disproportionation.

We also mentioned (Ch. 9) that the steeper the line joining any two neighbours in a Frost diagram, the stronger will be the oxidizing power of the redox couple. From the Frost diagrams of halogens, it appears that the halogen elements as well as their positive oxidation states are potentially oxidizing in nature.

It is also evident from the diagram that the oxidizing power of the oxoanions is greatly reduced in basic solution (less steep slopes). Thus, for the ClO_4^- ion,

$$pH = 0 \qquad ClO_4^- + 2H^+ + 2e \rightleftharpoons ClO_3^- + H_2O. \qquad E^\circ = 1.2\ V$$

$$pH = 14 \qquad ClO_4^- + H_2O + 2e \rightleftharpoons ClO_3^- + 2OH^- \qquad E^\circ = 0.37\ V$$

Apart from these thermodynamic considerations of the redox behaviour, rate factors appear to be equally important in guiding the ultimate behaviour of halogens and their oxoanions. These will be discussed in connection with the oxoanions.

Here we summarize the redox behaviour of halogens from thermodyanamic considerations.

(i) Oxidation states 0, +1 and +3 of the halogens (except fluorine) are expected to disproportionate in both acidic and basic media.

(ii) F_2 and Cl_2 have the thermodynamic potentiality to oxidize water to dioxygen (Section 9.5.1). F_2 is expected to cause oxidation more easily.

Oxidation State 0

$$X_2\,(aq) + 2OH^- \rightleftharpoons XO^- + X^- + H_2O$$

$$K = 7.5 \times 10^{15}\ (X = Cl);\ 2 \times 10^8\ (X = Br);\ 30\ (X = I)$$

In acid medium, the disproportionation is shifted largely to left, as exemplified by chlorine

$$Cl_2\,(aq) + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad K = 3.9 \times 10^{-4}$$

The equilibrium constants for Br_2 and I_2 are even less and both elements dissolve unchanged in water. The reaction with chlorine is very fast. Oxidation by chlorine takes place by both Cl_2 and HOCl. Usually HOCl is a more facile oxidizing agent than Cl_2.

HOF has been isolated and chracterized (Appleman) by reacting F_2 with ice at −40°C:

$$F_2\,(g) + H_2O\,(s) = HOF\,(g) + HF\,(g)$$

Oxidation State I

The representative equation may be written with chlorine :

$$3ClO^-\,(aq) \rightleftharpoons ClO_3^- + 2Cl^-. \qquad K = 1.5 \times 10^{27}$$

The reaction is slow at room temperature but becomes rapid on heating; it is used in the manufacture of chlorates (see later). BrO^- disproportionates at a much faster rate; for IO^-, the process is so rapid that it can be detected only as a reaction intermediate.

Oxidation State III

ClO_2^- and BrO_2^- disproportionate slowly in basic solution

$$2ClO_2^- \rightleftharpoons OCl^- + ClO_3^-$$

$HClO_2$ and $HBrO_2$ disproportionate rapidly.

$$2HClO_2\,(aq) = H^+ + HOCl\,(aq) + ClO_3^-\,(aq)$$

HIO_2 has been only recently identified as a transient species in aqueous solution.

Oxidation state V

The chlorate ion undergoes slow disproportionation in both acid and basic media

$$4ClO_3^-\,(aq) \rightleftharpoons 3ClO_4^-\,(aq) + Cl^-\,(aq) \qquad K = 1.4 \times 10^{25}$$

Bromates and iodates are thermodynamically unstable with respect to disproportionation.

Oxidation state VII

Both ClO_4^- and IO_4^- ions are well known but BrO_4^- has been discovered only in the late 1960s.

$$BrO_3^-\,(aq) + F_2\,(g) + 2OH^-\,(aq) \longrightarrow BrO_4^-\,(aq) + 2F^-\,(aq) + H_2O.$$

BrO_4^- is the strongest oxidizing agent in this oxidation state. As the ion can undergo facile electron transfer, its reduction is faster than that of ClO_4^-. In dilute acid solution, reduction of periodates appears to be the fastest.

Differences of fluorine from other halogens

Causes

We have already mentioned how fluorine differs remarkably from the remaining halogens. These may be summarized as follows :

(i) Small size of the fluorine atom and the fluoride ion (Table 24.4).
(ii) Highest electronegativity among all elements.
(iii) Low bond dissociation energy of F_2 (Table 24.4).
(iv) High bond energy of any element-fluorine bond (Table 24.6).
(v) Restriction of the valence shell to octet.

Consequences

(i) The low bond dissociation energy of F_2 and the small size of the F^- ion promote the formation of ionic fluorides, as may be appreciated from any Born-Haber cycle; the small size of the F^- ion ensures higher lattice energy and higher coordination number. Small size also results in a high negative enthalpy of hydration for the fluoride ion but where lattice energy is the principal determining factor, the fluorides are least soluble among all halides, as in LiF and CaF_2 (Chapter 17 and 18).

(ii) The small size of the fluorine atom makes it resistant to polarization — the electron cloud in molecular fluorine compounds are hard to deform, resulting in weak van der Waals' or London dispersion forces in such molecules. Consequently, molecular fluorides are volatile and low-melting, for example the fluorocarbons.

(iii) The low bond dissociation energy of fluorine results mainly from repulsion between the unshared pairs of electrons on two atoms. When fluorine forms a bond to an atom of another element with no unshared pair of electrons, the bond is always much stronger than the bonds formed by other halogens. The same situation arises when the other atom is sufficiently large so that the repulsion is negligible. Thus, reactions of fluorine are expected to be highly exothermic in nature and this is the cause of the vigorous reactivity of fluorine.

(iv) The high electronegativity (and small size) of fluorine gives rise to strong hydrogen bonding in hydrogen fluoride. In fact, the bifluoride ion has two equal H–F distances which has been explained on the basis of 3-center m.o.-s. Electronegativity is also the principal reason for stronger acidity of fluorine substituted carboxylic acids (e.g. CF_3COOH) and the lack of basic character in NF_3 and $(CF_3)_3N$. The reversal of electron displacement in covalent bonds has many other impacts in chemistry, for example, the difference in hydrolytic products of CH_3I and CF_3I, and the deactivating effect of the CF_3 group in electrophilic aromatic substitution.

(v) The octet limitation in the valence shell of fluorine is shown in the absence of compounds analogous to ClF_3, $HClO_3$ or $HClO_4$ or the oxides like Cl_2O_7. In many polymeric fluorides, fluorine may form M—F—M bridge bonds of 3-center-2-electron type which are longer than terminal 2-center-2 electron M—F bonds.

24.3 PRINCIPAL COMPOUNDS

24.3.1 Halides

Almost all elements in the periodic table except He, Ne and Ar form binary compounds with some or all of the halogens which give rise to a wide range of halides. The compounds may be simple ionic or molecular; several halides with polymeric structures are also known. In addition to such binary halides, oxohalides, hydroxohalides and complex halides are formed by several elements

We begin a brief survey of the various methods for the preparation of anhydrous halides.

Preparation of anhydrous' halides

(i) **Reaction with halogens**	$2Fe + 3F_2 = 2FeF_3$
F_2 often needs dilution, with, say N_2.	$Fe + I_2 = FeI_2$
Higher temperatures for heavier halogens.	$2CoCl_2 + 3F_2 = 2CoF_3 + 2Cl_2$
Solvents like THF favour reactions, but the products are solvated.	
(ii) **Reacting metal with anhydrous HF(*g*) or HCl(*g*)**	$2Al + 6HCl = 2AlCl_3 + 3H_2$
	$Cr + 2HF = CrF_2$
(iii) **Heating an oxide with carbon and halogen**	$TiO_2 + 2C + 2Cl_2 = TiCl_4 + 2CO$.
(iv) **Heating with halogen compounds.**	$W + 2ClF_3 = WF_6 + Cl_2$
	$Sc_2O_3 + 6NH_4Cl$
	$= 2ScCl_3 + 6NH_3 + 3H_2O$ (300°C)
	$3UO_2 + 4BrF_3 = 3UF_4 + 3BrO_2 + \frac{1}{2}Br_2$
(v) **Halogen exchange**	$PCl_3 + SbF_3 = PF_3 + SbCl_3$
	$TiCl_4 + 4KI = TiI_4 + 4KCl$ (in acetone)
(vi) **Dehydration of hydrated halides.**	$VCl_3.6H_2O + 6SOCl_2$
(Heating of hydrated halides often form oxohalides or oxides :	$= VCl_3 + 12HCl + 6SO_2$ (distill)
$MgCl_2, 6H_2O = Mg(OH)Cl + HCl + 5H_2O$	$CrF_3.6H_2O + 6CH_3C(OCH_3)_2CH_3^*$
(200°C)	$= CrF_3 + 12CH_3OH + 6CH_3COCH_3$
$Mg(OH)Cl = MgO + HCl$ (600°C)	*2,2-dimethoxypropane
$2CrCl_3, 6H_2O = Cr_2O_3 + 6HCl + 9H_2O$)	$FeCl_3.6H_2O + 6SOCl_2$
	$= FeCl_3 + 6SO_2 + 12HCl$

Covalent Halides (molecular halides)

Molecular halides are formed by hydrogen, most of the electronegative elements and metals in high oxidation state. We have already discussed many of them in the previous chapters, including polymeric halides (like Teflon) and halides with extended structure like TeF_4.

Most metal halides have predominantly ionic character but partial covalence develops depending upon charge and oxidation state of the metal as well as increasing size of the halogen. Thus

(i) When the energy available for the formation of an ionic lattice is insufficient, many metals in high oxidation states fail to form ionic halides, even with fluorine. Compounds like UF_6, WF_6 or OsF_6 are gases, volatile liquids or solids comparable to many covalent fluorides.

(ii) When a metal forms halides in various oxidation states, the halides in higher oxidation state tend to be more covalent e.g. $FeCl_3$ vs $FeCl_2$ or $PbCl_4$ vs $PbCl_2$. UF_4 is a solid of low volatility but UF_6 is a gas at ordinary temperature.

(iii) For halides of general formula MX_n, if n is small and M is relatively large, the halides are often essentially ionic. If n is large, the halide is likely to be molecular. Thus in the series NaF, MgF_2, AlF_3 and SiF_4 or KCl, $CaCl_2$, $ScCl_3$ and $TiCl_4$, the first three members are not volatile but SiF_4 is a gas and $TiCl_4$ is a molecular solid which can be easily vaporized. Of course, there lies the danger of quick conclusions from such oversimplified generalizations since the bulk physical properties are determined, in addition to ionicity of bonds, by mode of packing and related factors. Thus AlF_3 forms a giant molecule with Al–F bonds which can be described as intermediate between ionic and covalent. Aluminium chloride is also a low melting solid (193°C) with an extended structure which melts to a molecular liquid (Ch–20). The bonding in the solid is again intermediate between "ionic" and "covalent" extremes.

The enthalpy terms in the formation of a covalent fluoride MF_n of an element M are as follows :

$$\begin{tikzcd}
 & M \arrow[r, "\Delta H_1"] & M\,(g) \arrow[r, "\Delta H_2"] & M\ \text{(valence state)} \arrow[dr, "-nE_{M-F}"] & \\
MF_n & \text{Standard State} \arrow[l, "\Delta H_f"'] \arrow[u, dash] \arrow[d, dash] & & & MF_n \\
 & \frac{1}{2}n\,F_2\,(g) \arrow[rr, "\frac{n}{2}D_{F_2}"] & & n\,F\,(g) \arrow[ur] &
\end{tikzcd}$$

ΔH_1, ΔH_2 : Enthalpies of atomization and excitation; ΔH_f : Enthalpy of formation; D_{F_2} : bond dissociation energy of difluorine; E_{M-F} = M – F bond energy.

For a stable fluoride to be formed, we want a negative ΔH_f value (exothermic compound) :

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \frac{n}{2} D_{F_2} - nE_{M-F}$$

For ΔH_f to be negative, we require

$$nE_{M-F} > \Delta H_1 + \Delta H_2 + \frac{n}{2} D_{F_2}$$

Thus high M–F bond energy and low dissociation energy of fluorine will favour the formation of a fluoride.

Hydrogen Halides

The hydrogen halides or the halogen hydracids have been known to the chemists since antiquity. These gases may be conveniently prepared by reactions of the following type :

$CaF_2 + H_2SO_4\,(conc) = CaSO_4 + 2HF$ (heat)

$NaCl + H_2SO_4\,(conc) = NaHSO_4 + HCl$ (heat)

$P_4 + 2X_2 + 12H_2O = 4H_3PO_3 + 12HX$ (heat; X = Br, I).

Industrial production and uses of these acids are discussed later.

Only hydrogen fluoride is a low boiling liquid associated through H-bonding. Others are gases, and all are colourless.

TABLE 24.8

Physical Properties of HX

	HF	HCl	HBr	HI
m.p./°C	−83	−115	−88.6	−51
b.p./°C	19.5	−84	−67	−35
Density (g cm^{-3}; near m.p.)	1.23	1.19	2.60	2.85
Dielectric constant	84 (0°)	9.28 (−95°)	7.0 (−85°)	3.39 (−50°)
Dipole moment (D)	1.74	1.07	0.79	0.38
ΔH_f^0 (kJ mol^{-1})	−271.1	−92.3	−36.4	26.48
d_{H-X}, pm	92	127	141	161
Bond diss. enthalpy, kJ mol^{-1}	574	428	362.5	295

Extensive H-bonding results in a low-vapour pressure and hence relatively high boiling point of HF. However, there is no 3-dimensional network of H-bonding as in H_2O, H_2SO_4 or H_3PO_4, and the viscosity of HF (0.26 cp at 0°C) is rather low. In spite of stronger H-bonding, the boiling point of HF is lower than that of water as the vapour consists essentially of cyclic $(HF)_6$ - i.e., the number of H-bonds broken at the time of boiling is less. Crystalline HF is polymeric with a planar zig-zag chain structure (Fig. 7.42, Ch. 7).

All the acids are freely soluble in water. Crystalline hydrates $H_2O.nHF$ ($n = 1,2,4$) show the presence of H_3O^+ ion in tight H-bonded association with F^-, HF_2^- or $H_3F_4^-$ ions. The acidity of the hydracids has been discussed in detail in section 10.4.2. High H–F bond strength makes HF a weak acid in dilute aqueous solution:

$$HF + H_2O \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_1\ (298\ K) = 6.7 \times 10^{-4}$$

$$HF + F^- \rightleftharpoons HF_2^- \qquad K_2\ (298\ K) = 3.86$$

The strongly H-bonded HF_2^- and similar species $H_2F_3^-$, $H_3F_4^-$ ions increase with increase in concentration of HF and thus HF behaves as a strong acid in concentrated solution.

HCl, HBr and HI also form a number of crystalline hydrates at low temperatures. Some of these have been studied by X-ray crystallography. $HCl.H_2O$ (m.p. −15°C) is actually $H_3O^+Cl^-$; $HCl.2H_2O$ (mp −25°C) is $H_5O_2^+Cl^-$; $HCl.3H_2O$ (m.p. −70°C) is $[H_5O_2^+Cl^-].H_2O$; $HCl.6H_2O$ (m.p. −70°C) is $[H_9O_4^+Cl^-].2H_2O$. Structures of the hydrated oxonium ions are given in Chapter 17.

Weaker bond dissociation energy (section 10.2.4) makes all three hydracids strong acids in aqueous solution; approximate *pK* values are HCl : −7; HBr : −9, HI : −10.

The HX molecules are covalent though their aqueous solutions conduct electricity owing to extensive ionization. In poorer ionizing solvents like anhydrous acetic acid, the degree of ionization of different HX molecules may be studied by conductance measurement. It is found that the acidity order is HI > HBr > HCl.

HF and its vapours are highly poisonous; they violently attack the skin and form sores. The sores are to be immediately treated with magnesium hydroxide. On inhalation, the vapour causes permanent loss of voice and finally death.

The aqueous solution attacks all metals except the noble ones and evolves hydrogen. It also attacks glass and porcelain. The use of HF in etching glass is based on the reaction

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The acid may be handled in teflon apparatus or if absolutely dry, in copper or stainless steel vacuum lines. Surprisingly, the dry and concentrated acid (>80%) has little corrosive action.

Detection of fluorides

Fluorides are detected by heating the sample with concentrated H_2SO_4 and sand in a dry glass test tube when bubbles of SiF_4 rise along the walls of the test tube, giving it an oily appearance. A drop of water held in the fume turns opaque due to the formation of insoluble silicic acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$3\ SiF_4 + 4H_2O = 2H_2SiF_6 + Si\ (OH)_4$$

Soluble fluorides in aqueous solution give a white precipitate with barium chloride solution, insoluble in concentrated HCl.

HF vapour is absorbed by KF (or NaF) forming bifluoride. KHF_2 is known as *Fremy's salt*.

$$KF + HF = KHF_2$$

Liquid HF as a solvent

Liquid hydrogen fluoride may be considered a good ionizing solvent comparable with water in its dielectric constant and dipole moment :

	HF	H_2O
Dielectric constant	84 (0°C)	78.5 (25°C)
Dipole moment	1.74 D	1.84 D

However, extreme chemical reactivity converts most salts into fluorides only a few of which are soluble.

(a) Alkali, alkaline earth, silver and Thallium(I) fluorides dissolve to form acid fluorides :

$$KF + HF = KHF_2.$$

The solutions are highly conducting. Solubility increases with increasing size of the metal ion and decreases with increase in ionic charge : TlF is more than 7000 times as soluble as TlF_3; AgF is more than 150 times as soluble as AgF_2.

Fluoroborates and perchlorates also dissolve producing the same ions as in water.

(b) *Solvolysis* usually occurs with other inorganic solutes. Chlorides, bromides and iodides readily evolve HX and give the corresponding fluorides.

Alkali sulphates and periodates give sufficiently stable anions and may result in precipitation reactions :

$$Na_2SO_4 + 2AgF = Ag_2SO_4 + 2NaF.$$
$$KIO_4 + AgF = AgIO_4 + KF.$$

The number of ionic species may vary with solvolysis at different temperatures, e.g.

$$K_2SO_4 + HF = 2K^+ + 2HF_2^- + H_2SO_4\ (-80°C)$$

Total number of solute particles from cryoscopic study is shown to be 5. At 0°C, this increases to 6 by the additional reaction :

$$H_2SO_4 + 3HF = H_3O^+ + HSO_3F + HF_2^-$$

The presence of HSO_3F at 0° has been shown by ^{19}F nmr study.

Solvolysis of KNO_3 similarly produces NO_2^+ and HF_2^- :

$$KNO_3 + 6HF \longrightarrow K^+ + NO_2^+ + H_3O^+ + 3HF_2^-$$

(c) Since pure HF is a very strong acid, it protonates a number of organic and inorganic compounds, including HNO_3 :

$$HNO_3 + 2HF \rightleftharpoons H_2NO_3^+ + HF_2^-$$

$$H_2O + 2HF \rightleftharpoons H_3O^+ + HF_2^-$$

$$RCOOH + 2HF \rightleftharpoons RCOOH_2^+ + HF_2^-$$

$$RCH_2OH + 2HF \rightleftharpoons RCH_2OH_2^+ + HF_2^-$$

(d) Fluoride ion acceptors act as Lewis acids in HF

$$AsF_5 + 2HF \rightleftharpoons H_2F^+AsF_6^-$$

SbF_5 and BF_3 behave similarly, BF_3 giving BF_4^-.

Fluoride ion donors like XeF_6, SF_4, ClF_3 etc. behave as Lewis bases in anhydrous HF.

Neutralization may be allowed to take place between a Lewis acid and a Lewis base in anhydrous HF :

$$BrF_2^+HF_2^- + H_2F^+AsF_6^- \longrightarrow BrF_2^+AsF_6^- + 3HF$$

(e) The F_2 — F^- reduction potential in HF is very high :

$$\frac{1}{2}F_2 + e \rightleftharpoons F^- \qquad E^\circ = 2.71\ V\ (0°C)$$

This enables preparation of several fluoro compounds by electrolysis in HF. Thus electrolysis of CH_3COOH produces CF_3COOH; NH_4F may be electrolyzed to prepare NFH_2, NF_2H and NF_3; and electrolysis of $NaClO_4$ gives ClO_3F.

Other molecular halides

Molecular halides are known for most elements in periodic groups 13(III) to 16(VI) and also for some heavy elements, for example tungsten (WF_6) and uranium (UF_6). Molecular fluorides are often formed exothermically by direct reaction — a consequence of the high energy of the bonds formed (plus the low F—F bond dissociation energy). Exception occurs when the combining element itself has a high bond dissociation energy as for example N_2 or O_2. NF_3 is exothermic ($\Delta H \simeq -109$ kJ mol^{-1}) but it is better made indirectly. Formation of heavier halides, particularly iodides, becomes energetically unfavourable in many cases owing to weakness of the bonds formed. We recall that NCl_3 is endothermic and NI_3 is an explosive solid. For oxygen, compounds of the heavier halogens are more appropriately classed as oxides.

Fluorine being highly electronegative, the bonds in fluorides are polar and we have noted the effect of fluorine substitution in several compounds, for example,

(i) change in dipole moment and basic character in NF_3.

(ii) lack of reactivity in fluorocarbons, SF_6 etc. We have also noted that such reluctance is kinetic rather than thermodynamic.

(iii) attainment of highest coordination number by certain elements, e.g., SF_6.

Q. 24.2 *Among the molecular halides, fluorides of both metals and nonmetals are usually gases or volatile liquids. Comment. When do you expect a deviation from this trend?*

Hint : Polarizability of F is very low. Weak van der Waals forces are the only intermolecular interaction, no suitable outer orbital being available for other types of attraction.

Deviations are expected in polymeric compounds with M—F—M bridges (see later).

Among the very few metal fluorides which are molecular, the importance of UF_6 in the separation of uranium isotopes by gaseous diffusion is noteworthy.

As one moves to heavier halogens, decreasing bond polarity as well as bond strength may change the nature of bonding. Some elements forming ionic fluorides form chlorides etc. which are essentially covalent e.g., HgF_2 vs. $HgCl_2$. In general, the molecular halides undergo ready hydrolysis whenever nucleophilic attack by water is favourable.

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

We have already noted the reluctance of CCl_4, CF_4 or SF_6 toward such hydrolysis, the reason being kinetic. SeF_6 and TeF_6 are hydrolyzed at room temperature as the central elements can expand their valence shell to welcome the nucleophilic attack by water.

Q. 24.3 *What species are present in solutions of the following in anhydrous HF?*

(a) H_2SO_4; (b) $HClO_4$; (c) HNO_3; (d) BF_3.

Hint : (a) $HSO_3F + H_2O$; (b) $H_2F^+ClO_4^-$; (c) $H_2NO_3^+F^-$; (d) $H_2F^+BF_4^-$.

Q. 24.4 *SbF_5 dissolves readily in anhydrous HF producing heat. The solution dissolves copper and readily reacts with AgF forming a clear solution. Give equations.*

Hint : $SbF_5 + HF \rightleftharpoons HSbF_6$ *(acid)*

$Cu + 2HSbF_6 = Cu(SbF_6)_2 + H_2$

$HSbF_6 + AgF$ *(base)* $= Ag(SbF_6) + HF$

Q. 24.5 *The following equilibria exist in aqueous solutions of HF :*

$$HF \rightleftharpoons H^+ + F^-;\ HF + F^- \rightleftharpoons HF_2^-.$$

Given $K_1 = 7 \times 10^{-4}$ mol liter^{-1} and $K_2 = 5$ liter mol^{-1}, calculate the concentrations of different species present in (a) 1M and (b) 0.1 M solutions of HF.

Answer : Let $[H^+] = x$, $[F^-] = y$, $[HF_2^-] = z$

(a) : 1*M solution* : $[HF] = 1 - x - z$

Let us first neglect x and z with respect to 1. This gives $[HF] = 1$.

$$\therefore K_1 = \frac{[H^+][F^-]}{[HF]} = xy = 7 \times 10^{-4};$$

$$K_2 = \frac{[HF_2^-]}{[HF][F^-]} = \frac{z}{y} = 5 \text{ or, } z = 5y.$$

By electroneutrality principle,

$$[H^+] = [F^-] + [HF_2^-]$$

or, $x = y + z = 6y$

$\therefore\ 6y^2 = 7 \times 10^{-4}$ or, $y = 1.08 \times 10^{-2}$

Hence, $x = 6.48 \times 10^{-2}$; $z = 5.4 \times 10^{-2}$

Now we may use these values of x, y and z to obtain further refined values :

$$[HF] = 1 - 0.0548 - 0.054 = 0.8812$$

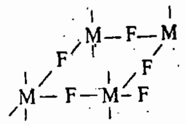
Proceeding as before, one gets

$$x = 0.0578,\ y = 0.0107,\ z = 0.0471 \text{ mol lit}^{-1}.$$

Other properties of molecular halides have been discussed in relevant groups.

Bridged Halides

Halogens may frequently form bridges between two atoms e.g. in gaseous Al_2Cl_6 dimer and polymeric $BeCl_2$. Fluoride bridges are also known, as in glassy BeF_2 which has infinite ...F...Be...F...Be chains with bent bridges (~ 125°). Linear M—F—M bridge is found in F-bridged cyclic tetramers NbF_5 and TaF_5 (24-III). VF_5 forms an infinite chain polymer. The preference of fluorine for linear bridges may be partly due to the fact that the smaller fluorine atom gives rise to greater M—M repulsion in a bent bridge. The linear bridges may also have some π-character.



24-III

Bridges by other halogens may be both linear and bent. Several halo complexes of Rh, Pd, Cu etc. transition metals are known to contain halogen bridges.

In the valence bond formalism, the bridges may be considered to have one normal covalent bond to the halogen and a coordinate covalent bond from a lone pair of electrons on the halogen. A three centre four electron molecular orbital description is satisfactory in most cases.

The halogen bridges are easily cleaved by strong Lewis bases like pyridine or tertiary phosphines.

Ionic Halides

The formation of ionic halides is primarily controlled by the lattice energy of the compound concerned. This may be readily understood with reference to a Born-Haber cycle for the formation of a halide from the elements (P 535). The heats of formation of the halide ions from the gaseous X_2 molecules

$$\tfrac{1}{2}X_2\,(g) + e \longrightarrow X^-\,(g)$$

vary little from one halogen to another (Table 24.9) and hence play only a minor role. The small size of the F^- ion makes it very suitable to form ionic lattices.

TABLE 24.9

Heats of formation and hydration energies of X^- ions (kJ mol^{-1})

	ΔH° (formation) $\tfrac{1}{2}X_2\,(g) \longrightarrow X^-\,(g)$	ΔH° (hydration) $X^-\,(g) \longrightarrow X^-\,(aq)$
F^-	–260	–506
Cl^-	–233	–369
Br^-	–234	–335
I^-	–226	–293

The radius of the fluoride ion (1.19 A°) is comparable to that of the oxide ion (1.26 A°) and we find that fluorides and oxides with similar stoichiometry often possess similar structure e.g. CaO and NaF (NaCl type). However, the oxides have a higher lattice evergy than the fluorides due to higher charge factor (when inter-ionic distances are similar) and usually have higher melting point and lower solubility (MgO vs NaF).

The solubility trend among ionic halides has been discussed in Chapters 6, 18 and 19. While the solubility of fluorides in water is favoured by large hydration enthalpy (Table 24.9), high lattice energy stands against. Fluorides of Li, Ca, Sr and Ba are sparingly soluble in water, while those of the lanthanide and actinide elements (+3 and +4 oxidation states) are insoluble. We have also discussed the solubility trend among the halides and the different roles played by lattice energy and hydration energy with change in ionic radii (Ch. 6). In general, solubility varies as

(a)	iodide > bromide > chloride > fluoride	when all four halides are essentially ionic. (halides of alkali and alkaline earth metals and lanthanum).
(b)	fluoride > chloride > bromide > iodide	when covalence dominates as in the halides of Ag (I) and Hg (I).
(c)	CsF > RbF > KF > NaF > LiF	Lattice energy increases more rapidly than hydration energy of the ions.
(d)	LiI > NaI > KI > RbI > CsI	Lattice energy decreases less rapidly than hydration energy.

PbClF is sparingly soluble in water.

The ionic halides have a wide range of crystal structure. The crystal structures of NaCl and CsCl have become two representative structures which are adopted by a large number of monohalides, including AgF, AgCl, AgBr, TlCl and TlBr which are likely to involve some covalent interaction. CuCl, CuBr, CuI and AgI adopt wurtzite structure.

While most difluorides have the CaF_2 or rutile structure, most dichlorides and almost all dibromides and diiodides have layer structures represented by $CdCl_2$ or CdI_2.

Q. 24.6 *In absence of any solvent, halogen exchange reactions of the type*

$$\rangle C{-}Cl + MF \longrightarrow \rangle C{-}F + MCl$$

are best carried out by CsF. Comment.

Hint : Consider a relevant Born-Haber cycle in terms of the following steps :

(a) cleavage of the C—Cl bond and conversion of Cl (g) to Cl^- (g).

(b) rupture of the MF lattice into $M^+(g)$ and $F^-(g)$; conversion of F^- (g) to F(g).

(c) formation of C—F bond and MCl lattice.

The main contributors to the enthalpy term are thus

(a) C—Cl bond energy and electron attachment enthalpy of Cl.
(b) Lattice energy of MF and electron attachment enthalpy of F.
(c) C—F bond energy and lattice energy of MCl.

If other things are kept constant, the overall enthalpy will be determined by the difference of lattice energy between MF and MCl. Since the F^- ion is smaller, fluorides will have higher lattice energy, which means that we have to supply more energy to split the lattice of MF and less energy is released in the formation of MCl. The less this difference, the greater will be the amount of heat released and the more favourable (thermodynamically) will be the process.

Now, lattice energy (U) depends inversely on interionic distance ; (for ions of same charge and structure)

$$U_{MF} \propto \frac{1}{r_{M^+} + r_{F^-}} ; \quad U_{MCl} \propto \frac{1}{r_{M^+} + r_{Cl^-}}$$

The difference between the U-values will be minimum when r_{M^+} is as large as practicable for the same crystal type. Hence among the alkali metal fluorides, CsF will be the best choice.

Q. 24.7 *Comment on the following reactions :*

$AgX + \frac{1}{2}X_2 \longrightarrow AgX_2$ *goes only for X = F*

$CuX_2 \longrightarrow CuX + \frac{1}{2}X_2$ *goes only for X = I at room temperature.*

Assume all the halides to be completely ionic and the same Madelung constant for all X (= F, Cl, Br, I).

Hint : For processes $MX\,(s) + \frac{1}{2}X_2\,(g) \longrightarrow MX_2\,(s)$, we have to consider the additional enthalpy-contribution from (i) second ionization energy of M and (ii) difference in Madelung constant and lattice energies for MX and MX_2 crystals.

If we vary X keeping M unchanged, the lattice energy will be related to interionic distance as

$$U_{MX_2} \propto \frac{A_2}{r_{M^{2+}} + r_{X^-}} ; \quad U_{MX} \propto \frac{A_1}{r_{M^+} + r_{X^-}} . \quad A_1,\ A_2 \text{: corresponding Madelung constants.}$$

Neglecting other factors, it may be concluded that the main contribution to the enthalpy of the oxidative halogenation will come from the difference $\left(U_{MX_2} - U_{MX}\right)$. Since A_2 is greater than A_1, the value of U_{MX_2} will be highest when r_{X^-} is smallest, implying the most exothermic process. This is the case with AgX when X = F^-.

On the other hand, a large r_X makes the difference in lattice energy smaller, implying a process which will be less exothermic or even endothermic. In fact, the reverse process occurs with CuI_2 where the loss of additional lattice energy (by forming CuI against CuI_2) is more than compensated by the saving on second ionization energy of Cu.

Q. 24.8 *What are the structural types of the following chlorides :* Al_2Cl_6 (g); $AsCl_3$; $BeCl_2$; $CaCl_2$; $CdCl_2$; $CrCl_3$; CsCl; $PdCl_2$; SCl_2; $SiCl_4$; UCl_3.

Hint : (a) molecular, essentially covalent : Al_2Cl_6 (g), $AsCl_3$, $SiCl_4$, SCl_2.
(b) chains : $PdCl_2$, $BeCl_2$ (c) layers : $CrCl_3$, $CdCl_2$
(d) essentially ionic : rest.

Q. 24.9 *How do the structures of the following compounds change on passing from solid to the vapour : (a) CuCl (b) $FeCl_3$ (c) SnI_4?*

Ans. : CuCl (c) : Zinc blende structure; CuCl (g) cyclic trimer Cu_3Cl_3 at 450°C.
$FeCl_3$ (c) : layer structure with octahedral Fe; $FeCl_3$ (g) : dimers like Al_2Cl_6 in equilibrium with monomers.
SnI_4 solid and gas : tetrahedral molecules.

[Sec. 24.3.2 *H-bonded complexes*]

Halide ions as ligands

The halide ions can function as ligands, some common examples being $[SiF_6]^{2-}$, $FeCl_4^-$ and HgI_4^{2-} etc. Generally for a given central atom, stability of the halo complexes decreases as F>Cl>Br>I, but the reverse trend is also known. Charge-size ratio of the metal ion and polarizability of the halide ion seem to control the trend.

The fluoro complexes often show a higher coordination number : e.g., FeF_6^{3-} vs $FeCl_4^-$; CoF_6^{3-} vs $CoCl_4^{2-}$ and so on. This is ascribed mainly to steric factors, though this should not be taken as the only reason for such observations.

Many fluorocomplexes are extensively hydrolyzed, particularly when the oxidation state is high. The iodo complexes are often unstable in aqueous solution where they dissociate. In non-aqueous solvents like liquid HI or CH_3NO_2, it is possible to prepare iodocomplexes of even oxidizing metal cations by reactions like

$$[MCl_6]^{(6-n)-} + 6HI = [MI_6]^{(6-n)-} + 6HCl.$$

The higher free energy of formation of HCl over HI drives the equilibrium to right, aided by the greater volatility of HCl.

24.3.2 H-bonded Complex of Halide ions

The halide ions are able to establish hydrogen bonds with some protonic species. The hydrogen dihalide ions, $(X—H—X)^-$, formed by the hydrogen halides HX with excess X^- ions are the simplest representatives of this class. Though known most commonly for the F^- ion, other halide ions also form such complexes with stability decreasing in the order

$$F^- \gg Cl^- > Br^- > I^-$$

The anions containing heavier halide ions are stabilized by large cations which offer minium loss in lattice energy :

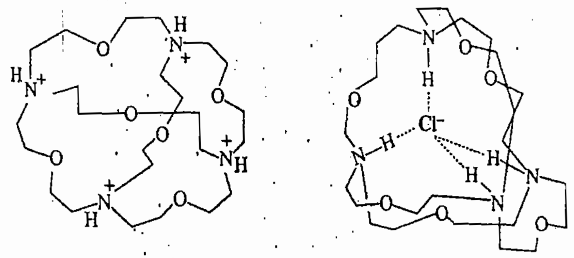
$$KF + HF\,(l) \longrightarrow K^+\,[F—H—F]^-$$

$$NMe_4X + HX\,(l) \longrightarrow NMe_4^+\,[X—H—X]^- \quad (X = Cl, Br)$$

$$(n-Bu)_4NI + HI\,(g) \xrightarrow{CH_2Cl_2} (n-Bu)_4N^+\ (I—H—I)^-$$

$$NMe_4F + HX\,(l) \longrightarrow NMe_4^+\,[F—H—X]^- \quad (X = Cl, Br, I)$$

Halide ions may also be encapsulated by protonated macropolycyclic ligands of the type H_4L^{4+} (Fig. 24.6). Thus, one of the four chloride ions in the salt hydrate $H_4L^{4+}(Cl^-)_4.7H_2O$ is hydrogen-bonded with the protons of the four quaternary nitrogen atoms :



(a) (b)

Fig. 24.6 The macropolycyclic ligand H_4L^{4+} (a) and the complex cation $[ClLH_4]^{3+}$ (b).

The pyramidal cation $[(pyH)_3Cl]^{2+}$ (Fig. 24.7) also contains a chloride ion H-bonded to three protonated pyridine rings.

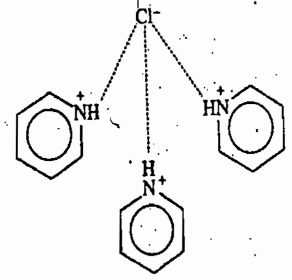


Fig. 24.7

The $[(pyH)_3Cl]^{2+}$ ion in $[(pyH)_3Cl]$ $(AlCl_4)_2$.

24.3.3 Oxides

The binary compounds of oxygen and fluorine have been discussed under oxygen fluorides (Chapter 23). Oxides of other halogens (Table 24.10) are unstable compounds, the higher oxides being rather more stable than the lower ones. Stability is greatest for the oxides of iodine, then chlorine, while the oxides of bromine are the least stable.

TABLE 24.10

Oxides of the halogens

	Nature	Preparation
Cl_2O b.p. −4°C m.p. −116°C	Yl-brown gas. Sol. in water. Bent (110°)	$2Cl_2 + 2HgO = Cl_2O + HgO.HgCl_2$
Cl_2O_3	Explodes below 0°C.	
ClO_2 b.p. −10°C m.p. −6°C	Yl, paramagnetic gas. Highly explosive; sol. in water; hydrolyzes to chlorite and chlorate (disproportionates) : $2ClO_2 + 2OH^- \longrightarrow ClO_3^- + ClO_2^- + H_2O$; Bent (117.6°)	$2KClO_3 + 2H_2C_2O_4 = 2ClO_2 + 2CO_2 + K_2C_2O_4 + 2H_2O$ The CO_2 dilutes the gas and makes it non-explosive.
Cl_2O_4	Highly unstable, actually $ClOClO_3$	
Cl_2O_6 m.p. 3.5°C	Red oil soluble in water $Cl_2O_6 + 2OH^- = ClO_3^- + ClO_4^- + H_2O$. Solid : $\overset{+}{ClO_2}\overset{-}{ClO_4}$ Gas : $O_3Cl\text{—}O\text{—}ClO_2$ (bent)	$ClO_2 + O_3$ (0°C)
Cl_2O_7 b.p. 82°C m.p. −91.5°C	Colourless liq. Water and OH^- gives ClO_4^-. $Cl_2O_7 + H_2O = 2HClO_4$. $O_3Cl\text{—}O\text{—}ClO_3$ (bent, 119°).	Dehydration : $2HClO_4 + P_2O_5 = Cl_2O_7 + 2HPO_3$ (at −10°C).
(No stable oxide of bromine at ordinary temperature).		
Br_2O	Dark brown solid below −18°, dec. above −60°. Gives OBr^- with alkali. Bent (symmetrical).	$HgO + Br_2$ or, low temp. decomposition of BrO_2 in vac.
BrO_2	Pale yellow solid unstable above −40°C. Decomp. violent at 0°C. $6BrO_2 + 6OH^- = 5BrO_3^- + Br^- + 3H_2O$	$Br_2 + 4O_3 \longrightarrow 2BrO_2 + 4O_2$ (in CF_3Cl at −78°C)
I_2O_4	Lemon yellow crystal; Decomp. to I_2O_5 above 85°C. $5I_2O_4 = 4I_2O_5 + I_2$ Polymeric I—O chains cross-linked by IO_3 groups. $[IO]^+[IO_3]^-$	Partial hydrolysis of $(IO)_2SO_4$.
I_4O_9	Hygroscopic yl powder. Decomp. to I_2O_5 above 75°C. $2I_4O_9 \longrightarrow 3I_2O_5 + I_2 + \frac{3}{2}O_2$ $I^{III}(I^VO_3)_3$	$I_2 + O_3$
I_2O_5 m 300°C	White, hygr. crystal. Very soluble in water $I_2O_5 + H_2O = 2HIO_3$. Dec. at 300° to $I_2 + O_2$. Ox. agent (H_2S, HCl, CO). $I_2O_5 + 5CO = I_2 + 5CO_2$ O_2IOIO_2 units having IO_3 pyramids sharing one O.	Dehydration of HIO_3 by heating (~240°C)

Oxides of Chlorine

Chlorine monoxide Cl_2O

The brownish yellow gas is formed when dry chlorine gas is passed through a cold tube containing yellow precipitated mercuric oxide. Basic 'mercuric oxide' (brown) remains in the tube.

$$2HgO + 2Cl_2 = HgCl_2.HgO + Cl_2O.$$

Reaction may also be carried out with chlorine dissolved in CCl_4.

The same reaction is used commercially at a higher temperature (~ 300°C); the Cl_2 is diluted wih dry air.

The gas condenses in a freezing mixture to an orange liquid. When heated or sparked, it explodes to the elements. 1*M* solution in CCl_4 may be safely handled.

The gas readily dissolves in water (~140 g per 100 g H_2O at −9.5°C) to form hypochlorous acid.

Cl_2O is a powerful and selective chlorinating agent for organic compounds. It is an oxidizing agent, too.

$$3Cl_2O + 10NH_3 = 2N_2 + 6NH_4Cl + 3H_2O.$$

The molecule is bent (111°) — the Cl-O distance is 1.71 A°. The central oxygen atom may be supposed to use sp^3 hybrid orbitals for bonding (with two lone pairs).

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The gas is mainly used to produce hypochlorites, e.g. $NaClO_2$ or $Ca(OCl)_2$ which are useful bleaching agents. It is also used to make chlorinated solvents.

Chlorine dioxide, ClO_2

The explosive gas is prepared by heating (90°C) potassium chlorate with moist oxalic acid. The liberated CO_2 dilutes the gas which is an advantage.

$$2KClO_3 + 2H_2C_2O_4 = 2ClO_2 + 2CO_2 + K_2C_2O_4 + 2H_2O.$$

Commercially the gas is prepared by reacting sodium chlorate with sulfur dioxide in 4 - 4.5 *M* H_2SO_4 containing a little NaCl (0.05 – 025 *M*) :

$$2NaClO_3 + SO_2 + H_2SO_4 = 2ClO_2 + 2NaHSO_4$$

HCl may also be used as the reducing agent, but this contaminates the product with Cl_2.

Pure ClO_2 is obtained by the reduction of $AgClO_3$ with chlorine :

$$2AgClO_3 + Cl_2 = 2ClO_2 + O_2 + 2AgCl \quad (90°C)$$

The yellowish gas condenses to a deep red liquid (b.p. 11°C) which explodes above –40°C. The gas itself detonates readily when the partial pressure exceeds about 50 mm Hg. It also explodes in contact with reducing agents. Hence the gas is always prepared in situ and diluted with carbon dioxide.

ClO_2 is soluble in water, the dark green solutions up to $8gL^{-1}$ are stable in the dark. In presence of light, these decompose slowly (HCl and $HClO_3$). Crystalline clathrate hydrates approximately ClO_2, $8H_2O$ (±2) may be obtained by cooling the solution.

ClO_2 dissolves in alkali to form chlorite and chlorate; it is a mixed anhydride

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O.$$

It is a powerful oxidizing and chlorinating agent. Powdered metals in aqueous suspension (Mg, Zn, Ni, Cd and Al) are converted to their chlorites at ordinary temperature :

$$Mg + 2ClO_2 = Mg(ClO_2)_2; \quad Al + 3ClO_2 = Al(ClO_2)_3.$$

Ozone oxidizes ClO_2 to Cl_2O_6 : $2ClO_2 + 2O_3 = Cl_2O_6 + 2O_2$

Alkaline hydrogen peroxide (or Na_2O_2) reacts with ClO_2 to give sodium chlorite which is used as a manufacturing process :

$$2ClO_2 + 2NaOH + H_2O_2 = 2NaClO_2 + O_2 + 2H_2O.$$

$NaClO_2$, $2H_2O$ is used in bleaching textiles and paper pulp (*textone*). F_2 at –50°C or AgF_2 at 20°C converts ClO_2 to chloryl fluoride, $FClO_2$, a colourless gas (b.p. –6°C).

The ClO_2 molecule is bent with O—Cl—O angle 118°. The bond lengths (1.47 A°) are equal and shorter than for single bonds. Though the molecule contains an odd number of valence electrons (2 × 6 + 7 = 19), it shows little tendency to dimerize. This shows that the odd electron is more extensively delocalized over the entire skeleton in comparison to other odd molecules like NO_2. Indeed, there is no evidence of dimerization even in the liquid or solid phases or in solution.

[Sec. 24.3.3 *Chlorine oxides*]

Huge quantities of ClO_2 (≑ 200,000 tonnes p.a.) are produced for bleaching wood pulp and cellulose, purifying drinking water and for making $NaClO_2$ (also used in bleaching wood pulp and textiles).

Dichlorine tetraoxide, Cl_2O_4 is actually $Cl^IOCl^{III}O_3$, chlorine perchlorate, which is prepared at –45°C by the reaction

$$CsClO_4 + ClOSO_2F \text{ (chlorine fluorosulphate)} = CsSO_3F + Cl_2O_4$$

It decomposes at room temperature into O_2, Cl_2 and Cl_2O_6.

Dichlorine hexoxide, Cl_2O_6

This can be made by ozonolysis of ClO_2 :

$$2ClO_2 + 2O_3 = Cl_2O_6 + 2O_2$$

The unstable red oil freezes (3.5°C) to a solid which is yellow at –180°C.

Cl_2O_6 reacts with water and alkali to form chlorates and perchlorates.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

$$Cl_2O_6 + 2NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O.$$

Anhydrous HF reversibly gives $FClO_2$ and $HClO_4$:

$$Cl_2O_6 + HF \rightleftharpoons FClO_2 + HClO_4.$$

NO or NO_2 give nitrosyl or nitryl perchlorates respectively :

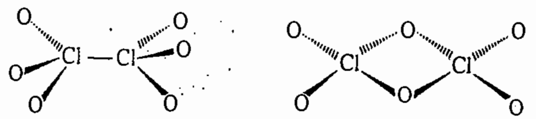
$$Cl_2O_6 + NO \longrightarrow ClO_2 + [NO]^+[ClO_4]^-$$

$$Cl_2O_6 + NO_2 \longrightarrow ClO_2 + [NO_2]^+[ClO_4]^-$$

Cl_2O_6 may be used to prepare anhydrous metal perchlorates according to the scheme

$$\left.\begin{array}{l} MCl_2 + Cl_2O_6 \longrightarrow ClO_2M(ClO_4)_3 \\ M(NO_3)_2 + Cl_2O_6 \longrightarrow NO_2M(ClO_4)_3 \end{array}\right] \xrightarrow{heat} M(ClO_4)_2$$

The structure of Cl_2O_6 is not known with certainty. The solid has the ionic compositon $ClO_2^+ ClO_4^-$ confirmed by X-ray study. The liquid may have either of two possible structures (24-IV).



24-IV

Dichlorine heptaoxide, Cl_2O_7

The most stable oxide of chlorine, it is made by careful dehydration of perchloric acid with phosphorus pentoxide at –10°C, followed by cautious vacuum distillation at –35°C and 1 mm Hg pressure.

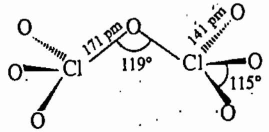
$$4HClO_4 + P_4O_{10} = 2Cl_2O_7 + 4HPO_3$$

Care is necessary as the colourless oily liquid is shock-sensitive.

Cl_2O_7, the anhydride of perchloric acid, reacts with water to form the acid. Alkalis produce perchlorates.

The oxide is less reactive than other chlorine oxides and does not ignite organic compounds at ordinary temperature. Alkyl perchlorates $ROClO_3$ are formed by reaction with alcohols; these are useful intermediates in synthesis.

Cl_2O_7 has a bent structure with a bridging O-atom (24-V). The terminal Cl—O bonds are substantially shorter than the bridge Cl—O bonds, showing appreciable double bond character.



24-V

Oxides of Bromine

The oxides of bromine are less numerous and have no practical importance. None are stable at ordinary temperature.

Dibromine monoxide, Br_2O, is prepared similar to Cl_2O by reacting Br_2 with HgO. It is also formed by low-temperautre decomposition of BrO_2 in vacuum. Br_2O is a dark brown liquid, m.p. –17.5°C with decomposition. The solid is stable at –60°C.

It gives OBr^- with aqueous alkali and oxidizes I_2 to I_2O_5 and benzene to 1, 4-quinone.

The structure is similar to Cl_2O.

Bromine dioxide, BrO_2, is prepared by oxidizing bromine with ozone in CF_3Cl at –78°C. The pale yellow crystals decompose violently, at 0°C to the elements and are thermally unstable above –40°C. It disproportionates in alkali :

$$6BrO_2 + 6OH^- \longrightarrow Br^- + 5BrO_3^- + 3H_2O.$$

It gives $FBrO_2$ with F_2.

Several other unstable bromine oxides have been reported but these are not well characterized.

Oxides of Iodine

I_2O_5 is the most stable oxide formed by the halogens. I_2O_4 and I_4O_9 are the two relatively less stable oxides of iodine.

I_2O_4 is obtained as a lemon-yellow diamagnetic solid by partial hydrolysis of iodosyl sulphate, $(IO)_2SO_4$. It starts to decompose above 85°C into I_2O_5 and I_2; the process is rapid at 135°.

$$5I_2O_4 \longrightarrow 4I_2O_5 + I_2.$$

It has a network of polymeric I—O chains cross-linked by IO_3 groups. It is thus formulated as $[IO]^+[IO_3]^-$.

I_4O_9 may be obtained by oxidizing I_2 with O_3. The yellow hygroscopic solid decomposes above 75° C into I_2O_5 and I_2.

$$4I_4O_9 \longrightarrow 6I_2O_5 + 2I_2 + 3O_2.$$

It is formulated as $I^{III}(I^VO_3)_3$.

Diiodine Pentoxide, I_2O_5, is obtained by dehydrating iodic acid at ~ 200°C in dry air.

$$2HIO_3 = I_2O_5 + H_2O.$$

I_2O_5 is a white hygroscopic solid; it dissolves in water forming HIO_3. Commercial I_2O_5 contains some HIO_3 formed by absorbed moisture and has a composition like $I_2O_5 . HIO_3$ or HI_3O_8.

The oxide decomposes to I_2 and O_2 on heating to 300°C. It is a strong oxidizing agent. Carbon monoxide is oxidized to carbon dioxide at room temperature :

$$I_2O_5 + 5CO = I_2 + 5CO_2 \quad \textit{(Ditte's reaction)}$$

The reaction is quantitative and very sensitive (1 vol CO in 30,000 vol air); it may be used to detect and estimate carbon monoxide, car exhaust etc.

I_2O_5 also oxidizes H_2S to S and HCl to Cl_2 :

$$I_2O_5 + 5H_2S = I_2 + 5S + 5H_2O.$$

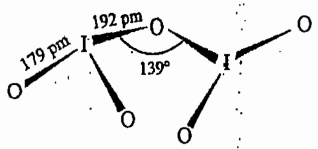
$$I_2O_5 + 10HCl = 2ICl_3 + 2Cl_2 + 5H_2O$$

Fluorinating agents like F_2, BrF_3 or SF_4 converts I_2O_5 to IF_5.

$$2I_2O_5 + 10F_2 = 4IF_5 + 5O_2$$

I_2O_5 consists of cross-linked chains of O_2IOIO_2 units (24-VI).

The unit may be supposed to consist of two pyramidal IO_3 units joined by sharing an oxygen at an apex. The bridge I—O bond-lengths (192 pm) correspond to usual single bonds while the terminal I—O bonds are somewhat shorter (177—183 pm).



24-VI

24.3.4 Oxoacids and their salts

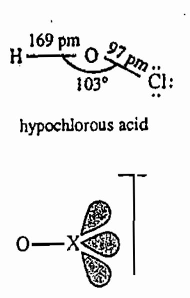
The halogens form oxoacids in oxidation states +1, +3, +5 and +7 most of them being stable only in aqueous solution or as salts. Fluorine forms only HOF.

TABLE 24.11

Oxoacids of the halogens

+1 HOX	+3 HOXO (HXO_2)	+5 $HOXO_2$ (HXO_3)	+7 $HOXO_3$ (HXO_4)
HOF			
HOCl	HOClO	$HOClO_2$	$HOClO_3$
HOBr	—	$HOBrO_2$	$HOBrO_3$
HOI	—	$HOIO_2$	$HOIO_3$

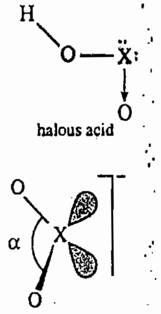
The oxoacids and their anions may be supposed to be derived through sp^3 hybrid orbitals on the halogens linking one or more oxygen atoms; the remaining orbitals are occupied by unshared pairs, ("lone pairs") of electrons of the halogen. The skeleton arrangement of the oxoacids and their anions are then as follows :



hypochlorous acid

hypohalite ion

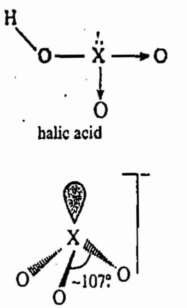
24-VII



halous acid

halite ion
$\alpha = 111°$ (Cl)
$= 105°$ (Br)

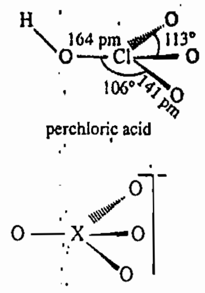
24-VIII



halic acid

halate ion

24-IX



perchloric acid

perhalate ion

24-X

Although iodine forms HIO_4 and the corresponding tetrahedral IO_4^- ion, a variety of other periodic acids and their derivatives are also known. This is a consequence of the tendency of the large I atom to attain higher coordination number (c.f. telluric acid). Ortho-periodic acid, H_5IO_6 has an octahedral environment of 5 OH groups plus an O atom. O-bridged dimers are also formed at higher pH (see text).

Strong *p-d* pi-bonding between filled 2*p* orbitals on oxygen and empty *d*-orbitals on the halogens (their energy lowered by the presence of the O-atoms) further stabilize the bonds. The nonexistence of oxoacids of fluorine (except HOF) may be related to this bonding description since fluorine cannot form *p-d* π-bonds owing to absence of acceptor orbitals. However, we have noted that stable molecules such as PF_5 or SF_6 may be described even without the involvement of *d*-orbitals.

Steric congestion around the small fluorine atom also appears to be responsible for the "non-existence" of higher oxoacids containing fluorine.

The stability of the oxoacids and their anions in aqueous solution are determined by an intricate interplay of several redox systems, together with significant kinetic influences. We have already mentioned the standard potentials for the various oxidation states of the halogens. We shall use some of those data to illustrate the involvement of several equilibrium present.

Two principal equilibria primarily involved are :

(i) dissolution of the halogen in water

$$X_2\,(g, l \text{ or } s) \rightleftharpoons X_2\,(aq) \qquad \text{equlibrium constant} = K_1$$

$$K_1\ (25°C) : Cl_2\ 0.062;\ Br_2\ 0.021;\ I_2\ 0.0013$$

(ii) disproportionation of $X_2\,(aq)$ in solution :

$$X_2\,(aq) + H_2O \rightleftharpoons H^+(aq) + X^-(aq) + HOX \qquad \text{equilibrium constant} = K_2$$

Values of K_2 can be determined from the relevant $E°$ values (Table 24.6).

$$K_2\ (25°C) : Cl_2\ 4.2 \times 10^{-4};\ Br_2\ 7.2 \times 10^{-9};\ I_2\ 2.0 \times 10^{-13}.$$

[Sec. 24.3.4 *Oxoacids*]

For saturated aqueous solutions of halogens at 25°C, the concentrations (mol L^{-1}) of HOX would be : HOCl : 0.03; HOBr : 1.15×10^{-3}; HOI : 6.4×10^{-6}.

Thus, a very negligible concentration of HOI is present in a saturated solution of I_2 in water.

Acid strengths of the oxoacids increase with increasing oxidation state of the halogen (section 10.2.4). Approximate pK_a values are : HOCl 7.52; HOClO 1.94; $HOClO_2$ −3; $HOClO_3$ −10. Acid strength among related acids by different halogens follows the sequence Cl < Br < I.

Some standard reduction potential values (aqueous) pertinent to the behaviour of halogens in aqueous solution (Volts) are given below (also see Table 24.7).

Acid Solution

$O_2 + 4H^+ + 4e = 2H_2O \quad (E° = 1.23V)$

	F	Cl	Br	I
$\frac{1}{2}X_2\,(g, l, s) + e = X^-$	2.85	1.36	1.06	0.53
$HOX + H^+ + e = \frac{1}{2}X_2 + H_2O$	—	1.63	1.59	1.45
$HOXO + 3H^+ + 3e = \frac{1}{2}X_2 + 2H_2O$	—	1.64	—	—
$XO_3^- + 6H^+ + 5e = \frac{1}{2}X_2 + 3H_2O$	—	1.47	1.52	1.20
$XO_4^- + 8H^+ + 7e = \frac{1}{2}X_2 + 4H_2O$	—	1.42	1.59	1.34

Basic Solution

$O_2 + 2H_2O + 4e = 4OH^- \quad (E° = 0.40V)$

$XO^- + H_2O + 2e = X^- + 2OH^-$	—	0.89	0.76	0.49
$XO_2^- + 2H_2O + 4e = X^- + 4OH^-$	—	0.76	—	—
$XO_3^- + 3H_2O + 6e = X^- + 6OH^-$	—	0.63	0.61	0.26
$XO_4^- + 4H_2O + 8e = X^- + 8OH^-$	—	0.56	0.69	0.39

We can use the above data in several ways. For example,

1. $E°$ for $XO_4^- - XO_3^-$ couples (T 24.7) and $XO_4^- - X_2$ suggest that perbromates should be *thermodynamically* the strongest oxidizing agent among the perhalates (see later).

2. We have : $X_2 + 2e = 2X^- \qquad E° = E_1$ V say

$H_2O = \frac{1}{2}O_2 + 2H^+ + 2e \qquad E° = -1.23$ V

$$X_2 + H_2O = \frac{1}{2}O_2 + 2H^+ + 2X^- \qquad E° = (E_1 - 1.23)\ \text{V}$$

With relevant values for different halogens, one gets $E°$ (volt) for different halogens in the reaction $X_2 + H_2O = \frac{1}{2}O_2 + 2H^+ + 2X^-$ as **F** : 1.62; **Cl** : 0.13; **Br** : −0.17; **I** : −0.70.

Thus we conclude (thermodynamically) that fluorine and chlorine should oxidize water to oxygen while oxygen would oxidize bromide and iodide in aqueous solution. We have already noted that the oxidation of water by chlorine is extremely slow; fluorine also can be made to form difluorine monoxide with dilute aqueous alkali.

3. pH-dependence of the $E°$ values for the formation of HOX suggests that it should be possible to stabilize the OX^- ion in basic media. Thus, for bromine,

$$\begin{array}{lr} Br_2 + 2e = 2Br^- & E° = 1.06\ V \\ Br^- + 2OH^- = BrO^- + H_2O + 2e & = -0.76\ V \\ \hline Br_2 + 2OH^- = BrO^- + H_2O + Br^- & +0.30\ V \end{array}$$

$\log K = 2FE/2.303\,RT = 10.17$

Thus, the formation of OBr^- is highly favoured in basic medium where the equilibrium expression involves square of hydroxyl ion concentration.

However, disproportionation adds complicacy :

$$\begin{array}{lr} 3BrO^- + 3H_2O + 6e = 3Br^- + 6OH^- & 0.76\ V \\ Br^- + 6OH^- = BrO_3^- + 3H_2O + 6e & -0.61\ V \\ \hline 3BrO^- \;=\; 2Br^- + BrO_3^- & +0.15\ V \end{array}$$

The reaction is quite slow at 0°C, so that hypobromites may be prepared at low temperature.

Similar disproportionation of OCl^- is slow at room temperature but OI^- disproportionates rapidly at temperatures down to the freezing point of its solution and hence the reaction of iodine with base gives only iodide and iodate.

4. Disproportionation of halate ions

$$4XO_3^- \longrightarrow X^- + 3XO_4^-$$

is thermodynamically very much favourable for chlorine; but the reaction occurs so slowly that perchlorate is not formed even at the boiling point of water. Careful heating of solid $KClO_3$ results in $KClO_4$ + KCl but here we cannot apply the solution potentials to interpret the observation. Disproportionation of bromates and iodates is unfavourable in the thormodynamic sense. Thus chlorates, bromates and iodates are quite stable in aqueous solution, though with different reasons : chlorates are stable for kinetic reason while bromates and iodates are stable owing to thermodynamic reasons.

The Frost diagrams for the halogens (Fig. 24.5) clearly indicate the tendency of the oxoanions to disproportionate - the species lying above the line joining the immediate neighbours on either side. The steeply sloping lines also suggest strongly oxidizing nature of the oxoanions.

Clearly, perhalates are not expected to disproportionate as there is no oxidation-state of halogens higher than VII.

The Frost diagrams of the halogen oxoanions in alkaline solution show much less steepness in slope, indicating that the species become much less strongly oxidizing.

Q. 24.10 *Calculate E′ for the $ClO_4^- - ClO_3^-$ couple at pH = 14.*

Given E° at $[H^+]$ = 1M is + 1.0 V.

Solution : $ClO_4^- + 2H^+ + 2e \longrightarrow ClO_3^- + H_2O$

(all ions are aquated)

$$E = E° - \frac{0.059}{2}\log\frac{[ClO_3^-]}{[ClO_4^-][H^+]^2} = E° - 0.059\ pH - \frac{0.059}{2}\log\frac{[ClO_3^-]}{[ClO_4^-]}$$

At pH = 14 and when $\frac{[ClO_3^-]}{[ClO_4^-]} = 1$

$E° = 1.20 - 0.059 \times 14 = 0.37$ V.

However, rates of oxidation by the oxoacids and their ions appear to *decrease* with increase in the oxidation number of the halogen :

$$OCl^- (\approx Cl_2) >> ClO_2^- > ClO_3^- > ClO_4^-$$

$$OBr^- (\approx Br_2) >> BrO_3^- > BrO_4^-$$

$$I_2 > IO_3^- > IO_4^-$$

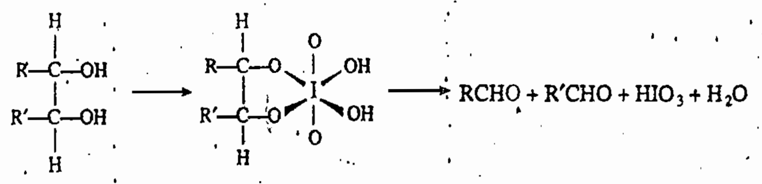
Thus Fe(II) is rapidly oxidized by aqueous solutions containing chlorine or hypochlorites, but it is fairly stable toward perchlorate solutions in absence of dissolved oxygen.

Rates of oxidation by different oxoanions containing the halogens in same oxidation state increase from Cl to Br to I :

$$IO_4^- > BrO_4^- > ClO_4^-$$

This is different from the trend suggested by $E°$ values : $BrO_4^- > IO_4^- > ClO_4^-$.

Thus perchlorates are often slow in their oxidizing reaction while **periodates** react very promptly. BrO_4^- is reduced faster than ClO_4^- since it undergoes electron-transfer more rapidly. It is likely that the rate-determining step involves cleavage of halogen-oxygen bond(s). As we expect, these bonds are strongest with chlorine owing to highest overlap as well as back bonding. The great speed of oxidizing reactions by periodates may also be associated with the ease with which iodine can expand its coordination sphere and form an adduct with the reducing agent, for example,



In acid medium, higher reduction potentials are further aided by ease of X—O bond rupture, presumably via protonation. The rate equation in the oxidation of bromide by bromate,

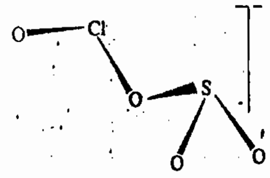
$$rate = K \cdot C_{BrO_3^-} \cdot C_{Br^-} \cdot C_{H^+}^2$$

shows the great influence of concentration of H^+ ion on the rate. The probable mechanism has been discussed in section 15.3.3.

Redox reactions of the halogen oxoanions may occur usually by inner sphere atom or electron transfer, though outer sphere electron transfer also takes place in some cases.

Inner-sphere O-transfer

The oxidation of SO_2 (*aq*) by chlorite probably involves an O-bridged intermediate (24-XI); the oxygen transfer has been confirmed using labelled oxoanion :



24-XI

$$ClO_2^-(aq) + 2SO_2(aq) + 2H_2O \longrightarrow Cl^-(aq) + 2SO{\cdot}O_3^{2-}(aq) + 4H^+(aq)$$

Inner-sphere electron transfer is illustrated by the oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ by periodate. The transfer may take place via a CN bridge linking Fe (III) and Fe(II).

Outer sphere electron transfer may occur through hydrated electrons, *e* (*aq*), produced as short-lived species by the action of γ-rays on water. These react rapidly with BrO_3^-, BrO_4^- or IO_4^- (but not with ClO_3^- and ClO_4^-).

Hypohalous acids (HOX) and their salts

HOF (*hypofluorous acid*) has been prepared in weighable quantities only in 1971. Fluorine at very low pressure (~ 100 mm Hg) was passed over ice at –40°C.

$$F_2 + H_2O \rightleftharpoons HOF + HF$$

The HOF was quickly removed from the reaction zone to avoid further reaction; water vapour and HF were arrested in u-tubes cooled to –50°C and –79°C respectively and the HOF was finally trapped in a tube at –180°.

Hypofluorous acid is an unstable white solid, m.p. –117°C. It decomposes spontaneously to HF and O_2; reaction with water also gives HF, O_2 and H_2O_2. The formal anhydride of the acid, OF_2, cannot be obtained by simply dehydrating it; but OF_2 is formed when HOF reacts with F_2 in presence of water.

$$F_2 + HOF = OF_2 + HF.$$

HOF is a bent molecule, the angle HOF (= 97.2°) is notably small in comparison to common bond angles found at oxygen :

H—O—H	F—O—F	H—O—Cl
104.7°	103.2°	103° ± 3

NMR data indicate a charge of + 0.5*e* at H and –0.5*e* at F. Electrostatic attraction between these two terminal atoms may be partly responsible for the reduced bond angle.

Several compounds with covalently bound –OF groups may be classed as covalent hypofluorites, for example, O_3ClOF, FSO_2OF, O_2NOF. The compounds may also be considered as fluorine perchlorate, fluorine fluorosulphate and fluorine nitrate respectively.

HOCl (*hypochlorous acid*) has been known to the chemists since the time of Scheele (1774). It may be prepared by reacting Cl_2O with water at 0°C. HgO or Ag_2O removes the Cl^- ion formed (as insoluble HgO. $HgCl_2$ or AgCl) and drives the equilibrium to right :

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-.$$

Industrially, aqueous solutions of HOCl containing chlorides may be obtained by reacting chlorine with cold aqueous alkali. The HOCl may be extracted by polar solvents (ketones, nitrites etc.).

A suspension of chalk or sodium bicarbonate also reacts similarly :

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HOCl + CO_2$$

$$NaHCO_3 + Cl_2 = NaCl + CO_2 + HOCl.$$

HOCl, being weaker than carbonic acid, cannot decompose a carbonate.

HOCl is a very weak acid, $K_a = 2.9 \times 10^{-8}$ at 20°C, even less than that of "carbonic acid" ($K_a = 4 \times 10^{-7}$). The acid is unstable, and may decompose to different products depending upon pH, temperature and presence of other substances :

$$2HOCl = 2H^+ + 2Cl^- + O_2$$

$$3HOCl = 3H^+ + 2Cl^- + ClO_3^-.$$

[Sec. 24.3.4 Hypochlorites]

Platinum black, manganese dioxide, cobalt oxide etc. catalyze the decomposition. HOCl dissolves magnesium with liberation of hydrogen. Fe and Al liberate both Cl_2 and H_2 while Co, Ni and Cu liberate Cl_2 and O_2.

Hypochlorites are similarly unstable, most stable ones being the solid salts of Li, Ca, Sr and Ba. NaOCl and KOCl are much less stable and cannot be isolated. Magnesium forms a basic hypochlorite. In solution, hypochlorites decompose less readily than the free acid, indicating stabilization in basic solutions. Some common hypochlorites have been separately discussed below.

HOCl as well as hypochlorites are strong oxidizing agents. *E*° for HOCl-Cl_2 (*g*) is 1.63 V while E° for $OCl^- - Cl^-$ is only 0.89 V, clearly showing the stronger oxidizing nature of HOCl. HOCl oxidizes Br^- to Br_2 and I^- to I_2; OCl^- gives OBr^-/OI^- and BrO_3^-/IO_3^- with Br^- or I^-. S is oxidized by HOCl to SO_4^{2-} and NH_3 is oxidized to NCl_3. Hypochlorites oxidize NH_3 to chloramine, NH_2Cl. In alkaline medium, IO_3^- is converted to IO_4^-, Cr(III) to CrO_4^{2-} and even Fe(III) to $FeO_4^=$. Organic aminocompounds are also oxidized to chloramines. The odour of water sterilized by hypochlorites is primarily due to such chloramines formed by the oxidation of bacteria.

Q. 24.11 *How can you differentiate between a solution containing chlorine and a solution containing hypochlorous acid?*

Hint : By shaking the solutions (separately) with mercury. Chlorine forms white mercurous chloride, insoluble in HCl. HOCl gives a light brown precipitate of basic mercuric chloride, soluble in HCl.

$$2Hg + Cl_2 = Hg_2Cl_2$$

$$2Hg + 2HOCl = HgO, HgCl_2 + H_2O.$$

Q. 24.12 *How would you estimate chlorine and hypochlorous acid in a solution ?*

Hint : By titrating the iodine liberated from KI in a medium of *known acidity*.

$$2KI + Cl_2 = 2KCl + I_2$$

$$2KI + HOCl + HCl = 2KCl + I_2 + H_2O.$$

The total iodine liberated is thus a measure of the chlorine and hypochlorous acid. Now, each mole of HOCl consumes one mole of acid. Hence moles of HCl consumed is a measure of HOCl present.

Q. 24.13 *How can you estimate free HOCl in presence of hypochlorite?*

Hint : Hypochlorous acid oxidizes H_2O_2 giving HCl, O_2 and water :

$$HOCl + H_2O_2 = HCl + H_2O + O_2$$

The HCl formed is a measure of the hypochlorous acid present.

The H—O—Cl bond angle in hypochlorous acid is 103 ± 3° with O—Cl distance 169 pm and H—O distance 97 pm.

Hypochlorites

Sodium hypochlorite is formed by passing chlorine into cold dilute NaOH solution. It is manufactured in large quantities by electrolysis of cold brine so that the products of electrolysis, chlorine and NaOH, may interact to produce hypochlorites :

$$Cl_2 + 2OH^- = Cl^- + OCl^- + H_2O.$$

Other side reactions may also occur, for example,

(i) discharge of OH^- producing oxygen

(ii) discharge of OCl^- followed by reaction with water :

$$ClO^- - e = ClO$$

$$6ClO + 3H_2O = 4HCl + 2HClO_3 + 3O$$

(iii) hydrolysis of OCl^- to form HOCl, ultimately giving chlorate :

$$ClO^- + H_2O = HOCl + OH^-$$

$$2HOCl + NaOCl = NaClO_3 + 2HCl$$

The formation of hypochlorite is favoured with

(i) neutral brine. (ii) high concentration of NaCl. (iii) low temperature (below 40°C). (iv) high current density, and (v) platinized electrodes. Addition of a little K_2CrO_4 in the bath prevents reduction of NaOCl by nascent hydrogen.

Solutions of NaOCl are extremely unstable and cannot be concentrated since they decompose to chlorate and chloride. Hydrates like NaOCl, $7H_2O$ m.p. 19°, NaOCl, $5H_2O$ m.p. 45° are however known.

Calcium hypochlorite is made by chlorinating milk of lime in cold. Vacuum evaporation yields the crystalline hydrate $Ca(OCl)_2, 2H_2O$. It is stable and does not spoil on keeping, and is completely soluble in water.

Bleaching powder, $CaCl_2$, $Ca(OCl)_2$, $Ca(OH)_2$, $2H_2O$, is obtained by chlorinating dry slaked lime in cold (35 – 40°C).

$$3Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O.$$

All hypochlorites are largely used for bleaching and sterilization in house hold work, paper and cloth industry and in municipal water supply.

Available chlorine : The efficiency of hypochlorite bleaching compounds is expressed in terms of available chlorine. It is the weight of chlorine that would liberate the same amount of iodine from HI as does a given weight of the compound. Thus, for $Ca(OCl)_2, 2H_2O$, we have the stoichiometric relations :

$$Ca(OCl)_2, 2H_2O + 4HI = 2I_2 + CaCl_2 + 4H_2O$$

and $2Cl_2 + 4HI = 2I_2 + 4HCl.$

1 mol or 179 g $Ca(OCl)_2, 2H_2O \equiv 2 \times 71$ g Cl_2

or, $$100 \text{ g } Ca(OCl)_2, 2H_2O \equiv \frac{2 \times 71 \times 100}{179} \text{ g } Cl_2$$

$$\equiv 79.32 \text{ g } Cl_2$$

∴ The percent available chlorine of pure $Ca(OCl)_2, 2H_2O = 79.32\%$.

Powdered calcium hypochlorite (~ 70% available chlorine) is used to sterilize swimming pools. The bleach liquor commonly used in paper and pulp industry contains a solution of $Ca(OCl)_2$ and $CaCl_2$ which releases about 85 g available chlorine per litre.

Bleaching powder usually contains 35% available chlorine.

LiOCl has high percentage of available chlorine (121% pure) and is diluted with sulphates to about 40% available chlorine. This is used where calcium is undesirable, for example, in treating hard water and in some dairy applications.

Domestic and laundry bleaches consist of alkaline solutions of NaOCl having 5-10% available Cl. Chlorinated sodium phosphate $4(Na_3PO_4.11H_2O)$, NaOCl is efflorescent, used in dishwashing powders and dairy cleaners.

Several molecular hypohalites are also known, for example $ClONO_2$, $ClOClO_3$, $ClOSeF_5$ etc.

Hypobromous/hypoiodous acids and their salts

The acids may be prepared in aqueous solution by reaction of the halogens on cold suspension of HgO :

$$2X_2 + 3HgO + H_2O = 2HgO.HgX_2 + 2HOX$$

The free acids are unknown. As already mentioned, both are weak acids, (pK ≈ 8) and strong oxidizing agents.

As usual, solutions containing hypobromites/hypoiodites may be obtained by reacting the halogens with cold aqueous alkali

$$X_2 + 2OH^- = X^- + OX^- + H_2O$$

They disproportionate rapidly even at 0°C, hypoiodites being faster.

$$3OX^- = XO_3^- + 2X^-.$$

Hydrated solid hypobromites $NaOBr.nH_2O$ (n = 5, 7) and $KOBr.3H_2O$ may be obtained; no solid metal hypoiodites have been prepared.

Solutions containing hypobromites act as oxidizing agents and are used in the estimation of H_2O_2 and urea :

$$H_2O_2 + NaOBr = NaBr + H_2O + O_2$$

$$O = C(NH_2)_2 + 3NaOBr = 3NaBr + CO_2 + N_2 + 2H_2O.$$

[In alkaline medium, the CO_2 will be actually converted to carbonate :

$$2NaOH + CO_2 = Na_2CO_3 + H_2O].$$

Halous acids, HOXO and halites XO_2^-

$HClO_2$ (*Chlorous acid*) is obtained in aqueous solution by acidifying a cold aqueous suspension of barium chlorite with dilute H_2SO_4 :

$$Ba(ClO_2)_2 + H_2SO_4 = 2HClO_2 + BaSO_4$$

[The barium chlorite may be prepared by the reactions

$$Ba(OH)_2\,(aq) + H_2O_2 + 2ClO_2 = Ba(ClO_2)_2 + 2H_2O + O_2$$

$$BaO_2 + 2ClO_2 = Ba(ClO_2)_2 + O_2]$$

The colourless solution of chlorous acid soon turns yellow due to chlorine dioxide formed on decomposition. It is a moderately strong acid, K_a (25° C) = 10^{-2}.

Chlorous acid, $HClO_2$, and bromous acid, $HBrO_2$, disproportionate as follows :

$$2HClO_2\,(aq) \longrightarrow ClO_3^-\,(aq) + HOCl\,(aq) + H^+\,(aq); \quad E° = 0.52 \text{ V}$$

$$2HBrO_2\,(aq) \longrightarrow BrO_3^-\,(aq) + HOBr\,(aq) + H^+\,(aq); \quad E° = 0.50 \text{ V}$$

HIO_2 is even more unstable and has only recently been identified as a transient species in aqueous solution. Other products of disproportionation are also formed.

The products of decomposition/disproportionation of chlorous acid depend upon several factors like pH, concentration, presence of chloride ions etc. The principal mode of disproportionation, catalyzed by Cl^- ions, is

$$5HClO_2 \longrightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O.$$

Other products are formed as follows :

$$3HClO_2 \longrightarrow 2ClO_3^- + Cl^- + 3H^+$$

$$HClO_2 \longrightarrow O_2 + Cl^- + H^+$$

Metal chlorites are prepared by reducing ClO_2 in presence of alkali, usually by H_2O_2. Colourless to pale yellow, they are soluble in water except silver and lead salts. Anhydrous $NaClO_2$ crystallizes above 37°C; below this, the crystals contain the trihydrate. Chlorites of Ag(I), Hg(I), Tl(I), Pb(II), Cu(II) and NH_4^+ tend to explode or detenate when heated or struck.

Solutions containing chlorites are also susceptible to disproportionation :

$$3ClO^-(aq) = 2Cl^- + ClO_3^-(aq). \quad K = 1.5 \times 10^{27}$$

However, neutral and alkaline aqueous solutions of $NaClO_2$ are kinetically stable except in boiling condition. On the other hand, rapid photochemical decomposition occurs to ClO_3^-, Cl^-, O_2 as well as ClO_4^- (in acid medium).

With two bond pairs and two lone pairs of electrons, the $OClO^-$ ion is nonlinear, angle O—Cl—O = 111°.

$NaClO_2$ is produced and used in thousands of tonnes per annum in bleaching of textiles and in oxidizing noxious pollutants like H_2S, HCN, mercaptans etc. from industrial flue gases.

Bromous and iodous acids are too unstable to be isolated. $Ba(BrO_2)_2.H_2O$ and $Sr(BrO_2)_2 . 2H_2O$ have been prepared by reacting Br_2 with hypobromites at 0°C in an alkaline medium, followed by slow evaporation. They decomposes rapidly into bromate and bromide.

Halic acids ($HOXO_2$) and halates

$HClO_3$, chloric acid (known in solution only) may be obtained by reacting barium chlorate with dilute H_2SO_4.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4\downarrow + 2HClO_3$$

The aqueous solution may be concentrated up to 40% in vacuum; decomposition occurs on further concentration or on warming :

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

$$8HClO_3 = 4HClO_4 + 2H_2O + 2Cl_2 + 3O_2$$

Chloric acid is a strong acid, $pK_a \le 0$.

Chloric acid and chlorates are strong oxidizing agents

$$3KClO_3 + 4HCl = 2KCl + Cl_2 + 2ClO_2 + 2H_2O.$$

The mixture of Cl_2 and ClO_2 is known as *euchlorine*.

Chlorates

Chlorates are formed by the action of chlorine on hot concentrated alkali. **Potassium chlorate** is prepared via calcium chlorate since milk of lime is much cheaper than KOH and $KClO_3$ is much less soluble. Chlorine is bubbled through hot milk of lime in cast iron vats; powdered KCl is then added to the clean supernate :

$$6Cl_2 + 6Ca(OH)_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

$$Ca(ClO_3)_2 + 2KCl \longrightarrow CaCl_2 + 2KClO_3.$$

Sparingly soluble $KClO_3$ (4.7% at 5°C) separates on cooling, which may be purified by recrystallization.

However, only 1 mole of Cl_2 out of every 6 moles reacted in the first step is converted to chlorate. Hence, electrolytic methods are preferable.

Sodium chlorate is manufactured by electrolysis of brine; conditions favourable are :

(i) brine (80-100 gl^{-}), 60-80°C, little HCl and sodium dichromate.

(ii) mild steel cathode and TiO_2 coated with platinum as anode in a lead-lined steel cell.

(iii) The chlorine liberated at the anode is allowed to interact with the OH^- ion formed at the cathode. OCl^- ion results, which undergoes further disproportionation or anodic oxidation :

$$H_2O \rightleftharpoons H^+ + OH^-$$

Cathode : $H^+ + e \longrightarrow \frac{1}{2}H_2$

Anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$

$Cl_2 + 2OH^- \longrightarrow Cl^- + OCl^- + H_2O$

Disproportiontion : $3OCl^- \longrightarrow ClO_3^- + 2Cl^-$

Further oxidation : $OCl^- + 2H_2O \longrightarrow ClO_3^- + 2H_2$

On concentration of the electrolysed solution, NaCl crystallizes first, followed by $NaClO_3$.

$KClO_3$ may be precipitated from a solution of $NaClO_3$ by adding KCl.

Barium chlorate may be prepared by adding barium chloride to sodium chlorate solution. Concentration first deposits NaCl, followed by crystals of $Ba(ClO_3)_2$.

The chlorates are colourless crystalline solids. $NaClO_3$ is fairly soluble in water but $KClO_3$ is only sparingly soluble :

	Water at 0°C	Water at 20°C
$NaClO_3$ g/kg water	820	990
$KClO_3$ (")	31	72

When fused, the alkali metal chlorates decompose through disproportionation. $LiClO_3$ (m.p. 125°C) decomposes at 270°C, $NaClO_3$ (m.p. 248°C) at 265° and $KClO_3$ (m.p. 368°C) at 400°.

$$4KClO_3 = 3KClO_4 + KCl$$

The $KClO_4$ decomposes at higher temperatue to KCl and O_2. In presence of MnO_2 as catalyst, $KClO_3$ begins to decompose to KCl and O_2 at 70°C; the reaction is used in the laboratory preparation of O_2.

When heated with concentrated sulphuric acid, chlorates form perchloric acid and the explosive gas chlorine dioxide.

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O.$$

Chlorates oxidize bromide (and iodide) to bromine (or iodine) :

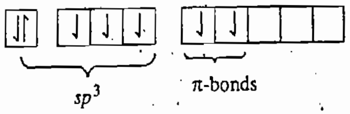
$$ClO_3^- + 6Br^- + 6H^+ \longrightarrow Cl^- + 3Br_2 + 3H_2O$$

The mechanism of such reactions has been discussed under section 15.3.3, On the other hand, iodine can displace chlorine from solid $KClO_3$ to form the more stable (thermodynamically) iodate.

$$I_2 + 2KClO_3 = Cl_2 + 2KIO_3.$$

The ClO_3^- ion is pyramidal with O—Cl—O bond angle around 106° (X-ray of $KClO_3$). In valence bond description, the bonding may be described in terms of sp^3 hybridization of an excited chlorine atom :

Cl^* (sp^3 hybridized) :



One hybrid orbital accomodates the lone pair while three others form three σ-bonds with three O-atoms. The two electrons in the *d*-orbitals excluded from hybridization form two π-bonds with two of these three O-atoms. Resonance makes all three bond lengths equal (148 pm) which are slightly shorter than single bond distances.

Sodium chlorate is used in huge quantities in bleaching paper pulp (via ClO_2). It is also used in making other chlorates and perchlorates and as a herbicide. Being hygroscopic in nature, it cannot be used as an oxidizer in fireworks and similar applications. $KClO_3$, non-hygroscopic, can be used in such cases. The tips of "safety match" sticks contain $KClO_3$, S and Sb_2S_3 with powdered glass.

$HBrO_3$, bromic acid, known only in solution, can be obtained by reacting barium bromate with dilute H_2SO_4. $Ba(BrO_3)_2$ may be prepared by adding bromine in slight excess to hot concentrated baryta. $Ba(BrO_3)_2 \cdot H_2O$ separates on cooling.

$$6Br_2 + 6Ba(OH)_2 = Ba(BrO_3)_2 + 5BaBr_2 + 6H_2O.$$

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3.$$

Excess H_2SO_4 may be neutralized by adding baryta water. $BaSO_4$ is filtered out.

An aqueous solution of $HBrO_3$ may also be obtained by shaking bromine water with silver bromate. The precipitated AgBr is filtered out.

$$3Br_2 + 5AgBrO_3 + 3H_2O = 5AgBr + 6HBrO_3.$$

The dilute solution of bromic acid may be concentrated on a water bath up to about 5%; in a vacuum desiccator, the concentration may be raised to 50% beyond which the acid tends to decompose :

$$4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O.$$

Bromates are usually prepared by oxidizing bromides with hypochlorites (Cl_2 + alkali) or by reaction of bromine with hot concentrated alkali.

$$3Cl_2 + KBr + 6KOH = KBrO_3 + 6KCl + 3H_2O$$

$$3Br_2 + 6KOH = KBrO_3 + 5KBr + 3H_2O.$$

Bromine vapours may also be passed through potassium carbonate solution saturated with chlorine :

$$Br_2 + 6KOCl = 2KBrO_3 + 4KCl + Cl_2.$$

The preparation of $Ba(BrO_3)_2$ has been stated earlier.

$AgBrO_3$ is formed as a white precipitate in the reaction.

$$AgNO_3 + KBrO_3 = AgBrO_3 + KNO_3.$$

Bromates of Tl(I), Ag, Ba and Pb have very low solubility (0.5 g/100 g water at 20°C); those of alkali and alkaline earth metals, Hg(I) and Zn are somewhat more soluble (50 g/100 g H_2O at 20°C).

[Sec. 24.3.4 *Bromates*]

Solid bromates decompose on heating, ammonium and lead bromate being explosive. The products formed on decomposition depend upon the relative stabilities of the metal bromide and oxide, for example.

(i) $MBrO_3 \longrightarrow MBr + O_2$ M = K, Hg(I), Ag

(ii) $M(BrO_3)_2 \longrightarrow MO + Br_2 + O_2$ M = Mg, Zn (also Al)

(iii) $M(BrO_3)_2 \longrightarrow MO + MBr_2$ M = Pb, Cu(II)

Bromic acid is a strong acid in aqueous solution ($pK_a \leq 0$). Both the acid and its salts are strong oxidizing agents. $E°$ values suggest the order

$$BrO_3^- > ClO_3^- > IO_3^-$$

though kinetically the rates of reaction follow the sequence

$$IO_3^- > BrO_3^- > ClO_3^-$$

Some oxidation reactions are

$$2HBrO_3 + 5SO_2 + 4H_2O = Br_2 + 5H_2SO_4$$

$$8HBrO_3 + 5H_2S = 4Br_2 + 5H_2SO_4 + 4H_2O$$

$$2BrO_3^- + 2Cl^- + 12H^+ = Br_2 + Cl_2 + 6H_2O$$

$$BrO_3^- + 6I^- + 6H^+ = Br^- + 3I_2 + 3H_2O$$

Some more examples of oxidizing action are oxidation of

AsO_3^{3-} to AsO_4^{3-}, PH_3 to H_3PO_4, Cr_2O_3 to CrO_4^{2-}, S (S, H_2S, SO_3^{2-}, $S_2O_3^{2-}$ etc.) to SO_4^{2-}, N_3H to N_2 and N_2O and OCl^- to ClO_4^- (slowly). The BrO_3^- ion undergoes oxygen exchange with $H_2\,^{18}O$.

A bromate-bromide mixture liberates bromine quantitatively on acidification :

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O.$$

The reaction is extensively used in volumetric analysis.

However, bromates are oxidized to perbromates by F_2 (or XeF_2) :

$$NaBrO_3 + F_2 + 2NaOH = NaBrO_4 + 2NaF + H_2O$$

$$NaBrO_3 + XeF_2 + H_2O = NaBrO_4 + 2HF + Xe.$$

Q. 24.14 *How will you standardize a solution of sodium thiosulphate using pure $KBrO_3$? 0.1024 g pure $KBrO_3$ liberates iodine from excess KI (dilute acid medium). The iodine requires 41.4 ml of a thiosulphate solution. What is the molarity of the thiosulphate solution?*

Hint : $BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$

$3I_2 + 6S_2O_3^{=} \longrightarrow 6I^- + 3S_4O_6^{2-}$

$\therefore$ 1 mol $KBrO_3 \equiv$ 6 mol $S_2O_3^{=}$

0.1024 g $KBrO_3 \equiv$ 0.1024/167.01 mol = 0.6134 millimol.

$\therefore$ mols of $S_2O_3^{=}$ (in 41.4 mL) = 6 × 0.6134 = 3.68 mmol.

$$\therefore M_{S_2O_3^{=}} = \frac{3.68 \text{ mmol}}{41.4 \text{ mL}} = 0.089 \text{ mol L}^{-1}.$$

(This is also the normality of the thiosulphate solution)

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Like chlorates, bromates may also oxidize I_2 to IO_3^- in acid medium (pH ~ 2) :

$$I_2 + 2BrO_3^- \longrightarrow Br_2 + 2IO_3^-$$

The reaction has an induction period during which HOBr is probably formed as a catalyst. The overall reaction then probably occurs in stages :

(i) $I_2 + BrO_3^- \longrightarrow IBr + IO_3^-$

(ii) $3IBr + 2BrO_3^- + 3H_2O \longrightarrow 5Br^- + 3IO_3^- + 6H^+$

(iii) $5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O.$

Certain oxidation reactions by bromate provide interesting examples of "*oscillating reactions*" in which the concentrations of certain species undergo periodic variations. Thus in a solution containing cerium(IV) sulphate, $KBrO_3$ and malonic acid in sulphuric acid, the concentrations of Ce^{4+} and Br^- can be made to fluctuate repeatedly; the time period may be adjusted from seconds to minutes by adjusting the concentration and temperature (Belousov, B.P. 1959). Similar other reactions (Zhabotinskii, 1964) also involve bromate oxidation of an organic substrate with an active methylene group under the catalytic influence of Ce^{IV}/Ce^{III} or Mn^{III}/Mn^{II} couple. Iodates also give some oscillating reactions (see The Chemical clock).

HIO_3, iodic acid, may be prepared by electrolytic oxidation of I_2 in aqueous suspension. I_2 may also be oxidized by fuming nitric acid, chlorine or chloric acid. Colourless orthorhombic crystals may be obtained by crystallization from acidic soluions.

Iodates may be prepared by reacting iodine with hot concentrated alkali. Potassium iodate may also be made by heating iodine with potassium chlorate in slightly acidic solution. The cyrstals first separated consist of the acid salt $KIO_3.HIO_3$ (sparingly soluble). This is dissolved in hot water and neutralized (KOH); KIO_3 crystallizes on cooling. Barium iodate, $Ba(IO_3)_2$, being sparingly soluble, may be obtained as a precipitate by adding barium chloride to a solution of potassium iodate.

Iodic acid is a colourless solid, highly soluble in water. In concentrated aqueous solution, equilibrium exists between undissociated HIO_3 and IO_3^- :

$$IO_3^- + HIO_3 = [H(IO_3)_2]^-$$

Acid salts, e.g. $KH(IO_3)_2$, *potassium biiodate*, crystallize from solutions of KIO_3 containing excess HIO_3. Tri-iodates, e.g., $KH_2(IO_3)_3$ are also known ($KIO_3.2HIO_3$).

When heated to 100°C, HIO_3 partly dehydrates to $HIO_3.I_2O_5$ (H-bonded). Complete dehydration to I_2O_5 occurs at 200°C.

Iodic acid is a strong oxidizing agent. The solid acid inflames on heating with finely divided characoal, sulphur, phosphorus or organic matter. In solution, it oxidizes SO_2, H_2S and HI (or iodide) :

$$2HIO_3 + 5SO_2 + 4H_2O = I_2 + 5H_2SO_4$$

$$2HIO_3 + 5H_2S = I_2 + 5S + 6H_2O$$

$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

As already noted, $E°$ for the $IO_3^- - I_2$ system is lowest among the halates, but iodates are kinetically the fastest to react.

Potassium bi-iodate, $KH(IO_3)_2$, may be crystallized from a boiling solution of potassium iodate and iodic acid acidified with HCl. The crystals are filtered and washed with cold water.

Potassium biiodate is moderately soluble in water and forms a good primary standard acid since,

(i) it is anhydrous and non-hygroscopic;

(ii) its aqueous solution is stable for long periods;

(iii) it has a high acidimetric equivalent weight (equal to molecular weight, 389.91).

Its oxidimetric equivalent weight is much less — M/12 (see Question 24.15).

Q. 24.15 *How can you standardize a solution of sodium thiosulphate by potassium biiodate?*

Hint : A weighed amount of $KH(IO_3)_2$ is reacted with excess KI in presence of acid. The liberated iodine is titrated by thiosulphate.

$$KH(IO_3)_2 + 10KI + 11HCl = 6I_2 + 11KCl + 6H_2O$$

$$I_2 + 2S_2O_3^= = 2I^- + S_4O_6^=$$

$$1 \text{ mole } KH(IO_3)_2 \equiv 12 \text{ mole or } 12 \text{ equivalent } S_2O_3^=.$$

Metal iodates decompose on heating to give different products :

$$2KIO_3 \longrightarrow 2KI + 3O_2$$

$$2Ca(IO_3)_2 \longrightarrow 2CaO + 2I_2 + 5O_2$$

$$5Ba(IO_3)_2 \longrightarrow \underset{\text{"periodate"}}{Ba_5(IO_6)_2} + 4I_2 + 9O_2$$

$$2NH_4IO_3 \longrightarrow N_2 + I_2 + O_2 + 4H_2O.$$

A solution containing IO_3^- gives a curdy white procipitate with $AgNO_3$; it is readily soluble in dilute ammonia but difficultly soluble in dilute HNO_3. Dropwise addition of SO_2 - water to the ammonia solution precipitates silver iodide which is not soluble in concentrated ammonia (*difference from bromate*). Iodates also form a white precipitate of mercuric iodate with mercuric nitrate solution. Barium nitrate also gives white precipitate of barium iodate, sparingly soluble in dilute HNO_3.

HIO_3 forms orthorhombic crystals which consist of H-bonded pyramidal $HOIO_2$ molecules with O—I—O angle 101.4° and O—I—(OH) angle 97°. The I—O distance is 181 pm and I—OH distance 189 pm. The IO_3^- ion is pyramidal with angles 97-105°.

The Chemical Clock

[**Sec. 24.3.4** *Chemical clock*]

We have already mentioned the oscillating chemical reactions given by bromates. The reduction of iodate by bisulphite in presence of excess iodic acid is similarly periodic in nature - providing an interesting example of a chemical clock which was first reported by H. Landolt in 1885. The overall observation is due to a sequence of reactions which occur with different speeds.

1. In acid solution, iodate is only slowly reduced by bisulphite :

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3HSO_4^-$$

2. Iodate reacts moderately rapidly with iodide to give I_2 :

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O.$$

3. The liberated iodine is very rapidly reduced by the bisulphite :

$$I_2 + HSO_3^- + H_2O \longrightarrow 2I^- + HSO_4^- + 2H^+.$$

With an excess of bisulphite, free iodine appears periodically (giving blue colouration with a little starch) - the time period varies with concentration and temperature. At 23°C, the time T is approximately given by the relation

$$T = \frac{3.7 \times 10^{-3}}{[IO_3^-]\,[HSO_3^-]}\ \text{sec}\quad [\textit{concentrations in molarity}]$$

The reaction between H_2O_2 and HIO_3 (Bray, 1921) similarly gives rise to periodic appearance of I_2 (blue colouration with starch) :

$$5H_2O_2 + 2HIO_3 \longrightarrow I_2 + 5O_2 + 6H_2O$$

The iodine is reoxidized to HIO_3 :

$$5H_2O_2 + I_2 \longrightarrow 2HIO_3 + 4H_2O.$$

Lecture Demonstration

An easy demonstration of such a periodic reaction may be arranged according to the following recipe*

Weigh about 0.12 g of gallic acid in a clean 250 mL conical flask, add 10 mL 4—6 (N) H_2SO_4, followed by 2 drops of ferroin. Then add 10 mL of 0.2 M $KBrO_3$ solution. Gently shake the conical flask — a purple colour appears in 3—5 minutes which slowly disappears and then again returns in a periodic manner.

Perhalic acids and perhalates

Perchloric acid, $HClO_4$, is prepared by reacting sodium perchlorate with conc HCl. NaCl is precipitated; on distillation, the filtrate forms an azeotrope (203°C) containing 71.6% $HClO_4$ corresponding to $HClO_4.2H_2O$. This may be distilled at low pressure (<1mm Hg) in presence of fuming sulphuric acid avoiding all contact with oxidizable substances to obtain the anhydrous acid.

Pure perchloric acid is a colourless mobile hygroscopic liquid (sp. gravity 1.76 at 25°) which explodes on shock. In concentrations greater that 72%, the solution is unstable towards loss of Cl_2O_7. It forms several crystalline hydrates with 1, 2, 2.5, 3 and 3.5 molecules of water of crystallization. $HClO_4.H_2O$ consists of $[H_3O^+]\,[ClO_4^-]$ crystals melting at 50°C. Other hydrates similarly contain $[H^+ (H_2O)_n]$. The anhydrous acid as also all forms except the azeotrope decompose on heating at 1 atm pressure before boiling.

Perchloric acid is a very strong acid. It dissolves electropositive metals like Mg, Zn and Fe, evolving H_2 (the acid is not reduced by nascent hydrogen).

Aqueous solutions of perchloric acid and perchlorates are not good oxidizing agents at ordinary temperature owing mainly to kinetic reasons. Strong reducing agents like Sn(II), Ti(III), $S_2O_4^=$ etc. react slowly with perchlorates at room temperature, but H_2S, HNO_2, SO_2, HI and even Cr(II) remain unaffected. On heating, perchloric acid and perchlorate solutions turn violently oxidizing and may cause explosion with any oxidizable substance, e.g., alcohol.

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Perchlorates are formed by a large number of metals; these are thermally stable, e.g., $LiClO_4$ to 300°; $KClO_4$ to 400°. NH_4ClO_4 deflagrates at 200° with a yellow flame

$$2NH_4ClO_4 = N_2 + Cl_2 + 2O_2 + 4H_2O$$

Sodium and magnesium perchlorates are hygroscopic. The solubilities of various perchlorates in water vary as expected for a large anion (chapter 6) :

$$NaClO_4 > LiClO_4 > KClO_4 > RbClO_4 > CsClO_4.$$

Potassium (and also Rb/Cs) may be estimated gravimetrically as perchlorate. $AgClO_4$ on the other hand, has a very high solubility, ~ 557 g per 100 g water at 25°C.

Sodium perchlorate, $NaClO_4$, is prepared by electrolytic oxidation of $NaClO_3$ solution (60 - 70%) at smooth platinum anode and steel cathode (container itself).

$$\textit{Anode}:\quad ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e$$

$$\textit{Cathode}:\quad 2H^+ + 2e \longrightarrow H_2.$$

The platinum electrode prevents electrolysis of water as it has a high overpotential for O_2.

Cells usually operate at 30° - 50°C with a high anode current density. A small amount of $Na_2Cr_2O_7$ is added to inhibit reduction of the perchlorate at cathode.

All other perchlorates and perchloric acid are prepared from $NaClO_4$ by double decomposition.

$$NaClO_4 + NH_4Cl = NH_4ClO_4 + NaCl$$

$$NaClO_4 + KCl = KClO_4 + NaCl.$$

Direct anodic oxidation of $KClO_3/NH_4ClO_3$ is not advantageous since they are much less soluble than $NaClO_3$.

$NaClO_4$ is used mainly in the production of $HClO_4$ and other perchlorates. It has limited application in explosives.

$KClO_4$ is used in fireworks. A mixture of $KClO_4$, S and Al (dangerous) produce big bangs and flashes while $KClO_4$ and Mg produce white flash. Colours may be obtained using Li_2CO_3, $SrCO_3$ or $CuCO_3$.

NH_4ClO_4 is now largely used in space shuttle programme. The solid propellant for the two booster rockets contains nearly 700 tons of NH_4ClO_4 each — this oxidizes the Al-powder acting as the fuel.

Mg $(ClO_4)_2$ is used as a desiccant (*anhydrone*) and as the electrolyte in dry cells.

Perchlorates should be handled with extreme care since their oxidation reactions are usually slow, but once inititated by mechanical action, heat or static electricity, may suddenly lead to dangerous explosions, quite unexpectedly. Such explosions have injured many chemists and plant workers who had handled the same compound several times before such disaster.

Both perchloric acid and perchlorates contain the tetrahedral ClO_4 unit, but with varying dimensions :

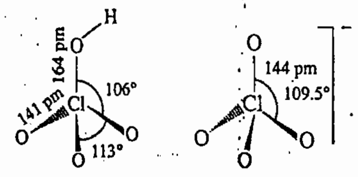


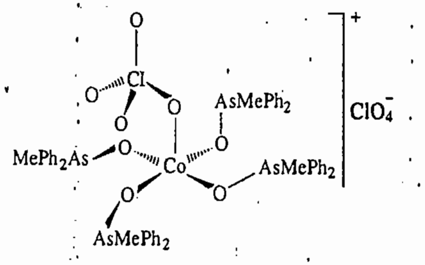
Fig. 24.8
Structure of $HClO_4$ and ClO_4^-.

The perchlorate ion is an extremely weak coordinating ligand (strong Cl—O π-bonding) and the first structural evidence for a coordinated ClO_4^- was obtained only in 1965 in the 5-coordinate Co(II) complex $[Co(OAsMePh_2)_4(\eta^1\text{-}OClO_3)_2]$ (24-XII). Several complexes of ClO_4^- acting as monodentate, bidentate and bridging ligand are now known for transition metals (Co^{II}, Ni^{II}, Cu^{II}, Ag^{I}) as well as *s*-, *p*- and *f*-block elements (Na, Ba, Sn^{II}, Sn^{IV}, Sm^{III}). Some examples are

(i) $[Ni(\eta^1-OClO_3)_2L_4]$ L = 3, 5-dimethylpyridine

(ii) $[Ba(\eta^1-OClO_3)(\eta^6\text{-benzo-18-C-6})(H_2O)_2]$

(iii) $[Sm(\eta^1-OClO_3)_2(\eta^2-O_2ClO_2)(\eta^6\text{-dibenzo-18-C-6})]$



24-XII

Perbromic acid and perbromates were supposed to be non-existent until in 1968 their existence was indicated by the radioactive β-decay of $^{83}SeO_4^{2-}$. The resulting $^{83}BrO_4^-$ decayed to ^{83}Kr and O_2 with a half-life of about 2.4 hour. From thermochemical data, $E°$ (red) calculated for the half-cell reaction

$$BrO_4^- + 2H^+ + 2e \rightleftharpoons BrO_3^- + H_2O$$

is 1.74 V, implying that only very strong oxidizing agents should be able to oxidize BrO_3^- to BrO_4^-. O_3 ($E° = 2.07$ V) and $S_2O_8^{2-}$ (2.01 V) do not appear to be effective, may be due to kinetic reasons. F_2/H_2O ($E° \simeq 2.8$ V) and XeF_2/H_2O ($E° = 2.64$ V) are effective.

Perbromates can be prepared by oxidation of BrO_3^- by F_2 or XeF_2 :

$$RbBrO_3 + XeF_2 + H_2O \longrightarrow RbBrO_4 + Xe + 2HF \text{ ...... (10\% yield).}$$

$$KBrO_3 + F_2 + 2KOH \longrightarrow KBrO_4 + 2KF + H_2O \text{ ...... (20\% yield).}$$

Excess bromate and fluoride may be separated by precipitation as $AgBrO_3$ and CaF_2 respectively.

Electrolytic oxidation of $LiBrO_3$ in aqueous solution also produces little BrO_4^- (~ 1%).

A dilute solution of $HBrO_4$ may be prepared by passing the solution of $KBrO_4$ through a cation exchange resin. The acid is stable up to a concentration of 6*M* even at 100°C, but more concentrated solutions are unstable. A crystalline hydrate $HBrO_4.2H_2O$ is known.

Dilute solutions of BrO_4^- are weakly oxidizing at 25° — they slowly oxidize Br^- and I^- only. This is in contrast to the calculated $E°$ value of 1.74 V for the BrO_4^- - BrO_3^- couple. In 3*M* concentration the acid can oxidize stainless steel; 12*M* acid readily oxidizes Cl^-.

[**Sec. 24.3.4** *Periodates*]

The perbromate salts have fair thermal stability — for example $KBrO_4$ decomposes at ~ 275°C (into $KBrO_3$ and O_2); NH_4BrO_4 decomposes at ~ 170°C. These salts are isomorphous with their perchlorate analogues.

Perbromates appear to be thermodynamically less stable than either perchlorates or periodates, as shown by the following thermodynamic data for the potassium compounds :

	$KClO_4$	**$KBrO_4$**	**KIO_4**
ΔH_f^0 (kJ mol^{-1})	−432	−288	−461
ΔG_f^0 (kJ mol^{-1})	−302	−174	−349

Thus, both ΔH_f^0 and ΔG_f^0 values of perbromates have smaller numerical values. Since entropy effects are not expected to differ much, the Br—O bond in BrO_4^- should be considerably weaker than either Cl—O or I—O bonds in the other perhalates. In this respect bromine follows the trend set by its previous post-$3d^{10}$ elements, i.e., As and Se. Again, no mass spectral evidence of Br_2O_7 was obtained on heating $HBrO_4$, instead the decomposition products showed the presence of BrO_2. It seems that the filled $3d^{10}$ core makes it extremely difficult to oxidize As, Sb and Br; also the 4*d* orbitals appear less efficient at back-bonding than the 3*d* orbitals in the previous period. This would make arsenates and perbromates strongly oxidizing.

The Br—O distance in the tetrahedral BrO_4^- ion is 161 pm.

Periodic acids and periodates

Like antimony and tellurium in preceding groups, iodine also exhibits a tendency to attain higher coordination number and forms H_5IO_6 ($O = I(OH)_5$).

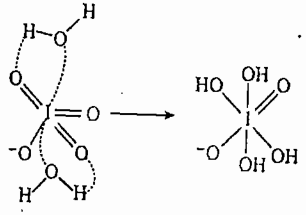
For the process

$$\underset{\text{4-coord}}{IO_4^-} + 2H_2O \rightleftharpoons \underset{\text{6-coord}}{H_4IO_6^-}$$

$\Delta H° = -62$ kJ mol^{-1}; $\Delta S° = -236$ J mol^{-1}.

$\Delta H°$ is negative since two extra I—O bonds are formed. Greater order in the 6-coordinated species makes $\Delta S°$ also negative.

$\Delta G°_{298} = -8.33$ kJ mol^{-1}; $K \simeq 29$.



IO_4^- $H_4IO_6^-$

The stability order : $HClO_4 > HIO_4 > HBrO_4$ may also be related to this tendency of IO_4^- to hydration in aqueous solution. Ordinarily one may expect a steady decrease in oxygen (*p*) to halogen (*d*) π-bonding from Cl—Br—I (size increase) and hence a stability sequence $HClO_4 > HBrO_4 > HIO_4$. The large size of the I atom and the consequent tendency of IO_4^- to strong hydration appears to reverse the trend between $HBrO_4$ and HIO_4.

The parent acid appears to be H_5IO_6 (orthoperiodic acid; also called paraperiodic acid) based on IO_6 octahedra; the formal analogue of other perhalic acids, HIO_4 (metaperiodic acid) has the tetrahedral IO_4 unit, and may be obtained by dehydration of H_5IO_6. Other species are derived from sharing of IO_6 octahedral units. There is also a square pyramid IO_5^{3-} ion in K_3IO_5.

Orthoperiodic acid may be prepared via its salts by oxidizing iodate in alkaline solution by chlorine or through electrolysis.

$$NaIO_3 + Cl_2 + 4NaOH = Na_3H_2IO_6 + 2NaCl + H_2O$$

The sparingly soluble acid salt is treated with barium nitrate in presence of dilute nitric acid :

$$2Na_3H_2IO_6 + 3Ba(NO_3)_2 = 6NaNO_3 + Ba_3[H_2IO_6]_2$$

When the barium salt is treated with concentrated nitric acid, barium nitrate is thrown down; the solution containing H_5IO_6 may be concentrated on water bath and dried in a vacuum desiccator to yield colourless monoclinic crystals of H_5IO_6.

In the electrochemical oxidation, electrolysis is carried out in a porous pot with platinum cathode and a lead anode coated with PbO_2.

Iodates of alkaline earth metals disproportionate on heating to form periodates :

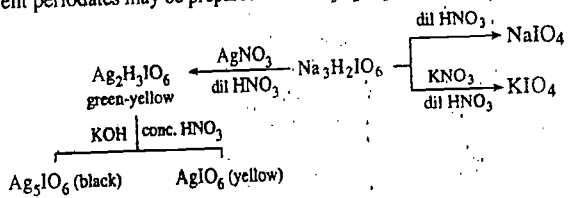
$$5Ba(IO_3)_2 \xrightarrow{\Delta} Ba_5(IO_6)_2 + 4I_2 + 9O_2$$

Crystals of H_5IO_6 may be dehydrated at reduced pressure to yield metaperiodic acid, HIO_4.

$$H_5IO_6 \longrightarrow HIO_4 + 2H_2O \; [100°C, 12mm\ Hg]$$

Dehydration of H_5IO_6 at 120° yields $H_7I_3O_{14}$. Decomposition begins above 138°C with the evolution of O_2 and ultimately I_2O_5 is formed; the non-existent I_2O_7 is not obtained.

Different periodates may be prepared from $Na_3H_2IO_6$, for example



In aqueous solution, H_5IO_6 rapidly establishes a series of equilibria like

(i)	$H_5IO_6 = H^+ + H_4IO_6^-$	K (25°C) ≃ 5×10^{-4}	(deprotonation)
(ii)	$H_4IO_6^- = H^+ + H_3IO_6^{2-}$	≃ 5×10^{-9}	(deprotonation)
(iii)	$H_4IO_6^- = 2H_2O + IO_4^-$	≃ 29	(dehydration)
(iv)	$2H_4IO_6^{2-} = 2H_2O + H_2I_2O_{10}^{4-}$	≃ 820	(dimerization)

Deprotonation (i, ii), dehydration (iii) and dimerization (iv) proceed gradually as pH increases - dimerization occurs in the pH range 10-11. On the other hand, in strong acid medium like concentrated $HClO_4$, H_5IO_6 is protonated to give the $[I(OH)_6]^+$ cation. When H_5IO_6 is dissolved in concentrated H_2SO_4 (or H_2SeO_4) at 120°, crystals of $[I(OH)_6][HSO_4]$ may be obtained by slowly cooling the solution.

Periodic acid and the periodates are strong oxidizing agents, particularly in acid solution. Thus Mn(II) is oxidized to permanganate in acid medium

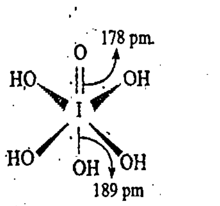
$$2Mn^{2+} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+$$

(1, 2-diols and related compounds (α-diketones, α-ketols etc.) are specifically oxidized by periodic acid - a cyclic intermediate being formed (page 553). Accordingly, only *cis*-difunctional groups are oxidized in a rigid system.

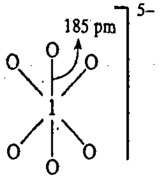
The octahedral IO_6^{5-} group can also act as a bidentate chelating group. Several transition metals form stable complexes in unusual oxidation states, e.g.

$Na_7[H_4Mn^{IV}(IO_6)_3].17H_2O$	6-coordinate Mn^{IV}
$Na_3K[H_3Cu(IO_6)_2].14H_2O$	4-coordinate (sq. planar) Cu^{III}

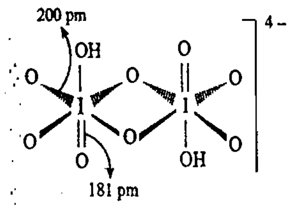
The octahedral geometry of H_5IO_6 and IO_6^{5-} ion is consistent with sp^3d^2 hybridization of the central I atom - the lone pair forming a coordinate bond to one oxygen (or a double bond). The dimensions of the H_5IO_6/IO_6^{5-} ion are shown in 24-XIII and 24-XIV.



24-XIII



24-XIV



24-XV

In the dimeric $H_2I_2O_{10}^{4-}$ ion formed at high pH, two octahedra share an edge (24-XV). The potassium salt of the anion may be crystallized from KOH solution as $K_4H_2I_2O_{10}.8H_2O$.

A face-sharing meso-periodate anion is present in $K_4I_2O_9$. Triperiodates and large polyanions formed by fusion of several octahedra are also known.

24.3.5 Interhalogen Compounds

A remarkable feature of the halogen chemistry is the large number of compounds formed by union of different halogens. Such interhalogens may be (i) neutral molecules, (ii) cationic and (iii) anionic species. A few covalent organo derivatives like CH_3IF_2 and $C_6H_5ICl_2$ are also known.

Neutral Interhalogen Molecules

These are mostly binary compounds of the general formula XX_n where X is the heavier halogen and n is an odd number (1, 3, 5 and 7). Some important members are given in Table 24.12.

TABLE 24.12
Some Interhalogen molecules

ClF Colourless gas	ClF_3 Colourless gas	ClF_5 Colourless gas	
BrF Pale brown gas	BrF_3 Yellow liquid	BrF_5 Colourless liquid	
IF Unstable	IF_3 Yellow solid	IF_5 Colourless liquid	IF_7 Colourless gas
BrCl Red-brown gas			
ICl Red crystal	I_2Cl_6 Yellow solid		
IBr Black crystal			

XY type interhalogens

The diatomic XY type molecules are the simplest interhalogens which may be prepared by direct reaction under controlled conditions, for example

Room temperature	$I_2 + Cl_2 \longrightarrow 2ICl$ $I_2 + Br_2 \longrightarrow 2IBr$	Purified by fractional crystallization. The brown red β-form of ICl (m.p. 140°) readily transforms to ruby red α-form (m.p. 27°).
High temperature	$Cl_2 + F_2 \xrightarrow{225°} 2ClF$	Higher fluorides are also formed (fractional distillation).
	$Br_2 + F_2 \longrightarrow 2BrF$	At room temperature, BrF disproportionates ($Br_2 + BrF_5$).
Low temperature (−45°,in CCl_3F)	$I_2 + F_2 \longrightarrow 2IF$	Rapid disproportionation to ($I_2 + IF_5$) at room temperature.

These interhalogenes may also be prepared by reacting a halogen on a higher interhalogen, e.g.

High temperature	$Cl_2 + ClF_3 \longrightarrow 3ClF$.	(300°C; superior method)
Low temperature	$I_2 + IF_3 \longrightarrow 3IF$	− 78°C; in CCl_3F
	$I_2 + AgF \longrightarrow AgI + IF$	0°C.

ICl is also prepared by boiling iodine with aqua regia and extracting the diluted solution with ether—the oily liquid crystallizes on cooling.

The reaction

$$X_2\,(g) + Y_2\,(g) \longrightarrow 2XY\,(g)$$

involves slight increase in entropy given by

$$\Delta S = R\ln 2 = 5.9\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The actual values (= 4.6 – 5.4 J K^{-1}) are close to this value. Since ΔS is almost constant for all these diatomic interhalogen molecules, the ΔH terms will provide a measure of the stability (thermodynamic) of the compounds. Now, ΔH increases with increasing electrostatic contribution to the bond : $X^{\delta+}$–$Y^{\delta-}$ (Y more electronegative). This is reflected in the values of ΔH_f^0 (298 K) for the various diatomic interhalogens. The bond lengths are equal to the sum of the covalent radii of X and Y only when their electronegativities are not widely different.

TABLE 24.13

Some physical data for XY type interhalogen molecules

	M.P. °C	B.P. °C	ΔH_f^0 kJ mol^{-1}	Bond length pm.	Diss. energy kJ mol^{-1}	Dipole moment (g)D
ClF	− 156	− 100	− 56.5 (*g*)	163	252.5	0.88
BrF	(−33) disprop.	(20)	− 58.5 (*g*)	176	248.6	1.29
IF	disprop.	–	− 95 (*g*)	191	~ 277	–
BrCl	(− 66) disss.	(5)	+ 14.6 (*g*)	214	215	0.57
ICl	27(α) 14(β)	~ 100	− 35.3 (α, s)	232	208	0.65
IBr	41 diss.	~ 116	− 10.5(*s*)	248.5	175.4	1.21

Q. 24.16 ***The values of ΔH_f^0 (Table 24.13) suggest the stability sequence IF> BrF>ClF>ICl>IBr>BrCl, with IF as the most stable diatomic interhalogen molecule. In fact, IF is a very unstable compound—known only in minute amounts observed spectroscopically. Comment.***

Hint : The ΔH_f^0 values refer only to thermodynamic stability *with respect to the parent halogen molecules*. IF readily disproportionates as

$$5IF \longrightarrow 2I_2 + IF_5 \qquad \Delta G_0 = -\,166.5\ \text{kJ per mol of } IF_5.$$

A little IF_7 is also formed.

[Sec.24.3.5
Interhalogens]

The diatomic interhalogens are highly reactive species — usually they are more reactive than the halogens (weaker bond). All are extensively hydrolyzed by water (and alkali).

$$ClF + H_2O \rightleftharpoons HF + HOCl.$$

ICl dissolves in water giving iodine and iodic acid :

$$5ICl + 3H_2O \rightleftharpoons 2I_2 + HIO_3 + 5HCl.$$

ICl and IBr ionize slightly in the liquid state and in solutions :

$$3\ ICl \rightleftharpoons I_2Cl^+ + ICl_2^- \text{ (or, } 2ICl \rightleftharpoons I^+ + ICl_2^-\text{)}$$

The conductivity is greatly enhanced by the addition of alkali metal halides or aluminium halides :

$$ICl + MCl \rightleftharpoons M^+\,[ICl_2]^- \qquad \text{(halide ion donor)}$$

$$2\ ICl + AlCl_3 \rightleftharpoons [I_2\ Cl]^+\,[AlCl_4]^- \qquad \text{(halide ion acceptor).}$$

Similar halide ion transfer takes place in other adducts also, e.g., $[pyI]^+\,[ICl_2]^-$, $[I_2Cl]^+\,[SbCl_6]^-$ and $[PCl_2]^+\,[ICl_2]^-$. Solvoacid solvobase reactions may be followed conductimetrically by titrating solutions of RbCl and $SbCl_5$ in ICl :

$$Rb^+[ICl_2]^- + [I_2Cl]^+\,[SbCl_6]^- \longrightarrow Rb^+\,[SbCl_6]^- + 3ICl.$$

The main reactions of these interhalogens may be broadly classified as (i) halogenation and (ii) Lewis acid-base interaction.

(i) **Halogenation** : ClF and BrF are strong fluorinating agents (ClF > BrF) ; many metals and nonmetals are converted to their fluorides at room temperatue and above:

$$W + 6ClF = WF_6 + 3Cl_2\ ;\ Se + 4ClF = SeF_4 + 2Cl_2$$

Addition of both Cl and F (chlorofluorination) may also take place, accompanied by oxidation.

$$SF_4 + ClF \longrightarrow SF_5Cl \qquad \text{(in presence of CsF)}$$

$$SO_2 + ClF \longrightarrow ClSO_2F$$

$$CO + ClF \longrightarrow COFCl$$

$$(CF_3)_2CO + ClF \longrightarrow (CF_3)_2\,CFOCl \qquad \text{(in presence of MF, M = K, Rb, Cs)}$$

Even ICl and IBr react vigorously with most metals including Pt and Au ; B, C, Cd, Pb, Nb, W, Mo are however not attacked.

Q. 24.17 *ICl vapour chlorinates phenol and salicyclic acid but in nitrobenzene solution, iodination takes place. Comment.*

Hint : The vapour may be supposed to react by homolytic dissociation and formation of I_2 and Cl_2. Cl_2 is more reactive.

A solvent with high dielectric constant like nitrobenzene facilitates heterolytic fission followed by electrophilic iodination by I^+.

Remarks :

1. In a solvent of low dielectric constant, like CCl_4, iodination predominates but some chlorination occurs through Cl_2 or ICl.
2. IBr dissociates more readily in solution into I_2 and Br_2 and hence acts almost exclusively as a brominating agent.

A solution of ICl in glacial acetic acid (**Wij's reagent**) is used in the estimation of unsaturation in oils and fats through their "Iodine Value".

$$—CH = CH— + ICl = —CHI—CHCl—$$

(ii) **Lewis acid-base character :**

Lewis acid : $NOF + ClF \longrightarrow [NO]^+ [ClF_2]^-$

Lewis base : $BF_3 + 2ClF \longrightarrow [Cl_2F]^+ [BF_4]^-$

$AsF_5 + 2ClF \longrightarrow [Cl_2F]^+ [AsF_6]^-$

XY_3 type interhalogens (ClF_3, BrF_3, IF_3, I_2Cl_6)

The three fluorides ClF_3, BrF_3, IF_3 and the only chloride I_2Cl_6 are known in this category. All are formed by direct union of the elements under appropriate conditions :

ClF_3	$3F_2+Cl_2 = 2ClF_3$ (or ClF)	200 – 300°C, Cu or Ni tube
BrF_3	$3F_2 + Br_2 = 2BrF_3$	Room temperature, purified by distillation.
IF_3	$3F_2 + I_2 = 2IF_3$	I_2 suspended in CCl_3F at – 45°.
	$3XeF_2 + I_2 = 2IF_2 + 3Xe$	low temperature.
I_2Cl_6	$3Cl_2 + I_2 = I_2Cl_6$	– 80°C, liq. Cl_2 in excess, low temp. evaporation of Cl_2.

Essential physical properties of the compounds are summarized in Table 24.14.

TABLE 24.14

Some properties of XY_3 type interhalogens

	M.P. °C	B.P. °C	ΔH_f^0 kJ mol^{-1}	Sp. Conductivity (25°C) Ohm^{-1} cm^{-1}	Mean bond energy kJ mol^{-1}	Dipole moment D
ClF_3	– 76	12	– 164 (*g*)	3.9×10^{-9}	174	0.56
BrF_3	9	126	– 300 (*l*)	8×10^{-3}	202	1.19
IF_3	decomp > –28	–	– 485(*est*)	–	275(*est*)	–
I_2Cl_6	101 (16 atm)	–	– 89.3(*s*)	8.6×10^{-3}	–	–

est = estimated (102°)

ClF_3 is a highly reactive fluorinating agent, BrF_3 is somewhat less vigorous. Both react explosively with water and organic and inorganic substances ranging from hydrocarbons, wood, asbestos to several metals and nonmetals. H_2, P, As, S, K, Te etc. ignite spontaneously in ClF_3. Na, Mg, Al, Zn, Sn and Ag react at ordinary temperature but soon gets protected by a layer of fluoride; vigorous reaction continues on heating. Pt, Pd and Au are also attacked. Mild steel, nickel, monel metal and copper (below 300°C) are least attacked by it. Both ClF_3 and BrF_3 are used as fluorinating agents:

$$AgCl + ClF_3 \longrightarrow AgF_2 + ClF + \tfrac{1}{2}Cl_2$$

$$3NiO + 2ClF_3 \longrightarrow 3NiF_2 + Cl_2 + \tfrac{3}{2}O_2$$

$$U(s) + 3ClF_3(l) \longrightarrow UF_6(l) + 3ClF(g) \quad (50° – 90°C) \text{ Note 1}$$

$$3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 2Br_2 + O_2 \quad \text{Note 2}$$

Note 1 : Extensively used in the processing of nuclear fuels— e.g., in the separation of volatile UF_6 from involatile PuF_4. BrF_3 is also used.

Note 2 : Small amounts of oxygen (or nitrogen) in metals and alloys of Li, Ti, U etc. may be estimated by this type of reaction. Refractory oxides like MgO, CaO, NiO, CeO_2 etc are only partially fluorinated. $KBrF_4$ and $[BrF_2]$ $[SbF_6]$ are more effective for these compounds.

Oxygen in carbonates and phosphates may also be estimated through similar reactions.

I_2Cl_6 dissociates readily into ICl and Cl_2; it acts as a vigorous chlorinating agent.

ICl and I_2Cl_6 are completely decomposed by aqueous alkali :

$$3ICl + 6KOH \longrightarrow 3KCl + 2KI + KIO_3 + 3H_2O$$

$$3I_2Cl_6 + 24KOH \longrightarrow 18KCl + 2KI + 4KIO_3 + 12H_2O$$

Electrical conductivities indicate that ClF_3 undergoes little self-ionization. However, BrF_3 and I_2Cl_6 have appreciable electrical conductivity, suggesting self-ionization as

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-; \quad I_2Cl_6 \rightleftharpoons ICl_2^+ + ICl_4^-$$

The conductivity of BrF_3 decreases at high temperature due to instability of the ions. Addition of fluoride ion donor increases the conductivity through the formation of solvo bases :

$$KF + BrF_3 \rightleftharpoons KBrF_4 \qquad \text{(Similarly AgF, NOF, BaF}_2\text{ etc.)}$$

Solvoacids are similarly formed by F^- ion acceptors, e.g. $BrF_2^+SbF_6^-$, $BrF_2^+AuF_4^-$, $BrF_2^+PdF_6^-$ etc. The solvoacids and solvobases may be titrated conductimetrically. The ICl_2^+ ion is present in the crystalline products $[ICl_2]$ $[AlCl_4]$ and $[ICl_2]$ $[SbCl_6]$.

ClF_3 also exhibits Lewis acid-base character by forming stable solid compounds with donors/acceptors of F^- ions :

$$PtF_5 + ClF_3 \longrightarrow [ClF_2][PtF_6] \quad \text{m.p. } 171°$$

$$BF_3 + ClF_3 \longrightarrow [ClF_2][BF_4] \quad \text{m.p. } 30°$$

$$KF + ClF_3 \longrightarrow K[ClF_4] \quad \text{dec. } 350°\text{; also RbF/CsF.}$$

XY_5 and XY_7 type interhalogens (ClF_5, BrF_5, IF_5 and IF_7) :

Preparation of these halogen fluorides mostly involve direct fluorination under varying conditions. Some representative reactions are

$$KCl + 3F_2 \longrightarrow KF + ClF_5 \quad (200°\text{; bomb})$$

$$Cl_2 + 5F_2 \longrightarrow 2ClF_5 \quad \text{(excess Cl}_2\text{; 350°/250 atm).}$$

$$Br_2 + 5F_2 \longrightarrow 2BrF_5 \quad (\text{excess } F_2;\ 200°)$$

$$KBr + 3F_2 \longrightarrow KF + BrF_5 \quad (25°)$$

$$I_2 + 5F_2 \longrightarrow 2IF_5 \quad (25°)$$

$$I_2\,(g) + 7F_2 \longrightarrow 2IF_7 \quad (300°)$$

$$KI + 4F_2 \longrightarrow KF + IF_7 \quad (250°)$$

$$PdI_2 + 8F_2 \longrightarrow PdF_2 + 2IF_7.$$

ClF_5 and IF_7 are colourless gases while others are colourless liquids at ordinary temperature. Some of their physical properties are listed below.

TABLE 24.15

Some physical properties of ClF_5, BrF_5, IF_5 and IF_7

	M.P. °C	B.P. °C	$\Delta H_f^0\,(g)$ kJ mol^{-1}	Sp. Conductivity Ohm^{-1} cm^{-1}	Mean X–F bond energy kJ mol^{-1}	Dipole moment D
ClF_5	− 103	− 13	− 255	–	154	–
BrF_5	− 60	41	− 430	9×10^{-8} (25°)	187	1.5
IF_5	9	105	− 843	5×10^{-6} (25°)	269	2.2
IF_7	6.5	–	− 962	–	232	0

All except IF_7 are highly vigorous fluorinating agents (though somewhat less than ClF), and react vigorously with SiO_2, water or organic substances.

$$ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF$$

$$BrF_2 + 3H_2O \longrightarrow HBrO_3 + 5HF$$

$$IF_5 + 3H_2O \longrightarrow HIO_3 + 5HF$$

BrF_5 attacks glass and silicates on heating (450°C) :

$$SiO_2 + 2BrF_5 \longrightarrow SiF_4 + 2BrF_3 + O_2$$

IF_5, somewhat less vigorous, may be handled in glass apparatus. However, this also inflames in contact with B, P, As and Sb and reacts vigorously with the alkali metals. Mo and W inflame on heating.

IF_5 forms adducts with XeF_2 and XeF_4 : the adduct $XeF_2 . 2IF_5$ is formed at low temperature (~ 5°) while $XeF_4 . IF_5$ is formed at room temperature. The latter splits above 92°.

IF_5 undergoes slight self-ionization, as supported by its low conductivity.

$$2\,IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

As expected, conductivity increases on dissolving KF, NOF or SbF_5 and $[IF_4]^+\,[SbF_6]^-$ can be titrated with KIF_6. Similarly, BrF_5 forms a 1:2 adduct with SbF_5 which consists of $[BrF_4]^+\,[Sb_2F_{11}]^-$. CsF yields $Cs^+\,[BrF_6]^-$, a white crystalline solid stable upto 300°.

IF_7 is a stronger fluorinating agent than IF_5. It reacts with most elements in cold or on warming, including glass or silica (100°C)

$$SiO_2 + 2IF_7 \longrightarrow SiF_4 + 2IOF_5$$

Vapours of IF_7 undergo smooth hydrolysis to HIO_4 and HF; an oxofluoride is formed with less amount of water at room temperature

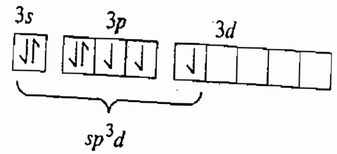
$$IF_7 + H_2O \longrightarrow IOF_5 + 2HF.$$

Compounds $[IF_6]^+[MF_6]^-$ have been isolated (M = As, Sb) with fluoride ion acceptors like AsF_5 and SbF_5. The adducts of CsF and NOF have been formulated as $Cs^+\,[IF_8]^-$ and $[NO]^+[IF_8]^-$ from Raman spectroscopy.

Structure and bonding

The bonding and molecular shapes of the interhalogen molecules can be successfully described in terms of the valence bond approach and they conform to the expectations from the VSEPR theory. Thus, the shapes of ClF_3 and BrF_3 may the readily arrived at from the following approach exemplified with ClF_3.

Valence shell of Cl, excited state



Assuming enough contraction of the $3d$-orbitals in presence of the electronegative F-atoms, the Cl-atom can now form three bonds using its sp^3d hybrid orbitals; three F-atoms may use their respective unpaired electron in a $2p$ a.o. of suitable symmetry. The chlorine now has a total of five electron pairs—three bond pairs plus two non-bonding pairs (or "lone pairs"). These are expected to be directed along the corners of a trigonal bipyramid - the lone pairs occupying equatorial positions for minimum repulsion (Ch. 7). The actual T-shaped structure established from microwave spectroscopy conform to this description—the influence of lone-pair-bond pair repulsion is reflected in squeezing the bond angle from 90°. As expected, the equatiorial bonds are slightly longer than the axial bond : ClF_3 170 pm and 160 pm; BrF_3 181 pm and 172 pm.

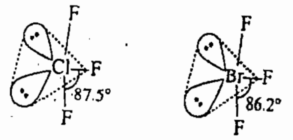
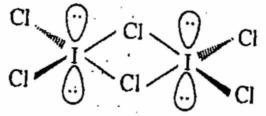


Fig. 24.9

Molecular structures of ClF_3 and BrF_3.

The structure of ICl_3 gas is not know since it decomposes into ICl and Cl_2. The solid consists of I_2Cl_6 molecules built through two Cl bridges. Each atom has seven valence electrons-making a total of 56 i.e., 28 pairs. A reasonable Lewis structure with two bridge Cl-atoms (24-XVI) puts four bond pair around each I. These correspond to a V.B. desciption involving sp^3d^2 hybridization at the I atoms, with two lone pairs on each. In accordance with the VSEPR theory, this octahedral disposition of the valence orbitals of I will put the lone pairs in nonadjacent trans-positions. The molecule is thus expected to be planar, consistent with X-ray study on single crystals. The bridge I—Cl distances are somewhat longer (~ 270 pm) than the terminal ones (~ 238 pm).



24-XVI

The structure of AX_5 type interhalogens may be similarly understood in terms of sp^3d^2 hybridization of the central halogen. One of the octahedrally disposed valence orbitals is occupied by a lone pair of electrons — conferring a square-based pyramidal structure of the molecules. The lone pair slightly pushes the basal A-X bonds upward (Chapter 7, problem 7.10). The structures are same for gaseous and crystalline molecules.

IF_7 has the pentagonal bipyramid structure expected for 7 valence shell electron pairs around I involving sp^3d^3 hybridization.

The Polyhalogen and Interhalogen Cations

Polyhalogen Cations

Removal of an electron from the highest occupied π^* m.o. of the halogen molecules gives rise to X_2^+ cations. Various salts containing I_2^+ and Br_2^+ are known while Cl_2^+ has been characterized only in the gas phase. Few other cationic X_n^+ (n = 3,5) and I_4^{2+} are known.

I_2^+, I_3^+, I_5^+ and I_4^{2+} ions can be generated by oxidizing I_2 in fluorosulphonic acid, FSO_3H, with the very powerful oxidizing agent bis(fluorosulphuryl)peroxide FO_2SOOSO_2F ($SO_3 + F_2$, 160°, AgF_2 catalyst); stoichiometric amount of the oxidant leads to different products :

$$2I_2 + FO_2SOOSO_2F \longrightarrow I_2^+ + SO_3F^-$$
$$3I_2 + FO_2SOOSO_2F \longrightarrow I_3^+ + SO_3F^-$$
$$5I_2 + FO_2SOOSO_2F \longrightarrow I_5^+ + SO_3F^-$$

The bright blue solution obtained by dissolving I_2 in oleum contains I_2^+ cation not I^- as thought earlier.

Subsequent addition of SbF_5 to these cations gives rise to stable salts like $[I_2^+][Sb_3F_{16}^-]$. Salts containing Br_2^+ may be similarly produced.

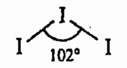
AsF_5 may also be used as the oxidant, sometimes in liquid SO_2 as solvent.

$$Cl_2 + ClF + AsF_5 \xrightarrow{-78^\circ} Cl_3^+AsF_6^-$$
$$Br_2 + BrF_3 + AsF_5 \longrightarrow Br_3^+AsF_6^-$$
$$3I_2 + 3AsF_5 \longrightarrow 2I_3^+AsF_6^- + AsF_3$$
$$5I_2 + 3AsF_5 \longrightarrow 2I_5^+AsF_6^- + AsF_3$$
$$2I_2 + 3AsF_5 \longrightarrow I_4^{2+}(AsF_6^-)_2 + AsF_3$$

The salts containing Br_2^+ have bright red colour while those of I_2^+ are bright blue. Cl_3^+ is yellow, Br_3^+ brown and I_3^+ is dark brown. The salts have considerable thermal stability, e.g., $[Br_2^+][Sb_3F_{16}^-]$ m.p. 85°; $[I_2^+][Sb_2F_{11}^-]$ m.p. 127°.

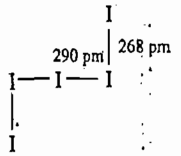
When the deep blue solution containing I_2^+ is cooled to about −70°C, there occurs a drop in paramagnetic susceptibility and electrical conductivity, accompanied by reversible colour change to red. This has been ascribed to dimerization of I_2^+ to I_4^{2+}, presumably through overlap of half-filled π^* orbitals on two I_2^+ units.

The structural features of some of the iodine cations are shown in 24–XVII to 24–XIX. These have been determined from their salts with various polyfluoroanions. The bond length in I_2^+ (256 pm) is *less* than that in free I_2(266 pm), consistent with the loss of an electron from the antibonding π^* m.o.. There is a corresponding increase in the I—I stretching frequency (238 cm⁻¹ vs 213 cm⁻¹).



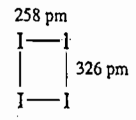
I_3^+

24-XVII



I_5^+ (planar)

XVIII



I_4^{2+}

24-XIX

Interhalogen Cations

At least 15 interhalogen cations are now known (Table 24.16); all of them are unipositive and except $IBrCl^+$, they consist of only two different halogens. Fifty per cent of these have iodine as the central atom; fluorine being the most suitable accompanying element.

TABLE 24.16

Interhalogen cations

Type	XY_2^+, XYZ^+		XY_4^+	XY_6^+
	ClF_2^+	I_2Cl^+	ClF_4^+	ClF_6^+
	Cl_2F^+	IBr_2^+	BrF_4^+	BrF_6^+
	BrF_2^+	I_2Br^+	IF^+	IF_6^+
	IF_2^+	$IBrCl^+$		
	ICl_2^+			

The cation $I_3Cl_2^+$ is also known (see later).

The cations are prepared by reacting the corresponding interhalogen (or its constituents) with a halide ion acceptor, for example a strong Lewis acid like SbF_5, $SbCl_5$, AsF_5, BF_3 etc.

$$ClF_3 + SbF_5 \longrightarrow [ClF_2^+][SbF_6^-] \quad \text{m.p. } 78^\circ$$
$$BrF_5 + 2\,SbF_5 \longrightarrow [BrF_4^+][Sb_2F_{11}^-] \quad \text{m.p. } 60^\circ$$
$$I_2 + 3Cl_2 + 2SbCl_5 \longrightarrow 2\,[ICl_2^+][SbCl_6^-] \quad \text{m.p. } 83^\circ$$

ClF_6^+ and BrF_6^+ cannot be prepared by similar reactions since ClF_7 or BrF_7 do not exist. These may be prepared by oxidizing ClF_5/BrF_5 as follows :

$$2ClF_5 + 2PtF_6 \xrightarrow[\text{dec.at } 140^\circ]{} [ClF_6^+][PtF_6^-] + [ClF_4^+][PtF_6^-]$$

$$BrF_5 + [KrF^+][AsF_6^-]^* \longrightarrow [BrF_6^+][AsF_6^-] + Kr$$

*[Prepared from $KrF_2 + AsF_5$]

73

The cation $[I_3Cl_2^+]$ can be prepared by reacting stoichiometric quantity of I_2 with $SbCl_5$ in liquid chlorine at −78°C.

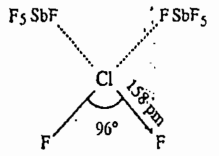
The interhalogen cations may be isolated as stable salts, as evident from the melting points of some compounds given above. The fluorocations are colourless to pale yellow, while the heavier members may be wine-red, orange or dark purple in colour. As expected, the heavier fluorocations are strongly oxidizing in character, e.g.,

$$O_2 + [BrF_6^+][AsF_6^-] \longrightarrow [O_2^+][AsF_6^-] + BrF_5 + \tfrac{1}{2}F_2$$

$$Rn + IF_6^+SbF_6^- \longrightarrow [RnF^+][SbF_6^-] + IF_5$$

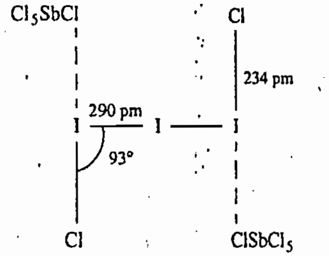
$$NO_2 + IF_6^+SbF_6^- \longrightarrow [NO_2^+][SbF_6^-] + IF_5$$

The cations have structures consistent with the VSEPR theory. Thus BrF_4^+ has a structure similar to SF_4 (4 b.p. + 1 l.p. in equatorial position) while BrF_6^+ is octahedral. X-ray diffraction of the crystals show that the cations are in close contact with the anions via halogen bridges as for example in $[ClF_2^+][SbF_6^-]$ (24-XX). The structure of $I_3Cl_2^+$ is similar to that of I_5^+ (24-XXI).



$[ClF_2^+][SbF_6^-]$

24-XX



$[I_3Cl_2^+][SbCl_6^-]$

24-XXI

Polyhalide anions

The dihalogens and several inter-halogens may act as Lewis acids by accepting an electron pair into their LUMO (lowest unoccupied m.o.). When the donor Lewis base is also a halide ion, the adduct is a polyhalide ion. Polyiodides $[(I_2)_nI^-]$ formed by I_2 as the Lewis acid and I^- or I_3^- as the Lewis base are the most interesting polyhalide anions. Some dinegative polyiodides of the general formula $[I^-(I_2)_nI^-]$ are also known. Several other polyhalides like Cl_3^-, Br_3^- and those derived from interhalogens have also been characterized.

Polyiodides

These are mostly uninegative of the general type $[(I_2)_nI^-]$ with n = 1–4 or dinegative of the type $[I^-(I_2)_nI^-]$, n = 1–3. I_{16}^{4-} is also known, which may be regarded as a linked chain of $I_3^-...I_2...I^-...I_2...I_2...I^-...I_2...I_3^-$. The most stable member of this series is the triiodide ion, I_3^-. This is also the only important polyiodide ion in aqueous solution and is responsible for the high solubility of I_2 (*s*) in aqueous KI :

[Sec. 24.3.5 *Polyhalides*]

$$I_2 + I^- = I_3^- \qquad K = 700\ (25°C)$$

The I_3^- ion is linear in both solution and in crystals. But though the ion is considered symmetrical in solution with both I–I distances equal (and longer than in I_2), in crystals, it is symmetrical only when present in combination with a large cation like $[NMe_4]^+$ or $[Ph_4As]^+$. Even Cs^+ ion, slightly smaller than the $[NMe_4]^+$ ion, cause significant distortion in the I_3^- ion (24 – XXII).

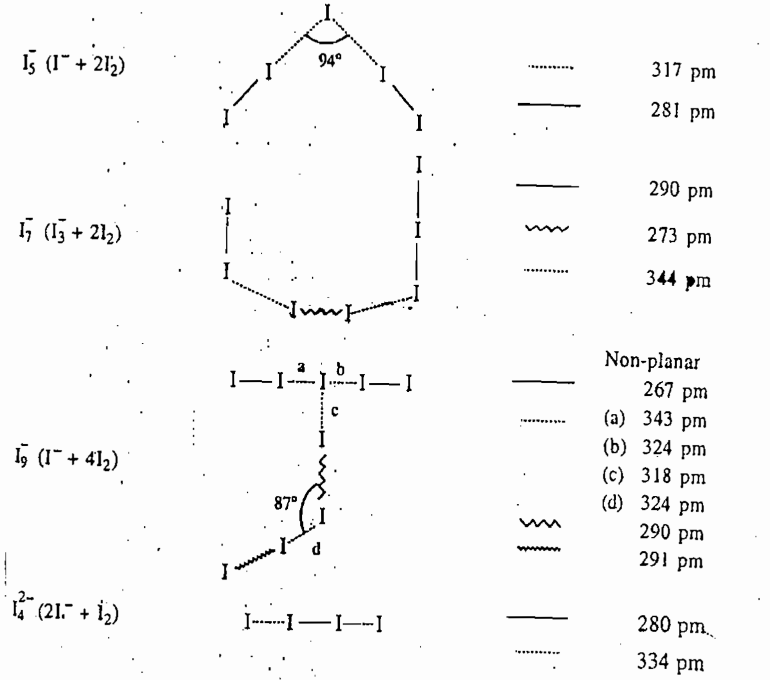
$$\left[I \overset{283}{—} I \overset{303}{—} I\right]^- \qquad \left[I \overset{290}{—} I \overset{290}{—} I\right]^-$$

24. XXII 24.XXII

(a) I_3^- in CsI_3 (distance in pm) (b) I_3^- in $As(C_6H_5)_4^+I_3^-$ (distance in pm)

Et_4NI_3 has two forms, both with linear I_3^- ions, but one having symmetrical (293 pm) and one unsymmetrical (291 and 296 pm) I–I distance. The anion structure is thus determined by the crystal environment, not simply the cation size. Still smaller cations form unstable tri-iodides, e.g., NaI_3 is known in aqueous solution only; evaporatin of the water leads to decomposition to NaI + I_2.

The other higher polyiodides are also stable in combination with large cation. The structures of the anions in crystals depend highly on the counter-cation. Weak I...I interactions link these anions into polymeric chains as in $C_5H_5NH^+I_5^-$. The structural motiff in a few polyiodide are shown below :



Iodine-doped polyacetylene contains I_3^- and I_5^- chain anions by transfer of electrons from the π-orbitals of the polymer; such ions increase the electrical conductivity of the polymer.

Other polyhalides

Homonuclear triatomic polyhalides Cl_3^- and Br_3^- are known in solution and also as solids with large cations. Cl_3^- ion is formed in solution with other polyhalide anions in methanol :

$$2Cl_2 + 2I_2 + 2Cl^- + 2I^- = Cl_3^- + I_3^- + ICl_2^- + I_2Cl^-$$

The ion may also be formed in concentrated aqueous solution

$$Cl_2 + Cl^- (aq) \longrightarrow Cl_3^- (aq).$$

The Br_3^- ion does not exist in aqueous solution but the reaction

$$Br_2 + Br^- \longrightarrow Br_3^-$$

has a large formation constant in liquid SO_2.

F_3^- has been detected spectroscopically in an inert matrix at very low temperature.

Equilibrium constants of the reaction $X^- + X_2 \rightleftharpoons X_3^-$ are as follows :

X =	Cl	Br	I
K_{298}	0.2	16	700.

Several heteronuclear interhalogen anions are known, the central atom being mostly the heavier halogen. The principal species are shown in Table 24.17. As expected, use of a large cation helps to minimize the loss in forming the polyhalide (against the simpler halide) and hence stabilize the polyhalide. All known salts of Cl_3^-, I_5^- and I_7^- contain cations like NR_4^+, Ph_4As^+ etc. Br_3^- and I_3^- ions may also be prepared as the cesium salt.

TABLE 24.17

Principal polyhalide anions (heteronuclear) (central atom on extreme left)

Trinuclear	Pentanuclear		Heptanuclear
$BrCl_2^-$	ClF_4^-	$I_2BrCl_2^-$	BrF_6^-
$I\,Cl_2^-$	BrF_4^-	$I_2Br_3^-$	IF_6^-
$I\,Br_2^-$	ICl_4^-	I_4Cl^-	
$I\,BrCl^-$	ICl_3F^-	I_4Br^-	
$I\,ICl^-$	$IBrCl_3^-$		
	$I_2Cl_3^-$		

We have already come across such species in discussing the chemistry of various interhalogens. In fact, the polyhalide anions may be readily synthesized from nearby interhalogen molecules either by direct halogenation or by halide ion (mainly F^-) transfer, e.g.,

$$NR_4^+I^- + Cl_2 \longrightarrow NR_4^+ICl_2^-$$

$$NR_4^+ICl_2^- + Cl_2 \longrightarrow NR_4^+ ICl_4^- \quad (R = n\text{–Bu, e.g.})$$

$$CsF + ClF \longrightarrow Cs^+ ClF_2^-$$

$$CsF + ClF_3 \longrightarrow Cs^+ ClF_4^-$$

$$CsF + IF_5 \longrightarrow Cs^+ IF_6^-.$$

$$CsF + IF_7 \longrightarrow Cs^+ IF_8^-.$$

For a given cation, the stability of a polyhalide anion is found to increase with (i) the size of the central atom and (ii) symmetrical disposal of the adjacent halogen atoms. Thus, we have the approximate sequence of symmetry decreasing as

$$I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_3^- > BrCl_2^- > Br_2Cl^-.$$

Polyhalides containing two different halogens decompose thermally to form the halide having the highest lattice energy, for example.

$$RbICl_2 \longrightarrow RbCl + ICl$$

$$KBrF_4 \longrightarrow KF + BrF_3.$$

Gross structures of the polyhalide anions follow our expectations from simple VSEPR considerations. As observed earlier for I_3^- ion, other triatomic species are also linear. Like I_3^-, the Br_3^- ion is also found in symmetrical and unsymmetrical forms. The Br–Br distances are

$$Me_4NBr_3 : 254\ pm;\ CsBr_3 : 244\ and\ 270\ pm.$$

The linear structures of the trihalide ions are consistent with a 10-electron valence shell of the central atom with a trigonal bipyramid disposal — the lone pairs occupying equatorial positions (Ch. 7). However, increased bond length and decreased i.r. stretching frequency suggest that the bonds in such polyhalide anions are much weaker than the bonds in related halogen or interhalogen molecules. For example,

I_2	215 cm^{-1}	I_3^-	113, 135 cm^{-1}
ICl	384 cm^{-1}	ICl_2^-	267, 222 cm^{-1}.

If the bonds in I_2 or ICl are taken as normal single bonds (i.e. two-center two-electron bonds), then the bond in I_3^- or ICl_2^- are definitely weaker. We recall the valence shell electron configuration of I atom and I^- ions :

$$I\ \underset{s}{\boxed{\uparrow\downarrow}}\quad \underset{p_x\ p_y\ p_z}{\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow}}\qquad I^-\ \underset{s}{\boxed{\uparrow\downarrow}}\quad \underset{p_x\ p_y\ p_z}{\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow}}$$

The formation of an I_3^- may now be treated from the combination of the p_z orbitals of two I atoms and one I^- ion. (z-axis taken as internuclear axis). In all, three m.o.-s are formed as shown, and the four electrons occupy the lower bonding and nonbonding m.o.-s. The net bond order between each pair of atoms is thus only half, consistent with the observed lowering in stretching frequency.

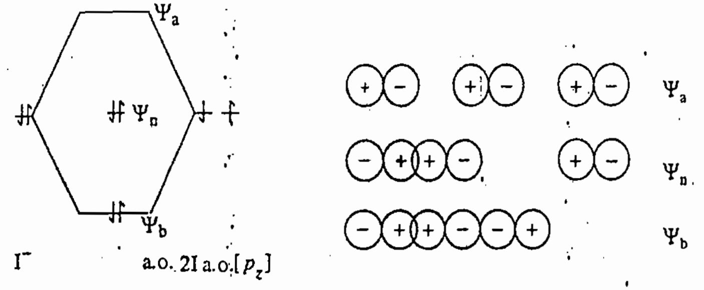


Fig. 24.10

M.O. energy level diagram for I_3^- ion:

Such multicentered molecular orbital approach to bonding is now favoured over *d*- orbital participation.

The structures of penta-atomic polyhalides (e.g., IF_4^-, BrF_4^-, ICl_4^-) are all planar and corresponds to a 12-electron ditribution around the central atom, lone pairs in trans positions. The VSEPR theory suggests a pentagonal bipyramind disposal of valence electrons (one lone pair) for BrF_6^- and IF_6^- ions. Spectroscopic studies indicate that the ions are not octahedral but complete elucidation of the structure is still awaited. The structure of IF_8^- ion, known only as $CsIF_8$, NO $[IF_8]$ and $NO_2[IF_8]$, is also not known.

24.3.6 Pseudohalogens (Halogenoids)

A number of uninegative ions are known which show close resemblance to the halides (see below); some of these may even be oxidized to a dimeric molecule corresponding to the oxidation of halides to the dihalogen molecules. These uninegative ions are called pseudohalides and the related molecules are called pseudohalogens. The common pseudohalides and their respective pseudohalogens (where they exist) are shown below :

Pseudohalide		Pseudohalogen	Hydracid
CN^-	*cyanide*	*Cyanogen* $(CN)_2$	HCN
SCN^-	*thiocyanate*	*thiocyanogen* $(SCN)_2$	HSCN
$SeCN^-$	*selenocyanate*	*selenocyanogen* $(SeCN)_2$	—
$SCSN_3^-$	*azidodithiocarbonate*	*azidocarbondisulphide* $(SCSN_3)_2$	—
$TeCN^-$	*tellurocyanate*	—	—
OCN^-	*cyanate*	—	HOCN
NCO^-	*isocyanate*	—	HNCO
CNO^-	*fulminate*	—	HCNO
N_3^-	*azide*	—	N_3H

The main points of similarity between pseudohalogens and halogens are

(i) Like the dihalogen molecules, the pseudohalogens undergo thermal and photochemical dissociation : for example,

$$(CN)_2 \longrightarrow 2CN^{\cdot}$$

The reactions of these radicals are similar to those of halogen atoms, including chain reaction :

$$H_2 + CN^{\cdot} \longrightarrow HCN + H^{\cdot}$$

$$H^{\cdot} + (CN)_2 \longrightarrow HCN + CN^{\cdot} \text{ ... and so on.}$$

(ii) The pseudohalide anions may be oxidized easily to the pseudohalogen :

$$(CN)_2(aq) + 2e \rightleftharpoons 2CN^-(aq) \qquad E^\circ = 0.27\text{ V}$$

$$(SCN)_2(aq) + 2e \rightleftharpoons 2SCN^-(aq) \qquad E^\circ = 0.77\text{ V}$$

Thus, thiocyanogen may be prepared by heating HSCN with MnO_2 (compare preparation of HCl)

$$MnO_2 + 4HSCN = (SCN)_2 + Mn(SCN)_2 + 2H_2O.$$

Thiocyanogen would oxidize iodide to I_2 :

$$(SCN)_2 + 2I^- = 2SCN^- + I_2.$$

(iii) Pseudohalogens react with aqueous alkali similar to the halogens :

$$(CN)_2 + 2NaOH = NaCN + NaOCN + H_2O$$

$$(SCSN_3)_2 + 2NaOH = NaSCSN_3 + NaOSCSN_3 + H_2O.$$

[*compare :* $[Cl_2 + 2NaOH = NaCl + NaOCl + H_2O]$

However, the cyanate ion is not like the OCl^- ion.

(iv) Solubility of the silver salts of pseudohalides in water resembles those of silver halides, e.g., AgCN is insoluble in water but dissolves in aqueous ammonia.

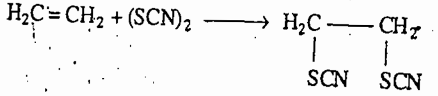
(v) The pseudohalogens can also form interhalogens and interpseudohalogens, for example ClCN, ICN, CNN_3. Interhalogen pseudohalogens are also known

$$CNBr + NaN_3 = NaBr + CNN_3,$$

$$Cl_2 + (SCN)_2 = 2SCNCl \text{ (in chloroform; white crystals).}$$

(vi) The pseudohalides may from stable complexes similar to the halocomplexes e.g. $[Cu(CN)_4]^-$, $K_2[Hg(SCN_4]$ etc.

(vii) Pseudohalogens can add to C = C double bonds, e.g.



$$H_2C{=}CH_2 + (SCN)_2 \longrightarrow \underset{SCN}{H_2C}\!-\!\!-\!\underset{SCN}{CH_2}$$

(viii) Similar to halogen hydracids, there are hydracids corresponding to many pseudohalides. However, these are considerably weak acid, e.g., HCN : $pK_a = 9.2$, $N_3H : pK_a = 4.92$.

(ix) The mode of decomposition of many pseudohalides resembles that of metal halides :

$$Pb(SCN)_4 = Pb(SCN)_2 + (SCN)_2$$

$$[PbCl_4 = PbCl_2 + Cl_2]$$

$$Cu(CN)_2 = CuCN + \tfrac{1}{2}(CN)_2$$

$$[CuI_2 = CuI + \tfrac{1}{2}I_2]$$

Pseudohalogens may also form compounds similar to the halogens, e.g. $SO_2(N_3)_2$, analogue of SO_2Cl_2; $CO(N_3)_2$, analogue of $COCl_2$.

However, there are some inherent differences between the halogens and pseudohalogens. Thus,

(i) most pseudohalogen and pseudohalides are strong coordinating agents (in contrast, the halides are weak ligands).

(ii) Many of them are also ambident bases, having two alternative sites for coordination. The thiocyanate ion SCN^- has nitrogen as the hard base site and sulphur at the soft base site. Both nitrogen and carbon in cyanide (CN^-) are hard base sites, but the C atom is the stronger hard base.

(iii) The pseudohalides are good π-acids and occupy higher positions than the halides in the spectrochenical series (see chapter 27).

$$CN^- > N_3^- > -NCS^- > NCSe^- > F^- > Cl^- > Br^- \simeq SCN^- > I^-$$

(iv) On the other hand, most halides are more polarizable than many of the pseudohalides which is reflected in the nephelauxetic series (chapter 27)

$$CN^- > I^- > Br^- > -SCN^- > Cl^- > N_3^- > NCO^- > F^-$$

(v) The hydracids formed by pseudohalide anions are all extremely weak, e.g. HCN $(pK = 9.2)$; HNCO $(pK = 3.5)$; $(pK = 4.9)$.

The hydracids formed by pseudohalide anions are all extremely weak, e.g. HCN $(pK = 9.2)$; HNCO $(pK = 3.5)$; N_3H $(pK = 4.9)$.

Thus, the comparison of pseudohalogens with halogens is a matter of convenience and obviously has its own limitations. The comparison should not be dragged too much.

Preparation and properties of cyanogen, thiocyanogen, cyanides and thiocyanates have been described in section 21.3.8.

24.3.7 Basic Properties of Halogens

The general trend of increasing basic character of the elements down any group in the periodic table is also observed among the halogen group, though somewhat less pronounced than in the previous groups. The basic properties of iodine are much less marked than those of tin, antimony and tellurium–the elements preceding it in the same period. This may be associated, at least partly, with the observed increases in non-metallic character as one moves toward right along any period –a consequence of increasing nuclear charge. Astatine, the last member of the group, is expected to show the most pronounced basic character but little is known about the chemistry of this unstable element.

We have already discussed the polyhalogen cations like I_2^+, Br_2^+ etc. Complexes containing positive iodine are numerous, as we have already encountered :

ICl in pyridine : $2ICl + 2py \rightleftharpoons [Ipy_2]^+ [ICl_2]^-$

ICl melt + $AlCl_3$: $2ICl + AlCl_3 \rightleftharpoons [I_2Cl]^+ [AlCl_4]^-$

ICN (melt) : $3ICN \rightleftharpoons [I_2(CN)]^+ [I(CN)_2]^-$

Similarly, we have species like $[Brpy_2]^+NO_3$, $[Clpy_2]^+ NO_3$, $[BrF_2^+]$ $[BrF_4^-]$ etc. with the halogen atom in a positive oxidation state. The ionization schemes shown above are confirmed by electrical conductance studies.

The action of ICl on acetanilide and salicyclic acid produces 4–iodoacetanilide and 3, 5- diiodosalicylic acid respectively. As the attack occurs at electronrich sites, the iodine may be taken to be positive.

Compounds containing I^I

Compounds containing I^I may be generally prepared by reacting stoichiometric quantities of iodine with excess of pyridine and a silver salt in chloroform :

$$AgNO_3 + 2py + I_2 = [Ipy_2]^+NO_3^- + AgI$$

The precipitated AgI is removed by filtration and the complex isolated. Electrolysis of the chloroform solution liberates iodine at the cathode in consistence with the cationic nature of iodine.

Direct reaction of iodine with pyridine produces $[Ipy_2]^+I_3^-$; X-ray study shows the ion $[py - I - py]^+$ to be planar. A similar cationic species is obtained by grinding thiourea (NH_2.CS. NH_2, abbreviated tu) and iodine :

$$2I_2 + 2tu \longrightarrow [tu - I - tu]^+ I_3^-$$

The I^+ cation may be retained on a cation exchange resin by passing a solution of iodine in an inert solvent. The bound I^+ may be subsequently eluted with KI—this gives an estimate of the bound I^+. The cation may also be eluted with other reagents :

$$I - I + H^+ Resin^- \longrightarrow I^+Resin^- + HI$$

$$I^+ - Resin^- + KI \longrightarrow I - I + K^+ Resin^-$$

$$2I^+ - Resin^- + H_2SO_4\,(\textit{anhydrous}) \longrightarrow I_2SO_4 + 2H^+ Resin^-$$

$$I^+ - Resin^- + HNO_3\,(\textit{alcohol}) \longrightarrow INO_3 + H^+ Resin^-$$

In aqueous solution, the I^+ reacts readily with OH^- ions :

$$I^+ + OH^- \longrightarrow HOI$$

$$2HOI + OI^- \longrightarrow IO_3^- + 2I^- + 2H^+$$

I^+ has also been stabilized by macrocylic ligands, e.g. [2,2,2]-cryptate. The follwing reaction in chloroform has an equilibrium constant greater than 10^7.

$$I_2 + [2,2,2] \rightleftharpoons ([2, 2, 2]I)^+ + I^-$$

Unstable covalent compounds of the type $BrNO_3$, INO_3, ClO_3 are also known for Br(I) and I(I). These are formed by disproportionation of Br_2 or I_2 in presence of silver salts in nonaqueous solutions, e.g., ether.

$$I_2 + AgNO_3 = INO_3 + AgI$$

The compounds hydrolyze in accordance with a positive halogen center.

$$IClO_4 + HOH = HOI + HClO_4$$

This is supported by reactions of the type.

$$KNO_3 + INO_3 = K\,[I(NO_3)_2]$$

Compounds of I^{III}

Though there is no structural evidence for I_3^+, it is formally present in compounds like $I(CH_3COO)_3$, $I(ClO_4)_3$, IPO_4 and $I(SO_3F)_3$. Iodine(III) acetate is obtained when I_2 is oxidized by fuming nitric acid in acetic anhydride.

The phosphate is obtained if phosphoric acid is also present. Oxidation may also be caused by ozone, e.g.

$$2\,I_2 + 3AgClO_4 \longrightarrow I(ClO_4)_3 + 3AgI \text{ (in ether; } -85°C)$$

$$I_2 + 6HClO_4\,(\textit{anhydrous}) \xrightarrow{O_3} 2I(ClO_4)_3 + 3H_2O$$

$$I_2 + HNO_3\,(\textit{fuming}) + (CH_3CO)_2O \longrightarrow I\,(CH_3\,COO)_3$$

$$I_2 + HNO_3\,(\textit{conc}) + H_3PO_4 \longrightarrow IPO_4.$$

The salts containing I(III) are well-defined crystalline compounds — iodine(III) acetate forms colourless **hexagonal** crystals, the phosphate is yellow and the perchlorate is greenish-yellow in colour. **Results** of electrolysis of the acetate in acetic anhydride (silver electrode) is consistent with the ionization scheme :

$$I(CH_3COO)_3 \rightleftharpoons I^{3+} + 3CH_3COO^-$$

Three faradays of electricity are required for the formation of one mole of AgI at the cathode : $I^{3+} + Ag + 3e \longrightarrow AgI$.

The salts are moisture sensitive and get readily hydrolyzed with disproportionation :

$$5\,IPO_4 + 9H_2O \rightleftharpoons I_2 + 3HIO_3 + 5H_3PO_4$$

$$3\,I(NO_3)_3 + 6H_2O \rightleftharpoons HI + 2HIO_3 + 9HNO_3.$$

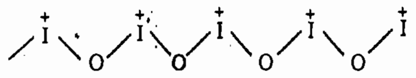
They contain essentially covalent I—O bonds.

Bromine (III) is present in the compounds $Br(OSO_2F)_3$ and $K[Br(OSO_2F)_4]$.

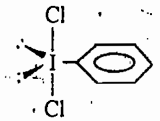
Iodosyl compounds contain the IO^+ group which contains I^{III}. These are obtained by reacting I_2O_5 and I_2 in concentrated acids to give salts like $[IO^+]_2SO_4$, $[IO^+]_2S_2O_7$, $[IO^+]_2SeO_4$ etc.

$$3I_2O_5 + 2I_2 + 5H_2SO_4 = 5(IO)_2SO_4 + 5H_2O.$$

Such compounds are also formed when iodine is oxidized with ozone in strong acids. $(IO)NO_3$ and $(IO)SO_3F$ have also been prepared in this manner. Not much is known about the compounds or their structure. Iodosyl sulfate, $(IO)_2SO_4$, is a yellow solid which may have a zig-zag chain of I – O – I – cross-linked by the anion (24-XXIII)



24-XXIII



24-XXIV

A large number of organic compounds containing I^{III} are well known, e.g., triphenyliodine, $(C_6H_5)_3I$ and salts of the type $(C_6H_5)_2I^+\,X^-$ (X^- is any common anion). Iodo-benzene reacts directly with chlorine to give $C_6H_5ICl_2$ in which the phenyl group occupies an equatorial position in a trigonal bipyramid geometry (24-XXIV). Iodosylbenzene, I(Ph)O is a polymeric solid containing – I(Ph) – O –I(Ph) – O – chains. Many other compounds with substituted aryl groups are also remarkably stable.

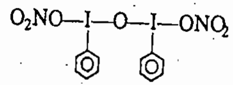
I^V is known in many compounds like $I(OTeF_5)_5$, $O = I(OTeF_5)_3$ and $F_xI(OTeF_5)_{5-x}$. Selenium analogs of these compounds are also known.

Iodyl Salts contain the IO_2^+ ion; the sulfate is produced by reacting I_2O_5 with SO_3;

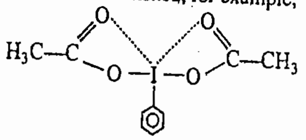
$$I_2O_5 + SO_3 = (IO_2^+)_2\,SO_4^{2-}$$

Peroxodisulfuryl diflouride, $S_2O_6F_2$ yields $[IO_2]^+\,[SO_3F]^-$ with I_2O_5.

Several organocompounds containing I^V are also well established, for example,



24-XXV



24-XXVI

24.3.8 Aqueous Solution Chemistry

Halogens present a broad as well as complicated aqueous solution chemistry, much of which we have encountered in connection with the oxoacids and their anions. The standard potentials for the halogens (p. 531) present several disproportionation modes. however, not all inferences from redox potential data fit real experiences. As already pointed out, kinetic factors, pH etc. play important roles in determining the ultimate course of a reaction; a few typical examples are discussed.

(i) Reduction potential values suggest that both bromide and iodide should be oxidized by oxygen at $[H^+] = 1$. Thanks to the slowness of the process, we can reasonably handle aqueous solutions containing these halides in titrimetric analysis, though with precaution. Aereal oxidation of iodide is catalyzed by tansition metal ions.

(ii) $E°$ for the half-reaction.

$$ClO_2^- + 6H^+ + 6e \rightleftharpoons Cl^- + 3H_2O$$

is calculated at 1.45 V. Nevertheless, the reaction does not occur in aqueous solutions.

(iii) The disproportionation equilibrium

$$3OCl^- \rightleftharpoons ClO_3^- + 2Cl^-$$

depends largely on pH though H^+ ions do not appear in the above equation. We recall that HOCl is a weak acid, while $HClO_3$ and HCl are both strong. Hence, in acid medium, the concentration of OCl^- ion is largely reduced and disproportionation is suppressed. Disproportionation of the hypochlorite ion (i.e., in alkaline medium) on the other hand, is more pronounced.

(iv) HOI readily disproportionates into IO_3^- and I_2. But in presence of HCl, the fairly stable ICl_2^- ion is formed :

$$HOI + 2HCl \longrightarrow ICl_2^- + H^+ + H_2O.$$

The relevant potentials are :

$$IO_3^- \xrightarrow{+1.23\,V} ICl_2^- \xrightarrow{+1.06\,V} I_2.$$

Iodate in presence of hydrochloric acid is used in a large number of iodimetric determination :

$$IO_3^- + 2Cl^- + 6H^+ + 4e \rightleftharpoons ICl_2^- + 3H_2O$$

The iodate is first reduced to I_2 which concentrates largely in an organic solvent like CCl_4 (added to the titrating mixture). At the end-point, the I_2 is fully oxidized to $H_3O^+\,ICl_2^-$ and is transferred to the aqueous layer, leaving the organic layer colourless.

Q. 24.18 *One mole of IO_4^- reacts with excess I^- in neutral solution to form one mole of I_2. If the reaction mixture is subsequently acidified, further three moles of I_2 are liberated. Derive equations for the reactions involved.*

Hint : $IO_4^- + 2I^- + H_2O \longrightarrow IO_3^- + I_2 + 2OH^-$

$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

(v) The disproportionation of chlorate to perchlorate and chloride in aqueous solution according to the reaction

$$4ClO_3^- \longrightarrow 3ClO_4^- + Cl^-$$

is energetically favourable. But the disproportionation is not found to occur noticeably even at the boiling point of water, Solid $KClO_3$ readily diproportionates on heating.

(vi) Liberation of O_2 from water in basic solution involves a low reduction potential.

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^- \quad E^\circ = 0.40\ V$$

So it appears that in basic solution all halogens (except At) should be able to liberate O_2 from water. But the reaction occurs extremely slowly even with fluorine (initially forming F_2O).

Q. 24.19 *Bromine reacts with ice-cold base to give bromide and hypobromite; at room temperature and above, the products are bromide and bromate. But iodine reacts with base at all conditions to give iodide and iodate. Comment.*

Hint : hypoiodite ions disproportionate too rapidly to be isolated.

24.3.9 Oxohalogen Fluorides (Halogen oxide fluoride)

These are compounds with a larger halogen atom linked to fluorine and oxygen, F_nXO_m. They are also called halogen oxofluorides. Removal or addition of F^- ions to the neutral molecules give rise to cations and anions corresponding to these compounds. Some of these compounds and their correspnding ions are shown in Table 24.18.

TABLE 21:18

Oxohalogen fluorides F_nXO_m and ions derived from them

Formal ox.no of X	X = Cl		X = Br		X = I	
III	FClO		–	–	–	–
V	$FClO_2$	ClO_2^+	$FBrO_2$	BrO_2^+	FIO_2	$F_2IO_2^-$
		$F_2ClO_2^-$		$F_2BrO_2^-$		
	F_3ClO	F_2ClO^+	F_3BrO	F_2BrO^+	F_3IO	–
		F_4ClO^-		F_4BrO^-		–
VII	$FClO_3$	–	$FBrO_3$	–	FIO_3	–
	F_3ClO_2	$F_2ClO_2^+$	–	–	F_3IO_2	–
					F_5IO	

FClO is an extremely unstable gas which may be prepared by photolysis of a mixture of ClF and O_3 in argon at 4-15 K. It rapidly decomposes at room temperature :

$$2FClO \longrightarrow FClO_2 + ClF$$

The molecule is bent with two lone pairs on the Cl-atom.

$FClO_2$ (chlorine dioxide fluoride) is obtained in good yield by reacting $NaClO_3$ with ClF_3 at room temperature for one day.

$$4ClF_3 + 6NaClO_3 \longrightarrow 6FClO_2 + 6NaF + 2Cl_2 + 3O_2$$

It is a colourless gas (b.p. –6°) thermally stable at room temperature and may be kept dry in quartz vessels. It decomposes appreciably above 300°

$$FClO_2 \longrightarrow ClF + O_2$$

The gas also undergoes slow hydrolysis at room temperature

$$2FClO_2 + H_2O \longrightarrow 2HF + 2ClO_2 + 1/2\ O_2$$

$$FClO_2 + 2OH^-(aq) \longrightarrow ClO_3^- + H_2O.$$

Otherwise the compound is highly reactive even at very low temperatures. It ignites with liquid ammonia (–78°) forming NH_4Cl and NH_4F. It explodes with SO_2 (–40°) and HBr (–110°). Some other reactions are :

$$HCl(l) + FClO_2 \longrightarrow HF + ClO_2 + \tfrac{1}{2} Cl_2 \quad (-110^\circ)$$

$$HOSO_2F + FClO_2 \longrightarrow HF + ClO_2OSO_2F \quad (-78^\circ)$$

$$SO_3 + FClO_2 \longrightarrow ClO_2OSO_2F \quad (-10^\circ)$$

The last reaction is different from the others (*insertion*).

As expected, $FClO_2$ is a good fluorinating and oxidizing agent : it oxidizes SF_4 to SF_6(SF_4O and SF_2O_2 above 50°); UF_4 is oxidized to UF_5 (room temp) and UF_6 (100°). Fluorination may occur with or without oxidation.

$$AsF_3 + 3FClO_2 \longrightarrow [ClO_2]^+ [AsF_6]^- + 2ClO_2$$

$$SbF_5 + FClO_2 \longrightarrow [ClO_2]^+ [SbF_6]^-$$

$$2SbF_5 + FClO_2 \longrightarrow [ClO_2]^+ [Sb_2F_{11}]^-$$

$FClO_2$ may also act as a fluoride ion accepter :

$$CsF + FClO_2 \longrightarrow Cs^+ [F_2ClO_2]^-$$

The product is a white solid stable at room temperature.

The $FClO_2$ molecule is pyramidal with one lone pair of electrons on the central Cl atoms.

F_3ClO (chlorine trifluoride oxide) is made by direct fluorination of Cl_2O or of $ClONO_2^*$.

$$Cl_2O + 2F_2 \longrightarrow F_3ClO + ClF \text{ (in presence of NaF; –78°).}$$

$$ClONO_2 + 2F_2 \longrightarrow F_3ClO + FNO_2 \text{ (–35°).}$$

$$(Cl_2O + N_2O_5 \longrightarrow 2ClONO_2 \text{ (0°).}$$

The first method is risky for bulk preparation since liquid Cl_2O is highly explosive in nature.

F_3ClO is a colourless volatile liquid (b.p. 28°) stable at room temperature though it reacts rapidly with glass/quartz. Teflon or passivated metal containers may be used to store it. It decomposes to ClF_3 and O_2 above 300°. It is hydrolyzed first to HF :

$$F_3ClO + H_2O \longrightarrow FClO_2 + 2HF$$

$$F_3ClO + HF \longrightarrow [F_2ClO]^+ [HF_2]^-$$

It also acts as a fluoride ion donor (Lewis base) as well as acceptors (Lewis acid) forming stable solid adducts :

$$F_3ClO + AsF_5 \longrightarrow [F_2ClO]^+ [AsF_6]^-$$

$$F_3ClO + CsF \longrightarrow Cs^+ [F_4ClO]^-$$

It is a good fluorinating agent at room temperature, rapid on heating :

$$Cl_2 + F_3ClO \longrightarrow 3ClF + \tfrac{1}{2} O_2 \ (200°)$$

$$Cl_2O + F_3ClO \longrightarrow 2ClF + FClO_2 \ (\text{room temp}).$$

It acts as both fluorinating and oxidizing/oxygenating agent towards a number of chemicals. For example, SF_4 is oxidized (in presence of CsF,25°) to SF_6 together with other products like SF_5Cl, SF_4O (and $FClO_2$); N_2F_4 yields (100°) NF_3, FNO and ClF.

F_3ClO acts as a reducing agent towards PtF_6

$$F_3ClO + PtF_6 \longrightarrow [F_2ClO]^+ [PtF_6]^- + \tfrac{1}{2} F_2$$

The molecule has a trigonal bipyramid disposal of the valence orbitals of chlorine with one lone pair.

$FClO_3$ (perchloryl fluoride) is best prepared by the reaction of a superacid like $SbF_5 - HOSO_2F$ or $SbF_5 - HF$ on $KClO_4$

$$KClO_4 + SbF_5 + 2HF \longrightarrow FClO_3 + KSbF_6 + H_2O \ (40° - 50°)$$

It may also be prepared by (i) electrolysis of $NaClO_4$ in anhydrous HF (ii) the action of F_2 on $NaClO_3$ *(aq)*.

$FClO_3$ is a colourless toxic gas (bp – 46.7°) which is thermally stable to about 450°C. The stability must be kinetic in origin since $\Delta \overset{0}{G}_f$ for the gas at 298K is + 48·1 kJ mol^{-1}.

The compound is notably inert, particularly at room temperature, and undergoes slow hydrolysis only at 250 – 300°C with concentrated aqueous NaOH:

$$FClO_3 + 2NaOH \longrightarrow NaClO_4 + NaF + H_2O$$

However, alcoholic KOH reacts appreciably at 25°.

$FClO_3$ does not form adducts with either Lewis acids or bases – it appears that the tetrahedral geometry is preferred in comparison to planar ClO_3^+ or trigonal bipyramidal $F_2ClO_3^-$ ions.

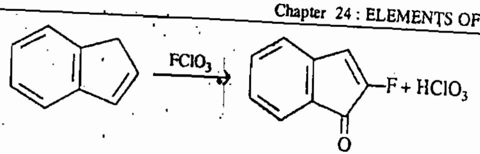
[In contrast, F_3ClO has a pseudo trigonal bipyramidal disposal of the valence orbitals around Cl and is readily converted to more stable F_2ClO^+ (pseudotetrahedral) or F_4ClO^- (pseudo-octahedral)].

$FClO_3$ is highly susceptible to nucleophilic attack at Cl and may be used to introduce ClO_3 group in an organic compound :

$$FClO_3 + C_6H_5^- Li^+ \longrightarrow LiF + C_6H_5ClO_3$$

$$FClO_3 + RO^- \longrightarrow F^- + ROClO_3.$$

It may also be used as an oxidant at high temperature and as a fluorinating agent. H in CH_2 groups may be replaced by F; sometimes it also acts as a 2-center electrophile leading to oxofluorination, as for example with the cyclic double bond conjugated to an aromatic ring in indene.



$FClO_2$ has the potentiality of an oxidizer in rocket propellant fuels like hydrazine. It is also useful as an insulator in high-voltage systems — its resistance to dielectric breakdown is much greater than that of SF_6.

F_3ClO_2 is highly reactive in comparison to the other Cl(VII) species, i.e., $FClO_3$. It is prepared by reacting $FClO_2$ with PtF_6 :

$$2FClO_2 + 2PtF_6 \longrightarrow [F_2ClO_2]^+ [PtF_6]^- + [ClO_2]^+ [Pt\,F_6]^-$$

Reaction with FNO_2 now gives both F_3ClO_2 and $FClO_2$. The latter is slightly less volatile than F_3ClO_2 and may be removed by fractional condensation at –112°. F_3ClO_2 may be further purified by forming a stable adduct with BF_3.

$$FClO_2 + BF_3 \longrightarrow [ClO_2]^+ [BF_4]^- \ (\text{dissociates})$$

$$F_3ClO_2 + BF_3 \longrightarrow [F_2ClO_2]^+ [BF_4]^- \ (\text{stable})$$

F_3ClO_2 is regenerated by reaction with FNO_2.

It is a colourless, corrosive gas (b.p. – 21.6°C) which must be handled in Teflon or sapphire apparatus. It is a strong oxidizing as well as fluorinating agent. Stable adducts are formed by Lewis acids like BF_3, AsF_5 etc.fluoride ion donors.

[Sec. 24.3.9
Bromine oxofluorides]

Bromine Oxofluorides

$FBrO_2$, F_3BrO and $FBrO_3$ are the only recognized bromine oxide fluorides. All of them are reactive. Some important informations about these compounds are summarized below :

$FBrO_2$ **Bromyl fluoride**	**F_3BrO** **Bromine oxide trifluoride**	**$FBrO_3$** **Perbromyl fluoride**
(a) ***Preparation***		
(i) $5BrF_5 + 2I_2O_5 = 5FBrO_2 + 4IF_5$	(i) $K[F_4BrO]^* + HF(\text{anhy.}) \xrightarrow{-72°C} F_3BrO + KHF_2$	(i) $KBrO_4 + 2AsF_5 + 3HF \longrightarrow FBrO_3 + KAsF_6 + [H_3O]^+ [AsF_6^-]$
(b) ***Nature***		
Colourless liquid (mp –9°), rapid decomp. above 55° ($BrF_3 + Br_2 + O_2$). Attacks glass at room temp. Hydrolysed violently : $FBrO_2 + 2OH^- \longrightarrow BrO_3^- + F^- + H_2O$ $AsF_5 + FBrO_2 \longrightarrow [BrO_2]^+ [AsF_6]^-$	Colourless liquid, freezes at –5°. Slowly decomp. at room temp.($BrF_2 + O_2$). $AsF_5 + F_3BrO \longrightarrow [F_2BrO]^+ [AsF_6]^-$	Colourless gas, Freezes at 2.4°. Slow decomp. at room temp. Attacks glass. Rapid hydrolysis $FBrO_3 + H_2O \longrightarrow BrO_4^- + HF + H^+$

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*Prepared by : $KBrO_3 + KBrF_6 \longrightarrow K[F_2BrO_2]\downarrow + K[F_4BrO]$

The structures of these compounds and the derived ions are in conformity with VSEPR expectations.

Iodine Oxofluorides

There is no compound containing I(III), e.g. FIO is not known, I(V) compounds include FIO_2 and F_3IO; I(VII) compounds are FIO_3, F_3IO_2 and F_5IO.

FIO_2 and F_3IO : These are prepared from I_2O_5:

$$I_2O_5 + F_2 \longrightarrow 2\,FIO_2 + 1/2\,O_2\ (\textit{anhydrous HF; } 20°C)$$

$$I_2O_5 + 3IF_5 \longrightarrow 5\,F_3IO\quad (105° \textit{ followed by cooling})$$

FIO_2 is a colourless polymeric solid; it decomposes without melting above 200°. Hydrolysis is rapid with alkali :

$$FIO_2 + 2\,OH^- \longrightarrow IO_3^- + F^- + H_2O$$

Fluoride ion transfer forms $F_2IO_2^-$ ion

$$KF + FIO_2 \longrightarrow K^+[F_2IO_2]^-\ (\text{in HF})$$

KF_2IO_2 is also formed by reacting KIO_3 with concentrated (40%) HF. The ion $F_2IO_2^-$ has axial F atoms at 200 pm; the lone pair in the equatorial plane suppresses the OIO angle to 100°.

F_3IO is a colourless crystalline solid; it disproportionates above 110°

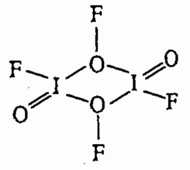
$$2F_3IO \longrightarrow FIO_2 + IF_5$$

FIO_3 and F_3IO_2 are prepared by fluorination of (i) HIO_4 with $F_2/HF(l)$ and (ii) $Ba_3H_4(IO_6)_2$ with HSO_3F respectively. FIO_3 is a white crystalline solid which decomposes on heating to 100°.

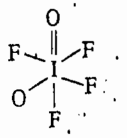
$$FIO_3 \longrightarrow FIO_2 + \tfrac{1}{2}O_2$$

It forms adducts like $[IO_3]^+[BF_4]^-$ and $[IO_3]^+[AsF_6]^-$

F_3IO_2 is a low melting yellow solid (mp 41°). It also forms adducts with AsF_5 etc. The solid as well as the vapour at room temperature consists of centrosymmetric dimers formed by sharing of two O atoms (24-XXVII); the environment around each I is octahedral (X-ray and vibration spectrum). Dissociation into monomers begins at 100° and is nearly complete at 185°. Solution of F_3IO_2 in BrF_3 (–48°) shows F–19 nmr and Raman spectra indicating the presence of O-bridged trimers. $(F_3IO_2\,SbF_5)_2$ is cyclic with alternating SbF_4 and IF_4 units linked through O.



24-XXVII



24-XXVIII

F_5IO has no chlorine or bromine analogue. It results from the reaction of IF_7 with water, I_2O_5 or even glass or silica. It is a colourless solid (mp 45°C) stable towards hydrolysis. The octahedral environment around I (24.XXVIII) has been confirmed by vibrational spectrum and 19F nmr studies. This rules out the alternative formulation containing I(V) in 5-coordination, F_4IOF.

24.3.10 Halogen Derivatives of Oxoacids

Replacement of hydrogen(s) in oxoacids by halogens produces a large number of compounds. Our discussion will be limited to the halogen perchlorates, nitrates and fluorosulphates.

Halogen perchlorates ($XOClO_3$, X = F, Cl, Br, I?) may be prepared through reactions like:

$$NF_4ClO_4 \longrightarrow NF_3 + FOClO_3 \quad (\text{heat})$$

$$CsClO_4 + ClOSO_2F \longrightarrow ClOClO_3 + CsSO_3F \quad (-45°)$$

$$ClOClO_3 + Br_2 \longrightarrow BrOClO_3 + BrCl_2 \quad (-45°)$$

[Iodine reacts with $ClOClO_3$ at –50° to form a polymeric white solid $I(OClO_3)_3$ which cannot be purified].

The chlorine and bromine compounds are extremely unstable and shock sensitive – decomposition temperatures 20°C and –20°C respectively. $FClO_4$ obtained by the action of F_2 on concentrated $HClO_4$ explodes, on freezing but the pure compound obtained from NF_4ClO_4 is a colourless gas stable to about 100° above which it decomposes to oxygen, ClF and $FClO_2$. The compound adds to C = C double bonds in fluorocarbons to form perfluoroalkyl perchlorates :

$$F_2C{=}CF_2 + FOClO_3 \longrightarrow F_3C.CF_2OClO_3$$

It is also useful in the synthesis of anhydrous metal perchlorates.

Halogen fluorosulfates ($XOSO_2F$, X = F, Cl, Br, I) are known for all four halogens. $FOSO_2F$ is obtained by direct addition of F_2 to SO_3; others are conveniently made by reacting the appropriate X_2 with equimolar quantity or peroxodisulfuryl difluoride, FO_2SOOSO_2F ($S_2O_6F_2$) Excess of $S_2O_6F_2$ produces $Br(OSO_2F)_3$ and $I(OSO_2F)_3$ with bromine and iodine respectively.

$FOSO_2F$ is a colourless gas (b.p. –31.3°); $ClOSO_2F$ is a yellow liquid (b.p. 45°); $BrOSO_2F$ is also a red-brown liquid (b.p. 117.3°) while $IOSO_2F$ is a black solid (m.p. 51.5°). All are thermally unstable, moisture sensitive and highly reactive compounds.

$Br(OSO_2F)_3$ and $I(OSO_2F)_3$ are pale yellow solids (m.p. 59° and 32° resp.). They decompose on heating to form respective $XOSO_2F$.

Halogen nitrates ($XONO_2$, X = F, Cl, Br, I) may be made by reacting alcoholic solutions of the halogens with silver nitrate at low temperature.

$$AgNO_3 + Cl_2 = AgCl + ClONO_2$$

(Excess $AgNO_3$ gives $Br(ONO_2)_3$ with Br_2/I_2 respectively).

Other reactions used are like :

$$F_2 + KNO_3 \longrightarrow FONO_2$$

$$Cl_2O + N_2O_5 \longrightarrow 2ClONO_2 \quad (0°C)$$

$$ClF + HONO_2 \longrightarrow ClONO_2 + HF \quad (0°C)$$

$$BrF_5 + LiNO_3\ (\text{excess}) \longrightarrow BrONO_2 \quad (0°C)$$

All halogen nitrates are thermally unstable and explosive gases. $FONO_2$ and $ClONO_2$ are colourless, while the bromine and iodine compounds are yellow. $ClONO_2$ may be used to convert metal chlorides to anhydrous metal nitrates.

SUMMARY

Introduction : The halogens, particularly chlorine, play a major role in our civilization. F—19 is very suitable for nmr studies.

Fluorine is obtained by electrolysing molten mixtures of KF and HF around 70-100°C in mild steel cells. Chemically, fluorine may be prepared by the reaction

$$3SbF_5 + K_2MnF_6 \longrightarrow 2KSbF_6 + MnF_3 + \frac{1}{2}F_2 \ (150°C)$$

Chlorine is obtained mainly as a by-product in the electrolytic preparation of sodium hydroxide. Bromine and iodine are prepared by chlorinating brine.

Fluorine is used in the manufacture of UF_6 in nuclear power plants. Chlorine is used mainly as an industrial bleaching agent and in the manufacture of chlorinated organo compounds (e.g. polyvinyl chloride). Bromine is used in making several organo compounds used as pesticides and as flame retardant in fabrics. Silver bromide is extensively used in photography. Iodine is used in making several organic and inorganic chemicals. Sodium iodide and iodate are added to edible common salt to supplement natural iodine deficiency.

General Properties : The colour of gaseous diatomic halogen molecules arise due to absorption of visible radiation for the $\pi^* \rightarrow \sigma^*$ transition which is normally forbidden (singlet-triplet) but is gradually relaxed with heavier halogens. Also, the separation between the two levels decreases from F_2 to I_2, shifting the absorption to lower frequencies; I_2 transmits strongly in the violet region. This is also the colour of I_2 in nonpolar solvents (e.g. CCl_4). In polar solvents, solvent I_2 charge transfer occurs at a higher frequency and shifts to the blue end of the spectrum, and the solution appears brown.

Reactivity of the halogens decreases from fluorine to iodine. Fluorine is highly reactive, mainly because of the low bond dissociation enthalpy of F_2. Its small size and highest electronegativity gives rise to some unique features in its chemistry.

The halogens form ionic and covalent halides, fluorides being most ionic owing to lattice energy stabilization. Besides the common oxidation state I, Cl, Br and I show positive oxidation states in their oxoacids : HOX, HOXO, $HOXO_2$, $HOXO_3$ and $I(O)(OH)_5$ or H_5IO_6.

In all oxidation states except +VII, the halogens have marked tendency to disproportionate.

Halides : Almost all elements in the periodic table (except He, Ne and Ar) form binary compounds with halogens. The compounds may be simple ionic or molecular, sometimes polymeric. These may be prepared mostly by direct reaction or by heating a metal in dry HCl or its oxide with carbon and chlorine. For halides of general formula MX_n, the halides are often essentially ionic when n is small and M is relatively large. If n is large, the halide is likely to be molecular.

The hydrogen halides are all strong acids in aqueous solution except HF which has high bond energy and forms strong H-bond. Acid strength decreases in the order H—I > H—Br > H—Cl > H—F, the bond energy being the principal factor. Liquid HF is a good nonaqueous ionizing solvent.

Molecular halides are known for most elements in periodic groups 13—16 and also for heavy elements, for example WF_6 and UF_6. The halide ion may act as a bridge in some molecular halides, for example, in gaseous Al_2Cl_6 dimer and polymeric $BeCl_2$. Fluoride bridges are also known, as in glassy BeF_2 (infinite F—Be—F—chains); cyclic tetramers of NbF_5 and TaF_5 (linear M—F—M bridge) and VF_5 (infinite chain polymer).

Oxides : Binary compounds of fluorine and oxygen are better described as oxygen fluorides. Oxides of other halogens are unstable, the higher oxides being more stable than the lower ones. Stability is greatest for the oxides of iodine, then chlorine, the oxides of bromine being the least stable.

$$2HgO + 2Cl_2 = HgCl_2.HgO + Cl_2O$$
$$2KClO_3 + 2H_2C_2O_4 = 2ClO_2 + 2CO_2 + K_2C_2O_4 + 2H_2O$$
$$2ClO_2 + 2O_3 = Cl_2O_6 + 2O_2$$
$$4HClO_4 + P_4O_{10} = 2Cl_2O_7 + 4HPO_3$$
$$2HIO_3 = I_2O_5 + H_2O \quad (200°C)$$

Cl_2O is a powerful chlorinating agent. ClO_2 is used in bleaching wood pulp and cellulose and in purifying drinking water.

Oxoacids and Salts : The oxoacids and their anions may be supposed to be derived through sp^3 hybrid orbitals on the halogen atoms linking one or more oxygen atoms; unshared pairs of electrons occupy remaining orbitals. Strong p-d π-bonding between filled $2p$ orbitals on oxygen and empty d-orbitals on the halogens further stabilize the bonds. Fluorine forms only HOF at very low temperature (–40°C).

The oxoacids and their salts are mostly prepared by reacting the halogens with alkali or by electrochemical oxidation. All of them are good oxidizing agents. Rates of oxidation appear to decrease with increase in the oxidation number of the halogen :

(i) $OCl^- (\sim Cl_2) >> ClO_2^- > ClO_3^- > ClO_4^-$

(ii) $OBr^- (\sim Br_2) >> BrO_3^- > BrO_4^-$

(iii) $I_2 > IO_3^- > IO_4^-$

Rates of oxidation by different oxoanions with the halogen in same oxidation state increase from Cl to Br to I :

(i) $IO_4^- > BrO_4^- > ClO_4^-$

(ii) $IO_3^- > BrO_3^- > ClO_3^-$

However, $E°$ values suggest a different order : (i) $BrO_3^- > ClO_3^- > IO_3^-$; (ii) $BrO_4^- > IO_4^- > ClO_4^-$.

Interhalogen Compounds : Different halogens may combine between themselves to form interhalogen compounds which may be neutral molecules, cations or anions.

XY type interhalogens like ClF, ICl etc. may be prepared by direct reaction. Their properties are intermediate between those of the constituent halogens and they are usually more reactive. They are good halogenating agents. The XY_3, XY_5 type interhalogens and IF_7 are also vigorous fluorinating agents, sometimes slightly less than ClF. The shapes of the molecules are consistent with the VSEPR theory.

Pseudohalogens : A number of uninegative ions like CN^-, SCN^-, $SeCN^-$, etc. show close resemblance with the halide ions in chemical properties; some of them may even be oxidized to dimeric molecules (e.g. $(CN)_2$, $(SCN)_2$ etc.) like the oxidation of halides to free halogens. These ions and molecules are called pseudohalides/pseudohalogens.

Basic Properties : Only iodine (and astatine) shows some definite basic character in oxidation states +I and +III.

$$AgNO_3 + 2py + I_2 = I\overset{+}{p}y_2NO_3^- + AgI$$

The I(I) may be retained on a cation exchange resin and stabilized by macrocyclic ligands like 2, 2, 2-crypt. I(III) is formally present in $I(CH_3COO)_3$, $I(ClO_4)_3$, $I(PO_4)$ and $I(SO_3F)_3$. I(III)-acetate is obtained by oxidizing I_2 with fuming HNO_3 in acetic anhydride. It may be electrolysed in acetic anhydride in accordance with the ionization scheme

$$I(CH_3COO)_3 \rightleftharpoons I^{3+} + 3CH_3COO^-$$

EXERCISE

1. *Consult Figures 24.2 and 24.3. From the following enthalpy of formation of I_2-solvent complexes, predict the maximum change in the colour of iodine in these solvents :*

	I_2—C_6H_6	I_2—CH_3OH	I_2—Et_2O	I_2—Et_3N
ΔH^0_{298}, *kJ mole*$^{-1}$	–5.9	–7.9	–18.0	–50.2

[Ans. : Et_3N; colour changes to yellow]

2. *Bond energies of H_2 and other halogen molecules are as follows :*

	H_2	F_2	Cl_2	Br_2	I_2
E (kJ mol^{-1})	435	154.8	242.7	192.46	150.6

(a) *How do you account for the much greater bond energy in H_2?*

(b) *The bond energies in halogens first increase and then decrease along the group. Explain.*

3. *Note the following bond angles in some hydrides and fluorides :*

	X—C—X	X—N—X	X—O—X
C_2H_4	120°	NH_3 107°	H_2O 104.5°
C_2F_4	114°	NF_3 102°	F_2O 101.5°

Comment on the decreasing bond angles in fluorine compounds.

4. *Iodine dissolves in cyclohexane to give a violet solution. When benzene, dioxan or pyridine are added to this solution, its colour changes, and the apparent dipole moment of the iodine in solution increases. The moments of the dipolar species formed in the presence of the above three solvents are 1.8, 3.0 and 4.5 D repectively, with the cyclohexane solution as reference zero. Explain.*

[**Hint :** Donor strength increases in the order benzene < dioxan < py. Greater interaction implies greater electron transfer and hence a higher dipole moment.]

5. *What happens when*

(i) *Chlorine water is added to an aqueous solution of KBr and the mixture is shaken with CCl_4.*

(ii) *KI is shaken with an aqeous suspension of AgCl.*

(iii) *KIO_3 reacts with KI in (a) dilute and (b) concentrated HCl medium.*

(iv) *Manganese (II) sulfate is treated with periodic acid in acid medium.*

(v) *Potassium chlorate is gently heated with oxalic acid.*

(vi) *Iodine is added to silver nitrate solution in presence of an excess of pyridine in chloroform solution.*

6. *Explain :*

(a) *Of the three XO_4^- anions (X = Cl, Br, I), BrO_4^- is the strongest oxidizing agent.*

(b) *O_2F_2 has comparatively short O—O bond and long O—F bonds.*

	OF_2	H_2O_2	O_2	O_2F_2
$d_{O—O}$ (pm)	—	148	121	122
$d_{O—F}$ (pm)	142	—	—	158

(sum of covalent radii : O—O 148 pm; O—F 145 pm).

(c) *Perchloric acid is $HClO_4$ but common form of periodic acid is H_5IO_6.*

(d) *Interhalogen compounds are always diamagnetic, covalent and more reactive than constituent halogens.*

(e) *Acidity of $HClO_x$ increases as x increases from 1 to 4.*

(f) *Colours of the halogen vapours change from pale yellow in F_2 to intense violet in I_2.*

(g) *Neither BrF_5 nor AsF_5 are good conductors of electricity but a mixture of the two makes a good conductor.*

(h) *$KH(IO_3)_2$ may be used as a primary standard oxidant as well as a primary standard acid.*

(i) *Iodine forms purple solution in cyclohexane or CCl_4 but brown solutions in ether or pyridine.*

(j) *ClO_2 is a free radical with one unpaired electron but it has no tendency to dimerize like NO_2.*

(k) *Thermal decomposition of $Et_4N[ClHI)]$ gives tetraethylammonium iodide and hydrogen chloride.*

(l) *AgCl and AgI are both soluble in saturated aqueous solution of potassium iodide but insoluble in saturated aqueous potassium chloride.*

(v) *The ionic radius of Cl^- is greater than the mean of the radii of F^- and Br^-, but that of Br^- is less than the mean of the radii of Cl^- and I^-.*

(n) *In covalent compounds, a bromide has a higher boiling point than the corresponding chloride but the reverse is generally true for ionic compounds.*

(o) *CF_3COOH is a very strong acid and $(CF_3)_3N$ has no basic properties.*

7. *Describe the shapes of the following molecules in the vapour state :*

$$ClF_3, BrF_5, I_2Cl_6,$$

What is the probable hybridization of the central atom in each?

8. *Name one cationic, one neutral and one anionic interhalogen compound. Which atom is considered central in species containing three or more atoms?*

9. *Using the VSEPR theory, predict the probable structures of IF_6^+ and IF_6. Suggest an equation leading to the formation of $[IF_6][SbF_6]$.*

10. *Point out the principal points of similarity between halogens and pseudohalogens. Illustrate your answer with equations for the reactions of (i) $(CN)_2$ with aqueous NaOH (ii) excess SCN^- with MnO_2 in acid solution.*

11. (a) *What species are present in solutions of the following in anhydrous HF : (i) H_2SO_4 (ii) $HClO_4$ (iii) HNO_3 (iv) BF_3?*

(b) *What happens when the following compounds are added to anhydrous HF : (i) NH_4F (ii) KCN (iii) $AlCl_3$ (iv) $CuCl_2$.*

[**Ans. :** (a) (i) $HSO_3F + H_2O$ (ii) $H_2F^+ClO_4^-$ (iii) $H_2NO_3^+F^-$ (iv) $H_2F^+BF_4^-$ (b) (i) dissolves (ii) solvolysis — HCN evolved (iii) solvolysis — AlF_3 (insoluble) + HCl↑ (iv) no reaction].

12. *Write equations for*

(a) *the self-ionization of ICl*

(b) *the production of a basic solution when KCl is dissolved in ICl*

(e) *the neutralization between solution in (b) and (c).*

13. *Write equations with conditions for the preparation of (a) $KBrO_4$ (b) I_2O_5 (c) $KH(IO_3)_2$ (d) KIO_4 (e) BrF_3 (f) HOF (g) ClO_2 (h) $Ca(ClO_2)_2$.*

14. *The standard reduction potentials (volt) for astatine are as follows :*

$$H_5AtO_6 \xrightarrow{1.6} AtO_3^- \xrightarrow{1.5} HOAt \xrightarrow{1.0} At \xrightarrow{0.3} At^-$$

(a) *What is the likely product of reaction between At^- ions with $Cr_2O_7^{=}$/acid?*

(b) *What do you expect when magnesium powder is added to a solution containing H_5AtO_6?*

[**Ans. :** (a) HOAt (b) At^-]

15. *Arrange the following reactions in order of increasing rate in IM aqueous acid medium at ordinary temperature.*

(a) $IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O$

(b) $BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$

(c) $ClO_4^- + 12I^- + 8H^+ \longrightarrow 4I_3^- + Cl^- + 4H_2O$

(d) $HOI + 2I^- + H^+ \longrightarrow I_3^- + H_2O$

[**Ans. :** c < b < a < d]

CHAPTER TWENTY FIVE

ELEMENTS OF GROUP 18(VIII A or O)

He, Ne, Ar, Kr, Xe, Rn

(The Noble Gases)

OBJECTIVES

25.1 Introduction.
- Abundance and occurrence [25.1.1]
- Isolation [25.1.2]
- Properties and uses [25.1.3-25.1.4]

25.2 Chemistry
- Introduction, diatomic cations [25.2.1]
- Fluorides of xenon [25.2.2]
- Xenon oxides, xenates and perxenates [25.2.3]
- Miscellaneous compounds of xenon [25.2.4]
- The chemistry of krypton [25.2.5]
- The chemistry of radon [25.2.6]

25

ELEMENTS OF GROUP 18(VIIIA or O)

25.1 INTRODUCTION

The noble gases in the periodic table were discovered through their physical properties like spectral behaviour and gas density. The first observation in this connection dates back to the time of Henry Cavendish (1785) who observed that a sample of air always leaves a small residue (about 1/120th part) even after repeated sparking with excess oxygen. The first discovery of a noble gas took nearly one hundred years after this observation. The main events in this connection are summarized below.

1868	A new yellow line was observed close to the Sodium-D lines in the spectrum of the sun's chromosphere recorded during the total solar eclipse on 18th August. Lockyer and Frankland assigned this to a new element which they named *helium* (Greek *helios* = sun). *This was the only element found extraterrestrially before being found on the earth.*
1881	The same line was observed by L. Palmieri in the spectrum of volcanic gases from Mt. Vesuvius.
1891	Lord Rayleigh observed that nitrogen isolated from atmospheric gases was about 0.5 per cent heavier than nitrogen prepared chemically.
1895	Ramsay identified helium in the gas occluded in uranium minerals. He also identified a new element (*argon* = lazy) in the residue left after heating atmospheric nitrogen with magnesium.
1896	Ramsay suggested that helium and argon belong to a new group (Group zero) in the periodic table and there should be three other inert gases to complete the table.
1898	Ramsay and Travers isolated three new elements by low-temperature distillation of liquid air : *neon* (Greek : *new*), *krypton* (Greek *hidden*) and *xenon* (Greek *strange*). These were characterized by spectral analysis.
1902	Rutherford and Soddy isolated radon (Latin *radius* = ray) from emanations given out by radioactive minerals.
1904	Lord Rayleigh awarded the Nobel Prize in Physics for investigations on gas densities and for the discovery of argon. W. Ramsay awarded the Nobel Prize in Chemistry for discovery of the inert gas elements in air and their place in the periodic system.

25.1.1 Abundance and Occurrence

The noble gases are present to the extent of about 1% in the earth's atmosphere, the chief component being argon.

Helium is the second most abundant element in the *universe* after hydrogen (H 76%; He 23%) as it is formed in thermonuclear reactions in stars :

$$4\,{}^{1}_{1}H = {}^{4}_{2}He + 2\beta^{+} + 2\nu$$

But it is present to a very negligible extent in the earth's atmosphere because of its extreme lightness.

Helium consists of two stable isotopes ^{4}He and ^{3}He. He–4 is formed on earth by α-decay of radioactive elements. He–3 is formed by nuclear reactions induced by cosmic radiation, for example

$${}^{14}_{7}N + {}^{1}_{0}n = {}^{12}_{6}C + {}^{3}_{1}H; \quad {}^{3}_{1}H = {}^{3}_{2}He + \beta^{-}$$

Helium occurs to the extent of 5.24 ppm by volume in dry air and 3×10^{-3} ppm by weight in igneous rocks. However, the most economical source of helium is natural gas which may contain as high as 7% He in some samples (USA) but is usually present to the extent of 0.1-2%. About 3400 tonnes of He are recovered annually in USA alone from natural gas, while in eastern Europe (mainly Poland) some 1000 tonnes of He are isolated in a year.

The thorium mineral, *monazite sand* (Chapter 31) contains about 1 ml of helium per gram, formed by α-decay of Th-232. The gas may be recovered by heating the sand in vacuum at 1000° or by digesting it with sulphuric acid.

Neon is present to the extent of about 18 ppm by volume in dry air and 7×10^{-5} ppm by weight in igneous rocks. This, as well as other noble gases are mainly obtained as by-products of the liquefaction of air.

It has three stable isotopes viz, ^{20}Ne, ^{21}Ne and ^{23}Ne.

Argon is the most abundant noble gas element in air, ~93 ppm by volume of dry air; in igneous rocks it is present to the extent of 4×10^{-2} ppm by weight.

Natural argon is also a mixture of three stable isotopes—^{40}Ar (99.6%), ^{38}Ar (0.063%) and ^{36}Ar (0.337%). ^{40}Ar is produced through K-electron capture by ^{40}K.

$$^{40}_{19}\text{K} + e^- \longrightarrow {}^{40}_{18}\text{Ar}$$

Krypton and **Xenon** are present in the atmosphere to the extent of 0.0001% and 0.00001% by volume respectively.

Radon-222 is the longest-lived isotope of the element with a half-life of 3.8 days. It is produced directly by α-decay of radium-226. Each gram of Ra produces about 0.64 mm^3 of Rn in 30 days. A small back-ground concentration thus persists in the earth's atmosphere; its concentration in uranium mines is still higher.

25.1.2 Isolation of the Elements

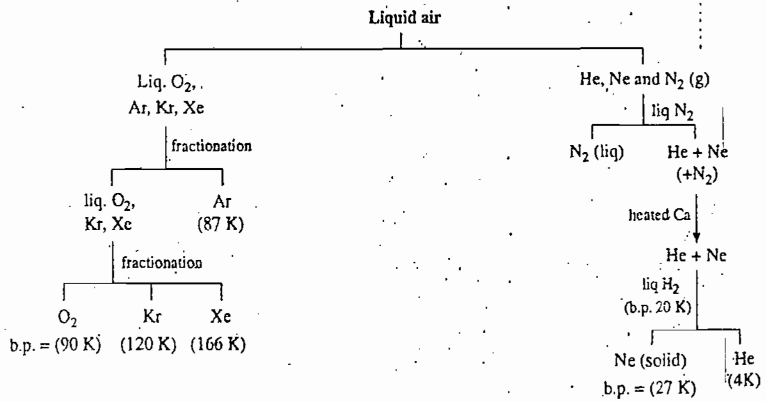
Helium is primarily obtained from natural gas. The hydrocarbons are liquefied at about –150° and the helium is pumped out.

Neon, Argon, Krypton and Xenon are mostly obtained from liquid air (see below). Some argon is also recovered from synthetic ammonia plants where the gas enters with nitrogen.

The boiling points (K) of the various constituents of liquid air are as follows :

He	Ne	Ar	Kr	Xe	N_2	O_2	
4	27	87	120	166	77	90	(K)

Fractionation of liquid air is carried out according to the following scheme



Radon is produced by the α-decay of an aqueous solution of radium chloride. The gas is largely diluted by ozone, hydrogen and oxygen produced by the α-irradiation of water. The mixture of gases is passed successively over heated copper and copper (II) oxide and finally dried with phosphorus pentoxide to obtain pure radon.

[Sec. 25.1.3 *Physical Properties*]

25.1.3 Physical Properties

The noble gas elements are colourless*, odourless monatomic gases having C_p/C_v ratios close to 1.67. Their closed shell configuration develops little intermolecular attraction and hence they possess very low boiling and melting points (Table 25.1). As expected, the weak van der waals force (London force) between the molecules increases with increasing polarisability which is approximately in the proportion 1 : 2 : 3 : 12 : 20 from He to Xe. This is reflected in the increasing trend in m.p./b.p., enthalpy of vaporization as well as solubility in water. The forces of attraction between He atoms are so small that even the zero point vibration energy is sufficient to hinder solid formation.

In the solid state, Ne, Ar, Kr, Xe and Rn form face centered cubic lattice—the cubic close-packed structure being the most space-economizing. With atoms of small mass, the zero-point energy also exerts an influence on the crystal structure : at 1 K at 25 atm He-4 has a hexagonal closepacked structure but the lighter He-3 adopts the body-centered cubic arrangement. Helium-4 may be forced to adopt a cubic close-packed structure above 1100 atmosphere pressure.

TABLE 25.1

Some physical properties of the noble gases

	He	Ne	Ar	Kr	Xe	Rn
At. mass	4.0026	20.179	39.948	83.80	131.30	[222]
v.W. radius (pm)	140	154	192	200	218	—
B.P. (K)	4.2	27.1	87.3	120.3	166.1	208.2
Δ*H* (vap) (kJ mol^{-1})	0.09	1.8	6.3	9.7	13.7	18.0
I.E. (kJ mol^{-1})	2372	2080	1520	1351	1169	1037
Solubility (water) cm^3/L at 20°C	8.6	10.5	34	59	108	230

Superfluidity

Liquid helium (^{4}He), when cooled further below its normal b.p., undergoes a transition from He-I to He-II at 2.2 K when evaporation continues without turbulence; the thermal conductivity of the liquid rises abruptly by a factor of 10^6, the specific heat increases by a factor of 10 and the viscosity becomes effectively zero. It shows the peculiar property of "flowing up" along the wall when the bottom of an empty container is dipped in a bath of liquid He-II below 2.2 K — the process will continue until the levels of liquid are equal inside and outside. These behaviours, described as characteristics of a *superfluid*, may be explained to some extent by quantum theory.

Noble gases, specially helium, diffuse through many common materials like rubber and PVC. Helium diffuses even through most glasses.

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[*] Radon is colourless at ambient temperatures but when cooled below its melting point (202 K), it emits a brilliant yellow phosphorescence; the colour changes to orange-red as the gas is slowly cooled to liquid nitrogen temperature (77K).

25.1.4 Uses

Liquid helium is used in the laboratory as a refrigerant in low-temperature physics. It is mainly used to provide an inert atmosphere in welding metals and to some extent in meteorological balloons. Helium is also used as a substituent for nitorgen in the breathing gas for deep-sea divers — it is less soluble in blood than nitrogen and hence lessens the problem of degassing when the divers come to upper surface and are exposed to a much reduced pressure. Helium is also used as a coolant in high temperature nuclear reactors.

Neon is widely used in electronics for filling photoelectric cells, voltage stabilizers and similar instruments. The so-called "neon-lights" in advertisements contain an admixture of neon with other inert gases.

Argon is largely preferred over helium (because of its cheapness) in metallurgy and other systems requiring an inert atmosphere (arc-welding of aluminium and Al-Mg alloys). Argon is also used in fluorescent tubes, incandescent lamps, discharge tubes, ionization counters and similar instruments.

Krypton is used in electronics; a mixture with xenon is used to fill various lamps and tubes. Radioactive radon is used in testing metal castings and in radiation therapy.

25.2 CHEMISTRY OF NOBLE GASES

25.2.1 Introduction

Lack of chemical reactivity of the noble gases was the reason to call them inert. In fact, prior to 1962, no true chemical compound of these elements were known. The only "compounds" reported were some clathrates or cage compounds formed by Ar, Kr and Xe with para-quinol and water. When quinol is crystallized from aqueous or other solutions in presence of these gases at high pressure (10-40 atm), the noble gas molecules are physically trapped within the cavities formed in the quinol crystal through H-bonded network. Water molecules similarly encapsulate Ar, Kr and Xe when frozen under high pressure of the gas. Synthetic zeolites also form such cage compounds. These cannot be called true compounds since only weak van der Waals forces operate between the gas molecules and the quinol or water; the gases are liberated on melting or dissolution. The atoms of He and Ne are small as well as difficult to polarize; hence these elements do not form clathrates.

The complete s- and p- subshells in the valence shell (n) of the noble gas elements make a very stable configuration — the energy required for promotion of an electron to the next available vacant orbital, (n + 1) shell or nd/nf subshell, is quite large. For example, with xenon, the promotion energies are (kJ mol^{-1}) :

$$5s^2 5p^6 \longrightarrow 5s^2 5p^5 6s^1 : 795 \text{ kJ mol}^{-1};\ 5s^2 5p^6 \longrightarrow 5s^2 5p^5 5d^1 : 963 \text{ kJ mol}^{-1},$$

this shows that covalent bonding involving sp^3d or sp^3d^2 valence states is highly unfavourable.

Formation of an ionic compound of the type Xe^+F^- is similarly difficult, as apparent from the following Born-Haber cycle :

$$\begin{tikzcd}
Xe(g) + \frac{1}{2}F_2(g) \arrow[r, "\frac{1}{2}D"] \arrow[d, "\Delta H"'] & Xe(g) \arrow[d, "I_{Xe}"] & + F(g) \arrow[d, "E.A._F"] \\
XeF(s) & Xe^+(g) \arrow[l, "U_{XeF}"'] & F^-(g)
\end{tikzcd}$$

Assuming that the lattice energy of XeF is approximately equal to that of CsF, we get,

$$\begin{aligned} \Delta H &= \tfrac{1}{2}D + I_{Xe} + E.A._F + U_{XeF} \text{ (algebraic sum)} \\ &= (79 + 1162 - 333 - 720) \text{ kJ mol}^{-1} \\ &= +188 \text{ kJ mol}^{-1}. \end{aligned}$$

Except for an unusually high positive ΔS, ΔG for the formation of Xe^+F^- (s) will be positive, suggesting that its formation would be unlikely. The chlorides, bromides and iodides are similarly expected to be (thermodynamically) unstable since Cl_2 and Br_2 have higher bond dissociation energies; the lattice energies of these halides should also be smaller in magnitude.

As early as 1933, Linus Pauling had suggested from ionic radii considerations that it should be possible to prepare XeF_6 and KrF_6. Attempts to prepare these compounds failed until in 1962 xenon fluorides were first prepared by N. Bartlett.

Bartlett observed that PtF_6 changes colour on exposure to air. It was subsequently established that PtF_6 is a very strong oxidizing agent, capable of oxidizing O_2 to produce $O_2^+PtF_6^-$. Since the ionization energy of Xe is comparable to that of O_2 ($O_2 \longrightarrow O_2^+$; 1175 kJ mol^{-1}), it was natural to expect that PtF_6 would oxidize Xe also. In fact, Bartlett reported the formation of an orange solid on reacting Xe with PtF_6 vapour; he formulated this as "$XePtF_6$". Subsequently it was shown that the solid has a variable composition $Xe(PtF_6)_n$, n lying between 1 and 2. The exact nature of the substance has not been established; it may contain $[XeF]^+[PtF_6]^-$ and $[XeF]^+[Pt_2F_{11}]^-$.

This was the beginning of noble gas chemistry. Soon XeF_2 and XeF_4 were prepared. It was even observed that XeF_2 is formed when a mixture of Xe and F_2 in a sealed tube is simply exposed to sunlight. Chemists really took such a long time to remove the label of "inertness" from the noble gases.

[Sec. 25.2.1
Diatomic Cations]

Diatomic Cations

Cations like He^+ and He_2^+ are produced in mass spectrometers. At first He^+ is formed when a He atom collides with an energetic electron in a high vacuum

$$He + e^- \longrightarrow He^+ + 2e^-$$

Such ions are kept away from the walls of the vessel by magnetic and electric fields (else they would pick up electrons to form neutral atoms) and allowed to reach the collector plates of detector. If the pressure inside the spectrometer is suitably adjusted ($\approx 10^{-5}$ mm Hg), the He^+ ion will combine with a neutral He atom :

$$He^+ + He \longrightarrow He_2^+$$

Such species, stable in vacuum only, have a bond order of 0.5 and an unusually high bond energy :

	He_2^+	Ne_2^+	Ar_2^+	Kr_2^+	Xe_2^+
Bond Energy (kJ mol^{-1})	126	67	104	96	88

Xe_2^+ ion has also been characterized (Raman spectrum) in the green solution obtained by reducing $XeF^+Sb_2F_{11}^-$ with xenon in presence of excess SbF_5 :

$$3Xe + XeF^+Sb_2F_{11}^- + 2SbF_5 \longrightarrow 2Xe_2^+Sb_2F_{11}^-$$

The paramagnetic solution is stable at room temperature under a pressure of xenon gas.

Dark green crystals may be separated at –30°C. X-ray study at –143°C shows the Xe—Xe⁺ bond distance to be 308.7 pm, the longest known for an element-element bond.

Standard reduction potentials (aqueous) for xenon are given below.

Acid solution

$$\underbrace{\overset{+8}{H_4XeO_6\,(aq)} \xrightarrow{2.4\ V} \overset{+6}{XeO_3\,(aq)} \xrightarrow{2.12\ V} \overset{0}{Xe\,(g)}}_{2.18\ V}$$

Basic solution

$$HXeO_6^{3-} \xrightarrow{0.99\ V} HXeO_4^- \xrightarrow{1.24\ V} Xe\,(g)$$

It is evident that "perxenates" [hexaoxyxenate (VIII)] are strong oxidizing agents in both acidic and alkaline medium.

Important compounds of the noble gases are shown in Table 25.2.

TABLE 25.2

Compounds of noble gases

Oxidation States	+ 2	+ 4	+ 6	+ 8
Halides	KrF_2 XeF_2, $XeCl_2$ (RnF_2)	— XeF_4 (RnF_4)	— XeF_6 (RnF_6)	— — —
Oxides	—	—	XeO_3	XeO_4
Oxofluorides	—	—	$XeOF_4$ XeO_2F_2	XeO_3F_2
Fluoro-Complexes [M = Pt, Ir, Os Ru, Au, Nb, Ta, Sb]	$[KrF][MF_6]$ $[XeF][MF_6]$	— $[XeF_3][MF_6]$	$[XeF_5][MF_6]$ $[XeOF_3][MF_6]$ $Cs_2[XeF_8]$	$[XeOF_5][MF_6]$
Salts of Oxoacids	$Xe[ClO_4]_2$ $[XeF][NO_3]$	— —	— —	— —
Acids	—	—	H_2XeO_4	H_4XeO_6

25.2.2 Fluorides of Xenon

Xenon fluorides XeF_2, XeF_4 and XeF_6 are all thermodynamically stable, as shown by their standard enthalpies of formation. The mean Xe—F bond energies are also quite high :

	ΔH° (kJ mol⁻¹)	Xe—F bond energy (kJ mol⁻¹)
$Xe\,(g) + F_2\,(g) = XeF_2\,(s)$	–109	133
$Xe\,(g) + 2F_2\,(g) = XeF_4\,(s)$	–216	133
$Xe\,(g) + 3F_2\,(g) = XeF_6\,(s)$	–294	126

All the xenon fluorides are obtained by heating xenon and fluorine in varying ratios in sealed nickel vessels :

Preparation

		Xe : F_2 ratio	Condition
(i)	$Xe + F_2 = XeF_2$	2 : 1	400°C
(ii)	$Xe + 2F_2 = XeF_4$	1 : 5	6 atm/400°C
	($XeF_2 + F_2 = XeF_4$	—	400°C)
(iii)	$Xe + 3F_2 = XeF_6$	1 : 20	50 atm/300°C
	($XeF_4 + F_2 = XeF_6$	—	300°C)

Conversions are usually quantitative under the given conditions. XeF_6 may be completely separated from XeF_2 and XeF_4 by passing over dry NaF when XeF_6 alone is absorbed : $XeF_6 + 2NaF = Na_2XeF_8$; the complex decomposes on heating to give XeF_6.

XeF_2 is also formed by heating XeF_4 with Xe at 400°C. The formation of XeF_2 by the action of sunlight on a mixture of Xe and F_2 probably occurs via photochemical decomposition of F_2

$$F_2 \xrightarrow{h\nu} 2F;\ Xe + 2F \longrightarrow XeF_2$$

Caution : Complete exclusion of moisture is necessary in the preparation of xenon fluorides since XeF_4 and XeF_6 hydrolyzes to give the explosive product XeO_3.

Properties All three xenon fluorides are colourless volatile solids. XeF_6 is yellow in the liquid and gaseous phases. The fluorides form large crystals on standing in closed vessels. XeF_2 and XeF_4 can be handled conveniently in glass vacuum systems but XeF_6 attacks glass or quartz (see reactions). Their melting points, structures of gaseous molecules, and reactions with water are summarized in Table 25.3.

TABLE 25.3

The Xenon Fluorides

Compound	MP/°C	Structure	Reaction with water
XeF_2	129	Linear Xe—F = 200 pm	Soluble, 25 g dm⁻³ at 0°C. Fairly stable (half-life ~7 hrs) in absence of base; hydrolyzed to Xe, O_2, HF.
XeF_4	117	Sq. planar Xe—F = 195 pm	Instantly hydrolyzed to Xe, O_2, HF and XeO_3 (explosive).
XeF_6	49.5	Fluxional; distorted octahedral. Xe—F ≃ 184 pm	Vigorously hydrolyzed to XeO_3 and HF.

Hydrolysis All the xenon fluorides are readily hydrolyzed, the reaction of XeF_6 being most vigorous. Approximate stoichiometries of the reactions are :

$$XeF_2 + H_2O \longrightarrow Xe + \tfrac{1}{2}O_2 + 2HF$$

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + \tfrac{3}{2}O_2 + XeO_3 + 12HF$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Formation of the highly explosive XeO_3 has caused many accidents during the study of XeF_4 and specially XeF_6.

The formation of one-third mole of XeO_3 per mol of XeF_4 hydrolyzed indicates that the reaction does not occur through simple disproportionation as

$$2Xe^{IV} \longrightarrow Xe^{VI} + Xe^{II}.$$

Rather, one may think in terms of the intermediate formation of a Xe^{VIII} species :

$$\begin{array}{ccc} 3Xe^{IV} \longrightarrow & 2Xe^{II} & + Xe^{VIII} \\ & \downarrow & \downarrow \\ & 2Xe^{0} & Xe^{VI} \end{array}$$

Or, $$\begin{array}{ccc} 3XeF_4 + 6H_2O \longrightarrow & 2XeO & + XeO_4 + 12HF \\ & \downarrow & \downarrow \\ & 2Xe + O_2 & XeO_3 + \frac{1}{2}O_2 \end{array}$$

The stoichiometry may vary with variation of conditions.

With small quantities of water, XeF_6 gives xenon oxide-tetrafluoride which is a colourless liquid frezing at –46°C.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Further reactions often take place readily with XeO_3.

$$XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$$

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2 \text{ (m.p. 31° C).}$$

Oxidizing and Fluorinating action

All three fluorides are strong oxidizing and fluorinating agents, reactivity increasing from XeF_2 to XeF_6. Thus XeF_6 combines with H_2 and attacks glass at ordinary temperature, while others do so on heating. This is why XeF_6 cannot be handled in glass or quartz apparatus as it ultimately forms explosive XeO_3.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF \quad (400°C)$$

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF \quad (130°C)$$

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF \text{ (room temperature)}$$

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

Here XeF_6 behaves as an acid (oxide ion acceptor) according to the Lux-Flood definition.

Estimation

The reaction of xenon fluorides with H_2 or Hg may be used for their estimation :

$$XeF_6 + 3Hg \longrightarrow Xe + 3HgF_2$$

XeF_4 may also be analyzed by titrating the iodine liberated from KI :

$$XeF_4 + 4KI \longrightarrow Xe + 2I_2 + 4KF.$$

XeF_2 oxidizes Ag(I) to Ag(II), Cr(III) to Cr(VI) and even BrO_3^- to BrO_4^- :

$$BrO_3^- + XeF_2 + H_2O \longrightarrow BrO_4^- + Xe + 2HF$$

XeF_2 is widely used as a fluorinating agent in organic synthesis; many alkyl and aryl groups are stable towards it while the central atom in many organometalloid systems are simultaneously oxidized and fluorinated (*oxidative fluorination*) :

$$(C_6H_5)_2S + XeF_2 \longrightarrow (C_6H_5)_2SF_2 + Xe$$

$$CH_3I + XeF_2 \longrightarrow CH_3IF_2 + Xe$$

Reductive fluorination may also take place in certain cases, as in the following reaction :

$$XeF_2 + 2CrO_2F_2 \longrightarrow 2CrOF_3 + Xe + O_2$$

The reactivity of XeF_2 is remarkably enhanced in anhydrous liquid HF (probably owing to the formation of XeF^+ cation) :

$$S_8 + XeF_2 \longrightarrow SF_6; \quad Cr + XeF_2 \longrightarrow CrF_3 \longrightarrow CrF_4$$

$$Ir + XeF_2 \longrightarrow IrF_5; \quad OsBr_4 + XeF_2 \longrightarrow OsF_5 \longrightarrow OsF_6$$

XeF_4 is a stronger fluorinating agent :

$$Pt + XeF_2 \longrightarrow Xe + PtF_4; \quad 2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$$

XeF_6 is a still more stronger fluorinating agent, as exemplified by its reaction towards silica.

XeF_6 reacts with dry sodium nitrate to form $XeOF_4$ and XeO_2F_2 (see oxofluorides).

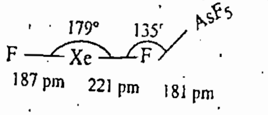
Xenon fluorides react with fluoride ion acceptors like the pentafluorides MF_5 (M = As, Sb, Bi, Nb, Ta, Ru, Os, Ir, Pt) forming complexes with stoichiometries $(XeF_n)_2MF_5$, XeF_nMF_5 and $XeF_n(MF_5)_2$. Thus XeF_2 gives three types of products : $2XeF_2.MF_5$ or $Xe_2F_3^+[MF_6]^-$; $XeF_2.MF_5$ or $XeF^+[MF_6^-]$ and $XeF_2.2MF_5$ or $XeF^+[M_2F_{11}]^-$. The compounds may be prepared by fusing the reactants together; a solvent like HF or BrF_5 may also be used.

$$XeF_2 + SbF_5 = [XeF]^+[SbF_6]^- \qquad XeF_4 + SbF_5 = [XeF_3]^+[SbF_6]^-$$

$$2XeF_2 + SbF_5 = [Xe_2F_3]^+[SbF_6]^- \qquad XeF_6 + AsF_5 = [XeF_5]^+[AsF_6]^-$$

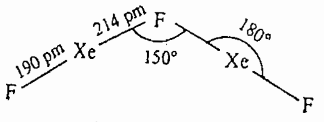
The xenon halides act as a base (F^- ion donor) to the strong Lewis acids MF_5. As expected, basic character decreases with increase in oxidation state of Xe, XeF_2 being most basic in behaviour.

However, these compounds formed with fluoride ion acceptors are not fully ionic since there is appreciable fluorine bridging between the cations and anions. The $[XeF]^+$ ions are attached to the anion with a linear F-bridge (25-I) : the F-Xe...F-M units have one short and one long Xe—F distance. The $Xe_2F_3^+$ ion is planar and angular (25-II).



$[XeF]^+[AsF_6]^-$

25-I

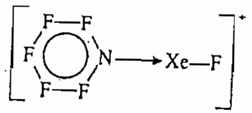


$Xe_2F_3^+$ in $[Xe_2F_3]^+[AsF_6]^-$

25-II

The XeF^+ ion is also formed by weak F^- ion acceptors like MOF_4 (M = W, Mo). The xenon atom in XeF^+ accepts an electron pair from Lewis bases like acetonitrile or pentafluoropyridine to give cations like

$[H_3CCN \longrightarrow Xe–F]^+$ and



The XeF_3^+ ion derived from XeF_4 in $XeF_3^+[Sb_2F_{11}]^-$ has Xe–F bond lengths 183 and 189 pm. XeF_6 mostly forms 1 : 1 complex in which the XeF_5^+ ion is square pyramidal as established from X-ray studies on salts like $XeF_5^+AsF_6^-$ — but some fluorine bridging is again present between cations and anions. The average Xe–F distance is 184 pm.

XeF_6 is amphoteric in the sense that it also accepts fluoride ion from more basic fluorides to form complexes such as $MXeF_7$ (M = Rb, Cs) and M_2XeF_8 (M = Na, K, Rb, Cs) :

$$CsF + XeF_6 = Cs\,[XeF_7]; \quad 2CsF + XeF_6 = Cs_2\,[XeF_8]$$

NOF similarly forms $[NO^+]_2\,[XeF_8]^{2-}$. It is the only salt of this category which has been fully characterized by X-ray crystallography. The square antiprism coordination around the xenon atom leaves no clearly defined position for the lone pair which must therefore be stereochemically inactive.

Na_2XeF_8 decomposes at 100°C while the salts of Rb and Cs decompose above 400° C :

$$Na_2XeF_8 \longrightarrow XeF_6 + 2NaF$$

XeF_2 also undergoes F/H metathesis with anhydrous acids :

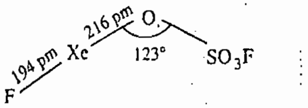
$$XeF_2 + HClO_4 = [XeF]\,[ClO_4] + HF$$

$$XeF_2 + 2HClO_4 = Xe[ClO_4]_2 + 2HF$$

Similar stepwise substitution of F is known with other strong acids HOY (Y = TeF_5, SeF_5, SO_2F, SO_2CF_3, SO_2CH_3, ClO_2, CF_3CO and possibly NO_2) :

$$XeF_2 + HOY \longrightarrow FXeOY \longrightarrow Xe(OY)_2$$

$FXeOSO_3F$ has the structure shown in 25-III. $Xe(OY)_2$ type compounds have a linear bridge as in $F_5SeO—Xe—OSeF_5$.



25-III

Structure

XeF_2 forms linear triatomic molecules in the gas phase, Xe—F distance = 200 pm. Solid crystals (density 4.32 kg m^{-3}) are also molecular and made up of linear XeF_2 units (Fig. 25.1).

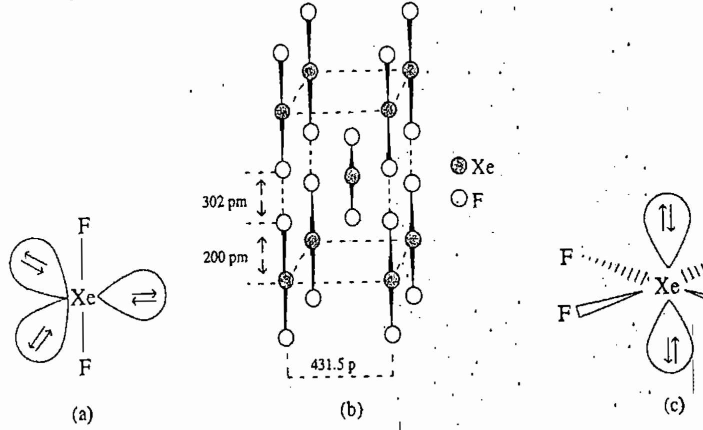


Fig. 25.1

Structure of (a) XeF_2 (g); (b) XeF_2 (s); (c) XeF_4 (g):

[Sec. 25.2.2 *Xenon fluorides*]

XeF_4 is a square planar molecule in the vapour, Xe—F = 195 pm. The solid (density 4.04 kg m^{-3}) also consists of molecular lattice consisting of square planar XeF_4 molecules.

The gaseous XeF_6 molecule does not have a static structure. In this non-rigid (or fluxional) molecule the valence shell of xenon contains six bond pairs and one lone pair of electrons. The lone pair continuously interchanges its position between various triangular faces and also among the centres of edges. The overall structure is thus a distorted octahedron.

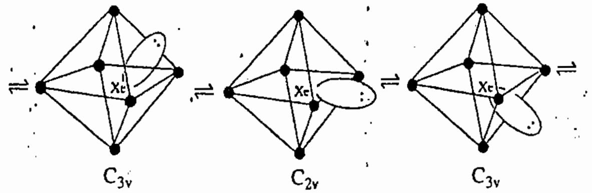


Fig. 25.2

Fluxional behaviour of XeF_6 (g) molecules.

Solid XeF_6 also possesses several structures which may be best described as aggregates of $XeF_5^+F^-$ molecular units. Four crystalline modifications are known, three of which essentially consist of four square pyramidal XeF_5 units, each bridged by two fluorine bridges to two other units (Fig. 25.3). The fourth form contains both tetramers and hexamers.

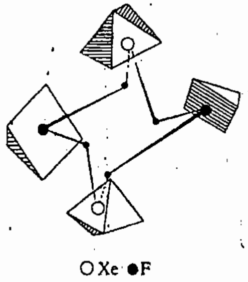


Fig. 25.3

Sketch for one tetrameric form of solid XeF_6.

Xe—F distance in XeF_5^+ : 184 pm

Xe—F bridge distance : 223–260 pm

In a variety of nonaqueous solvents xenon hexafluoride may be present as XeF_6 at ordinary temperatures but at very low temperatures (–118°C) tetramers are again indicated.

Bonding

The various promotion energies for xenon from $5s^25p^6$ ground state to different excited states are as follows :

Excited state configuration	$5s^25p^56s^1$	$5s^25p^55d^1$	$5s^25p^45d^2$	$5s^25p^45d^16s^1$
Energy (kJ mol^{-1})	795	963	1758	1926

In view of the high promotion energies required, a valence bond approach involving higher orbitals of xenon appears logically unjustified to describe the bonding in xenon fluorides. Nevertheless, the geometry of XeF_2 and XeF_4 is in keeping with expectations from the VSEPR theory :

77

(i) in XeF_2, xenon has 3 nonbonding pairs and 2 bond pairs of electrons in its valence shell; the molecule is linear with the lone pairs in equatorial positions (Fig. 25.1); (ii) in XeF_4, there are 4 bond pairs and 2 nonbonding pairs of electrons favouring a square planar arrangement of the F atoms. However, the structure of XeF_6 does not follow that expected for seven electron pairs; the molecule is fluxional as described earlier.

The molecular orbital description of bonding in the xenon fluorides uses the idea of 3-center 4-electron bonds involving only the valence shell 5*p* orbital of xenon. This is illustrated for XeF_2 as follows. Taking x-axis as the internuclear axis, we may combine the $5p_x$ a.o. of xenon with $2p_x$ orbitals from two F atoms to obtain one bonding, one nonbonding and one antibonding m.o. There are total four electrons for placement in these m.o.-s, two from the xenon and one each from the fluorine atoms. The four electrons occupy the bonding and non-bonding m.o.-s. In effect, the single bonding electron pair bonds all three atoms. The nonbonding orbital is localized closer to the F-orbitals, imparting some ionic character. This is equivalent to valence bond resonance among the structures $F—Xe^+F^- \leftrightarrow F^-Xe^+—F$.

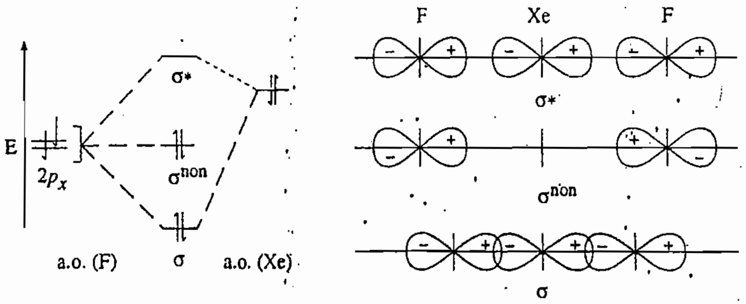


Fig. 25.4

3-center molecular orbitals in XeF_2.

The planar structure in XeF_4 is consistent with two 3-center four electron bonds in mutually perpendicular directions. XeF_6 may be similarly described in terms of three mutually perpendicular 3-center bonds, but this leads to a regular octahedral structure. The observed distortion is associated with a lone pair occupying a face of the octahedron in a fluxional role.

The stabilization caused by the electron pair in bonding m.o. clearly depends on the electronegativity of the element combined to xenon. Thus, only the most electronegative atoms like fluorine or oxygen succeed in forming compounds with noble gases. Again, since the central atom is providing an electron pair, bond strength may be expected to decrease with increase in its ionization energy. This explains why the stability of xenon compounds is high while He, Ne and Ar has no known compound.

The instability of KrF_2 also follows from this consideration : the first ionization enthalpies of Kr and Xe differ by ~ 182 kJ mol^{-1} while the $\Delta H°$ values for the two gasous fluorides differ by 172 kJ mol^{-1} :

$$Kr\,(g) + F_2\,(g) = KrF_2\,(g); \quad \Delta H° = 63 kJ\,mol^{-1}$$

$$Xe\,(g) + F_2\,(g) = XeF_2\,(g); \quad \Delta H° = -109\ kJ\,mol^{-1}$$

Xenon Oxofluorides

$XeOF_4$ and XeO_2F_2 are best characterized. $XeOF_4$ is a stable colourless liquid (m.p. −46°C) which is formed in the controlled hydrolysis of XeF_6. As explained earlier, explosive XeO_3 may be formed if the hydrolysis is allowed to go further.

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

A much more covenient and less hazardous route is to treat dry sodium nitrate with a slight excess of XeF_6 in stainless steel apparatus (70°C).

$$NaNO_3 + XeF_6 = NaF + XeOF_4 + FNO_2$$

Excess $NaNO_3$ leads to XeO_2F_2 :

$$NaNO_3 + XeOF_4 = NaF + XeO_2F_2 + FNO_2$$

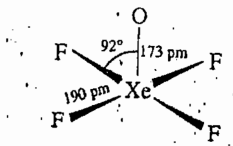
XeO_2F_2 forms metastable colourless crystals (m.p. 31°C) which are obtained by reactions like

$$XeO_3 + XeOF_4 = 2XeO_2F_2$$

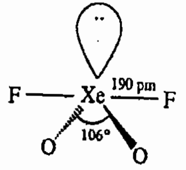
$$2XeO_3 + XeF_6 = 3XeO_2F_2$$

XeO_2F_2 decomposes into XeF_2 and O_2 on standing at room temperature.

$XeOF_4$ is square pyramidal, with the O-atom at apex (25-IV). XeO_2F_2 has a structure similar to those of SF_4 or $IO_2F_2^-$ with F atoms in axial positions (25-V).



25-IV



25-V

$XeOF_4$ (excess) reacts with dry CsF to form oxofluroanions :

$$3XeOF_4 + CsF \longrightarrow Cs[(XeOF_4)_3F] \longrightarrow CsXeOF_5 + 2XeOF_4$$

The $[(XeOF_4)_3F]^-$ anion has three $XeOF_4$ groups attached to a central fluorine. The $XeOF_5^-$ anion has a distorted octahedral geometry with a stereochemically active lone pair of electrons.

Other oxofluorides of xenon like $XeOF_2$ and XeO_3 are unstable. $XeOF_2$ is formed in a low temperature matrix by reacting xenon with OF_2 or by hydrolysis of XeF_4 at low temperature. It disproportionates in presence of CsF to give the anion $[XeO_2F_3]^-$. Stable white salts of $[XeO_3F]^-$ are formed by reacting aqueous XeO_3 with CsF or KF.

The oxofluorides also react with fluoride ion acceptors like AsF_5, SbF_5 etc. Thus, by direct reaction, or using SbF_5 as solvent, one may get species like $XeOF_4.SbF_5$, $XeOF_4.2SbF_5$ and $XeO_2F_2.2SbF_5$.

25.2.3 Xenon oxides, Xenates and Perxenates

Xenon trioxide, XeO_3 is the end product of hydrolysis of XeF_6 (and XeF_4). The violence of the reaction is controlled by sweeping XeF_6 vapour with dry N_2 into water.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

The oxide is not ionized in solution and concentrations upto 11*M* of XeO_3 are stable. On evaporation of water, the dangerously explosive solid XeO_3 is obtained.

XeO_3 is a white deliquescent solid (ΔH_f^0 at 298 K = + 402 kJ mol^{-1}). In strongly alkaline solutions (pH > 10.5), the xenate ion is formed.

$$XeO_3 + OH^- \rightleftharpoons HXeO_4^-; \quad K = 1.5 \times 10^3$$

The $HXeO_4^-$ ion forms salts like $NaHXeO_4$, 1.5 H_2O. However, in solution $HXeO_4^-$ undergoes slow disproportionation to perxenate and xenon gas

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

XeO_3 is one of the strongest oxidizing agents in aqueous media :

$$XeO_3 + 6H^+ + 6e \rightleftharpoons Xe + 3H_2O; \qquad E^\circ = 2.1\text{ V}$$

$$HXeO_4^- + 3H_2O + 6e \rightleftharpoons Xe + 7OH^-; \quad E^\circ = 1.2\text{ V}$$

Solutions of XeO_3 should thermodynamically oxidize water. But this reaction does not actually take place — this suggsts that there is a high activation energy barrier probably arising from the absence of any stable intermediate oxidation states of xenon between 0 and +6. XeO_3 oxidizes Mn(II) to MnO_2 over hours and to MnO_4^- over a few days. Reaction with KI is quantitative and can be used to estimate the oxide :

$$XeO_3 + 6H^+ + 9I^- \longrightarrow Xe + 3H_2O + 3I_3^-$$

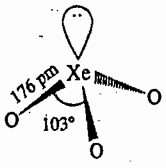
Estimation

Reactions with XeO_3 may also be followed by observing the pressure change (in a closed vessel) due to the xenon gas released. The pressure change is followed by a pressure transducer and the method is called ***pressuremetric titration***. Thus, in the reaction

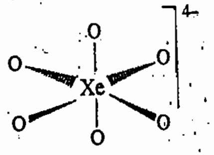
$$XeO_3 + 6H^+ + 6Fe^{2+} = Xe + 3H_2O + 6Fe^{3+}$$

the pressure increases linearly up to Xe : Fe ratio equal to 1 : 6 and then remains constant.

XeO_3 crystals consist of trigonal pyramidal XeO_3 units with the xenon at the apex (25-VI).



25-VI



25-VII

Perxenates are so called by analogy with periodates and are formed by disproportionation of XeO_3 and XeF_6 in alkaline solution (see above). They are best obtained by passing ozone into a dilute solution of XeO_3 in aqueous NaOH.

$$HXeO_4^- + 3OH^- + O_3 \longrightarrow XeO_6^{4-} + 2H_2O + O_2$$

A precipitate Na_4XeO_6, xH_2O ($x \approx 2.2$) is formed almost quantitatively. Perxenates of Li^+, K^+ as well as other cations like Ba^{2+}, Am^{3+} have also been prepared. All of them are colourless crystals stable thermally to above 200°C. Crystal structures of Na_4XeO_6, nH_2O (n = 6, 8) show the presence of octahedral XeO_6^{4-} ions (25-VII). This ion is also present in other salts.

Miscellaneous Xe-compounds]

Solutions of sodium perxenate are alkaline owing to hydrolysis :

$$XeO_6^{4-} + H_2O = HXeO_6^{3-} + OH^-$$

$$HXeO_6^{3-} + H_2O = H_2XeO_6^{2-} + OH^-$$

Study of equilibrium shows that the second step occurs much less in comparison to the first; thus $HXeO_6^{3-}$ is the main species up to about pH 11-13. H_4XeO_6 is an anomalously weak acid in comparison to H_5IO_6 and H_6TeO_6.

The potentials $H_4XeO_6 \xrightarrow{2.4V} XeO_3$ (*acid*) and $HXeO_6^{3-} \xrightarrow{0.94V} HXeO_4^-$ (*alkaline*) show that the perxenate ion is an extremely powerful oxidizing agent, particularly in acid medium. In fact, perxenates are both powerful and rapid oxidizing agents. They oxidize Fe^{2+} to Fe^{3+}, Cr(III) to Cr(VI), Ag(I) to Ag(II), iodate to periodate; Mn(II) is immediately oxidized to MnO_4^-. Water is oxidized slowly in alkaline solution but almost instantaneously in acid solution.

$$H_2XeO_6^{2-} + H^+ \longrightarrow HXeO_4^- + \tfrac{1}{2}O_2 + H_2O$$

The process involves hydroxyl radicals and H_2O_2.

Xenon tetroxide, XeO_4, is formed by the action of concentrated H_2SO_4 on sodium and barium perxenates.

$$4XeF_6 + 18Ba(OH)_2 = 3Ba_2XeO_6 + Xe + 12BaF_2 + 18H_2O$$

$$\therefore Ba_2XeO_6 + 2H_2SO_4 = 2BaSO_4 + XeO_4 + 2H_2O.$$

It is a yellow, highly explosive gas which may be condensed in liquid nitrogen temperature. The solid decomposes explosively even at –40°C :

$$XeO_4 \longrightarrow Xe + 2O_2.$$

The gas, under normal conditions, decomposes slowly into Xe, XeO_3 and O_2.

The XeO_4 ion is tetrahedral with the Xe atom at the center (Xe—O = 160 pm).

25.2.4 Miscellaneous compounds of Xenon

Xenon dichloride, $XeCl_2$ is not formed under usual conditions but may be formed when xenon and chlorine mixtures are passed through a microwave discharge and rapidly quenched to about 20K; infrared and Raman spectra of the resulting matrix show bands which are not observed when chlorine alone is subjected to such treatment. Detailed study of the fine structure of the bands establish the presence of linear $XeCl_2$ molecules formed by the isotopes ^{35}Cl and ^{37}Cl. $XeCl_2$, $XeBr_2$ and $XeCl_4$ have also been detected by Mössbauer spectroscopy in the products of β-decay of corresponding species formed by I–129. For example

$$\overset{*}{I}Cl_2^- \longrightarrow XeCl_2 + \beta^- + \bar{\nu} \qquad \overset{*}{I} = {}^{129}_{53}I$$

Besides these unstable compounds, the compounds $M_9(XeO_3Cl_2)_4Cl$ (M = Rb, Cs) are stable at room temperature. These are formed by reacting XeO_3 with RbCl/CsCl and consist of infinite chain anions—XeO_3Cl—Cl—XeO_3Cl—Cl, together with M^+ and Cl^- ions. The Xe atom has highly distorted octahedral environment of three O atoms and three Cl atoms (Xe—O ≈ 177 pm; Xe—Cl ≈ 296 pm).

Xenon also binds to NO_3, ClO_4, SO_3F, $OSeF_5$ and $OTeF_5$ substituents via Xe—O bonds to form several species which are often highly explosive. The most stable among these contain the pentafluorotellurate group :

$$3XeF_4 + 4B(OTeF_5)_3 \longrightarrow 3Xe(OTeF_5)_4 + 4BF_3 \quad (0°C).$$

$$XeF_6 + 2B(OTeF_5)_3 \longrightarrow Xe(OTeF_5)_6 + 2BF_3$$

$$OXeF_4 + B(OTeF_5)_3 \longrightarrow OXe(OTeF_5)_4$$

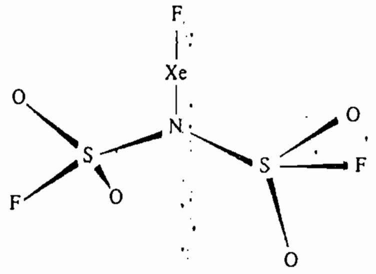
$$Xe(OTeF_5)_6 \xrightarrow{-10°C} Xe(OTeF_5)_4 \xrightarrow{-20°C\ (slow)} Xe(OTeF_5)_2$$

Compounds containing Xe—N bonds are also formed by replacing **F** atoms by $N(SO_2F)_2$ groups :

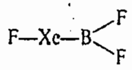
$$2XeF_2 + 2HN(SO_2F)_2 \longrightarrow 2F\text{-}Xe\text{-}N(SO_2F)_2 \quad (\text{in } CF_2Cl_2;\ 0°C,\ 4\ \text{days}).$$

This product (25-VIII) is a white solid decomposing at 70°C which undergoes ready hydrolysis. It reacts with further $HN(SO_2F)_2$ at −15°C in CF_2Cl_2 to give a compound with two Xe—N bonds :

$$FXe(NSO_2F)_2 + HN(SO_2F)_2 \rightleftharpoons Xe[N(SO_2F)_2]_2 + HF$$



25-VIII



25-IX

A compound containing Xe—B bond is formed in the reaction

$$O_2BF_4 + Xe \longrightarrow BXeF_3 \quad (-100°C)$$

$BXeF_3$ decomposes at −30° C into Xe and BF_3. It has a planar structure (25-IX) in which one F in XeF_2 is replaced by the BF_2 unit.

$XeCr(CO)_5$ has been characterized as a short-lived (half-life ~ 2s at −98°C) product in solution after uv photolysis of $Cr(CO)_6$ dissolved in liquid xenon. The compound has a formula comparable to $(N_2)Cr(CO)_5$.

Compounds containing Xe—C bonds are very few in number and contain CF_3 or C_6F_5 group :

$$Xe + {\cdot}CF_3\ (\text{radical}) \longrightarrow Xe(CF_3)_2$$

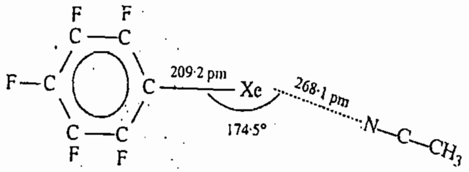
$$XeF_2 + B(C_6F_5)_3 \longrightarrow [C_6F_5Xe]^+ [C_6F_5BF_3]^- + [C_6F_5Xe]^+ [(C_6F_5)_2BF_2]^-$$

$Xe(CF_3)_2$ is a waxy solid which decomposes to XeF_2 and carbon fluorides (half-life ≈ 30 min at 20°C). In contrast, the pentafluorophenylxenonium cation is somewhat stable in CH_3CN solution and may be characterized by ^{19}F nmr spectroscopy. It is a strong oxidizing agent and readily transfers the fluorobenzene group :

$$Te(C_6F_5)_2 + [FXe(C_6F_5)]^+ \longrightarrow Te(C_6F_5)_3^+$$

$$C_6F_5I + [FXe(C_6F_5)]^+ \longrightarrow I(C_6F_5)_2^+$$

It has been possible to crystallize $[CH_3CN\ XeC_6F_5]^+ [(C_6F_5)_2BF_2]^-$ from acetonitrile solution. X-ray study confirms the presence of both Xe—C bond and coordination from CH_3CN (25-X).



25-X

A Xe—Xe bond (308.7 pm) has been established in the Xe_2^+ ion from X-ray analysis of $Xe_2^+Sb_4F_{21}^-$ at −143°C. The compound is formed in dark green crystals by reaction of Xe with $XeF^+Sb_2F_{11}^-$ in HF—SbF_5 ("magic acid") at −30°C.

25.2.5 The Chemistry of Krypton

The only known halide of krypton is KrF_2 which is an endothermic compound :

$$Kr\ (g) + F_2\ (g) \longrightarrow KrF_2\ (g) \qquad \Delta H° = +63\ \text{kJ mol}^{-1}$$

KrF_2 may be prepared by passing an electric discharge through a mixture of Kr and F_2 at low pressure in a U-tube immersed in liquid oxygen. KrF_2 freezes on the cold wall as it is formed. KrF_2 is also formed by the action of OF_2 on krypton in presence of sunlight.

KrF_2 is a colourless solid which dissociates into Kr and F_2 at room temperature. Being less stable than XeF_2, it is rapidly decomposed by water and is a stronger fluorinating agent. It will even fluorinate xenon or a noble metal like gold :

$$Xe + 3KrF_2 \longrightarrow XeF_6 + 3Kr$$

$$2Au + 7KrF_2 \longrightarrow 2KrF^+AuF_6^- + 5Kr$$

$$2KrF^+AuF_6^- \longrightarrow AuF_5 + Kr + F_2 \quad (60\text{-}65°C)$$

A mixture of KrF_2 and XeF_2 fluorinates many trivalent lanthanide compounds (Ln^{III}) to Ln^{IV} species like LnF_4, LnF_7^{3-} and $LnOF_2$ where Ln = Ce, Pr, Nd, Tb, and Dy.

KrF_2 reacts with strong fluoride ion acceptors like AsF_5 and SbF_5 to form compounds with KrF^+ and $Kr_2F_3^+$ cations, for example,

$$KrF_2 + 2SbF_5 \longrightarrow KrF^+ [Sb_2F_{11}]^-$$

$$2KrF_2 + AsF_5 \longrightarrow Kr_2F_3^+ [AsF_6]^-$$

Salts of KrF^+ may be used to fluorinate NF_3 to NF_4^+.

KrF_2 has a linear structure similar to that of XeF_2. The Kr—F distance is ~ 189 pm. The Kr—F bond energy is about 50 kJ mol^{-1} which is the lowest value known for a bond formed by any element to fluorine.

An example of Kr bonded to N is provided by the salt $HCNKrF^+ [AsF_6]^-$ which is made by reacting KrF_2 with $HCN^+[AsF_6]^-$ in HF solution. Other nitrile adducts are also known, for example, $[RC \equiv NKrF]^+$ where R = Me, CF_3, C_2F_5 and $n-C_3F_5$.

Kr—O bond is present in the thermally unstable compound $Kr(OTeF_5)_2$:

$$3KrF_2 + 2B(OTeF_5)_3 \longrightarrow 3Kr(OTeF_5)_2 + 2BF_3$$

The compound decomposes into Kr and $F_5TeOOTeF_5$.

25.2.6 The Chemistry of Radon

Inspired by the development in xenon chemistry, it is logical to expect a rich chemistry for radon from energy considerations. However, the longest-lived isotope of radon, Rn-222 has a half-life of only 3.8 days, making its study extremely difficult. Not only that, the availability of radon is also another problem - only about 1.2×10^{-6} g of it is produced from 1 g of Ra-226 in one day. Hence the study of radon chemistry is restricted to tracer studies. Radon may be easily detected by its radioactivity but it is often convenient to detect the more penetrating 1.8 MeV γ-radiation from $^{214}_{83}Bi$ produced from radon; the radiation can be detected through glass or metals. Radon itself is volatile above –80° C in vacuum, but radon compounds are not. Hence compound formation is indicated by any drastic reduction in its mobility.

When radon reacts with fluorine gas at room temperature (or liquid fluorine at –196° C), the reaction vessel retains some γ-activity after the volatile substances are pumped out. This suggests that an ionic fluoride might be formed, Rn^+F^- or $(RnF^+)F^-$. As the samples are very small, conventional analysis is not possible, but mass spectra show the presence of Rn^+. The fluoride is reduced by H_2 gas at 500° C to set free the radon.

Radon is also oxidized by several interhalogen cations to give Rn^+ or RnF^+ which may be retained on a cation exchange resin. Similar oxidation may be carried in liquid ClF_3 or BrF_3; on electrolysis, the radon is found to move to the cathode, showing that a cationic species has been formed. If cesium fluoride is now added to the solution, the radon moves towards both the cathode and the anode. This suggests that fluoro-anions have been formed:

$$Rn \longrightarrow RnF_2 \longrightarrow RnF^+ + F^-$$
$$RnF_2 \xrightarrow{CsF} Cs^+RnF_3^-$$

25.2.7 Can Helium form compounds

In view of their high ionization energies, we do not expect the lighter noble gases He, Ne and Ar to form compounds in positive oxidation states. However, it has been suggested that these elements may act as electron pair donors to strong Lewis acids. Some support to this idea comes through the characterization of several XHe^+ species in interstellar spaces, where X = an electron deficient radical. This is not unlikely since helium is the second most abundant element in the universe.

From calculations it has also been suggested that a number of acetylene derivatives of helium, including $(HeCCHe)^+$, may have sufficient stability. A compound is also likely to be formed when molecules of BeO (vaporizing solid BeO) are implanted into a helium matrix at low temperature.

All of these await confirmation.

SUMMARY

Abundance and Occurrence : After hydrogen, helium is the second most abundant element in the universe where it is formed by thermonuclear reactions. Helium accumulates in the earth's crust through alpha decay of radioactive minerals. It occurs dissolved in minerals and in natural gas. It may be obtained by fractionation of liquid air but is mainly obtained from natural gas.

Argon is the most abundant noble gas in air from which all the noble gases except radon may be isolated by fractionation of liquid air. Radon is produced by decay of radium-226.

Use : Argon and helium are widely used to create an inert atmosphere for welding of metals etc. Liquid helium is used as a refrigerant in low temperature experiments. Neon is widely used in electronics for filling voltage stabilizers and other instruments. Argon and neon are widely used in lamps and discharge tubes.

Compounds : Prior to 1962, only a few clathrates or inclusion compounds of the noble gases were known. High ionization energy of the elements is the main cause of their chemical inertness. Only xenon is known to form stable fluorides, oxides and oxoanions.

Xenon fluorides are formed by direct reaction under varying conditions

$Xe + F_2 = XeF_2$ 400°C, $Xe : F_2 = 2 : 1$

$Xe + 2F_2 = XeF_4$ 400°C, 6 atm, $Xe : F_2 = 1 : 5$

$Xe + 3F_2 = XeF_6$ 300°C, 50 atm, $Xe : F_2 = 1 : 20$

All three fluorides are colourless volatile solids forming molecular crystals. They are readily hydrolyzed—XeF_6 most vigorously.

$$XeF_2 + H_2O \longrightarrow Xe + \tfrac{1}{2}O_2 + HF$$

XeF_4, XeF_6 form Xe, O_2, HF and XeO_3; the last compound is highly explosive.

All three fluorides are strong oxidizing and fluorinating agents :

$$XeF_2 + BrO_3^- + H_2O \longrightarrow BrO_4^- + Xe + 2HF$$

$$XeF_4 + 4KI \longrightarrow Xe + 4KF + 2I_2 . \text{ (estimation)}$$

XeF_6 reacts with glass or quartz giving $XeOF_4$, XeO_2F_2 and finally XeO_3 :

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4.$$

The fluorides react with fluoride ion acceptors like AsF_5 etc. to form adducts like $XeF^+[AsF_6]^-$ etc. XeF_6 also *accepts* fluoride ion from more basic fluorides to form complexes like $CsXeF_7$ and Cs_2XeF_8. These are stable up to 400°C.

XeF_2 is linear, XeF_4 square planar, XeF_6 has a dynamic structure in which the lone pair on xenon occupies a face-center or edge-center of an octahedron of F atoms. The bonding in these compounds is best described in terms of 3-center 4-electron m.o.-s.

Xenon trioxide, XeO_3 is obtained by hydrolysis of XeF_6 :

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF.$$

The compound remains as molecules in solution and may be obtained as white deliquescent explosive solid by evaporation. It is one of the strongest oxidizing agents in aqueous solution ($E°$ for $XeO_3/Xe = 2.1$ V). But it does not oxidize water normally due to kinetic barrier.

XeO_4 is obtained by the action of anhydrous H_2SO_4 on barium perxenate :

$$Ba_2XeO_6 + 2H_2SO_4 = 2BaSO_4 + XeO_4 + 2H_2O.$$

The gas decomposes slowly at room temperature into XeO_3, Xe and O_2 but the solid explodes even at –40° C.

Perxenates are so called by analogy with periodates and result from disproportionation of XeO_3 and XeF_6 in alkaline solution.

$$XeO_3 + OH^- \rightleftharpoons HXeO_4^- \text{ (xenate)}$$

$$2HXeO_4^- + 2OH^- \rightleftharpoons XeO_6^{4-} + Xe + O_2 + 2H_2O \text{ (perxenate)}$$

Both perxenates and xenates are strong oxidizing agents.

Xenon chlorides and krypton fluorides are unstable.

EXERCISE

1. *Which of the noble gases is most abundant in the universe? Mention two uses of the gas.*
2. *Discuss the structures and bonding of xenon fluorides.*
3. *How xenon(VI) and Xenon(VIII) compounds are prepared? Discuss their structure and bonding.*
4. *The xenate ion disproportionates in basic solution to yield xenon, perxenate ion and oxygen. Give a balanced equation for this reaction.*
5. *Describe a procedure for the preparation of potassium perxenate and discuss its structure in the light of the VSEPR theory.*
6. *Write balanced equations for the following reactions :*
   - (a) *Oxidation of* $HXeO_4^-$ *by ozone.*
   - (b) *reduction of* XeO_3 *by iodide in acid medium to xenon.*
   - (c) *oxidation of HCl by* XeF_2.
   - (d) *fluorination by* XeF_2.
7. *Suggest the most suitable noble gas for each of the following uses :*
   - (a) *providing the least expensive inert atmosphere (b) a very low temperature liquid refrigerant (c) an electric discharge light source using a safe gas with low ionization energy.*

   [**Ans. :** (a) Ar (b) He (c) Xe.]
8. *Calculate the standard heat of formation of the hypothetical ionic compound* Xe^+F^- *(s) from the following informations only :*

   Lattice energy of XeF is equal to that of CsF. Ionization energy of Xe = $1170\ kJ\ mol^{-1}$, *of Cs =* $376.5\ kJ\ mol^{-1}$. *Heat of atomisation of Cs (s) =* $79.5\ kJ\ mol^{-1}$, *standard heat of formation of CsF =* $-531.4\ kJ\ mol^{-1}$.

   [**Hint :** Draw Born-Haber cycle for both CsF and XeF (Chapter 6).

   $$\frac{1}{2}D_{F_2} - E.A\,(F) - U = -987.4\ kJ.$$

   Ans. : $\Delta H = 182.6\ kJ\ mol^{-1}$.]

CHEMISTRY OF THE ELEMENTS

SECTION—III : THE d-BLOCK ELEMENTS

CHAPTER TWENTY SIX

COORDINATION COMPOUNDS—I

Introduction; Preparation; Stability; Isomerism

OBJECTIVES

26.1 Introduction.
- The transition elements [26.1.1]
- Coordination compounds [26.1.2]
- Werner's theory [26.1.3]
- Acceptors and donors [26.1.4]
- Detection of complex formation in solution [26.1.5]
- Some applications [26.1.6]
- Second coordination Sphere : supercomplex [26.1.7]

26.2 Preparation of complex compounds
- Reactions of aqua ions [26.2.1]
- Direct reaction in nonaqueous medium [26.2.2]
- Oxidation-reduction reactions [26.2.3]
- Template synthesis [26.2.4]

26.3 Stability of complex ions in solution
- Formation constants [26.3.1]
- The chelate effect [26.3.2]
- Determination of the composition and formation constants [26.3.3]

26.4 Coordination number and stereochemistry
- Examples of coordination numbers [26.4.1]
- Isomerism [26.4.2]
- Structural isomerism [26.4.3]
- Stereoisomersim [26.4.4]

26.5 Nomenclature
- Writing formula [26.5.1]
- Naming mononuclear coordination compounds [26.5.2]
- Polynuclear complexes [26.5.3]
- Names of ligands [26.5.4]

26

COORDINATION CHEMISTRY-I

26.1 INTRODUCTION

The Transition Elements

The majority of elements in the periodic table are metals among which the transition elements constitute the larger fraction. As we shall presently see, they are also most prominent in occurrence and importance among other metals. The transition elements or transition metals appear to have derived their name from the early periodic classification of Mendeleev. He observed that the elements Ti, V, Cr etc. required a separate subgroup to maintain the vertical similarity of properties among the elements in his 8-group periodic table. He further realized that any triad of elements in Group VIII (Fe, Co, Ni say) bear some resemblance to some of the elements in Group VII (here Mn) as well as to some elements in the beginning of the next row in Gr. I (Cu). Thus, the properties of the elements show a transitional character from one row to the next in the periodic table.

There has been some controversy in "defining" a transition element. It seems logical to categorize those elements as transitional which have partly filled d- shell in at least one of its common oxidation states and show certain distinct properties characteristic of such d-orbitals. Zinc, cadmium and mercury $[(n-1)d^{10}ns^2]$ are not classed as transition elements according to this criterion. Nevertheless, they belong to the d - block elements in the periodic table and will be discussed in a separate chapter.

The inner transition elements are similarly characterized by partly filled f-shells and are relatively less common. The next few chapters will be devoted to the chemistry of the transition elements, confined mainly to the first transition series. Before that, we shall have a glance into one important aspect of transition metal chemistry - the coordination or complex compounds.

26.1.1 Coordination Compounds

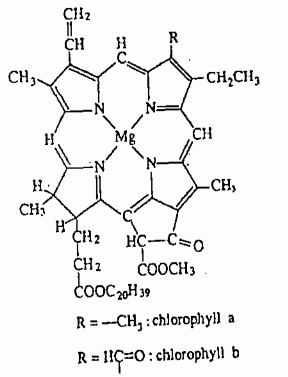


Fig. 26.1
Chlorophylls

Chlorophylls are a mixture of four pigments : chlorophyll (a)—(d); these are complexes of magnesium with macrocylic ligands derived from porphin (Fig. 19-XII). The central Mg^{2+} ion is ~ 30-50 pm above the plane of the 4 nitrogen atoms; one (or two) water molecules coordinate to the Mg and interconnect stacks of chlorophyll units through H-bonding.

Coordination compounds, often popularly called "complexes", play important roles in industry, in the synthesis of various organic chemicals and in polymerization processes. They are also involved in numerous biological processes in an extremely complicated but selective and systematic manner; study of model reactions involving similar but simpler compounds help us a lot to understand these processes of nature.

Ready examples of such widely occurring natural complex compounds are provided by chlorophyll, the magnesium(II) complex essential for plant photosynthesis and haemoglobin, the iron(II) complex that carries oxygen in blood without undergoing oxidation.

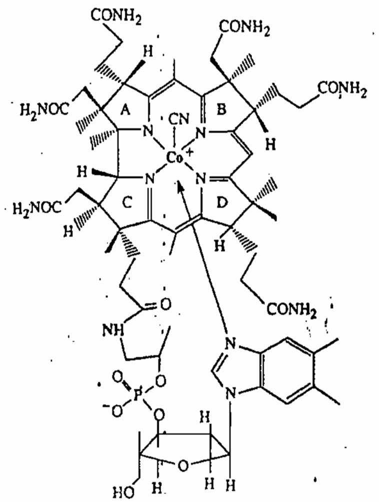
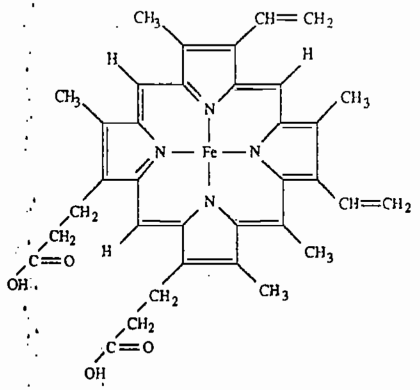


Fig. 26.2
Vitamin B_{12}

Vitamin B_{12} is a naturally occurring complex of cobalt (formal oxidation state III) coordinated to four N atoms of a corrin ring; the fifth coordination site of the cobalt is linked to an imidazole nitrogen and the sixth site is σ-bonded to a carbon in a deoxyadenosine moiety. The sixth coordination position is a labile site; the vitamin is isolated as ***cyanocobalamine*** in which this sixth site contains a cyamide ion. The vitamin occurs only in animals and micro organisms but not in plants. The vitamin is responsible for the supply of red blood cells in the liver.

Fig. 26.3
Haemoglobin

Haemoglobin is responsible for transporting oxygen in our body through blood. The Fe(II) atom is held by bonds to four N atoms in the *haem* group of haemoglobin. (A further bond can be made to part of a protein chain not shown in the diagram). The Fe(II) can reversibly bind a molecule of oxygen without undergoing oxidation presumably because of its strained environment. The oxygen is again released in our body.



What is a complex compound?

A formal definition of a complex or coordination compound is difficult to find. Informally, a complex is said to have formed when a central atom attaches to it a number of ions or molecules to form a distinct entity in which the number of atoms directly linked to the central atom usually exceeds its normal covalency. Thus $[BF_4]^-$ is a complex of boron but BF_3 is not because the normal covalency of boron, three, is not exceeded in the latter. A solution of ferrous sulphate contains the complex $[Fe(H_2O)_6]^{2+}$ and SO_4^{2-} (aquated) ions. The groups bonded to the central atom are called ligands; they contain one or more donor atoms which may be said to donate a pair of electrons to the central atom, forming coordinate bonds. The actual description of bonding is more sophisticated.

A complex may be neutral, cationic or anionic. Some examples are given below :

"Simple compound" or ion	Ligand	Complex
BF_3	Me_3N	Me_3NBF_3
AgCl	Cl^-	$[AgCl_2]^-$
Fe^{2+}	CN^-	$[Fe(CN)_6]^{4-}$
Cu^{2+}	NH_3, H_2O	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ abbreviated as $[Cu(NH_3)_4]^{2+}$
Cu^{2+}	NH_3	$[Cu(NH_3)_6]^{2+}$ *(in liquid NH_3)*.

A complex compound or ion is characterized by the discrete entity present either in solution or in the solid state. Thus the complex $[Fe(CN)_6]^{4-}$ ion dissociates only negligibly in solution to furnish $Fe^{2+}(aq)$ and CN^- ions.

Although the chemistry of complex or coordination compounds developed initially with metals as the central acceptor atom, nonmetal atoms and even molecules can play the same role. Thus species like BrF_4^-, ICl_4^-, XeO_3F^- and $H_3B.CO$ also fall under the category of complexes. Of course, the majority of complex compounds are formed by metals.

Double salts

"Double salts" appear to form an aggregate of two simpler salts, each capable of independent existence. The aggregate maintains the individuality of the salts and in solution the aggregate simply splits into the ions expected on the basis of the simple formula of the component salts. Thus potash alum is represented as $K_2SO_4.Al_2(SO_4)_3.24H_2O$ or $KAl(SO_4)_2.12H_2O$. This is a double salt as it splits in aqueous solution to K^+, Al^{3+} and SO_4^{2-} ions. Strictly speaking, however, the Al^{3+} ion is present as the complex $Al(H_2O)_6^{3+}$ ion and a more instructive way to write the formula is $K^+[Al(H_2O)_6]^{3+}(SO_4^{2-})_2.6H_2O$. Some more examples of double salts are

Ferric alum : $K_2SO_4.Fe_2(SO_4)_3.24H_2O$
Chrome alum : $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
Carnallite : $KCl.MgCl_2.6H_2O$
Mohr's salt : $(NH_4)_2SO_4.FeSO_4.6H_2O$
Tutton salt : $M_2SO_4.CuSO_4.6H_2O$ [M = Na, K]

Organometallic Compounds

Though precise definition of "organo" and "metallic" are lacking, a vast number of compounds are now included under this broad generalization and they represent a fast expanding realm of chemistry. These compounds also involve coordination to a metal by donor atoms in ligands but the term organometallic implies that there is at least one close M - C interaction. Hence complexes with CO, CO_2, CS_2 and CN^- are classed as organometallics. Compounds like NaCN or CH_3COONa which are basically ionic in nature, or metal carbides are excluded from this category. Metal alkoxides and complexes with organic ligands where the donor atom is not carbon (e.g. pyridine C_5H_5N) are also excluded. On the other hand, the domain of "metals" is often relaxed to include the elements B, Si, Ge, As, Sb, Se and Te.

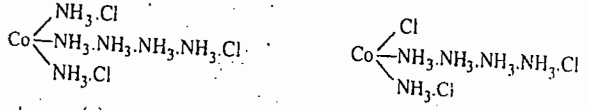
[Sec. 26.1.2 *Werner's work*]

In short, the term "complex" was restricted initially to compounds in which the bonds (between the metal and the ligand) were largely sigma bonds and the metal had oxidation number of +2 and above. The development of coordination chemistry was initiated by study of such compounds. In later periods, complexes have been recognised with π-bonding between the metal and ligand and having the metal in zero or even negative oxidation states; there are also complexes where the metal is encapsulated by macrocyclic ligands, e.g., the alkali metal complexes of crown ethers and cryptands mentioned earlier. A number of sandwich complexes like ferrocene and dibenzenechromium have also emerged.

26.1.2 Historical Development

Though the systematic understanding of complex compounds dates from the time of Alfred Werner (1893), many complex compounds were known to the chemists even in the eighteenth century. For example, the cyano complex "Prussian blue" was discovered in 1704. In 1798, Tassaert observed that solutions containing Co(II) in aqueous ammonia turned brown when exposed to air and the colour changed to wine red on boiling. Later, Fremy showed that the cobalt(II) had been oxidised to Co(III) and had associated with upto six NH_3 molecules. But formulations like $CoCl_3$, $6NH_3$ could not explain how the NH_3 molecules were attached to the neutral molecule $CoCl_3$. In 1827, Zeise isolated a compound of the composition $PtCl_2.KCl.C_2H_4$, later established as $K[PtCl_3(C_2H_4)]$ (*Zeise's salt*). With the exception of cyano compounds, this may be called the first organometallic compound of the transition metals. Many other salts were similarly named after their discoverers, e.g., *Magnus' green salt* (1828) : $PtCl_2.2NH_3$, now formulated as $[Pt(NH_3)_4][PtCl_4]$ and *Reinecke's salt* : $Cr(SCN)_3.NH_4SCN.2NH_3$ or $NH_4[Cr(NH_3)_2(NCS)_4]$. An example of application of complex formation in industry in the nineteenth century is provided by Mond's process of separation of nickel as volatile $Ni(CO)_4$ (1899).

Several theories were put forward to explain the formation of complex compounds. For example, Jörgensen followed the analogy of catenation in carbon compounds and proposed a structure like the following for the compound of stoichiometry $CoCl_3.6NH_3$ (26-Ia) and $CoCl_3.5NH_3$ (26-Ib). It was suggested that the chlorine atoms bonded to ammonia are *not* precipitated readily by silver ion (see below).



(a) (b)

26-I

Similar formulations were proposed for other such compounds known at the time. But these formultions could not explain many of the experimental facts already available. Werner built his revolutionary alternative to the chain theory of Jörgensen (then accepted widely), largely on Jörgensen's data. Later he isolated and studied a wide variety of complex compounds and developed a comprehensive theory for them. Some idea of his initial work may be gained from his studies on "metal-ammonia salts" like

$M(NH_3)_6X_3$	$M(NH_3)_5X_3$	$M(NH_3)_4X_3$
"Luteo salts" (yellow)	"Purpureo salts" (purple)	"Praseo salts" (green)

where M was most commonly Co(III), Cr(III), Rh(III) and X ("acid residue") was most commonly halides, nitrite etc.

Alfred Werner (1866 - 1919)

Alfred Werner, born in Switzerland, developed an active interest in Chemistry at an early age and set up a small laboratory to run different experiments. He studied chemistry in Karlsruhe and then in Zurich. Here A. Hantszch had found some nitrogen containing organic compounds having the same analytical composition but different properties. Werner explained this in his doctoral thesis (1890) as a case of isomerism by extending van't Hoff's theory of tetrahedral carbon atom to nitrogen.

Werner carried out extensive work on the constitution of inorganic compounds and forwarded his theory of bonding in coordination compounds in 1893. He became full Professor at the university of Zurich in 1893, at the age of twentyseven. For nearly the next twenty years he prepared and studied different coordination compounds which perfected and proved his theory of coordination compounds. He was the first to discover optical activity in coordination compounds and "inorganic" compounds. He was awarded the Nobel Prize in Chemistry in 1913.

Werner passed away in 1919 at the age of fifty-three.

Let us consider the four cobaltammines :

A : $CoCl_3.6NH_3$ (Orange-yellow : *Luteocobaltic chloride*).

B : $CoCl_3.\ 5NH_3,H_2O$ (Pink : *Roseocobaltic chloride*).

C : $CoCl_3.\ 5NH_3$ (Violet : *Purpureocobaltic chloride*).

D : $CoCl_3.\ 4NH_3$ (Violet : *Violeocobaltic chloride* and Green : *Praseocobaltic chloride*).*

Some observations on these compounds were as follows :

(i) Treatment of solid A with sulphuric acid, liberated *all* the chlorine as HCl, forming $Co_2(SO_4)_3.\ 12NH_3$. The ammonia molecules were not removed even when the solid was heated with hydrochloric acid at 100°C.

(ii) Compound B loses the water molecule only at 100°C or above, giving compound C.

(iii) Compound C loses only *two* chlorine on treatment with sulphuric acid and forms $CoClSO_4.5NH_3$.

Interesting observations were also obtained from conductance measurements on aqueous solutions of the compounds and estimation of the silver chloride precipitated immediately from such solutions with silver nitrate. The latter furnished the number of moles of AgCl precipitated per mole of the complex.

The electrical conductance of a solution depends (among other things) on the number of charge-carriers, i.e. ions, in the solution. For very dilute solutions, a simple relationship may be established between the number of ions furnished per "molecule" of the compound and the molar conductivity. Thus, molar conductivities (Λ_M) in water (at 10^{-3}M conc.) are about 120 $ohm^{-1}cm^2$ for NaCl which gives two mol of ions per mol of NaCl; $BaCl_2$, giving three ions, has $\Lambda_M \simeq 260\ ohm^{-1}cm^2$; $CeCl_3$, giving four ions, has $\Lambda_M \simeq 400\ ohm^{-1}cm^2$. The number of ions furnished by a complex compound may be similarly inferred by comparing the molar conductances of their dilute aqueous solutions. Conductance study on the above mentioned cobalt compounds, or corresponding bromides indicated different numbers of ions in solutions (Table 26.1).

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* The isomeric violeo salts were not discovered by Werner until 1907.

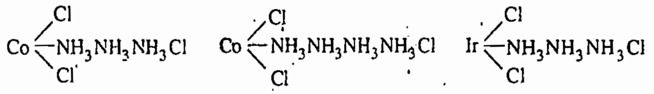
TABLE 26.1

Molar conductivity (0.001 *M* solution) and halide ions precipitated readily from solution

Compound	Molar Conductivity	No. of ions	No. of Cl^-/Br^- ions precipitated
(i) $CoCl_3.6NH_3$	431.6	4	3
(ii) $CoCl_3.5NH_3$	261.3	3	2
(iii) $CoBr_3^{\dagger}.5NH_3,\ H_2O$	412.9	4	3
(iv) $CoBr_3^{\dagger}.5NH_3$	257.6	3	2

Though each compound contained the principal component $CoCl_3$ (or $CoBr_3$), the number of Cl^-/Br^- ions furnished per atom of cobalt were not always three; the remaining halogen atoms were precipitated *only slowly* after long standing or boiling. This indicated a difference in the mode of attachment of the chlorine atoms.

These observations lead one to conclude that $CoCl_3.3NH_3$ should not produce any immediate precipitate with $AgNO_3$ solution. However, a compound of this stoichiometry could not be isolated. But a similar compound, $IrCl_3.3NH_3$ was found to have no ionizable chloride. This observation could not be explained by the chain theory mentioned before, since it predicts the same number of ionizable chlorides for $CoCl_3.3NH_3$, $CoCl_3.4NH_3$ and $IrCl_3,\ 3NH_3$:



26-II

Similar observations were recorded with corresponding compounds of chromium, platinum etc. It was shown by Werner that the number of ions inferred from molar conductivity and the number of chloride ions precipitated from the compounds could be interpreted on the basis of formulations of the following type for the cobalt compounds A—D :

A. **Luteocobaltic chloride**	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$
B. **Roseocobaltic chloride**	$CoCl_3.\ 5NH_3.H_2O$	$[Co(NH_3)_5H_2O]Cl_3$
C. **Purpureocobaltic chloride**	$CoCl_3.\ 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$
D. **Violeo- and Praseocobaltic chloride**	$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$

Data for platinum(IV) ammine complexes are also illustrative :

TABLE 26.2

Conductance of platinum(IV) ammines (0.001*M* solution)

Complex	Λ_M ($ohm^{-1}\ cm^2$)	No. of ions	Formulation
(a) $PtCl_4.6NH_3$	523	5	$[Pt(NH_3)_6]Cl_4$
(b) $PtCl_4.5NH_3$	404	4	$[Pt(NH_3)_5Cl]Cl_3$
(c) $PtCl_4.4NH_3$	229	3	$[Pt(NH_3)_4Cl_2]Cl_2$
(d) $PtCl_4.3NH_3$	97	3	$[Pt(NH_3)_3Cl_3]Cl$
(d) $PtCl_4.2NH_3$	7	0	$[Pt(NH_3)_2Cl_4]$
(e) $KPtCl_5.NH_3$	109	2	$K[Pt(NH_3)Cl_5]$
(g) K_2PtCl_6	256	3	$K_2[PtCl_6]$

[†] The corresponding chlorine compounds showed rapid water exchange in solution.

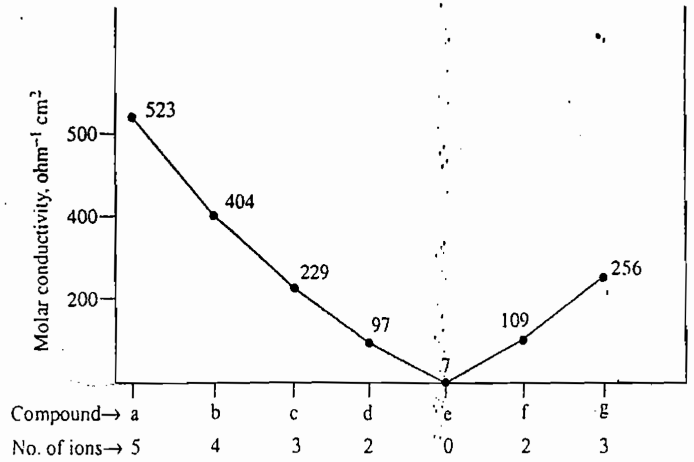


Fig. 26.4 **Molar electrical conductivity of platinum(IV) complexes.**

With these and several other experimental results, Werner put forward his theory of coordination compounds in the revolutionary papers* "Contribution to the constitution of inorganic compounds" published in 1893, at the age of twentyseven and subsequent publications. Werner verified each and every postulate of his theory by experiment. These were also supported by works of several other scientists working independently. He was awarded the Nobel Prize in Chemistry in 1913 in fitting recognition to his contributions.

26.1.3 Werner's Theory

In his attempt to explain the experimental facts gathered with cobaltammines and related compounds, Werner not only suggested formulations which are mostly held correct even today, but also developed a theory which is still applicable without gross alteration. This is a rare feature of any theory in science; not only that, what was a blooming bud at the time of Werner, has by this time covered a major area in the world of chemistry, the coverage increasing day by day at an enormous rate.

The basic postulates of Werner's theory may be summarized as follows :

1. *Metals possess two types of valency* :

(a) the primary or principal valency; this is the ionizable valency. (German Hauptvalenz; Haupt = principal).

(b) a secondary nonionizable valency (German *Nebenvalenz*; Neben = subsidiary).

2. *Every metal has a fixed number of secondary valencies.*

The number of secondary valencies of a metal is called its coordination number.†

3. *Primary valencies are satisfied by negative ions whereas secondary valencies may be satisfied by negative ions as well as neutral molecules and cations.* In some cases, a given negative group may have to satisfy both the valencies of a metal, but it is essential to satisfy the secondary valency of the metal.

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[*] It is said that Werner finalized this theory following a dream.

[†] This is, however, different from the coordination number (C.N.) used in connection with crystals where it denotes the number of nearest neighbours of a given atom/ion in the crystal. In coordination compounds, the term is used to indicate the number of groups associated through electron-pair bonding with a central metal atom (ion) in a coordination compound. However, corodination compounds are also formed without electron pair bonds e.g. sandwich complexes, crown ether complexes etc. (see later).

4. *The secondary valencies are directed in space around the central metal ion in definite geometrical disposition.*

[Sec. 26.1.3 *Werner's theory*]

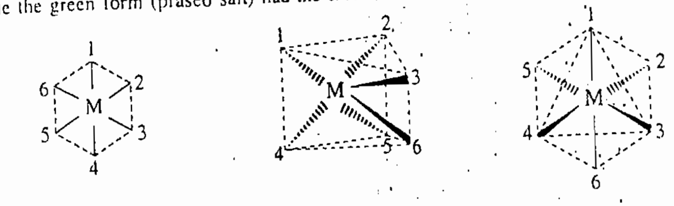
Explanation : The first three postulates of Werner's theory help us to rationalize the structural formulae of complex compounds like the cobaltammines or platinum compounds mentioned before. Thus the primary valency of cobalt in the cobaltammines (Table 26.1) is, always three and the secondary valency is six. For the platinum ammines the primary valency of Pt is four and the secondary valency is again six. So the coordination number of Co(III) or Pt(IV) in such compounds is six - the metals prefer to have six ligands directly attached to them. These are said to be in the coordination sphere of the metal. We see that the secondary valencies are satisfied by the negative chloride ion as well as the neutral groups like NH_3, H_2O etc. When a chloride ion enters the coordination sphere of a metal, it satisfies both the primary and secondary valency of the metal. The entire coordination sphere has an overall charge equal to the algebraic sum of the primary valency and the charge of ligands in the coordination sphere : for example,

Species	**Primary Valency**	**Charge of ligand(s)**	**Overall Charge**
$[Co(NH_3)_5Cl]^{2+}$	+3	−1	2+
$[Pt(NH_3)_4Cl_2]^{2+}$	+4	−1 × 2	2+
$[Fe(CN)_6]^{4-}$	+2	−1 × 6	4−
$[Ni(CO)_4]$	0	0	0

Clearly, the ions outside the coordination sphere are bonded ionically to the coordination sphere as a whole. When $[Co(NH_3)_5Cl]Cl_2$ is dissolved in water, we get the ions $[Co(NH_3)_5Cl]^{2+}$ and two Cl^-. The chlorine bonded coordinatively in $[Co(NH_3)_5Cl]^{2+}$ is not readily precipitated by silver nitrate. Similar considerations apply to other compounds of this type mentioned before.

The most significant part of Werner's theory lies in Postulate No. 4. It assumes directional character of the coordinate bonds established by the secondary valency of an element and as such predicts the occurrence of various types of stereo isomers. This has made enormous contribution to the development of inorganic stereochemistry. This part of the Werner theory was the most difficult to prove; it took Werner nearly twenty years to furnish an unquestionable proof of this by resolution of a "purely inorganic" complex into its predicted optical isomers (see optical activity). At that time, direct methods of structure determination were not established (for example X-ray study); Werner had to decide upon a structure on the basis of the number of stereoisomers obtainable from it. Thus the octahedral disposition of the six secondary valencies was based on the availability of only two isomers of the type MA_4B_2 (A, B = unidentate ligands).

Let us consider the possible ways in which six groups may be arranged in space around a central metal atom/ion. The simplest case arises when the groups are all identical, say for a compound of the formula-type MA_6. No isomers are expected for any conceivable geometrical arrangement of the identical ligands. For a complex of the type MA_4B_2, we expect 3 isomers for each of hexagonal planar or trigonal prismatic arrangement of the ligands around M (Figure 26.5). But the octahedral structure gives rise to only two isomers. Numerous complexes of the type MA_4B_2 were studied, and in no case more than two isomers could be isolated. Hence Werner concluded that the six groups were arranged at the six corners of a regular octahdron. The cobaltammines of the formula $[Co(NH_3)_4Cl_2]Cl$ were of this type, and we remember that they were isolated in two colour varieties. The violet compound (violeo-salt) was shown to have the two coordinated chlorines in adjacent positions (*cis*) while the green form (praseo salt) had the chlorines in diagonally opposite positions (*trans*).



	(i) hexagonal planar	(ii) prismatic	(iii) octahedral
MA_6	—	—	—
MA_5B	—	—	—
MA_4B_2	3 isomers 1, 2; 1, 3; 1, 4	3 isomers 1, 2; 1, 4; 1, 5	2 isomers 1, 2; 1, 6.

Fig. 26.5

Arrangement of six groups around a metal : (i) hexagonal planar (ii) trigonal prismatic (iii) octahedral. The number of possible isomers for some ligand combinations are also shown.

For a regular octahedron, any point can be taken as the vertex 1 and hence position 1, 2, is identical with 1, 3 or or 1, 4 (and so on). Similarly, 1, 6 is identical with 2, 4 or 3, 5. See Fig. 26.6.

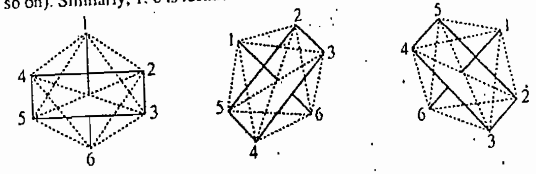


Fig. 26.6

Interrelation between different positions of an octahedron.

Werner also proved the octahedral structure for 6-coordinate complexes by resolution of complexes of the $M(aa)_3$ type into optical isomers (aa stands for a bidentate chelating agent, for example, ethylenediamine, $NH_2CH_2CH_2NH_2$). Neither the planar nor the trigonal prismatic structure would give optical iosmers for such types of complexes.

The first crystallographic confirmtion of octahedral geometry in $(NH_4)_2[PtCl_6]$ was published in 1921. Similarly, the square planar structures of Pt(II) complexes were established in the next year. In this latter case also, Werner had predicted the same geometry on the basis of two isomers for the type MA_2B_2, e.g., $[PtCl_2(NH_3)_2]$. A tetrahedral geometry would have produced only one form of such compounds.

Nevertheless, Werner's proof of the predicted stereochemistry on the basis of isolable isomers cannot be called fool proof. One cannot really conclude that an isomer does not exist because one could not prepare it. Thus, the third isomer for MA_4B_2 type complexes might have escaped Werner's methods of isolation. Luckily, the compounds of this formula type studied by him were all really octahedral and his inferences flawless. It may be mentioned in this connection that after nearly 70 years of Werner's proposal, a second variety of six-coordinte complexes has been established. In 1965, it was first shown that $[Re(S_2C_2Ph_2)_3]$ has trigonal prismatic geometry (see isomerism in C.N.6; Ph = phenyl). Since then, several complexes of this geometry have been characterized.

26.1.4 Acceptors and Donors in Complex Species

The formation of a complex species may be largely described as a Lewis acid-base type interaction between a central acceptor atom, mostly a metal, and peripheral donors, commonly called ligands.

Metal ions serving best as acceptors are those with small sizes and high ionic charges or effective nuclear charges and/or possessing incomplete acceptor orbitals like $(n-1)d$ or still inner f orbitals. The alkali and alkaline earth metals are known to form relatively fewer complexes, though in recent years many complexes of these elements have been prepared using macrocyclic ligands.

As mentioned earlier in connection with Hard-Soft Acid-Base classification, acceptor atoms may be divided into two broad clases : (i) class a acceptors which form most stable complexes with small, hard donor atoms (usually the lightest atom in a periodic group) like O or F present in ligands; (ii) Class b acceptors which form stable complexes with large, soft donor atoms like P or S. With minor deviations, this classification is also parallel to the hard-soft classification; a few examples :

Class A	Borderline	Class B
H^+, Na^+, K^+,	Fe^{2+}, Co^{2+}, Ni^{2+}	Pd^{2+}, Pt^{2+}, Pt^{4+},
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+},	Cu^{2+}, Zn^{2+}, Pb^{2+}	Cu^+, Ag^+, Au^+,
Al^{3+}, Sc^{3+}, La^{3+}, Ce^{4+}, Gd^{3+},	Sn^{2+}, Sb^{3+}, Rh^{3+},	Cd^{2+}, Hg_2^{2+}, Hg^{2+} etc.
Th^{4+}, U^{4+}, UO_2^{2+},	Ir^{3+} etc.	
Ti^{4+}, VO^{2+}, Cr^{3+}, Cr^{6+},		
Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+} etc.		

Ligands are essentially Lewis bases; they possess one or more pairs of electrons in addition to those used in bonding. Ligands with only one atom possessing such lone-pair electrons can bond through that atom and are called *monodentate ligands* (Latin *dentate* = having teeth) : for example, ammonia (NH_3), water (H_2O), halide ions (X^-) etc. Similarly when the molecule of a Lewis base possesses lone pair electrons on two such atoms, it may (not always) bond via both of them; it is then said to behave as a *didentate** *ligand*. Ethylenediamine, $\ddot{N}H_2CH_2CH_2\ddot{N}H_2$ and hydrazine $H_2\ddot{N}\ddot{N}H_2$ are such didentate ligands. On the same line, there may be ligands with three, four, five or six donor sites - these multidentate ligands are accordingly called tri-, tetra- etc. dentate ligands. The number of donor atoms is sometimes called *denticity* of the ligand. A ligand which shows different denticity is called a *flexidentate* ligand. Thus edta (Table 26.3), though a hexadentate ligand, sometimes function as a tetradentate or pentadentate ligand.

Most ligands normally coordinate through the same atom/atoms. Certain ligands however, can coordinate through either of two coordination sites giving rise to linkage isomerism (see later). Thus the thiocyanate ion coordinates through nitrogen forming $[Co(NCS)_4]^{2-}$ but it coordinates through sulphur in $[Hg(SCN)_4]^{2-}$. The nitrite ion also can coordinate through N (nitro complexes) or through O (nitrito complex). Such ligands are called *ambidentate* ligands. The cyanide ion is also ambidentate.

Some common polydentate ligands are shown in table 26.3.

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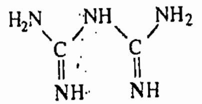
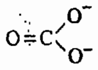
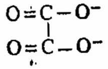
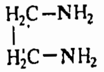
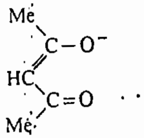
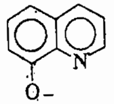
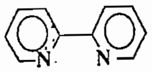
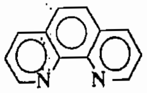
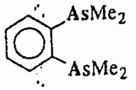
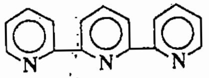
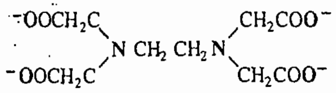
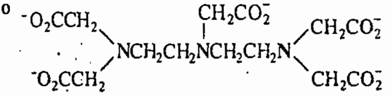
* Conventionally called bidentate. Both Latin (bi-, quadri-etc) as well as Greek prefixes (di-, tetra- etc.) were previously used (Greek prefix with Greek stem : *tetranuclear*; Latin prefix with Latin stem : *quadridentate*). The current trend is to use single set of prefixes - the Greek ones : mono-, di-, tri-, tetra-, penta-, hexa-, hepta......

TABLE 26.3

Some Common polydentate ligands*

Name	Formula (with donor sites)	Abbreviation	Denticity
Biguanide		(big H)	didentate
Carbonato		—	didentate
Oxalato		ox	didentate
(Ethylenediamine) 1,2-ethanediamine		en	didentate
(Acetylacetonato) 2,4-pentanedionato		acac	didentate
8-Hydroxyquinolinato (8-quinolinolato)		oxine	didentate
2,2'- Dipyridyl (bipyridyl)		dipy	didentate
1,10-phenanthroline		phen	didentate
Glycinato	$NH_2CH_2COO^-$	gly	didentate
Triphenylphosphine	$(C_6H_5)_3P$	Ph_3P	monodentate
o-phenylenebis(dimethylarsine)		diars	didentate
Diethylenetriamine	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	dien	tridentate
Terpyridine		terpy	tridentate
Triethylenetetraamine	$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	trien	tetradentate
Nitrilotriacetato	$N(CH_2COO)_3^{3-}$	nta	tetradentate
Tetraethylenepentaamine	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	tetraen	pentadentate
Ethylenediaminetetraacetato		edta	hexadentate (also tetra or pentadentate)
Diethylenetriaminepentaacetato		$dtpa^{5-}$	octadentate

Ligands may be classified according to the nature of donor atoms as follows :

(i) Ligands in which the donor atoms have one or more nonbonded electron pairs, e.g., H_2O, NH_3, F^-, H^- etc. Some ligands may have vacant orbitals (or orbitals which may be vacated) that can receive π-electron density from the metal, for example, CN^-, PR_3, I^- etc. Certain other ligands may have additional π-electronic charge density which may be delocalized into suitable metal orbitals, for example, OH^-, F^-, I^-.

(ii) Ligands in which the donor atoms do not possess nonbonded pairs of electrons but possess π-electronic charge density, for example, C_2H_4, C_6H_6, $C_5H_5^-$ (cyclopentadienide) etc.

We recall that NH_3, OH^-, F^-, Cl^- etc. are some of the hard bases while R_3P, CO, CN^-, SCN^-, I^- etc. are typical soft bases. This classification matches with the observed affinities of different metals towards these ligands. Hard base ligands are found to form more stable complexes with hard acceptor metals (class A) while, soft base ligands form more stable complexes with soft acceptors (class B). Ligands like CO, C_2H_4, CN^- etc. also act in metal to ligand dative bonding involving the lowest unoccupied mo (usually π^*) on the ligands. Such ligands are thus called π-acid or π-acceptor ligands.

Besides the above broad classification, there may be many uncommon donor species like H_2, N_2, O_2, P_4, polysulfide ions, $SnCl_3^-$, $Sn(CH_3)Cl_2$ etc. An example of the tetraphosphorus molecule acting as a ligand is the complex $[Rh(Cl)(P_4)PPh_3]_2$. An area of immense interest has been opened recently by the characterization of several dihaptodihydrogen complexes, for example,

$$Cr(CO)_6 + H_2 \xrightarrow[\text{liq Xe}]{h\nu\,(uv)} [Cr(CO)_5(\eta^2 - H_2)]$$

Examples of cations acting as ligands are rare, presumably because of the electrostatic repulsion involved with the metal ion. Typical examples of cationic donors are NO^+, $[Co(NH_3)_4(OH)_2]^+$ (see optical isomerism), $[(CH_3)_3\overset{+}{N}(CH_2)_2NH_2]$ (= L) in $[ML_6](ClO_4)_8$, where M = Ni^{2+}, Co^{2+} and $[(CH_3)_3\overset{+}{N}NH_2]$ (= L') in $[NiL_2'Cl_4]$.

Chelates

When a multidentate ligand coordinates to a metal ion from more than one donor site forming a ring with the metal (26-IV and 26-V) it is said to be a chelating ligand (Greek *crab's claw*) and the resulting compound is said to be a chelate complex

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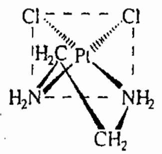
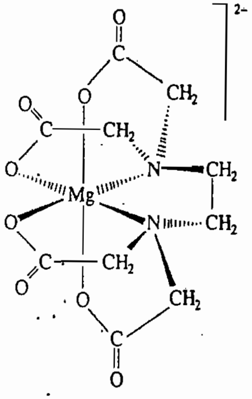
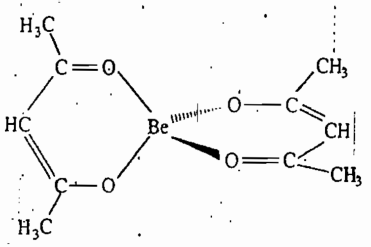
* A few more examples are given under analytical application p. 638.

(pronounced as **kelate**; 'ch' as in character *not* as in chair). A five-membered chelate ring is formed by ethylenediamine in which the NMN angle is about 90° and the C and N atoms retain near tetrahedral angles. As a consequence the chelate ring is puckered, as shown in skeleton in 26-III for $[PtCl_2en]$. The analytically important magnesium complex of edta is shown in 26-IV where the edta anion coordinates as a hexadentate ligand. The special stability associated with such chelate formation and their applications will be discussed in separate sections (application 26.1.6; chelate effect 26.3.4).


26-III

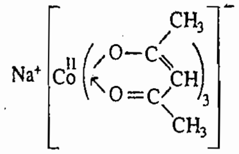

26-IV

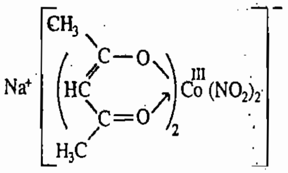

26-V

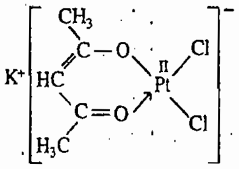
Chelating ligands having an anionic donor site may simultaneously satisfy the secondary valency (coordination site) and the primary valency or charge on the metal ion. Such chelate complexes where the coordination number and charge on a metal ion are internally compensated are sometimes classified as *inner metallic complexes* or *inner complexes.*

Chelate complexes in which the coordination number and charge on the metal ion are exactly balanced by the ligand are neutral in nature and are classed as inner complexes of the *first order*, bis(acetylacetonato)beryllium(II) (26-V) being an example of this kind. Bis(dimethylglyoximato)nickel(II) is another such example (see later). These neutral covalent complexes are low melting, volatile and mostly insoluble in water, but soluble in organic solvents. They often possess intense colours, too. These facts have led to their extensive use in analytical chemistry (section 26.1.6).

However, ligands with acidic donor sites may also form complexes in which the total anionic charge of the ligand does not exactly balance the charge on the metal ion. Such complexes with residual charge have been termed "*inner complexes of the second order*". These may also be formed by combination of a chelating ligand with other ligands. Some examples are given below :

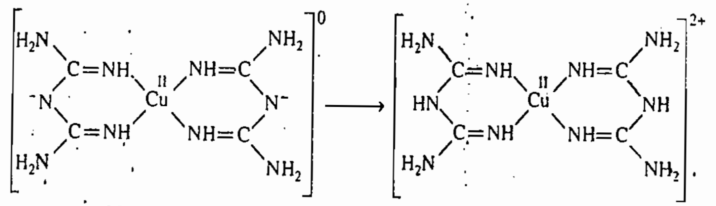

26-VI (a)


26-VI (b)

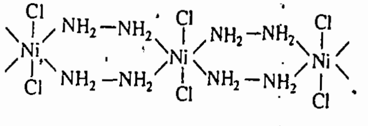

26-VI (c)

[Sec. 26.1.4 *Chelates*]

A *third order inner-metallic complex* is said to be formed when a neutral (first order), inner metallic complex is converted into a cationic species due to protonation of some negative centre in the ligand. Prof. P. Ray established such a third order complex when the first order complex of Cu(II) with biguanide (Table 26.3) is treated with HCl :


26-VII(a) 26-VII(b)

Chelating ligands can also coordinate to two different metal atoms from different donor sites when they form a bridge as in 26-VIII.


26-VIII

Q. 26.1 *Which of the following chelating ligands have the ability to form inner-metallic complexes with cobalt (II) and cobalt(III)?*

(i)	(ii)	(iii)	(iv)	(v)	(vi)
COOH | COOH	COOH | CH_2NH_2	CH_2NH_2 | CH_2NH_2	CH_2COOH | $CHNH_2$ | CH_2NH_2	CH_2COOH | NH | CH_2COOH	CH_2COOH | $N\text{-}CH_2COOH$ | CH_2COOH

Hint : $\overset{II}{Co}$: C.N.4 (ii) C.N.6 (iv); $\overset{III}{Co}$: C.N.6 (ii)

Here inner complexes of the first order only are implied. The "ability" may be arrived at by consideration of balance of charge and coordination number of the metal ion (usually 4 and 6) by coordination from all possible sites in the ligand. However, the real mode of coordination by the ligands and the preference of a metal ion for a particular coordination number remain untouched in such approach.

Macrocyclic Ligands

The crown-ethers (section 18.3.6) are examples of multidentate macrocyclic ligands which trap a variety of non-transition metal ions but form only a few stable complexes with the *d*-block transition metal ions. Similar macrocyclic ligands with nitrogen, sulfur or phosphorus donor atoms are also known which form stable complexes with *d*-transition metal ions. These ligands function by completely encapsulating the metal ion and are most stable when the metal ion exactly fits the size of the 'cavity' formed by the donor atoms. Since the ligands practically encapsulate the metal ion, such ligands have been termed *cryptands* (Greek *Kryptos* - hidden; to hide) or *sepulchrands* (Latin *sepulchruna* = to bury) and the complexes are often called cryptates or sepulchrates. The porphyrin and corrin ring systems found in nature are macrocyclic ligands (Fig. 26.1 and 26.2).

26.1.5 Detection of Complex Formation in Solution

Formation of a complex may be understood by following any property of the system which is related to the concentration of at least one species involved in the formation of the complex, e.g., H^+, metal ion, ligand or the complex itself. One may also adopt a number of other techniques like kinetic study, redox study, electrochemical migration, magnetic study, isotopic metal or ligand exchange, heats of reaction, molar refraction, infrared absorption spectra and nuclear magnetic resonance spectra. Only a few examples will be given.

(i) ***Chemical Properties*** : Complexation results in an alteration of the normal chemical properties of the metal ion in solution. For example,

(a) addition of alkali to an aqueous solution of Fe(II) in presence of edta does not precipitate $Fe(OH)_2$. The $[Fe(edta)]^{2-}$ complex is highly stable and the concentration of Fe^{2+} ion is insufficient to reach the solubility product of $Fe(OH)_2$.

(b) AgCl (sol. product $\simeq 10^{-10}$) is not precipitated by Cl^- ion from solutions of Ag^+ in aqueous NH_3; AgBr (S. P. $\simeq 10^{-12}$) is precipitated only with excess KBr; AgI (S.P. $\simeq 10^{-16}$) is precipitated even by dilute solutions of KI. One popular way of rationalizing these observations is to state ; silver chloride is more soluble in ammonia than silver iodide. Actually the stable $[Ag(NH_3)_2]^+$ complex furnishes too little Ag^+ ion which cannot reach the solubility product of AgCl. AgI has a much smaller solubility product which is exceeded by the small concentration of Ag^+ furnished by the ammine complex in presence of small concentrations of I^-.

Some other examples of abnormal solubilities due to complex formation are given below :

(c) Ag_2S dissolves in KCN solution but not in $Na_2S_2O_3$ solution. The stable complex $[Ag(CN)_2]^-$ does not furnish enough Ag^+ ion concentration to reach the solubility product of Ag_2S. But the complex $[Ag(S_2O_3)_2]^{2-}$ is somewhat less stable and the concentration of Ag^+ ion can exceed the solubility product of Ag_2S.

(d) Mercuric oxide, though insoluble in water, dissolves in KI solution :

$$HgO + 4I^- + H_2O \rightleftharpoons [HgI_4]^{2-} + 2OH^-$$

(e) The solubility of AgCl in water increases on adding NaI as the complex $[AgClI]^-$ is formed.

However, the changes in properties on complexation are best understood when the complex has high thermodynamic stability — the amount of metal ion remaining uncomplexed is relatively small. Similarly, kinetic aspects of the reactions under study may largely influence the chemical behaviour in many cases. Thus $[Cu(NH_3)_4]^{2+}$ gives all the reactions characteristic of NH_3, including the formation of NH_4^+ with acids. But $[Cr(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$ do not appear to react with H^+ or Nessler's reagent over a short time even at elevated temperatures. The primary factor responsible for this difference lies in the slowness of these latter complexes to react under the prevailing conditions.

(ii) ***Electrical Conductivity*** : As pointed out earlier (sec. 26.1.2), the number of charge carrying species in a solution may be inferred from the molar conductivities of solutions at infinite dilution. This procedure may be adopted to detect complex formation provided no appreciable decomposition or dissociation takes place during the experiment in the solution medium or where the complexes do not ionize to give $H^+ (aq)$ and $OH^- (aq)$ in solution.

Q. 26.2 *A species of composition $GoBr_3$, $2H_2O$, $4NH_3$ shows a molar conductivity 420 $ohm^{-1} cm^2$ at infinite dilution. Suggest the probable formulation.*

Hint : See Table 26.2, A 3:1 charge type is indicated. Of the various possible 6-coordination complexes :

(i) $[Co(NH_3)_4 (H_2O)Br]Br_2H_2O$

(ii) $[Co(NH_3)_4 Br_2]Br, 2H_2O$

(iii) $[Co(NH_3)_4 (H_2O)_2]Br_3$

the last one (iii) agrees with the charge type.

Q. 26.3 *Two moles of glycine, NH_2CH_2COOH is added to a solution of one mole of aqueous copper acetate. Explain whether the conductivity of the solution will (i) increase (ii) decrease (iii) remain unchanged.*

Hint : Glycine forms a chelate (see later) $[Cu(gly)_2]^o$ which is a nonelectrolyte. Acetic acid is produced which is also a weak electrolyte. Hence conductivity decreases.

(iii) ***Transport number*** of ions in solution may give an indication of complex formation, as in the case of concentrated aqueous solution of CdI_2. The concentration of Cd^{2+} around the cathode does not increase during electrolysis while the iodide ion concentration decreases sharply. The transport number of Cd^{2+} is found to be nearly zero in a 0.25 *M* solution of CdI_2 at 18°C and becomes negative at higher concentrations. In concentrated solution the complex anion CdI_4^{2-} is formed as

$$2\,CdI_2 \rightleftharpoons Cd^{++} + CdI_4^{2-}$$

The Cd^{2+} ion migrates to the cathode but the CdI_4^{2-} ion migrates to the anode. Since the anion is bulkier, its lower mobility gives rise to a negative transport number at higher concentrations. The transport number returns to normal values at concentrations less than 0.002 *M*.

(iv) ***Visible and uv absorption*** : Transition metal ions with incomplete *d*-shells usually absorb radiations in the visible and uv region mainly for electronic transitions between various energy levels. The separation of these energy levels is largely controlled by the ligands attached to the metal and as such, change from an aquo complex to some other complex is often associated with a marked change in the wavelengths of radiation absorbed. When the absorption takes place in the visible region, there is a colour change indicating complex formation. The intensity of light absorption also varies with change in the ligands (see later). In many cases the intensities actually increase many times when coordinated water molecules are replaced by a more basic ligand such as NH_3 or ethylenediamine :

$$\underset{\text{light blue}}{[Cu(H_2O)_6]^{2+}} + 4NH_3 \rightleftharpoons \underset{\text{deep blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}} + 4H_2O$$

$$\underset{\text{light blue}}{[Cu(H_2O)_6]^{2+}} + 2en \rightleftharpoons \underset{\text{deep purplish blue}}{[Cuen_2(H_2O)_2]^{2+}} + 4H_2O$$

$$\underset{\text{violet}}{[Cr(H_2O)_6]^{3+}} + Cl^- \rightleftharpoons \underset{\text{green}}{[Cr(H_2O)_5Cl]^{2+}} + H_2O$$

The extent of light absorption at the wavelength of maximum absorption of the complex may be taken as a measure of the concentration of the complex (see Job's method).

Ions which do not absorb in the visible region may show absorption in the ultraviolet region (200 - 390 nm). Often the ligand also absorbs and changes in intensity and frequency may be observed on coordination.

Q. 26.4 *A light pink aqueous solution of cobaltous chloride turns deep blue on adding concentrated HCl (or $CaCl_2$). The blue solution again turns pink on addition of $HgCl_2$ (or $ZnCl_2$). Comment.*

Hint : $[Co(H_2O)_6]^{2+}$ is light pink. Tetrahedral $[CoCl_4]^{2-}$ is deep blue. The intensity increases because transition probability is much higher in the tetrahedral environment which is non-centrosymmetric. (See later).

$$[Co(H_2O)_6]^{2+} + 2CaCl_2 \rightleftharpoons Ca(CoCl_4) + 6H_2O + Ca^{2+}$$

$$[Co(H_2O)_6]^{2+} + 4HCl \rightleftharpoons H_2[CoCl_4] + 6H_2O + 2H^+$$

$$[CoCl_4]^{2-} + HgCl_2 + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{2+}[HgCl_4]^{2-} + 2Cl^-.$$

(v) ***Change in* pH :** Many ligands contain acidic functional groups. Such groups release the proton while coordinating to a metal ion. The consequent change in hydrogen ion concentration can be used as a measure of complex formation. Oxine (8-hydroxy quinoline), salicylaldoxime and several other ligands possess such acidic sites :

$$Cu^{2+} + 2Hsal \rightleftharpoons Cu(sal)_2 + 2H^+ \quad (Hsal = salicylaldoxime)$$

Complexation is most conveniently followed by titrating the ligand with and without the metal ion against a standard base and observing the variation in pH. A typical graph is shown in Fig. 26.7.

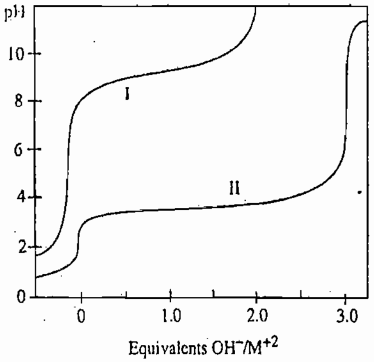


Fig. 26.7
pH-titration curves.

Ligand = 3-amino-3-methyl-2-butanoneoxime (L).
$M^{2+} = Ni^{2+}$

I : Titration curve for a mixture of the protonated ligand $[LH]^+$ and excess acid at total ligand concentration kept constant.

II : Similar titration in presence of Ni^{2+} at $2[Ni^{2+}]_{total} = [L]_{total}$ = constant.

In presence of Ni^{2+}, the pH rises more slowly, showing the removal of ligand into the complex.

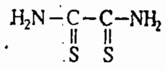
(vi) ***Ion Exchange* :** When a metal ion forms an anionic complex, it is no longer retained on a cation exchange resin. Thus an anion exchange resin will not normally absorb Zn^{2+} from aqueous solution but in presence of comparatively large excess of HCl, zinc forms the complex anion $ZnCl_4^{2-}$ which is strongly absorbed on the resin bed. The formation constant of $ZnCl_4^{2-}$ may be estimated by measuring the concentration of zinc in the resin and in an aqueous solution.

26.1.6 Some Applications of Coordination Compounds

We have already seen the involvement of some complex compounds in our life processes. Complex compounds have also found widespread analytical, technical, medicinal and other applications; a few representative examples are discussed here.

Analytical Applications

Complex compounds are extensively used in both qualitative and quantitative analysis. In the class room qualitative group separation of metals, AgCl is separated from Hg_2Cl_2 (Group I) as soluble $[Ag(NH_3)_2]^+$. The sulphides of Group IIB metal ions are separated as soluble tetrasulfido (thio) complexes like SbS_4^{3-} or SnS_3^{2-}. Chelate formation is also frequently used in qualitative anlysis. For example, copper in traces (at concentration limit 1 in 2,500,000) may be detected by the formation of a black precipitate with rubeanic acid (26-IX) from ammoniacal or weakly acid solution.

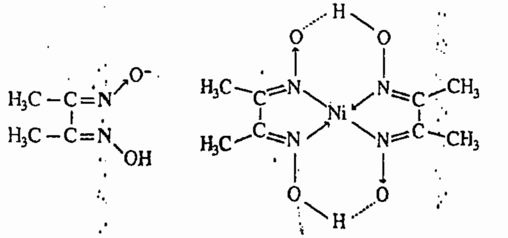


$$H_2N-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{C}-NH_2$$

26-IX

Rubeanic acid : A 0.5% solution in 95% ethanol is used. Hg(I) gives a black ppt with NH_3. Co and Ni also respond. The reagent was developed by Prof. Priyadaranjan Ray.

Dimethylglyoxime (26-X) is another useful reagent for both qualitative and quantitative estimation of Ni(II). A rose-red precipitate is readily formed in ammoniacal or acetate buffer medium by an 1% alcoholic solution of the reagent. Fe^{2+} gives a red colour, but may be oxidized to Fe^{3+} with say H_2O_2. Large excess of cobalt also interfere but may be avoided. The red chelate may also be dissolved in an organic solvent (e.g., $CHCl_3$) and nickel estimated spectrophotometrically.

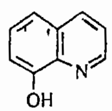


26-X

The anion of dimethylglyoxime, and bis(dimethylglyoximato)nickel(II).

The complex compound formed by dimethylglyoxime with nickel(II) has no net charge — it is an "inner metallic complex". This has a very low solubility in water (s.p. ≃ 2.3×10^{-25}) and hence may be used for gravimetric estimation of nickel. The interference of iron(III), aluminium or bismuth is prevented by the addition of a soluble tartrate or citrate; precipitation in a sodium acetate buffer medium is recommended when much cobalt, zinc or manganese is present.

Many other chelating agents are similarly used in the precipitation and estimation of metals, for example 8-hydroxyquinoline (oxine; 26-XI) in the estimation of several metals. It forms sparingly soluble precipitate with several metals in different pH range. The precipitates may be filtered, dried (at 105 - 110°C) and weighed as such but may also be ignited to the oxide of the metal and then weighed. Alternatively, the precipitate may be dissolved in dilute hydrochloric acid and titrated with a standard solution of potassium bromate (See estimation of aluminium, Chapter 20 for a typical procedure).



26-XI

Composition of precipitate :

$M(oxine)_2$: M = Mg, Zn, Cu, Cd, Pb, In

$M(oxine)_3$: M = Al, Fe, Bi, Ga

$M(oxine)_4$: M = Th, Zr

Few favourable pH ranges

Al 4.7 — 9.8

Ca 9.2 — 12.7

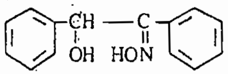
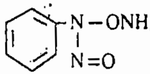
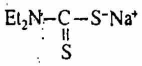
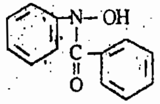
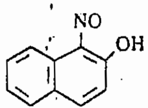
Mg >8.7

Zn >4.4

A few other common chelating agents used as precipitant are shown in Table 26.4

TABLE 26.4

Some organic chelating agents used in gravimetry

Reagent	Structure	Metals
(i) α-Benzoinoxime (cupron)		Cu(II) (ammonia and tartrate). Weighed as metal oxide after ignition. Mo(VI), W(VI) in acid medium.
(ii) Ammonium N-nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV); metal oxide is weighed.
(iii) Sodium N, N-diethyldithiocarbamate	 $Et_2N{-}\underset{\underset{S}{\parallel}}{C}{-}S^-Na^+$	Many metals from acid solution.
(iv) N-benzoyl-N-phenylhydroxylamine		Fe(III), Al(III), Cu(II) pH 3·6 - 6·0, Nb(V), pH 3·5 - 6·5 (tartrate); Ta(V) pH 1. Precipitate can be dried at 100°C or ignited to oxide.
(v) α-nitroso-β-naphthol		Co^{2+} in dilute HCl or acetic acid.

Complexometric titrations provide another nice application of complex compounds in analysis. The most important complexing agent used widely is 1,2-diaminoethanetetraacetic acid (ethylenediaminetetraacetic acid, edta, Table 26.3). It practically behaves as a dicarboxylic acid with two strongly acidic groups; two hydrogen atoms are probably held as zwitterions. Successive pK values (20°C) are $pK_1 = 2.0$, $pK_2 = 2.7$, $pK_3 = 6.2$ and $pK_4 = 10.3$. Several trivial names are used for the disodium salt e.g. Trilon B, Complexone III, Sequesterine, Versene and Chelaton 3. The flexible structure of the anion with six donor atoms enables it to satisfy all the six coordination numbers of metals (this C.N. is very frequently observed) with the formation of five-membered chelate rings having little strain. The structure of the magnesium-edta complex has been given in Fig. 26-IV. However, the C.N. attained may not be six in all metal-edta complexes. Favourable pH-range of some metal - edta complexes are

Fe^{3+} : pH 1 - 3

$Pb^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}$: pH 4 - 6

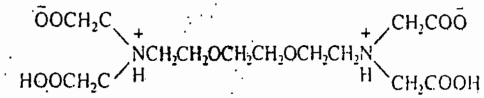
$Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}$: pH 8 - 10

Several other complexing agents are used in complexometric titration, for example,

(i) **nta** (Complexone I) : nitrilotriacetic acid (Table 26.3);

(ii) **egta** : ethyleneglycolbis(2-aminoethyl ether)N, N, N′, N′-tetraacetic acid (26-XII).

[Sec. 26.1.6
Analytical applications]



26-XII

If we represent the disodium salt of edta as Na_2H_2Y, the formation of a 1 : 1 metal-edta complex may be represented as

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$

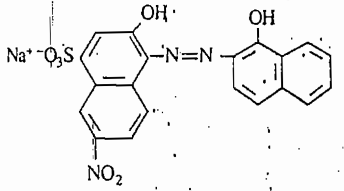
$$\text{or, } M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$

It is evident that the dissociation of the complex will be governed by the pH of the medium; lower pH will cause greater dissociation of the complex.

By adjustment of proper pH, the end-point in a complexometric titration is determined with metal ion indicators. These are dyestuffs which are themselves chelating agents and at the same time capable of undergoing colour change depending upon the pH of the medium. The role of the metal-ion indicator in edta titration may now be understood in terms of the following equilibrium (assuming 1 : 1 complexes for simplicity).

$$\text{M-In} + \text{edta} \rightleftharpoons \text{M-edta} + \text{In}$$

The equilibrium will proceed to right if the M-edta complex is more stable than the M-In complex. The colour of the free indicator will differ from the colour of M-In complex and depend upon the pH of the medium. Disappearance of the colour of the M-In complex will indicate the end-point. The important metal ion indicators usually fall into three categories : (a) hydroxyazo compounds (b) phenolic compounds and hydroxysubstituted triphenylethane compounds. (c) compounds containing an aminomethyldicarboxymethyl group. Solochrome Black (Eriochrome Black T, 26-XIII) is an extensively used indicator in edta titration.



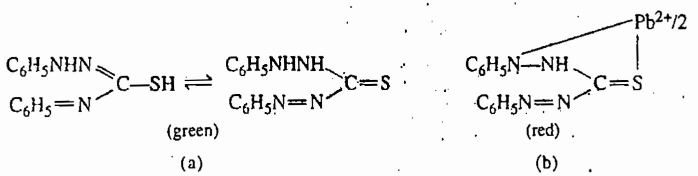
26-XIII

Solochrome Black (Eriochrome Black T)

In the pH range 7 - 11, the dye exhibits blue colour; but many metal ions, even in traces, form red complexes (e.g. $10^{-6} - 10^{-7}$ *M* Mg^{2+}). The indicator is used in the determination of total hardness of water.

Chelates also find use in **oxidation-reduction titrations.** One of the common-oxidation reduction indicators, ferroin, is the complex of Fe(II) with 1, 10-phenanthroline (*o*-phen), $[Fe(phen)_3]^{2+}$. It has a deep red colour but the corresponding Fe(III) complex is pale blue. Oxidation of ferroin at the end point of titration is marked by a colour change from red to pale blue ($E° = 1.06$ V at $[H^+] = 1M$).

Solvent extraction provides another very useful application of metal chelates in analytical chemistry. Many organic reagents form coloured chelates insoluble in water but soluble in a variety of organic solvents which may be used for extraction and spectrophotometric estimation of the metal. Since the chelating agent often has its own colour, its absorption spectrum may overlap on that of the chelate. A blank correction can be made or the interference may be overcome by other manipulations. Thus the red precipitate of bis(dimethylglyoximato)nickel(II) may be extracted with chloroform (pH range 7 - 12 in presence of citrate) and the concentration of Ni(II) may be determined spectrophotometrically by measuring the absorption at 366 nm. No interference is faced from iron(III) or aluminium; interference from cobalt, copper or manganese may be avoided by suitable means.



26-XIV

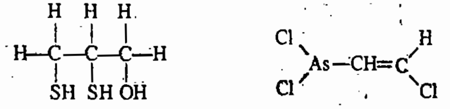
In a limited number of cases, quantitative analysis of trace quantities of metals has been achieved by solvent extraction of a volatile metal chelate followed by gas chromatographic analysis. Acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone form stable volatile chelates with aluminium, beryllium, chromium(III) and a number of other metal ions; these may be extracted in benzene and analyzed by gas chromatography.

An example of the use of solvent extraction in forensic chemistry is in the separation and determination of lead in blood. Diphenylthiocarbazone (dithizone, 26-XIVa) forms a chelate with Pb^{2+} (26-XIVb). The chelate may be extracted at pH 8 - 10 into methylene chloride and analysed spectrophotometrically (540 nm). To achieve selectivity, use of masking agents and proper adjustment of pH is necessary.

By adding a masking agent such as cyanide in alkaline medium, Zn^{2+}, Cd^{2+}, Hg^{2+} and Cu^{2+} may be complexed and their extraction can be prevented. Bismuth can be removed by extraction of its dithizone chelate into CH_2Cl_2 at pH 4 when lead (and thallium) is not extracted. Citrate is generally used to complex iron and prevent the precipitation of its hydroxide. Precipitation of calcium phosphate is prevented by sodium hexametaphosphate. Lead is now selectively extracted with the exclusion of thallium by carefully controlling the pH at 8.

Chelation Therapy

The presence of some metals in the body in excess of their normal requirement (or tolerable limit) may lead to serious physiological disorders. Some cases of such metal toxicity may be efficiently treated with chelating ligands which will bind strongly with the harmful metal and remove it through excretion. 2, 3 - dimercaptopropanol (26-XV (a)) is one of the early ligands developed for this purpose. During World War II, it was used as an antidote against the poison gas "Lewisite" [26-XV (b)]; hence its name British Anti-Lewisite or BAL.


(a) BAL (b) Lewisite

26-XV

The compound is itself toxic and has an extremely unpleasant smell, giving rise to nausea. However, the thiol groups in it, being uncharged, can readily pass through membranes and bind strongly with a range of metals, including Hg, Pb, Sn, Sb, Bi and Cu resulting in their removal from different parts of the body.

[Sec. 26.1.6 *Technical applications*]

Edta is a useful chelating agent not only in analytical chemistry but also in chelation therapy. However, its strong chelating ability may also cause leaching of essential elements like clacium and zinc from our body. This may be avoided by using the calcium complex $Na_2Ca(edta)$. In case of lead-poisoning the more stable lead-edta complex is formed as

$$Na_2Ca\text{ (edta)} + Pb^{2+} \longrightarrow Na_2Pb\text{(edta)} + Ca^{2+}$$

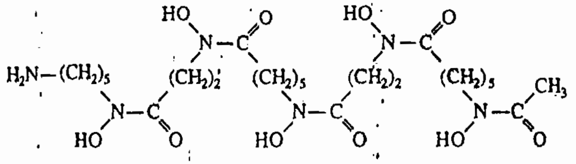
Both the lead complex and the unused drug are excreted in urine. Dermatitis from chromium or nickel salts is treated with edta ointment.

High concentrations of copper is deposited in several organs (particularly the liver and the brain) in the inherited disease known as Wilson's disease. This may be effectively tackled by lifelong doses of penicillamine (2-mercaptovaline; 26-XVIa) or trien [Table 26.3; 26-XVI (b)] both of which bind the copper and excrete it in urine.


(a) penicillamine (b) trien

26-XVI

Patients of thalassemia and certain other anaemic symptoms require regular blood transfusions; this causes accumulation of excess iron in the liver and other organs of the body (siderosis) and may ultimately lead to death. The excess iron may be removed through chelation therapy using the highly iron-specific ligands *desferrioxamine* (26-XVII) synthesized by microorganisms :



26-XVII

The platinum complex *cis*-diamminedichloroplatinum(II) (*cisplatin*) has been found effective in the treatment of cancer. It is likely that the platinum metal forms a chelate with two adjacent guanine bases in the DNA chain and interferes with cell-growth.

Technical and industrial applications

The Mond process for extraction of nickel via its volatile carbonyl complex (1899) and use of cyano-complexes in electroplating and metal extraction are some of the early applications of transition metal complexes in industry. At present, transition metal complexes have established their enormous potentiality in various organic chemical industry in the role of homogeneous catalysts; these afford quicker and easier conversions in an extremely cost-effective way. Thus, the complex $RhCl(PPh_3)_3$, known as Wilkinson's catalyst, is used in rapid homogeneous reduction of alkenes, alkynes and other unsaturated substances at 25°C and 1-atm pressure. The Ziegler-Natta catalyst (Ch. 20) is an example of a heterogeneous system used in the polymeristion of ehylene at 1 atm pressure and involves an alkene complex of Ti being formed. Several other homogeneous and heterogeneous catalysts have been developed for polymerization as well as other organic industrial processes like hydroformylation, carbonylation, water gas shift reaction and so on.

26.1.7 Second Coordination Sphere : Supercomplex

Werner conceptualized the coordination entity as a metal ion in direct contact with ligands. The ligands here may be said to form the *first coordination sphere* (FCS) around the metal. The complex species as a whole may now associate further solvent molecules or ions from the surrounding medium. Though this arrangement of the solvent molecules will be different from that in bulk, such associations are looked upon as simple solvation. However, certain macrocyclic ligands have been found to form a *second coordination sphere* (SCS) around the metal with a definite structural order which has been confirmed even by X-ray crystallography. Such complexes have been termed "supercomplex" by some authors. The "supercomplex" of (COD)Rh$(NH_3)_2$ (COD = cyclooctadiene) and dibenzo-24-crown-8 builds its second coordination sphere through hydrogen bonds between NH_3 in the FCS and O-atoms of the macrocycle. Such H-bonding may be supplemented by other secondary interactions like dipole-dipole, dipole-induced dipole etc. interactions. In some cases, such secondary interactions play the major role in bridging the FCS with SCS, as in the (super)complexes of (COD)$PtCl_2$ and (COD)$RhCl_2$ with cyclodextrins.

26.2 PREPARATION OF COMPLEX COMPOUNDS

Coordination compounds have been prepared by a wide variety of methods and techniques. We may at best have a summary overview of the general principles involved. Since the common medium of reaction is water, we start with replacement of water molecules from the coordination sphere of metal ions.

26.2.1 Reactions of aqua ions

In general, M^{2+} and M^{3+} cations of transition metals form octahedral (may be distorted) hexaaquo complexes in aqueous solution. The presence of such ions in solution has been confirmed from spectroscopic studies; some of them are also present in solid crystals as discrete species (X-ray study). Thus $NiSO_4$, $7H_2O$ actually contains the ion $[Ni(H_2O)_6]^{2+}$; one molecule of water is held by hydrogen bonds to an O-atom of SO_4 and the H-atom of a coordinated water molecule.

New complex compounds are formed from the hexaaquo ion mainly through substitution reactions.

Substitution of coordinated water molecules are sometimes carried out easily by adding an excess of the ligand. Thus, addition of concentrated (25%) aqueous ammonia to aqueous Nickel(II) produces $[Ni(NH_3)_6]^{2+}$. This may be precipitated as $[Ni(NH_3)_6]Cl_2$ using ammonium chloride/ammonia.

However, substitution may be partial in certain cases, as for example with Cu(II). Addition of concentrated aqueous ammonia to aqueous copper(II) replaces only four of the water molecules :

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O.$$

If ethanol is now added to induce precipitation, a precipitate of the composition $[Cu(NH_3)_4(H_2O)]SO_4$ is obtained with nearly square pyramid coordination of copper (see below). The strong ligand field of ammonia is primarily responsible for this behaviour and will be discussed in connection with bonding (Ch. 27). $[Cu(NH_3)_6]Br_2$ can be prepared readily using liquid ammonia.

However, reactions may proceed extremely slowly in certain cases, as in the following example

$$[Cr(H_2O)_6]^{3+} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6H_2O.$$

Thus both thermodynamic feasibility as well as kinetic aspects of a reaction has to be taken into account while preparing a particular complex compound through substitution.

In another variation of the method, organic ligands insoluble in water may be dissolved in alcohol and added to an aqueous solution of the metal ion :

$$[Fe(H_2O)_6]^{2+} + 3dipy \longrightarrow [Fe(dipy)_3]^{2+} + 6H_2O$$

Typical Examples

Preparation 1 : A double salt :

Cupric Ammonium Sulphate, $CuSO_4$, $(NH_4)_2SO_4$, $6H_2O$.

- **A.** Dissolve 0.02 mole $CuSO_4$, $5H_2O$ (249.5 g $mole^{-1}$) and 0.02 mole $(NH_4)_2SO_4$ (132 g $mole^{-1}$) in 10 ml. water. Heat gently until the salts dissolve.
- **B.** Cool the solution slowly to room temperature until crystals form. Slower the rate of cooling (leave overnight), the larger will be the crystals.
- **C.** Cool further in ice-water. Decant the mother liquor and dry the crystals on a piece of blotting paper.
- **D.** Observe the shape (monoclinic). Weigh the dry crystals.

Preparation 2. A complex salt

Tetraammineaquacopper(II) sulphate, $[Cu(NH_3)_4H_2O]SO_4$.

- **A.** Take 8 ml of 15 *M* ammonia (*aq*) ("liquor ammonia") in a small porcelain basin; dilute with 5 ml of distilled water.
- **B.** Weigh 0.02 mole of $CuSO_4$, $5H_2O$ (grind, if necessary). Add the powdered crystals to the ammonia solution; stir to dissolve.
- **C.** Slowly pour 10 ml of ethyl alcohol down the side of the basin so as to cover the solution with alcohol. *Do not stir or disturb.* Cover with a clock glass and let stand overnight.
- **D.** Stir slowly and gently to ensure complete precipitation. Allow the crystals to settle and discard the supernatant liquid. Filter the crystals by a filter paper (preferably on a small buchner funnel); rinse with 3-5 ml portions of a mixture of equal volumes of 15 *M* NH_3 (*aq*) and ethanol. Finally wash with 5 ml ethanol. Dry under gentle suction.
- **E.** Spread the crystals on a piece of blotting paper. Weigh the dry crystals.

When a solution contains two or more complex species, selective precipitation of a desired species may be facilitated by lattice energy considerations. In general, a complex ion is easily precipitated by an oppositely charged ion of approximately the same size. Thus Ni^{2+} (*aq*) reacts with high concentration of KCN to form both the species $[Ni(CN)_4]^{2-}$ and $[Ni(CN)_5]^{3-}$ in solution. The former ion predominates and crystallizes readily from solution as orange $K_2[Ni(CN)_4]H_2O$. If a large trivalent cation is used, say $[Cr(en)_3]^{3+}$, the $[Ni(CN)_5]^{3-}$ ion is precipitated as $[Cr(en)_3][Ni(CN)_5]$.$1.5H_2O$. Similarly other unusual coordination numbers may be stabilized : tris (propylenediamine) cobalt(III) cation precipitates solid $[Co(pn)_3][MCl_6]$ where M = Cr(III), Mn(III) and Fe(III). On the other hand, metals normally forming hexachloro species may be stabilized in a five-coordinate environment with appropriate cations, e.g., $[CuCl_5]^{3-}$ by $[Cr(NH_3)_6]^{3+}$, $[VCl_5]^-$ by $[PCl_4]^+$ and $[GeF_5]^-$ by $[AsPh_4]^+$.

26.2.2 Direct Reaction in Nonaqueous Medium.

The competition of water as a Lewis base towards metal cations may be avoided by the complete absence of water. Such reactions may be carried out in an inert solvent like hydrocarbon or by direct mixing if at least one component is a liquid. For example

$$VCl_4 + 2py \longrightarrow [VCl_4 \cdot (py)_2] \qquad \text{Toluene, } -20°C$$

$$SnCl_4 + 2Et_2O \longrightarrow [SnCl_4 \cdot (Et_2O)_2] \qquad \text{Benzene}$$

Complexes of ammonia may be prepared by reacting the metal salt with liquid ammonia and then evaporating the excess ammonia. This method is particularly helpful for metals which are precipitated as hydroxide by aqueous ammonia, for example.

$$FeCl_2 + 6NH_3(liq) \longrightarrow [Fe(NH_3)_6]Cl_2$$

Of course, ammonolysis reactions (similar to hydrolytic reaction in water) may also occur :

$$TiCl_4 + 6NH_3 \longrightarrow TiCl(NH_2)_3 + 3NH_4Cl.$$

26.2.3 Oxidation-reduction reactions

The stability of a metal in a given oxidation state may vary with the ligands attached to the metal. Thus, cobalt is present in aqueous solution as Co(II); Co(III) salts are oxidizing in aqueous solution. However, with ammonia as ligand, the +3 state is stabilized. The cobaltammines referred to in the beginning were prepared by bubbling air through solutions containing $Co^{2+}(aq)$ and NH_3.

$$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + O_2 \xrightarrow[\text{cat}]{\text{charcoal}} 4[Co(NH_3)_6]Cl_3 + 26H_2O.$$

The pentaammineaquo complex is obtained by using H_2O_2 instead of air in absence of charcoal.

$$2[Co(H_2O)_6]Cl_2 + 2NH_4Cl + 8NH_3 + H_2O_2 \longrightarrow 2[Co(NH_3)_5(H_2O)]Cl_3 + 12H_2O.$$

In many cases, the ligands are strong reducing agents, and the complex species contain the metal in a reduced state

$$K_2Cr_2O_7 + 7H_2C_2O_4 \longrightarrow 2K[Cr(C_2O_4)_2(H_2O)_2] + 6CO_2 + 3H_2O.$$

$$2CuCl_2 + 8N_2H_4 \longrightarrow 2Cu(N_2H_4)_2Cl + 2N_2H_4 \cdot HCl + 2NH_3 + N_2$$

The actual conditions often determine whether reduction will really take place or not. Thus potassium trisoxalatoferrate (III), $K_3[Fe(C_2O_4)_3]$ may be prepared (see below) in absence of sunlight; the compound gets reduced to Fe(II) in presence of sunlight, evolving CO_2. The extent of the reduction is proportional to the amount of light energy absorbed.

Preparation 3.

Potassium Trisoxalatoferrate(III)

A. Barium oxalate is prepared by mixing solutions of $BaCl_2$, $2H_2O$ (2.5g in 6 mL water) and sodium oxalate (1.5 g in 40mL water). The crystals are filtered and washed with cold water.

B. This barium oxalate is heated with 1.25g of ferric sulphate and 1.5g of potassium oxalate (in about 30 mL water) for several hours on a water bath. The precipitated $BaSO_4$ is filtered out and the filtrate is evaporated to a small volume (~ 5 mL). $K_3[Fe(C_2O_4)_3]$ separates on cooling. These are washed with water and then with ethanol and dried over conc. H_2SO_4 in a vaccuum desiccator.

Preparation 4.

Tetraamminecarbonatocobalt(III) nitrate.

A. Dissolve 4g of ammonium carbonate in 20 ml water in a small flask. Add 10 mL of 25% ammonia solution followed by a solution of 6g of cobalt nitrate (hexahydrate) in 12 mL water. Suck air through the solution for about one hour. (Fix a glass tube through cork reaching the bottom of the flask; fix another outlet tube through a second hole in the cork and connect it to the water-suction pump).

Filter the solution and evaporate on a water-bath, gradually adding 2g ammonium carbonate as crystallization begins. Filter any precipitate and leave the solution to crystallize.

Filter off the crystals in a Buchner funnel, wash with a small quantity of ice-water and then ethanol.

A transition metal may prefer a given oxidation state in combination with a particular ligand (or ligand type). This may lead to a different oxidation state of the metal in the complex produced. Ligands like 2, 2′-dipyridyl, pyridine etc. are not so strong reducing agents, but vanadium(IV) chloride reacts with excess of such reagents to give five coordinate complexes like $VCl_3(NMe_3)_2$ or six-coordinate complexes like VCl_3py_3 or $VCl_3(MeCN)_3$. But at low temperatures like −20°C, one can isolate the V(IV) complex $VCl_4(py)_4$ using excess VCl_4. It is likely that electron transfer occurs to the metal after coordination to give a radical anion $(VCl_4)^-$ and a radical cation $(Py)^+$. In the reductions of WCl_4 and WBr_5 with pyridine, 1-(4-pyridyl) pyridinium ion has been identified among the oxidation products of pyridine.

Liquid ammonia provides an excellent medium for the preparation of complexes containing metals in unusually low oxidation states. Thus $K_2Ni(CN)_4$ reacts with excess potassium in liquid ammonia to form a yellow precipitate of $K_4Ni(CN)_4$, potassium tetracynonickelate (0) :

$$K_2[Ni(CN)_4] + 2K = K_4[Ni(CN)_4]$$

If the nickel is in excess, a bright red precipitate, containing the binuclear Ni(I) ion $[Ni_2(CN)_6]^{2-}$ is formed.

Other complexes containing metals in formally zero oxidation state may be similarly prepared in liquid ammonia, for example $K_4[Co(CN)_4]$ and $K_3[Cr(CN)_6]$. As expected, these compounds are strongly reducing in nature - they liberate hydrogen from water and are rapidly oxidized in air.

Similar low oxidation state complexes by other ligands like carbon monoxide and phosphines may also be prepared with solution of alkali metals in liquid ammonia. These ligands are able to stabilize low oxidation states of metals via metal to ligand π-bonding. But low oxidation state complexes are also formed by ammonia itself acting as ligand, though it does not have the capacity to accept such π - backbonding. $[Pt(NH_3)_4]$ and $[Ir(NH_3)_5]$ are formed by reducing the metal bromides with potassium in liquid ammonia.

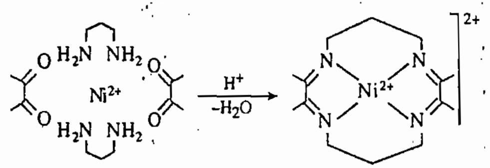
$$[Pt(NH_3)_4]Br_2 + 2K \longrightarrow [Pt(NH_3)_4] + 2KBr.$$

When heated, the compounds decompose to set free the ammonia.

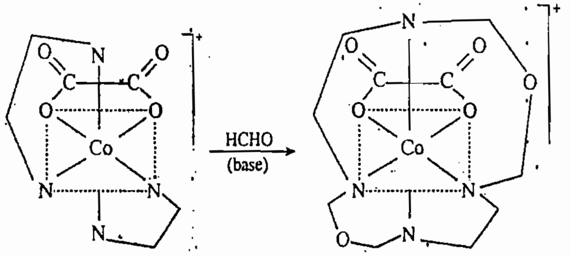
Complexes containing carbon monoxide and other organometallic compounds are prepared in numerous ways. Some mention will be found under appropriate sections.

26.2.4 Template Synthesis

In the methods described so far, the metal ion and the preformed ligand are allowed to react under appropriate conditions. In template type synthesis, the metal ion is used as a "template" (≡ mould for casting) for the formation of the chelate ring by reacting suitable reagents. Thus, cyclic condensation of an α-diketone with a 1,2- or 1,3-diamine in presence of Ni^{2+} results in complexes of the type



The method may be used with advantage for many macrocyclic cryptates and sepulchrates when organoligands already bonded to the metal are chemically altered to form an encapsulation around the metal e.g.



26.3 THE STABILITY OF COMPLEX IONS IN SOLUTION

We now consider the thermodynamic stability of a complex ion in terms of its tendency to be formed in solution from the metal ion and ligand(s). This is reflected in the equilibrium constant for relevant steps. Though somewhat approximate, equilibrium concentrations of the various species, rather than their equilibrium activities, will be used for simplicity.

26.3.1 Formation Constants (Stability Constants)

Interaction of a ligand L (assumed neutral, unidentate) with a metal ion $M^{n+}(aq)$ in aqueous solution results in successive replacement of water-molecules from the coordination sphere of the metal :

$$[M(H_2O)_6]^{n+} + L \rightleftharpoons [M(H_2O)_5L]^{n+} + H_2O$$

$$[M(H_2O)_5L]^{n+} + L \rightleftharpoons [M(H_2O)_4L_2]^{n+} + H_2O \text{ ......and so on.}$$

[Sec. 26.3.1 *Formation constants*]

To simplify, we may drop the water molecules and write down the equilibrium constant of each step in terms of the equilibrium concentrations of various species :

$$M + L \rightleftharpoons ML \qquad K_1 = [ML]/[M][L]$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 = [ML_3]/[ML_2][L]$$

$$\text{- - - - - - - - - - - -} \qquad \text{- - - - - - - - - - - - - -}$$

$$ML_5 + L \rightleftharpoons ML_6 \qquad K_6 = [ML_6]/[ML_5][L]$$

The equilibrium constants $K_1, K_2, ..., K_6$ are called the *stepwise formation constants* or *stability constants*. We may also be interested in obtaining the *overall formation constant* for a particular species, e.g.,

$$M + L \rightleftharpoons ML \qquad \beta_1 = [ML]/[M][L]$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = [ML_3]/[M][L]^3$$

$$\text{or, } M + 6L \rightleftharpoons ML_6 \qquad \beta_6 = [ML_6]/[M][L]^6$$

and so on. From the expressions of K_1, K_2, K_3 etc. written above, we find.

$$\beta_1 = K_1; \quad \beta_2 = K_1K_2; \quad \beta_3 = K_1K_2K_3; \quad ... \beta_6 = K_1K_2...K_6$$

In general.

$$\beta_n = [ML_n]/[M][L]^n = K_1K_2...K_n$$

$\beta_1, \beta_2, ...$ etc. (β_i 's) are called the *overall formation constants* (overall stability constants) for the relevant species.

In the strictest sense, formation constants should be expressed in terms of the activities of respective species rather than concentrations, as for example,

$$M^{n+} + L \rightleftharpoons [ML]^{n+} \qquad K_1 = a_{ML^{n+}} / a_{M^{n+}} \cdot a_L.$$

where a - terms denote activities. Since $a = m\gamma$ where m is the molar concentration and γ is the activity coefficient,

$$K_1 = \frac{[ML^{n+}]}{[M^{n+}][L]} \cdot \frac{\gamma_{ML^{n+}}}{\gamma_{M^{n+}}\gamma_L}$$

In most experimental studies, it is difficult to determine the γ - terms. Several ways to overcome this situation are in use :

1. The formation constants are determined at various total concentrations and the K - values are extrapolated to zero total concentration. Since activity coefficients approach unity at infinite dilution, the concentration equilibrium constant approaches the activity equilibrium constant.

2. The activity coefficients may be determined by extended Debye-Hückel equation.

3. The equilibrium constant may be determined in presence of large excess of an inert salt like 0.1 – 1.0 M $NaClO_4$ (ClO_4^- has feeble coordinating ability owing to stable π-delocalization). As the concentration of the salt does not vary at different steps of the equilibrium, the activty coefficients may be supposed to remain essentially constant. The concentration equilibrium constants may now be compared by varying the metal or the ligand. However, a comparison with another ionic medium is not possible since the activity coefficients will then change.

Q. 26.5 *A trivalent metal ion forms octahedral complexes with a neutral bidentate ligand. Write down the complex formation equilibria in aqueous solution. Give expressions for stepwise and overall stability constants and show the relation among them.*

Solution : Take note of the key words - bivalent metal ion, octahedral complex, neutral bidentate, aqueous solution.

Representing the metal by M and the ligand by LL, the equilibria are as follows with the corresponding stepwise stability constants.

$$\left[M(H_2O)_6\right]^{2+} + LL \rightleftharpoons \left[M(H_2O)_4LL\right]^{2+} + 2H_2O \qquad K_1 = \frac{\left[M(H_2O)_4LL^{2+}\right]}{\left[M(H_2O)_6^{2+}\right]\left[LL\right]}$$

$$\left[M(H_2O)_4LL\right]^{2+} + LL \rightleftharpoons \left[M(H_2O)_2(LL)_2\right]^{2+} + 2H_2O \quad . \quad K_2 = \frac{\left[M(H_2O)_2(LL)_2^{2-}\right]}{\left[M(H_2O)_4LL^{2+}\right]\left[LL\right]}$$

$$\left[M(H_2O)_2(LL)_2\right]^{2+} + LL \rightleftharpoons \left[M(LL)_3\right]^{2+} + 2H_2O \quad . \quad K_3 = \frac{\left[M(LL)_3^{2+}\right]}{\left[M(H_2O)_2(LL)_2^{2+}\right]\left[LL\right]}$$

Water molecules have been omitted from the expressions for K_1, K_2, K_3 since $a_{H_2O} = 1$. For other species, activity coeffecients are assumed to be 1. The overall stability constants relate to the overall equilibria

$$\left[M(H_2O)_6\right]^{2+} + LL \rightleftharpoons \left[M(H_2O)_4LL\right]^{2+} + 2H_2O \qquad \beta_1 = \frac{\left[M(H_2O)_4LL^{2+}\right]}{\left[M(H_2O)_6^{2+}\right]\left[LL\right]}$$

$$\left[M(H_2O)_6\right]^{2+} + 2LL \rightleftharpoons \left[M(H_2O)_2(LL)_2\right]^{2+} + 4H_2O \qquad \beta_2 = \frac{\left[M(H_2O)_2(LL)_2^{2+}\right]}{\left[M(H_2O)_6^{2+}\right]\left[LL\right]^2}$$

$$\left[M(H_2O)_6\right]^{2+} + 3LL \rightleftharpoons \left[M(LL)_3\right]^{2+} + 6H_2O \qquad \beta_3 = \frac{\left[M(LL)_3^{2+}\right]}{\left[M(H_2O)_6^{2+}\right]\left[LL\right]^3}$$

It is readily seen

$$\beta_1 = K_1;\ \beta_2 = K_1K_2;\ \beta_3 = K_1K_2K_3$$

A large value of the stability constant for a complex species implies that the concentration of the species at equilibrium is much greater than the concentrations of the species which form this.

$$Cd^{2+} + NH_3 \rightleftharpoons \left[Cd(NH_3)\right]^{2+} \qquad \log K_1 = 2.65$$

$$\left[Cd(NH_3)\right]^{2+} + NH_3 \rightleftharpoons \left[Cd(NH_3)_2\right]^{2+} \qquad \log K_2 = 2.10$$

$$\left[Cd(NH_3)_2\right]^{2+} + NH_3 \rightleftharpoons \left[Cd(NH_3)_3\right]^{2+} \qquad \log K_3 = 1.44$$

$$\left[Cd(NH_3)_3\right]^{2+} + NH_3 \rightleftharpoons \left[Cd(NH_3)_4\right]^{2+} \qquad \log K_4 = 0.93;\ \log \beta_4 = 7.12$$

As mentioned earlier, water molecules in the coordination sphere of the metal have been dropped for simplicity but those (or other solvating species) should be mentioned wherever necessary.

[Sec. 26.3.1 *Formation constants*]

We observe that there is a slow and gradual decrease in the magnitude of K_i - s (stepwise formation constants). This is further revealed in Table 26.5 where data for some more complexes are included :

TABLE 26.5

Stepwise and Overall Stability Constants (25°C)

M	Ligand	log K_1	log K_2	log K_3	log K_4	log β
Cu^{2+}	NH_3	4·17	3·53	2·88	2·08	log β_4 = 12·6
Cu^{2+}	en	10·55	9·05	–	–	log β_2 = 19·6
Ni^{2+}	NH_3	2·80	2·24	1·73	1·19	log β_6 = 8·7
Ni^{2+}	en	7·45	6·23	4·34	–	log β_3 = 18·0
Ag^{+}	NH_3	3·14	3·82	–	–	log β_2 = 7·0
Hg^{2+}	CN^-	18·0	16·70	3·83	2·98	log β_4 = 41·5
Hg^{2+}	I^-	12·87	10·95	3·67	2·37	log β_4 = 29·9

It is possible to make certain observations on the general trend in K - values in the table :

1. The successive K_i values show a steady decrease for simple substitution of coordinated water molecules when there is no change of stereochemistry and the metal ligand bond energies do not change appreciably with the number of ligands.

Several factors contribute to the observed steady decrease in successive K_i values :

(a) *Coulombic factor* : This factor involves increasing electrostatic repulsion between the ligands (their peripheral electrons), particularly when they are charged.

(b) *Steric hindrance* : If the ligands are bulkier than the water molecules which they replace, there will be steric hindrance in the formation of the complex. We shall get more examples of this kind later.

(c) *Statistical factor* : A species like $[Ni(H_2O)_6]^{2+}$ has six sites from which it can lose a molecule of H_2O; but $[Ni(H_2O)_5L]^{2+}$ has five sites from which it can lose a molecule of H_2O under identical conditions and hence has a lower probability for exchange of water molecule than $[Ni(H_2O)_6]^{2+}$. This applies to any step. Thus, for the general step

$$\left[Ni(H_2O)_x(NH_3)_{6-x}\right]^{2+} + NH_3 \rightleftharpoons \left[Ni(H_2O)_{x-1}(NH_3)_{6-x+1}\right]^{2+} + H_2O$$

the species on the left has higher probability of losing a water molecule and at the same time a lower probability of losing an ammonia molecule than the species on the right. If we consider the next step also in the same manner, it is found that K_{n+1}/K_n should be in the range 0.4 – 0.5. Experimental values for the $Ni^{2+}(aq)$ – NH_3 system show K_{n+1}/K_n ratios in the range 0.2 – 0.4, showing involvement of other factors.

2. Deviations from the observed general trend of decreasing K_i values may have several reasons like (i) a change in coordination number i.e. geometry of the complex species; (ii) special steric effects coming into operation at some later stage of coordination; (iii) a change in electron arrangement in the valence shell of the metal at some stage of complexation. Some examples will be given.

We observe a sudden large drop in the value from K_2 to K_3 for the complexes of Hg^{2+} with I^- or CN^-. This may be attributed to the change of linear HgX_2 to tetrahedral $[HgX_3(H_2O)]^{2+}$. The Hg(II) shows preference for linear coordination (*sp* hybridization; some contribution from d_{z^2} is also likely); change to the tetrahedral geometry (sp^3 hybridized) is thus met with reluctance.

The observed increase in the value of K_2 over K_1 for Ag^+–NH_3 system indicates similar greater stability of linear $[Ag(NH_3)_2]^+$ over nonlinear $[Ag(NH_3)(H_2O)_n]^+$ (n = 3 or 5).

3. In Table 26.5 we also observe that Ni^{2+} or Cu^{2+} has nearly $10^5 - 10^6$ times higher value of formation constants (K – values; the table shows log K values) with chelating ligands like en than with simple unidentate ligands like NH_3. This will be discussed in connection with the chelate effect (Sec. 26.3.2).

Many other generalizations are possible regarding the stability constants among complexes. Before we discuss them in the next section, it is worthwhile to mention that such stability correlations refer to equilibrium situations (mostly in aqueous solution). The formation constants provide a comparison of stabilities of various complex species *at equilibrium* but does not tell us anything about the rate at which the equilibrium is approached, that is, the time necessary for any appreciable complexation to occur. Thus, the reaction,

$$[\mathrm{Coen}_3]^{3+} + 6\mathrm{H}^+(aq) \rightleftharpoons \left[\mathrm{Co(H_2O)}_x\right]^{+3} + 3\left[\mathrm{enH}_2\right]^{2+} \quad K \simeq 10^{30}$$

has a high value of K (25°C), suggesting that addition of excess acid to $[Coen_3]^{3+}$ should give $[Co(H_2O)_x]^{3+}$ almost quantitatively. However, the reaction actually proceeds to less than 1% in one month at room temperature (in absence of a catalyst).

For a comparison of bond strength it would be certainly useful to have formation constants of reactions like

$$M^{2+}(g) + L(g) \rightleftharpoons [ML]^{2+}(g).$$

But such formation constants cannot be determined directly; in certain cases they may be calculated from the aqueous formation constant with appropriate hydration enthalpies for all species. However, such calculations are beyond the scope of this book.

Standard free energy change

Another useful way of looking at formation constants is in terms of the standard free energy change, $\Delta G°$, for each step of complex formation. As we all know, $\Delta G°$ is related to the equilibrium constant K and the enthalpy and entropy terms by the relations

$$\Delta G° = -RT \ln K; \quad \Delta G° = \Delta H° - T\Delta S°$$

It is possible to calculate $\Delta G°$ from experimental values of formation constants (section 26.3.3).

The heat of reaction may be measured directly or may be calculated from the variation of equilibrium constant with temperature :

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

[Sec. 26.3.1 *Formation constants*]

Here we assume that $\Delta H°$ remains constant over the temperature range from T_1 to T_2 which holds when the span is short.

From the values of $\Delta G°$ and $\Delta H°$, it is possible to calculate $\Delta S°$.

Let us now briefly summarise the various factors which influence the enthalpy and entropy terms in complex formation.

Enthalpy effects are mainly contributed to by (i) ligand-metal bonding interaction; this includes crystal field stabilization and related effects (Ch. 27); (ii) steric and electrostatic repulsion between the ligands; (iii) enthalpy of solution of the ligands and similar factors.

Entropy effects, related to thermodynamic probability or randomness associated with a system, are mainly contributed by (i) release of unbound solvent (water) molecules from the metal ion; (ii) entropy of solution of ligands and of the coordinated metal ion; (iii) entropy variations in uncoordinated ligands and configuration entropies of the ligand (iv) formation of chelate rings and their size, number and arrangement etc. We shall soon observe that in many ligand replacement reactions, particularly chelate formation, the major driving force is derived from the entropy effect (section 26.3.2 : the chelate effect).

Effect of ligands and metals on stability constants of complexes

We have already noted that certain metals favour nitrogen and oxygen donor ligands while some others favour phosphorus and sulphur donor atoms. If we assume at this stage that coordination involves donation of a pair of electrons from the ligand to the metal, the tendency of a metal ion to associate electron pairs will be reflected in its "ionic potential" or charge/radius ratio. Similarly, the ability of a ligand to donate electrons will depend on its polarizability. It may thus appear that high ionic potential of metal and high polarizability of ligand will result in most stable complexes. However, as both the factors increase, the negative charge accumulated on the metal opposes electron transfer and lowers the stability. Thus, a maximum is often found in the series : F, O, N, S, P. For many first transition series metals in low oxidation states the maximum is at nitrogen (e.g., V^{2+}, Ni^{2+}, Cu^+, Cu^{2+}); oxygen linked complexes are most stable for higher oxidation states and small size of metal (e.g., Fe^{3+}). Certain large ions of low charge (Cu^+, Ag^+, Au^+, Hg^+) form stable complexes with sulfur-containing ligands.

The combination of a ligand with a metal ion and with a hydrogen ion are comparable and as a first approximation we may expect large formation constants for strongly basic ligands. This expectation is sometimes found valid for closely related ligands with similar bond types. For many metal ions, the observed stability sequence is thus the same as the base strength order of the ligands :

$$F^- > NO_3^- > Cl^- > Br^- > I^- > ClO_4^- \simeq BF_4^-.$$

The formation constants also increase linearly with base-strength of the ligands, as has been found with various amines, β-diketones and amino acids. Plots of log$K$ against pK_a for the conjugate acids of the ligands give nearly straight lines with upward slopes. (Increasing value of pK_a for the conjugate acid implies weaker acid character and hence a stronger base character for the ligand. Complexes of secondary and tertiary amines have lower stability owing to steric hindrance between the ligands.

Steric congestion by bulky ligands reduces the stability of complexes, as may be seen from Table 26.6. The base strengths of the amines remain nearly the same but the formation constants decrease as bulkier groups are substituted on nitrogen. The effect is most prominent in the values of log K_3 due to strong steric inhibition by the bulky groups.

TABLE 26.6

Variation of stability constants with substitution in ethylenediamine (en)

		en	N,N′-dimethyl en	N,N′-diethyl en
Ni^{II}	logK_1	7·6	7·1	5·6
	logK_2	6·5	4·7	3·3
	logK_3	5·0	1·5	negligible
Cu^{II}	logK_1	11·3	11·2	10·8
	logK_2	9·9	8·3	7·8

2, 2′-dipyridyl forms tris-complexes with many metal ions (CN = 6). But 6, 6′-dimethyl - 2, 2′ - dipyridyl forms at best mono or bis complexes with these metals because of the steric hindrance from the methyl groups on the ligands.

The span which a multidentate ligand can cover is sometimes related to the stability of the complex. K_3 for the Cu^{2+} - en system is very small because of the strain involved in the third ethylenediamine molecule to stretch over two trans positions of the metal (see chapter 27, J-T distortion).

Similarly, the ligand *tren* (tris-(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$) can coordinate to four tetrahedral sites of a metal but is unable to form a square planar complex. But the ligand *trien*, (26-XVIb) can form a square-planar complex more easily.

Q. 26.6 *Both 2 - methyl and 5 - methyl 8 - hydroxyquinoline (oxine) are stronger bases than 8 - hydroxyquinoline itself. But while the 5 - methyl derivative forms a stronger complex wth Cu^{2+} than oxine itself, the complex formed by the 2 - methyl derivative is much less stable. - Comment.*

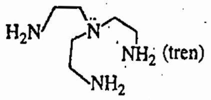
Hint : Draw structures. Consider steric congestion near the donor N-atom.

Q. 26.7 *For the reaction :*

$$M\ (trien)^{+2} + tren \rightleftharpoons M\ (tren)^{+2} + trien$$

logK is −1·6 for Cu^{II} and 2·55 for Zn^{II}. Comment.

Hint : As explained in the text, *trien* suits square planar geometry and *tren* suits tetrahedral geometry. Zn^{2+} forms tetrahedral complex.


(tren)

Q. 26.8 *Acetylacetonates of Cu^{II} and Fe^{II} are not formed when the substituent at the 3-position of the ligand is n-isopropyl group but typical chelates are formed when the substituent is a straight chain group like $-C_2H_5$. Explain.*

Hint : See Figure 26.8.

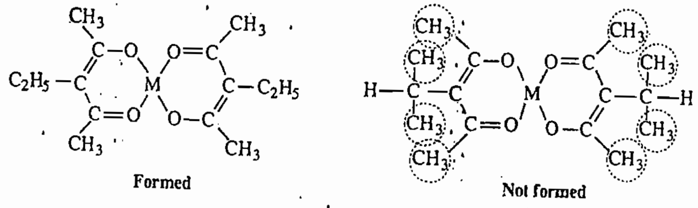


Fig. 26.8

Q. 26.9 *Explain*

(a) Pyridine, though a very weak base, forms much stronger complexes with many transition metal ions than the strongly basic piperidine.

(b) Ethylenediamine forms a purple paramagnetic complex wth Ni(II) but with C-substituted ethylenediamine, say tetramethylethylenediamine, Ni(II) forms a yellow diamagnetic complex.

Hint : (a) Ligands which are able to accept negative charge and/or offer stabilization through π-delocalization form very stable complexes.

(b) CN changes to 4 (square planar) with substituted ethylenediamines.

The stability of complexes of +2 ions follows a common order with various ligands under various conditions (Irving-Williams order) :

$$Pd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$$

The order remains practically unchanged with the nature of the donor atom (O, N, S or P). In the first transition series K_1 and K_2 for complexes of M^{2+} and most ligands rise steadily from Mn^{2+} to Cu^{2+} and then drops at Zn^{2+} (Fig. 26.9). The variation in ΔS for the complexes is negligible and the change in log *K* values may be associated mainly with enthalpy effects arising from crystal field stabilization (Ch. 27).

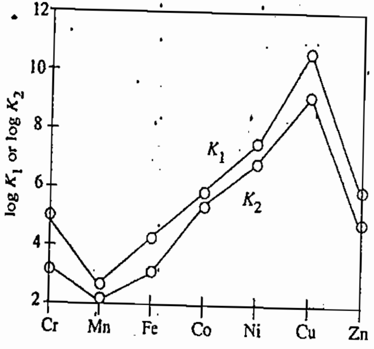


Fig 26.9

Variation of logK_1 and logK_2 among the first transition series.

(ethylenediamine-M^{2+} complex)

The plots are similar to that for hydration enthalpy of the ions (see Chapter 27).

Except with very soft ligands, it is generally observed that the formation constant increases with the oxidation state of the metal. To some extent this may be understood using a simple eletrostatic model for complex formation – interaction between a cation and the negative end of a dipole or an anion as ligand. We should then expect stronger interaction and hence greater stability when the interacting species are small or when they carry high charge. For soft acids and bases, however, polarization becomes significant and covalent bonding may be important. When the donor atom in the ligand is hard, stability constants increase as the oxidation state of the metal increases, as shown in Table 26.7 for some EDTA complexes. where EDTA acts as a hexadentate ligand;

TABLE 26.7

Stability constants ($\log K_1$) of EDTA complexes (25°C)

Ca^{2+}	Fe^{2+}	Fe^{3+}	Co^{2+}	Co^{3+}	V^{2+}	V^{3+}
10·8	14.3	25·1	16·1	36·0	12·7	25·9

26.3.2 The Chelate Effect

Chelate complexes are usually found to be more stable than comparable nonchelate complexes with same donor atoms. This extra stability of a complex species containing chelate rings is known as *"the chelate effect"*.

In Table 26.5, we have referred to the following equilibria

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O \qquad \log \beta_6 = 8.7$$

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O \qquad \log \beta_3 = 18.0$$

A difference of about 10 in the log value of the equilibrium constant implies tris (ethylenediamine) nickel(II) is nearly 10^{10} times more stable than $[Ni(NH_3)_6]^{2+}$. In both cases, the ligands have six nitrogen atoms as donor; but in $[Ni(en)_3]^{2+}$, presence of three chelate rings lead to greater stability—the chelate effect.

As mentioned earlier, the overall stability constant for a particular complex species is the relevant equilibrium constant K, in turn related to ΔG, ΔH and ΔS as

$$\Delta G^{\circ} = -RT \ln K;\ \Delta G = \Delta H - T\Delta S$$

In chelate formation, the $T\Delta S$ term contrtibutes significantly to make ΔG highly negative. This is expected from the equilibria written above for $Ni^{2+}(aq)$. In the first case, six NH_3 molecules release six H_2O molecules and there is no net change in the number of molecules. In the second case, three ethylenediamine molecules set free six water molecules, causing large increase in entropy. The $T\Delta S$ term may now even dominate over the ΔH term. The following cases are illustrative.

Equilibrium	ΔH°(kJ mol^{-1})	$T\Delta S^{\circ}$(kJ mol^{-1})
1. $[Ni(NH_3)_6]^{2+} + 3en \rightleftharpoons [Nien_3]^{2+} + 6NH_3$	−12.1	−55.1
2. $[Nien_2(H_2O)_2]^{2+} + tren \rightleftharpoons [Ni(tren)(H_2O)_2]^{2+} + 2en$	+13.0	−23.7

In reaction 1, the enthalpy change is nearly equal to that expected from enhanced crystal field stabilization energy (CFSE; see Ch. 27). The relatively large contribution of the $T\Delta S^{\circ}$ term is noteworthy.

In reaction 2, the ΔH° term is actually positive, disfavouring the forward equilibrium. But we see that the $T\Delta S^{\circ}$ term actually makes ΔG° ultimately negative.

The favoured ringsize in stable chelates of the transition elements appears to be a five-membered ring. Substitution of ethylenediamine by 1,3-propanediamine in $[Cu(en)_2]^{2+}$ results in a loss of free energy of formation by 16.3 kJ mol^{-1}.

26.3.3 Determination of the composition and formation constants of complexes

Several methods have been developed for the determination of composition of the complex species formed in solution and their formation constants. Things are often more complicated in reality because of the multiple equilibria involved. We shall discuss only the outline of a few methods which apply mostly to single equilibria. Besides the methods described below, a number of other approaches may be made in specialised circumstances like solvent distribution coefficients, conductance, refractive index, temperature changes, nuclear magnetic resonance, optical activity, dipole moment, polarography and so on.

The determination of the composition of a complex species is done by following the variation of any suitable property of the solution or reactants or products. We shall illustrate the procedure with three early approaches which are unsophisticated and yet helpful.

A. *Molar Ratio Method*

If a metal M and ligand L react to form complex M_xL_y having sufficient stability, then the physical properties of a solution containing M, L and the complex will change with a change in the ratio of the molar concentrations of the metal and the ligand; clearly, the concentration of the complex formed will be related to these concentration terms through the equilibrium.

$$xM + yL \rightleftharpoons M_xL_y$$

When the complex is sufficiently stable, the equilibrium proceeds almost completely to the right and the molar ratio of the ligand (L) to that of the metal (M) in solution is equal to the L : M ratio in the complex.

A number of solutions are prepared by mixing a fixed quantity of metal (T_M) and varying amounts of the ligand L (T_L). Any suitable physical property of the solution is now measured and plotted against the ratio of molar concentrtion of L and M (T_L/T_M; at constant T_M). The plot rises from the origin as a straight line and sharply changes the slope at the molar ratio corresponding to complex formation. Thus there are two linear portions mutually intersecting at such values of T_L/T_M representing the molar ratio of the complexes predominating in the solution under the experimental conditions. When more than one complexes are formed, the method can be applied only if the stabilities of such complexes vary widely.

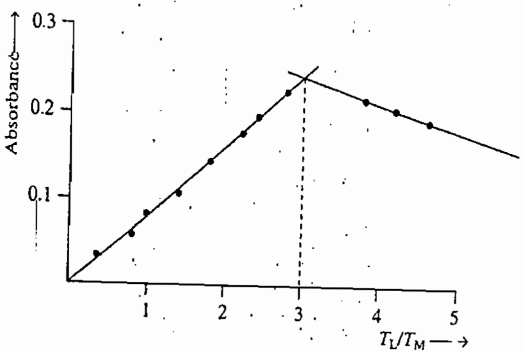


Fig. 26.10

Molar ratio method.

Plot of absorbance for solutions of Fe(II) with *o*-phenanthroline containing different mole ratios of the ligand and metal : (T_L/T_M).

(pH = 2.0; μ = 0.5)

A single complex of composition ML_3 is indicated.

B. *Solubility Method*

When a metal forms a relatively insoluble salt (of known solubility product) but a more soluble complex, the solubility of the salt will increase in presence of the ligand. Thus, silver acetate has relatively low solubility while its acetate complex is fairly soluble. If we allow excess silver acetate to reach equilibrium in presence of a known large concentration of acetate ion (at a constant temperature), the equilibria involved are (OAc ≡ acetate)

$$AgOAc(s) \rightleftharpoons Ag^+ + OAc^- \qquad K_{sp} = [Ag^+][OAc^-]$$

$$Ag^+ + 2OAc^- \rightleftharpoons [Ag(OAc)_2]^- \quad \beta_2 = [Ag(OAc)_2^-]/[Ag^+][OAc^-]^2$$

Hydrolysis of the acetate ion will be negligible if we use a basic medium. After equilibrium is reached, the solution may be freed from the excess undissolved salt (filtration) and the concentration of total silver in it (C_{Ag^+}) determined. Then,

$$C_{Ag^+} = [Ag^+] + [Ag(OAc)_2^-]$$

Since we have used a large excess of concentrated acetate ion, C_{OAc^-} remains practically unchanged and we have

$$[Ag^+] = K_{sp} / [OAc^-] = K_{sp} / C_{NaOAc}$$

Hence we can find out $[Ag(OAC)_2^-]$ and substitution of all the quantities in the expression of β_2 is possible :

$$\beta_2 = \frac{(C_{Ag^+} - K_{sp}/C_{NaOAc})}{(K_{sp}/C_{NaOAc})(C_{NaOAc})^2}$$

The constancy of β_2 may be checked by varying the concentration of sodium acetate.

C. *Spectral Methods*

Most complexes absorb light differently from the metal ions which form the complexes. Beer's law gives the absorbance A as

$$A = \log(I_o/I) = \varepsilon cl$$

I_o is the intensity of the radiation while entering the solution and I is the intensity of radiation while emerging from the solution; c is the concentration of the complex (moles liter^{-1}) and l is the length of the absorption cell. Knowing the absorbance with a spectrophotometer, it is possible to calculate c if ε, the molar extinction coeffecient, is known at that wave length.

Let us take an example of the complex formation

$$M^{2+} + L \rightleftharpoons ML^{2+} \qquad K = [ML^{2+}] \big/ [M^{2+}][L]$$

Typical absorption curves for M^{2+} and ML^{2+} are shown in Fig. 26.11. It is observed that the complex shows an absorption maxima at 550 mμ where absorption by the metal is negligible. A number of solutions containing known amounts of total M^{2+} and total L are allowed to reach equilibrium and the absorption of each solution is measured at 550 mμ. Then,

Total concentration of metal, $C_M = [M^{2+}] + [ML^{2+}]$

Total concentration of ligand, $C_L = [L] + [ML^{2+}]$

Absorbance, $A = \varepsilon[ML^{2+}].l$

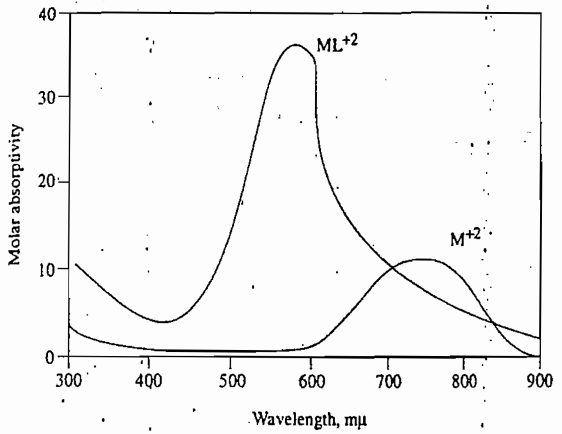


Fig. 26.11

Typical molar absorbance curve for ML^{2+} and M^{+2} (*aq*).

where ε is the extinction coefficient of the complex ML^{2+}. Knowing ε and l, we can determine $[ML^{2+}]$. Since we also know C_M and C_L, we can find out $[M^{2+}]$ and [L]. We are now in a position to put all the quantities in the expression of the formation constant K. The constancy of the value of 'K' may be checked by taking different concentrations of metal (C_M) and lignd (C_L).

We shall now illustrate two variations of this method : (i) The slope ratio method and (ii) Job's method. However, these methods are not necessarily limited to spectral analysis only; any variable physical property of the solution like conductance, pH - change etc. may be followed to apply the methods discussed.

(i) **Slope Ratio Method**

This method is generally used to determine the composition of a complex. Suppose a metal ion M reacts with a ligand L (charge on M and L omitted for simplicity) to give a sufficiently stable complex M_xL_y :

$$xM + yL \rightleftharpoons M_xL_y \qquad K = [M_xL_y] \big/ [M]^x[L]^y$$

In presence of large excess of either M or L, the dissociation of the complex will be negligibly small; hence at equilibrium its concentration will be proportional to the analytical concentration of the component which is not in large excess. That is,

Using large excess of L : $[M_xL_y] = C_M/x$

Using large excess of M : $[M_xL_y] = C_L/y$

Where C_M and C_L are total concentration of metal or ligand (analytical concentration) and $[M_xL_y]$ denote the equilibrium concentrations of the complex in respective cases.

Now if the complex M_xL_y is coloured and neither M nor L has any absorption at the wavelength of maximum absorption of M_xL_y, assuming Beer's law to hold in the concentration range under study, the absorbance A will be given by

$$A = \varepsilon[M_xL_y] \,.\, l,$$

where ε is the molar extinction coefficient of the complex at the wavelength of maximum absorption and l is the path length.

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For a series of solutions having a constant large excess of L and varying amounts of M(C_M), the absorbance A_L in each case will be given by

$$A_L = \varepsilon[M_xL_y] \, . \, l = \varepsilon.C_M/x. \, l.$$

i.e., A_L will be a linear function of C_M. Plot of A_L against C_M will then give a straight line having a slope

$$Slope_L = \varepsilon l/x$$

Similarly, for a series of solutions having a constant large excess of M and varying amounts of L (C_L), the absorbance in each case will be

$$A_M = \varepsilon[M_xL_y] \, . \, l = \varepsilon.C_L/y \, . \, l$$

Hence A_M will be a linear function of C_L and a plot A_M versus C_L will give a straight line with slope

$$Slope_M = \varepsilon l/y$$

The ratio of the two slopes now gives the ratio x/y :

$$\frac{Slope_L}{Slope_M} = \frac{y}{x}$$

This enables us to determine the composition of the complex M_xL_y.

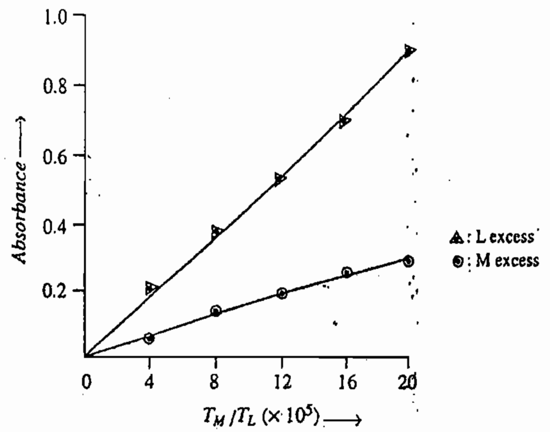


Fig. 26.12

The slope ratio method.

The slope-ratio for Fe(II)-1, 10-phenanthroline complex indicates formation of a 1 : 3 complex (pH = 2.0, μ = 0.5).

(ii) Job's Method

In Job's method of continuous variation, any property of the metal-ligand system is measured in a series of solutions having constant sum of the total concentration of metal (M) and ligand (L; $T_M + T_L$ = constant). In spectrophotometric method, light absorption is measured at the wavelength of maximum complex absorption and the absorbance is plotted against the concentration. It can be shown that maximum absorbance will occur when L : M ratio is equal to that in the complex.

The basic assumptions and requirements of the method are

(i) composition of the complex is the same as the composition of the solution actually studied.

(ii) the complex formed is highly stable and undergoes negligible dissociation.

(iii) only one complex is formed in the system.

(iv) there must be some variable physical property as a function of concentration of ligand or of the complex like colour intensity, optical absorbance, conductance etc.

The study of complex compounds by Job's method now consists of two parts :

1. Study of a series of equimolar solutions to obtain the composition of the complex.

2. Study of a series of nonequimolar solutions to determine the stability constant.

Let us consider the formation of a complex as follows :

$$xM + yL \rightleftharpoons M_xL_y$$

A number of experimental solutions are prepared in which the metal solution and the ligand solution are mixed in such a way that the total volume remaining the same, the mole fraction of M and L vary continuously. When the conditions laid down above are satisfied, the $x : y$ ratio in the complex at the point of maximum concentration of the complex is the molar ratio of the reactants that are taken for reaction.

Suppose we mix $(1 - v)$ volume of C molar solution of M with v volume of C molar solution of L. Since the total volume is unity, the volume of any component will be equal to its mole fraction.

Now, the total quantity of the metal or ligand (analytical concentration) must be equal to the sum of (i) the "free" metal or ligand and (ii) that present in the complex. In other words

$$T_M = (1 - v)C \text{ milimoles} = [M] + x\,[M_xL_y] \quad \ldots \text{(i)}$$

$$T_L = vC \text{ milimoles} = [L] + y[M_xL_y] \quad \ldots \text{(ii)}$$

From (i) and (ii)

$$[M] = (1 - v)C - x[M_xL_y]$$

$$[L] = vC - y[M_xL_y]$$

Since $K = \dfrac{[M_xL_y]}{[M]^x\,[L]^y}$, substitution gives,

$$K = \frac{[M_xL_y]}{\left\{ (1 - v)C - x[M_xL_y] \right\}^x \left\{ (vC - y\,[M_xL_y]) \right\}^y}$$

This shows that $[M_xL_y]$ is a function of v, the mole fraction of L. So we can find out a value of $v = v_{max}$ when the concentration of the complex is maximum. There cannot be an infinite concentration of the complex M_xL_y as [M] falls as [L] is raised - putting a limit to the formation of the complex.

Then, we may write,

$$\frac{d}{dv}[M_xL_y]_{v = v_{max}} = 0.$$

Determination of composition

Now we return to the equilibrium under study :

$$xM + y\,L \rightleftharpoons M_xL_y$$

As mentioned before, we have mixed $(1 - v)$ volume of C molar solution of M with v volume of C molar solution of L.

Let us assume that the equilibrium concentration of M, L and M_xL_y are C_1, C_2 and C_3 respectively. It is now possible to write the following relations

(i) Formation constant $K = \frac{C_3}{C_1^x C_2^y}$

$$\text{or,} \quad C_1^x \cdot C_2^y = \frac{1}{K} \cdot C_3 \quad \ldots (1)$$

(ii) From mass balance of M : $(1 - v)C = C_1 + xC_3$ ... (2)

(iii) From mass balance of L : $vC = C_2 + yC_3$ ... (3)

From these equations, differentiating, rearranging and substituting K, we get

$$\frac{x}{C_1} \cdot \frac{dC_2}{dv} + \frac{y}{C_2} \cdot \frac{dC_2}{dv} = \frac{1}{C_3} \cdot \frac{dC_3}{dv} \quad \ldots (4)$$

$$\frac{dC_1}{dv} + \frac{xdC_3}{dv} = -C \quad \ldots (5)$$

$$\frac{dC_2}{dv} + y \cdot \frac{dC_3}{dv} = C \quad \ldots (6)$$

As we have already explained, $\frac{dC_3}{dv} = 0$ at $v = v_{max}$, the point of maximum complex formation. Putting $dC_3/dv = 0$, equations (4), (5) and (6) give

$$C_2x - yC_1 = 0 \quad \ldots (7)$$

Now, from equation 2, 3 and 7

$$(1 - v)Cy - xvC = C_1y - C_2x = 0$$

$$\text{or,} \ \frac{x}{y} = \frac{1 - v}{v}$$

Thus, the composition of the complex M_xL_y may be found out from v (= v_{max}) using simplest numerical values of x and y.

Experimentally, the method involves the following steps :

(i) Determination of λ_{max} of the complex from a full length spectrum of the complex.

(ii) Plotting optical density versus concentration for the complex and finding the useful concentration range.

(iii) Preparation of several sets of solutions with varying volumes of M and L (at a constant μ and pH) and recording O.D. of each.

(iv) Plotting O.D. against the volume of ligand L and finding the maxima in the curve. This gives the x/y ratio for the complex M_xL_y (Fig. 26.13).

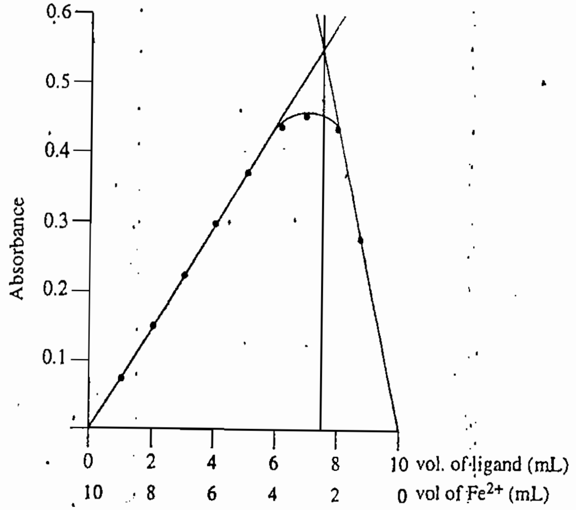


Fig. 26.13

Plot for Job's method.

Determining the composition of Fe^{2+}—1, 10-phenanthroline complex (pH = 2.0; μ = 0.5).

A 1 : 3 ratio of M : L is indicated.

In order to determine the formation constant (overall) of the complex, the same procedure may be used, but using metal and ligand solutions of different molarity. If $(1 - v)$ c.c. of C molar solution of the metal is equilibrated with nC molar solution of the ligand (v c.c.), the above process of calculation give

$$\frac{x}{y} = \frac{C(1 - v)}{nC\,v} \ \ldots\ldots \text{ at } v = v_{max}$$

where v is the theoretical value for maximum complex formation.

Experimentally, v is found to be different, showing that values of v are shifted. The shift is negligibly small for very strong complexes. For weak complexes, the shift in the value of v is appreciable. Thus the shift in the value of v is a measure of the stability of the complex. Greater the shift, less stable is the complex. We may write :

$$C_1 = \frac{C\{y - v(nx + y)\}}{y(1 - p)}$$

$$C_2 = \frac{vc\{n - v(nx + y)\}}{x(1 - n)}$$

$$C_3 = \frac{nc\{(x + y)x - y\}}{xy(1 - p)}$$

$$\therefore \ K = \frac{C^{m+n-1} . n^{y-1}\{y - v(nx + y)\}^{x+y}}{x^{n-1} . y^{m-1}(1 - v)^{m+n-1}} \{(x + y)v - y\}$$

Though the method is applicable when only one complex is formed, it has been extended to situation involving the formation of more than one complex.

The **Bjerrum Method** is more useful in the determination of formation constants. This takes advantage of the competition between hydrogen ions and metal ions for the ligand which may be a weak base or acid. The concentration of hydrogen ions can be precisely determined but often the concentration of the metal ions and ligands cannot.

Let us consider the equilibria involved when acid and metal ion are present in a solution containing a basic ligand :

$$L + H^+ \rightleftharpoons HL^+ \qquad K_a = [HL^+]/[L][H^+]$$

$$L + M^+ \rightleftharpoons ML^+ \qquad K_1 = [ML^+]/[M^+][L]$$

If the total amounts of acid, metal and ligand added in moles/liter (analytical concentrations) be C_H, C_M, and C_L respectively, we may write

$$C_H = [H^+] + [HL^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

$$C_M = [M^+] + [ML^+]$$

Solving these three equations with the acid association constant K_a, we get

$$[ML^+] = C_L - C_H + [H^+] - (C_H - [H^+])/K_a[H^+]$$

$$[M^+] = C_M - [ML^+]$$

$$[L] = (C_H - [H^+])/K_a[H^+]$$

Thus all of the concentrations necessary in the expression of formation constant can be determined if C_H, C_L, C_M, K_a and the hydrogen ion concentration are known. The last quantity is determined using a pH meter.

For precise results, the ligand must be a medium weak acid or base and the formation constant should lie within a factor of 10^5 of K_a, the acid association constant of the ligand. Successive stability constants are best obtained if they differ by a factor of at least 10^2.

26.4 COORDINATION NUMBER AND STEREOCHEMISTRY

The most significant part of Werner's theory lies in the postulate of directional nature of metal-ligand bonds. Werner had to depend on chemical methods for indirectly ascertaining the geometry of complexes. A number of physical methods are now available for elucidation of the structure of a complex compound; of these methods, the most direct is X-ray crystallography which can locate the actual position of various atoms in a crystal. Besides, there are other methods like electronic and vibrational spectroscopy, study of dipole moment, magnetic susceptibility measurement etc. In this section, we shall gain familiarity with the common geometries found in coordination compounds and the stereoisomerism associated with them.

Examples of coordination number 1 are rare. A metal coordinated to a single donor atom is always susceptible to further attack by more ligands. Thus the coordination number of vanadium in a transient VO^{2+} ion may be said to be 1; but it readily coordinates with further ligands, forming, e.g., $[VO(acac)_2]$ or $[VO(H_2O)_5]^{2+}$. A situation may also arise when a highly congested ligand creates steric shielding around the metal, preventing other ligands to approach. The complex $[Cu(2,4,6\text{-}Ph_3C_6H_2)]$ (Fig. 26.14) is an example of this type; it is appreciably stable when kept away from small ligands.

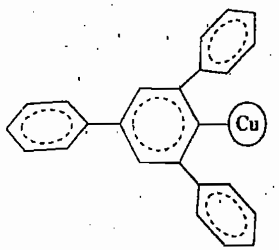


Fig. 26.14

Examples of C.N. 1.

[The benzene rings are not coplanar.]

A similar complex is known with Ag(I)]

[Sec. 26.4.1 *Coordination Number* 2]

Coordination numbers encountered in most complex compounds range from 2 to 12, among which 4 and 6 are most common.

26.4.1 Examples of Common Coordination Numbers

Coordination Number 2

This coordination number is also relatively uncommon since a two-coordinate metal is normally "open" to attack by other ligands. It is commonly exhibited by +1 ions of Gr IB cations i.e., Cu(I), Ag(I) and Au(I) and also Hg(II) : for example, $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Au(CN)_2]^-$, $Hg(CN)_2$, $[AuCl(PEt_3)]$ etc. Even bidentate ligands may form linear 2 - coordinated complexes by bridging e.g.,

$$Cl - Ag - NH_2CH_2CH_2NH_2 - Ag - Cl.$$

The preference of mercury (II) for coordination number 2 is reflected in the sudden fall of formation constant of complexes at K_3 (Table 26.5). Linear coordination is also present in solid $HgCl_2$ and $Hg(CN)_2$.

Although $CuCl_2^-$ and $[Cu(NH_3)_2]^+$ are linear, most complexes of Cu^+ are tetrahedral. In solid $K[Cu(CN)_2]$, the coordination number of Cu^+ is 3(see below); other solid halide complexes are usually tetrahedral.

The 2-coordinate complexes of Ag^+ and Hg^{2+} may react with additional ligands to form tetrahedral complexes, but the complexes of Au^+ hardly show this tendency.

$$[Ag(NH_3)_2]^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_4]^+$$

In solution, MX_2 species are strongly solvated to attain an effective coordination number 4.

Infrared studies on $HgCl_2$, $HgBr_2$ and HgI_2 vapour show very low bending force constants; this suggests that the bonding orbitals have weak directional properties. The occurrence of CN. 2 with Hg(II) and Au(I) may be explained by considering participation of d_{z^2} orbital in bonding. High effective nuclear charge brings the energies of 5*d* and 6*s* atomic orbitals close enough for *d* - *s* hybridization to take place, favouring linear complex formation. But *d* - orbital participation is not favourable in lighter elements in the group (e.g. Zn^{2+} and Cd^{2+}) since the $(n-1)d$ and *ns* orbitals are widely different in energy. Hence coordination occurs primarily through sp^3 hybrid orbitals.

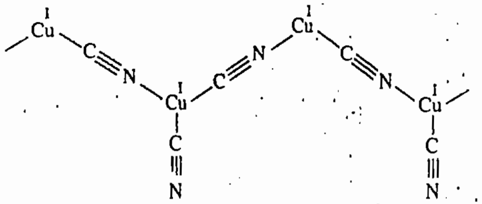
Q. 26.10 *Ethylenediamine complexes are usually much more stable than those of ammonia. But* $[Ag(NH_3)_2]^+$ *is more stable than* $[Ag(en)]^+$. *Comment.*

Hint : The ethylenediamine molecule cannot stretch enough to fulfill linear coordination around the Ag^+ ion.

Coordination Number 3

This coordination number is also very uncommon and occurs with metal ions in low oxidation number with bulky ligands or in solids. Thus, planar trigonal coordination is present in $K[Cu(CN)_2]$, HgI_3^-, $Pt[P(C_6H_5)_3]_3$ and similar complexes with $SP(CH_3)_3$, $SC(NH_2)_2$ etc. $N[SiMe_3]_3$ is another bulky ligand (= L) which forms three-coordinate molecules ML_3 with Fe^{3+}, Cr^{3+}, Mn^{3+}, Co^{3+} etc.

In $K[Cu(CN)_2]$, and $[Bu_4N]\ [Cu(CN)_2]$ the anion exists as polymeric chains with bridging cyanide groups; the copper atoms are trigonally coordinated, each by two carbon atoms and one nitrogen from three cyanide groups.



26-XVIII

The C-Cu-C angle is about 134° rather than 120° but the carbon and nitrogen atoms are almost coplanar with copper. The $Ag(CN)_2^-$ and $Au(CN)_2^-$ ions are, however, discrete anions with two coordinate metals. Also, $CsCuCl_3$ or $K_2Ni(CN)_3$ do not provide examples of 3 coordination. In $CsCuCl_3$, each copper is surrounded by four coplanar chlorines in a bridged structure $[Cl–MCl_2–Cl–MCl_2]$. The nickel complex is diamagnetic, suggesting that it exists as the dimeric anion $[Ni_2(CN)_6]^{4-}$.

Coordination Number 4

Four-coordinate complexes are obtained in two geometries — tetrahedral and square planar. Tetrahedral complexes are also formed by elements of the second period, particularly boron and beryllium, when they achieve their octet, e.g., BeX_4^{2-} and BX_4^-. Transitional elements form tetrahedral complexes when the ligands are bulky and weak, so that a square planar or octahedral complex would not be energetically favourable. But large metal ions in the 2nd and 3rd transition series (e.g., Pd^{2+} and Pt^{2+}) are free from steric congestion; at the same time they offer a large crystal field stabilization in forming a square planar complex. In fact, tetrahedral complexes are relatively uncommon for metals of the second and third transition series; in the first transition series also, this geometry is not common among d^3 and d^4 metal ions.

Tetrahedral complexes of transition metals are mostly anionic or neutral. Cationic complexes like $[Cd(NH_3)_4]^{2+}$ are not common. The formation of a tetrahedral complex in solution by substitution of water by halide ions may be written as

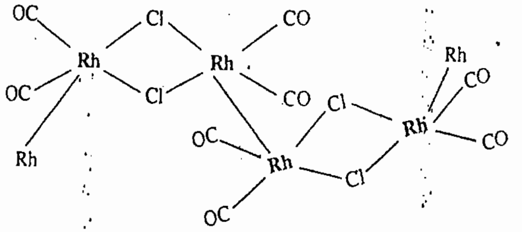
$$[M(H_2O)_6]^{n+} + 4X^- \rightleftharpoons [MX_4]^{(4-n)-} + 6H_2O$$

With some metals, tetrahedral complexes are formed even in presence of excess ligand. For example, when concentrated HCl is added to aqueous solutions containing Fe(III) or Co(II), Fe^{3+} and Co^{2+} form $FeCl_4^-$ and $CoCl_4^{2-}$ respectively, rather than $FeCl_6^{3-}$. Tetrahalo complexes of other metals may be prepared by using excess halide ions in media which are weakly coordinating. Thus VX_4^-, MnX_4^{2-} and NiX_4^{2-} may be isolated as crystalline salts from acetonitrile and alcohol solutions in presence of excess halide ions.

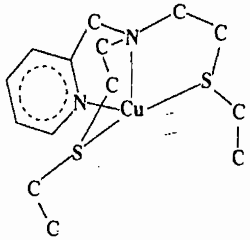
Tetrahedral complexes are also known with pseudohalogen anions, e.g., $[Co(NCS)_4]^{2-}$ and in mixed aquohalocomplexes, e.g., $[CoX_3(H_2O)]^-$. Tetrahedral complexes are common for Co(II), but they are unknown for $Co^{III}(d^6)$ and $Cr^{III}(d^3)$.

Neutral tetrahedral complexes are exemplified by $CoCl_2(py)_2$ and $NiBr_2(Ph_3AsO)_2$. However, the empirical formula of a compound does not indicate the stereochemistry. For example, $NiCl_2(py)_2$ contains six-coordinated nickel with chloride bridges.

Square planar complexes of the type PtX_2L_2 were recognized by Werner from their isomers. Cationic, neutral and anionic complexes of Pt(II) are square planar in the solid as well as in solution, for example, $[Pt(NH_3)_4]^{2+}$, $Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$. Rh^I, Ir^I, Pd^{II} and Au^{III} (all d^8) also form square planar complexes like $Ir(CO)Cl(PPh_3)_2$, $PdCl_4^{2-}$ and $AuCl_4^-$. Ni(II) also forms square planar complexes like $Ni(CN)_4^{2-}$ and $Ni(dmgH)_2$ (dmgH = dimethylglyoximate).



26-XIX



26-XX

$RhCl(CO)_2$ contains two square planar Rh(I) ions bridged by two chlorines. These dimeric units form chains with rather long Rh...Rh interaction, imparting an effective coordination number 5 for each Rh.

An unusual geometry in coordination no. 4 is shown by the trigonal monopyramidal 2-pyridylmethylbis(2-ethylthioethyl)amine complex of copper,

$[Cu\{N(CH_2CH_2SEt)_2\,CH_2py\}]$ (26-XX).

Most of the examples of square planar complexes given above contain metals with lowspin d^8 configuration (e.g., Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}). Co^{II}, d^7 low-spin, though mostly forms tetrahedral complexes, the *trans*- dimesitylbis(diethylphenylphosphine) complex of Co^{II} is square planar. The bis(benzyldiphenylphosphine) complex of Ni^{II}, $[Ni(PBzPh_2)_2Br_2]$ where Bz = benzyl, contains both planar and tetrahedral forms in one crystal.

Coordination Number 5

Though several arrangements of five ligands around a metal are possible, only two are commonly found - the trigonal bipyramid (TBP) and the square-base pyramid (SP). The VSEPR theory predicts the trigonal bipyramid structure in five-coordintion involving sp^3d hybridization. The structure is indeed found for the *s*-and *p*-block elements; but for complexes of the transition elements, difference of energy between the TBP structure and the alternative square pyramid structure is very small and the two forms may be readily interconverted (Fig. 26.15).

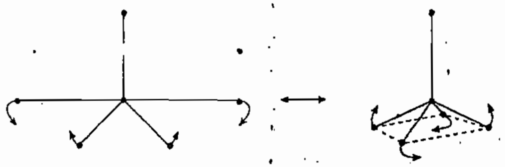
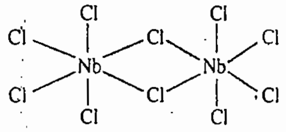


Fig. 25.15
Interconversion of TBP and SP structures.

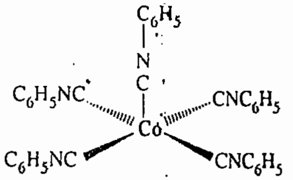
The TBP structure is generally found in compounds having five identical ligands. The pentachlorides of niobium, tantalum and molybdenum have this structure in the vapour phase but the solid state consists of dimeric molecules with slightly distorted octahedral coordination via chlorine bridges (26-XXI).



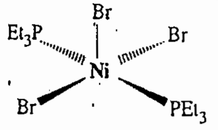
26-XXI

$SbCl_5$ retains its five coordination in the solid state. Other examples of TBP structure in five-coordination are provided by $Fe(CO)_5$, $[Mn(CO)_5]^-$, $[Pt(SnCl_3)_5]^{3-}$, $[Ni(CN)_5]^{3-}$, $CuCl_5^{3-}$ and $[Co(NCMe)_5]^+$. Substituted iron carbonyls like $Fe(CO)_4L$ and $Fe(CO)_3L_2$ and many complexes of vanadium(III) halides of the general formula VX_3L_2 also have structures based on TBP. Complexes of the general formula $MCl_3(NMe_3)_2$ (M = Ti, V, Cr) have the chlorine atoms in the equatorial positions of a TBP arrangement. Cs_2CoCl_5 actually contains the $CoCl_4^{2-}$ ion (distorted tetrahedral) and Cl^- ions in the lattice.

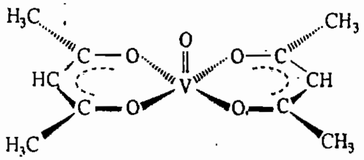
Square pyramidal structures normally contain the metal above the basal plane inside the pyramid and have a diferent ligand in their apex than the four ligands on the base. Common examples are $VO(acac)_2$, $Co(NO)(S_2CNR_2)_2$, $[NiBr(diars)_2]^+$, $[Co(CNPh)_5][ClO_4]_2$ and $Ni(PEt_3)_2Br_3$ (26-XXII and 26-XXIII).



26-XXII- (a)



26-XXII- (b)



26-XXIII

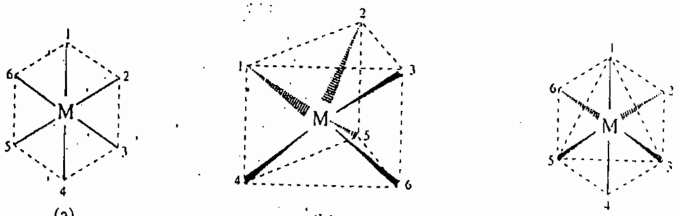
Square pyramid structures are also adopted when square 4-coordinate doubly charged complexes of d^8 configurations add a fifth ligand; the fifth ligand may be only loosely bonded to give rise to a slightly perturbed square structure; for example

$$[Pt(diars)_2]^{2+} + X^- \rightleftharpoons [Pt(diars)_2X]^+$$

Coordination Number 6

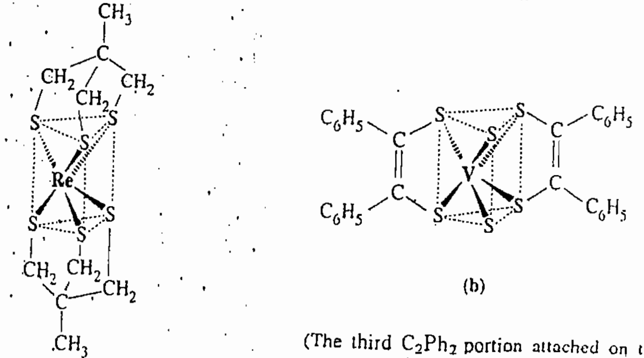
[Sec. 26.4.1
Coordination Number 6]

This is the most common as well as most important coordination number among transition metal complexes. Six coordinating groups may be arranged around a central metal atom in different arrangements, for example (i) hexagonal planar (ii) trigonal prismatic or (iii) regular octahedral. Of these, the hexagonl planar structure has not yet been found; the trigonal prismatic structure has been observed relatively recently (1965). It appears that some metals with d^0 configuration are more stable in the trigonal prismatic geometry rather than in the octahedral geometry, e.g., WMe_6. Of course, other examples are also known, e.g., $[Re\{S_3(CH_2)_3CMe\}_2]$, $[Re(S_2C_2Ph_2)_3]$ and $[V(S_2C_2Ph_2)_3]$.



(a) (b) (c)

Fig. 26.16
Different arrangement of six groups around a metal
(a) hexagonal planar (b) trigonal prismatic (c) octahedral.



(a) (b)

(The third C_2Ph_2 portion attached on the upper edge of the prism has been omitted for clarity.)

26-XXIV

The great majority of six-coordinate complexes have the octahedral structure. The regular or nearly regular octahedral environment of ligands is found with metal ions having electronic configurations ranging from d^0 to d^{10}, though distortions are also very common. Some examples of regular (or nearly so) octahedral structure are

d^0 $[TiF_6]^{2-}$
d^1 $[Ti(H_2O)_6]^{3+}$
d^2 $[V(H_2O)_6]^{3+}$
d^3 $[Cr(H_2O)_6]^{3+}$
d^4 $[Mn(H_2O)_6]^{3+}$
d^6 $[Fe(H_2O)_6]^{2+}$
d^6 $[Co(CN)_6]^{3-}$ (low spin)
d^6 $[Co(H_2O)_6]^{3+}$ (low spin)
d^7 $[Co(H_2O)_6]^{2+}$
d^8 $[Ni(H_2O)_6]^{2+}$

- d^4 $[Mn(CN)_6]^{3-}$ (low spin) d^9 $[Cu(NO_2)_6]^{4-}$
  d^5 $[Fe(H_2O)_6]^{3+}$ d^{10} $[Zn(H_2O)_6]^{2+}$
  d^5 $[Fe(CN)_6]^{3-}$ (low spin)

As evident from these examples, most of the regular octahedral complexes are high spin.

Distortion in octahedral complexes

Octahedral complexes often show notable distortions particularly with high spin d^4 and d^9 metal ions. Thus, CuX_2 (X = F, Cl) and CrX_2 (X = F, Cl, Br, I) have four neighbours in a plane and two more at a larger distance. The structures of individual halides are however different. Two types of distortions are common :

(i) **Tetragonal distortion :** The octahedron is either elongated or compressed along a fourfold rotational axis (C_4 axis, Fig. 26.17). This gives four equal bonds in the equatorial plane and two axial bonds which may be shorter or longer than these four (Fig. 26.18).

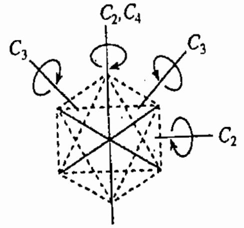


Fig. 26.17

Some of the symmetry axes of an octahedron.

Three fourfold C_4 axes pass through the center of symmetry and through opposite corners of the octahedron. Four threefold C_3 axes pass through the center and through the midpoints of opposite triangular faces.

Six twofold C_2 axes join the midpoints of opposite edges of the octahedron through the center. There is another set of C_2' axes coincident with the C_4 axes.

These distorted structural arrangements belong to the symmetry class D_{4h}. In the limiting case of tetragonal elongation, the ligands at the axial positions will be removed from the coordination sphere of the metal : a square planar complex will thus be formed.

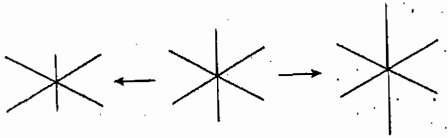


Fig. 26.18

Tetragonal distortions of an octahedral complex.

(ii) **Trigonal distortion** involves elongation or compression of the octahedron along any of the C_3 axes.

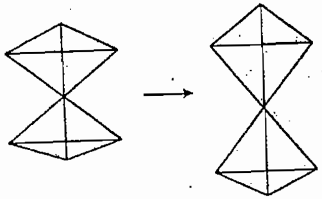


Fig. 26.19

Trigonal distortion of an octahedral complex.

This may be visualized by placing the ocahedron on a triangular base and stretching along the vertical C_3 - axis as shown in Fig. 26.19; compression along this axis will also produce similar distortion. The resulting trigonal antiprism structure belongs to the symmetry class D_{3d}.

Hexa-aquo complexes of some trivalent transition metal ions in the alums like $NH_4[V(H_2O)_6]^{3+}(SO_4)_2 \cdot 6H_2O$ provide examples of trigonal distortion.

Both trigonal and tetragonal distortions occur in the solid state as well as in solution as evidenced by x-ray and magnetic studies. The reasons for these distortions will be considered later.

Coordination Number 7

Coordination numbers greater than six are rarely found among complexes of the first transition series metals. For complexes of the second and third transition series metals, higher coordination numbers are more common; two reasons seem to be responsible : (1) larger size of the metal, (2) availability of orbitals which are energeticlly close enough to permit such co-ordination. Small electronegative unidentate ligands (like H^-, F^-, CN^-) and chelating agents containing electronegative donor atoms (N, O) are found to stabilize the higher coordination number. In many such complexes, the idealized shapes may be understood from the VSEPR theory, but the various possible structures often differ very little in energy and are readily interconvertible.

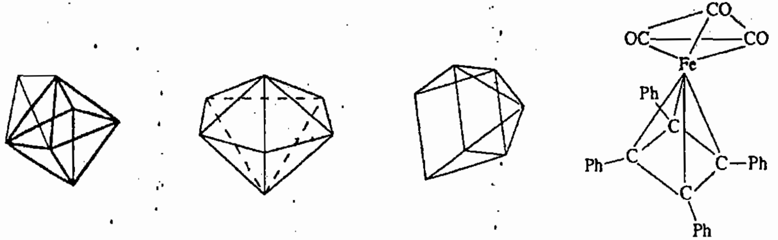
Four structures are possible in coordination number seven :

1. A *monocapped octahedron*, i.e., an octahedron with an extra atom on one of the faces (26- XXV a). $NbOF_6^{3-}$ ion has this structure.

2. A *pentagonal bipyramid* structure (26-XXV b), as found in $[UO_2F_5]^{3-}$, $[V(CN)_7]^{4-}$ and $[ZrF_7]^{3-}$

3. A *capped trigonal prism*, that is a seventh ligand added above one of the rectangular faces of a trigonal prism (26-XXV c); this is found in NbF_7^{2-} and TaF_7^{2-}.

4. *The tetrgonal base-trigonal base structure* (26-XXV d). This is illustrated for $Fe(CO)_3C_4Ph_4$.

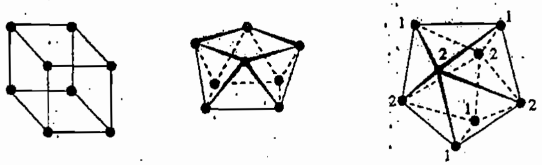


(a) monocapped octahedron (b) Pentagonal bipyramid (c) tetragonally capped trigonal prism (d) tetragonal base -trigonal base

26-XXV

Coordination Number 8

Of the several possible structures, only three have been actually recognized : the cube (26-XXVI a) the square antiprism (26 - XXVI b) and the dodecahedron (26 - XXVI c).



(a) (b) (c)

26-XXVI

The cubic coordination is not common due to greater inter-ligand repulsion; it has been found only in some fluoro complexes of actinide elements e.g., $[PaF_8]^{3-}$ and $[UF_8]^{3-}$.

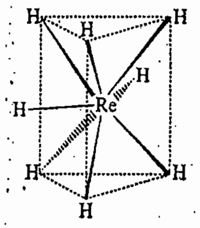
The square antiprism is formed when one square face of a cube is rotated by 45° relative to the face opposite to it. The structure occurs in $[M(acac)_4]$ ($M = Zr^{IV}, Ce^{IV}, Th^{IV}$) and TaF_8^{3-}, $[ReF_8]^{2-}$, $[W(CN)_8]^{3-}$ or $[Mo(CN)_8]^{3-}$. This structure appears more probable with larger ligands owing to greater inter-ligand separation.

The dodecahedral structure has two different types of positions in it (marked 1 and 2 in Fig. 26 - XXVI c); it occurs in $Na_4[ArO_4]$. $3H_2O$; $(Bu_4N)_3[Mo(CN)_8]$ and $K_4[Mo(CN)_8]$. $2H_2O$. Among the first transition series metals, only the dodecahedron is known in eight coordination involving bidentate ligands., e.g:, $[Ti(NO_3)_4]$, $[Cr(O_2)_4]^{3-}$, $[Mn(NO_3)_4]^{2-}$ and $[Fe(NO_3)_4]^-$.

Polymeric eight coordinate units are found in some cases, for example K_2ZrF_6 contains zirconium surrounded by eight fluorine atoms of which four are shared. A different structural type in eight coordination involves the planar hexagonal bipyramid structure found in actinide elements, particularly for uranyl (dioxouranium(VI) complexes) compounds like $Rb[UO_2(NO_3)_3]$: the OUO group is perpendicular to the three bidentate nitrate groups in a hexagonal plane with uranium at the center.

Higher Coordination Numbers

Coordination number nine is found to occur in a tricapped trigonal prismatic structure (26-XXVII), that is, a trigonal prism with one additional ligand centered on each of the rectangular faces, as in ReH_9^{2-} and TcH_9^{2-}. Aquated trivalent rare earth ions like $[Nd(H_2O)_9]^{3+}$ are also nine-coordinate.



26-XXVII

Coordination numbers ten, eleven and twelve occur principally with lanthanide and actinide ions. Ten coordination is known in $La[(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)CH_2CO_2]$. $4H_2O$.

$La_2(SO_4)_3$, $9H_2O$ provides an example of twelve coordination from the twelve oxygen atoms of the three sulphate ions in an icosahedral environment.

A few generalizations

After having a brief exposure to the different geometry of metal complexes, we observe that unlike compounds of the typical non-transition elements, the VSEPR theory cannot be applied in most cases to predict the geometry of transition metal complexes. The ions $[V(H_2O)_6]^{3+}(d^2)$, $[Mn(H_2O)_6]^{3+}(d^4)$, $[Zn(H_2O)_6]^{2+}(d^{10})$ and many others are all octahedral though the electron configurations of the central ions are different in each case. As we shall encounter in the next chapter on bonding, the structures of transition metal complexes are primarily determined by the nature of metal-ligand interaction, which in turn, depends on several factors like—

(i) electronic configuration and oxidation state of the metal; (ii) nature of the ligand; (iii) number of energetically accessible orbitals of the metal which may be involved in complex formation; (iv) size and steric effects.

The factors favouring low and high coordination number may now be summarized as follows. Low coordination number is favoured by

(i) *large, bulky ligands* : steric congestion will disfavour higher coordination number.

(ii) *soft ligands* : soft polarizable ligands may enter into π-bonding with the metal; this will, at least partly, compensate for the fewer sigma bonds present.

(iii) *low oxidation state* : in a low oxidation state, the electron density on a metal atom remains high. The metal is thus expected to be reluctant to receive electron density from additional ligands.

(iv) *counter ions of low basicity* : many anions are Lewis bases capable of acting as ligands. Hence in cationic complexes containing a metal in low coordination number, the metal may be further coordinated by a strongly basic counter ion. Nitrate, perchlorate, tetrafluoroborate and similar weakly coordinating ions are thus ideal partners for a complex cation having a metal in low coordination number.

Proceeding along the same line of argument as developed above, the factors forming high coordination number are expected to be

(i) *Small hard ligands*, (ii) *high oxidation state of metal*, (iii) *large, nonacidic cations* : A high coordination number with a large number of anionic ligands is expected to result in an anionic complex. The large anion is likely to form a stable crystal with a large cation. Small cations (like Li^+) may polarize the anion and ultimately abstract a ligand to favour hard-hard combination.

26.4.2 Isomerism among Coordination Compounds

When the same empirical formula applies to two or more complexes having different structures, either in atom connectivity or in the orientation of atoms in space, the compounds are referred to as *isomers*. Such isomers may be distinguished from one another only when their rates of interconversion are slower than the observation method; in many cases, the isomers may also be separated under appropriate conditions.

As we shall presently encounter, isomerism in complex compounds may arise in many ways. The number of isomers depend on the coordination number of the metal and the geometry adopted by it and also on the nature of the ligand. In one respect such isomerism differs from the isomerism observed in carbon compounds : the coordination number of carbon is limited to four except in few hypervalent compounds. The stereochemistry of the tetracovalent carbon is also tetrahedral only. In case of coordination compounds, a four-coordinate metal may have either tetrahedral or square planar geometry. Actually, the stereochemistry of coordination compounds is more varied since metals involve much larger number of orbitals (*s*, *p* and *d*) whose energy and spatial distribution are widely different.

The isomerism of coordination compounds may be classified into two general types :

(i) *constitutional isomerism* where two or more compounds with same empirical formula differ in atom linking sequences (bond connectivities). This is also called structural isomerism.

(ii) *stereoisomerism* in which the compounds have the same empirical formula and the same atom-to-atom link sequence, but different arrangement of the atoms in space.

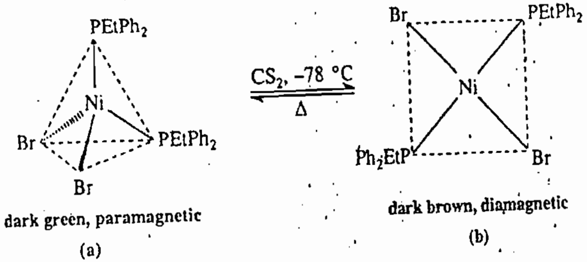
The main types within each category may be further classified as follows :

Isomerism

Constitutional Isomerism
1. Ionization
2. Hydrate
3. Coordination
4. Linkage
5. Polymerization
6. Ligand

Stereoisomerism
1. Geometrical
2. Optical

A third type of stereoisomerism has now been established among some complexes. This is called **polytopal isomerism**. Such isomers are actually conformational isomers (stereoisomers which can be interconverted without bond rupture) or *allogons* (*allos* ≡ different, *gonia* ≡ angle; the isomers differ only in ligand - metal-ligand angle) represented by compounds like [NiBr$_2$(PEtPh$_2$)$_2$] and [NiBr$_2$(PBzPh$_2$)$_2$] which may exist in both tetrahedral and square planar geometry (Bz = benzyl) :



26-XXVIII

[NiBr$_2$(PBzPh$_2$)$_2$] can simultaneously exist in a crystal in both geometries. Similarly, the crystal structure of [Cr(en)$_3$][Ni(CN)$_5$]. 1.5 H$_2$O shows the presence of both trigonal bipyramidal and square base pyrmidal [Ni(CN)$_5$]$^{3-}$ units.

26.4.3 Structural Isomerism

(i) ***Ionization Isomerism***

Coordination compounds with same empirical formula may have different ions in and outside the coordination sphere. The ions outside the coordination sphere act as counter ions for the complex species in the lattice. In solution, these counter ions ionize readily; for the various isomeric forms different ions are furnished in solution :

$$[PtCl_2(NH_3)_4]Br_2 \rightleftharpoons [Pt\,Cl_2(NH_3)_4]^{++} + 2Br^-$$

$$[(Pt\,Br_2(NH_3)_4)]Cl_2 \rightleftharpoons [Pt\,Br_2(NH_3)_4]^{++} + 2Cl^-$$

$$[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + NO_2^-$$

$$[Co(NH_3)_4Cl(NO_2)]Cl \rightleftharpoons [Co(NH_3)_4Cl(NO_2)]^+ + Cl^-$$

Outline for preparation of [Co(NH$_3$)$_5$Br]SO$_4$ and [Co(NH$_3$)$_5$SO$_4$]Br

$$CoBr_2 \xrightarrow[NH_4Br/NH_3aq]{O_2} [Co(NH_3)_5H_2O]Br_3 \xrightarrow{heat} [Co(NH_3)_5Br]Br_2 \xrightarrow{Ag_2SO_4} [Co(NH_3)_5Br]SO_4$$

violet

$$[Co(NH_3)_5Br]Br_2 \xrightarrow{conc\ H_2SO_4} [Co(NH_3)_5SO_4]HSO_4 \xrightarrow{BaBr_2} [Co(NH_3)_5SO_4]Br$$

red

The violet compound forms a white precipitate with BaCl$_2$ solution; the red compound gives a precipitate of AgBr with AgNO$_3$ solution.

The different symmetries of the free and coordinated sulphate ions may be distinguished by infrared spectroscopy. The violet form shows only one ir-active S-O stretching vibration while the red shows three such vibrations.

(ii) ***Hydrate Isomerism (Solvate isomerism)***

This is a special type of ionization isomerism in which water molecules (solvent) partly function as ligands and may be shifted outside the coordination sphere as if hydrate water:

[Cr (H$_2$O)$_6$] Cl$_3$	[CrCl (H$_2$O)$_5$] Cl$_2$.H$_2$O	[CrCl$_2$ (H$_2$O)$_4$] Cl.2H$_2$O
violet	**blue Green**	**green** (*trans*)

The three compounds are hydrate isomers. Note that they yield different number of Cl$^-$ ions on ionization.

Commercial chromium(III) chloride is a mixture of the two green forms, the *trans*-dichloro form predominating; it produces a green aqueous solution. On standing for a week or more, the green solution gradually turns violet. From this solution, one may crystallize violet [Cr(H$_2$O)$_6$]Cl$_3$.

(iii) ***Coordination Isomerism***

Ligands may be interchanged between the complex cationic and anionic parts of a compound to produce coordination isomers; for example,

[Co(NH$_3$)$_6$][Cr(CN)$_6$] and [Cr(NH$_3$)$_6$][Co(CN)$_6$]

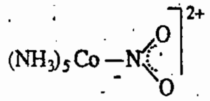
[Cr(NH$_3$)$_6$][Cr(SCN)$_6$] and [Cr(NH$_3$)$_4$(SCN)$_2$][Cr(NH$_3$)$_2$(SCN)$_4$]

[Pt^{II}(NH$_3$)$_4$][Pt^{IV}Cl$_6$] and [Pt^{IV}(NH$_3$)$_4$Cl$_2$][Pt^{II}Cl$_4$]

[Cu(NH$_3$)$_4$][Pt Cl$_4$] and [Pt(NH$_3$)$_4$][CuCl$_4$]

(iv) ***Linkage Isomerism***

While most ligands coordinate through a particular atom, some ligands may coordinate through either of two atoms. Such ligands are then called *ambidentate ligands*. Thus the nitro group usually coordinates through the N-atom, but in some cases coordination takes place through the O-atom :



Pentaammine(nitrito-*N*)cobalt(III) ion
or, Pentaammine(nitrito- κ *N*)cobalt(III) ion

$$[(NH_3)_5Co-O-N=O]^{2+}$$

Pentaammine(nitrito-*O*)cobalt(III) ion
or, Pentaammine(nitrito - κ *O*)cobalt(III) ion

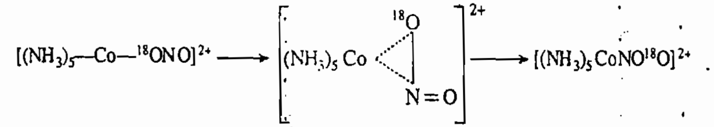
The pair of compounds thus represent a case of linkage isomerism. Cyanide (CN^-), thiocyanate (SCN^-) and sulphoxides ($R_2S=O$) may similarly give rise to linkage isomers :

M—SCN : thiocyanato-*S* M—NCS : thiocyanato-*N*
or, thiocyanato-κ*S* or, thiocyanato-κ*N*
M—CN : cyano-*C* M—NC : cyano-*N*
or, cyano-κ*C* or, cyano-κ*N*

Outline for preparation of $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$

$$\begin{tikzcd}
{[Co(NH_3)_5Cl]Cl_2} \arrow[r, "NaNO_2"] \arrow[d, "\text{dil } NH_3 \text{ aq.}"] & \underset{\textbf{red}}{[Co(NH_3)_5ONO]Cl_2} \arrow[d, shift right, "\text{let stand or warm, HCl}"'] \\
{[Co(NH_3)_5H_2O]Cl_3} \arrow[r, "NaNO_2\text{, conc HCl}"] & \underset{\textbf{yellow}}{[Co(NH_3)_5NO_2]Cl_2} \arrow[u, shift right, "\text{UV ray}"']
\end{tikzcd}$$

The red isomer is less stable than the yellow form and passes to it on standing or more rapidly on heating. The conversion occurs through an intramolecular rearrangement, as shown by ^{18}O study; no loss of ^{18}O is found even in presence of excess nitrite :



$$[(NH_3)_5—Co—^{18}ONO]^{2+} \longrightarrow \left[(NH_3)_5Co \cdots \begin{matrix} ^{18}O \\ | \\ N=O \end{matrix}\right]^{2+} \longrightarrow [(NH_3)_5CoNO^{18}O]^{2+}$$

The nitro-and nitrito-isomers of cobalt were first recognised by Jörgensen, Werner's contemporary, in 1894, but the compounds were known much before. The N-bonded isomer (yellow) was called the nitro-isomer and the O-bonded compound (red) was called the nitrito isomer. Other N-bonded complexes of cobalt, e.g., $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$ are yellow in colour; but the ions $[Co(H_2O)(NH_3)_5]^{3+}$ and $[Co(ONO)(NH_3)_5]^{2+}$ ions, containing one linkage via O-atom, are red. The M—ONO stretching vibrations of the red compounds are around 1060 cm^{-1}; the M—NO_2 frequency in the other compound lies around 820 cm^{-1}.

Such nitro-and nitrito isomers have also been established for Cr(III), Rh(III), Ir(III) and Pt(IV). Except Cr(III), in all other cases the nitrito isomer converts readily to the more stable nitro isomer.

[The nitrite ion can also coordinate in three other ways (see Ch. 22).]

The thiocyanate ion (SCN^-) is another example of an ambidentate ligand ; it can co-ordinate to metal atoms through the S or N-end. Sulphur-bonded complexes are usually formed by soft metals like Pd(II) and Hg(II); relatively hard metal ions like Cr^{3+} and Fe^{3+} form N-bonded thiocyanate complexes. Linkage iosmers like $[Pd(bipy)(NCS)_2]$ and $[Pd(bipy)(SCN)_2]$ have been prepared. They may be distinguished by infrared spectroscopy : in case of M—SCN bonding, the C—S stretching vibration lies in the range 690 - 720 cm^{-1}; for M—NCS bonding, the C—S stretching frequency is higher in the range 780 - 860 cm^{-1}. The C—N stretching absorption for S-bonded complexes is sharp and above 2000 cm^{-1} while it is broad and below 2000 cm^{-1} for N-bonded complexes.

[**Sec. 26.4.3** *Linkage isomerism*]

The cyanide ion (CN^-) is also an ambidentate ligand, but stable discrete complexes containing M-NC bonding are not known. But many solids (see Prussian Blue) contain metal ions bridged through cyanide groups, the C-end to one metal ion and the N-end to another metal ion.

$$\underset{\textbf{brick red}}{KFe^{II}[Cr^{III}(CN)_6]} \quad \text{and} \quad \underset{\textbf{dark green}}{KCr^{III}[Fe^{II}(CN)_6]}$$

are actually linkage iosmers which may be obtained by reactions like

$$FeSO_4 + K_3Cr(CN)_6 \longrightarrow \underset{\textbf{brick red}}{KFe^{II}[Cr^{III}(CN)_6]} + K_2SO_4$$

$$KFe^{II}[Cr^{III}(CN)_6] \xrightarrow{100^\circ} \underset{\textbf{dark green}}{KCr^{III}[Fe^{II}(CN)_6]}$$

The initial brick red precipitate contains Cr—CN coordination and a chain is formed with Fe^{III} coordinated by the available N-end :

$$—Fe^{II}—N \equiv C—Cr^{III}—C \equiv N—Fe^{II}—N \equiv C—Cr^{III}—$$

This rearranges to the dark green compound having Fe^{II} coordinated by carbon :

$$—Fe^{II}—C \equiv N—Cr^{III}—N \equiv C—Fe^{II}—C \equiv N—Cr^{III}—$$

The driving force for the change is largely derived from the greater crystal field stabilization energy (CFSE) of strong field C-linkage to the Fe(II) (low spin octahedral, t_{2g}^6 configuration) rather than to Cr(III) (t_{2g}^3 configuration) (see Chapter 27).

Q. 26.10 *Cr(III) - SCN bonded thiocyanato complexes slowly rearrange to give the N-bonded Cr(III) - NCS isothiocyanato complex. Comment.*

Hint : Cr^{3+} is a hard metal ion and hence prefers the hard donor N in preference to softer S donor.

Carbon monoxide always coordinates through the carbon end while functioning as a monodentate ligand. However, spectroscopic data at 6-10 K on cocondensation of Au atoms with large excess of CO indicated the formation of isocarbonyl(carbonyl)gold, $C \equiv O - Au - C \equiv O$. Cocondensation of Au and CO in rare gas matrix gives the normal isomer, $O \equiv C - Au - C \equiv O$.

When an ambidentate ligand preferentially coordinates through one end to a metal, the preference may be largely correlated to electronic or steric effects or both. Thus, we have the complexes

$$\underset{\textbf{(S-bonded)}}{cis\text{-}[Pt(SCN)_2(NH_3)_2]} \quad \text{and} \quad \underset{\textbf{(N-bonded)}}{cis\text{-}[Pt(NCS)_2(PR_3)_2]}$$

Ammonia is a good σ-donor ligand, but it cannot form π-bond as it has no vacant acceptor orbital to set up back-bonding. Hence the π-bonding *d*-orbitals on platinum are preferentially bonded to sulphur which can establish additional π-bond with the metal. But the phosphine ligands can establish stronger π-back-bonds, thereby engaging the *d*-orbitals of platinum. Coordination of thiocyanate now takes place through the nitrogen atom.

The "symbiotic" tendency, that is, hard ligands favouring coordination through hard donor atoms and so on, is observed in a number of complexes by ambidentate ligands, for example,

$$[Co(NH_3)_5(NCS)]^{2+} \quad \text{but} \quad [Co(CN)_5(SCN)]^{3-}$$

This general idea works satisfactorily for many octahedral complexes. In square planar complexes, however, the symbiotic tendency goes against the π-bonding competition : soft, π-bonding ligands should not encourage competition from other soft ligands; rather, they would prefer a high charge density on the metal through hard σ-donors. π-competition becomes more important in such cases. Tetrahedral complexes are also not adequately covered by the idea of symbiosis.

(v) "*Polymerization Isomerism*"

The name is applied to coordination compounds which have the same empirical formula but molecular weights which are multiples of a simple formula weight, for example,

$$[Co(NH_3)_4(NO_2)_2]\,[Co(NH_3)_2(NO_2)_4]$$
$$[Co(NH_3)_5NO_2]\,[Co(NH_3)_2(NO_2)_4]_2$$
$$\text{and}\ [Co(NH_3)_6]\,[Co(NO_2)_6]$$

have the same empirical formula $[Co(NH_3)_3\,(NO_2)_3]$.

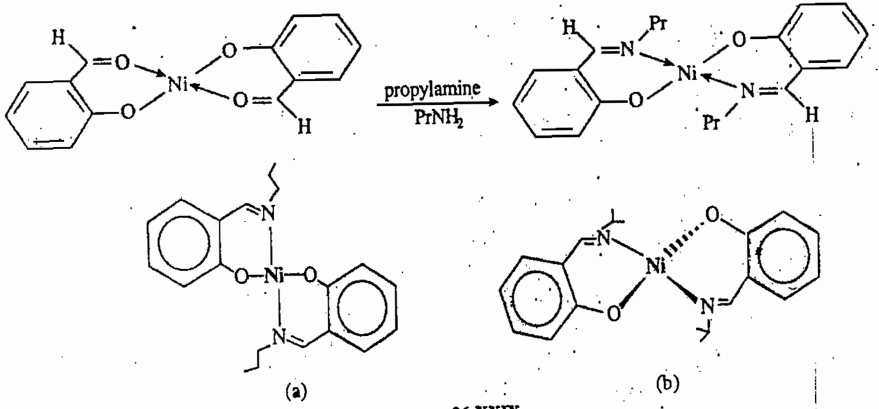
Similarly $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]\,[PtCl_4]$ have the same empirical formula. However, the term polymerization is not properly applied in this case since the compounds are not formed by repetition of any unit building block, as required in polymerization. Also, polymers are not isomers.

(vi) *Ligand Isomerism*

This is caused by coordination through isomeric ligands such as NMe_3 and $CH_3CH_2CH_2NH_2$. The following are examples of ligand isomerism.

$[CoCl_2(pn)_2]Cl$ and $[CoCl_2(tn)_2]Cl$ pn = propylenediamine
tn = trimethylenediamine
$[Ag(pic)_2]^-$ and $[Ag(nic)_2]^-$ pic = picolinate ion (pyridine 2-carboxylate)
nic = nicotinate ion (pyridine 3-carboxylate)

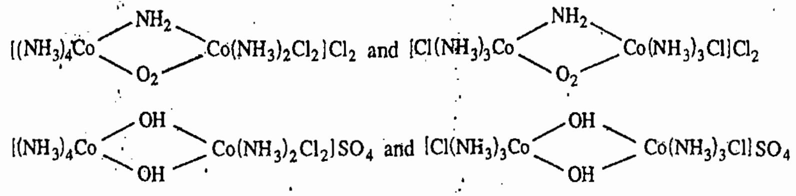
Changing an alkyl chain in a ligand from linear to a branched structure may sometimes siginificantly influence the structure of a complex. When *bis*-(salicylaldehydato)nickel(II) is reacted with *n*-propylamine, a square planar complex is obtained (26-XXIX a); but when isopropylamine is used, the geometry round Ni gets distorted towards tetrahedral structure owing to greater steric requirement of the isopropyl group (26-XXIX b).



26-XXIX

(vii) *Coordination Position Isomerism*

Such isomerism may occur in multinuclear complexes with different arrangement of the coordinating groups relative to the metal ions present, for example,

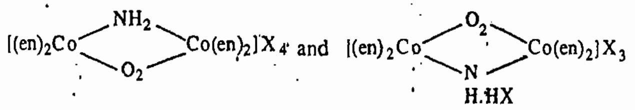


$$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\diamond}}Co(NH_3)_2Cl_2]Cl_2 \text{ and } [Cl(NH_3)_3Co\overset{NH_2}{\underset{O_2}{\diamond}}Co(NH_3)_3Cl]Cl_2$$

$$[(NH_3)_4Co\overset{OH}{\underset{OH}{\diamond}}Co(NH_3)_2Cl_2]SO_4 \text{ and } [Cl(NH_3)_3Co\overset{OH}{\underset{OH}{\diamond}}Co(NH_3)_3Cl]SO_4$$

(viii) *Valence Isomerism*

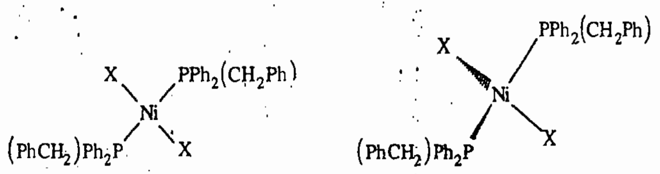
The term was used by Werner to complex species in which the same group is held in one compound by primary valency and in another compound by secondary valency, for example,



$$[(en)_2Co\overset{NH_2}{\underset{O_2}{\diamond}}Co(en)_2]X_4 \text{ and } [(en)_2Co\overset{O_2}{\underset{\underset{H.HX}{N}}{\diamond}}Co(en)_2]X_3$$

(ix) *Conformation Isomerism*

This may arise through different geometrical arrangement of the same donor atoms around a metal ion. A typical example is



Square Planar **Tetrahedral**

where X may be Cl, Br or I. Crystals of the paramagnetic complex $[NiBr_2\{PPh_2(PhCH_2)\}_2]$ contain both the square planar and the tetrahedral forms in the same unit cell.

26.4.4 Stereoisomerism

The most significant point in Werner's theory was the proposal of directional character of the secondary valencies of metals and the prediction of stereoisomers. Werner himself prepared numerous compounds to establish his theory.

As in carbon chemistry, stereoisomers which are not superimposable on their mirror images are called *enantiomers*; stereoisomers which do not possess mirror image relation are called *diastereoisomers*. A molecule without any symmetry (except C_1) is classified as an *asymmetric* molecule while a molecule without any rotation reflection axis (S_n - axis) is classed as a *dissymmetric* molecule (it may or may not possess a C_n axis). A complex is optically active if its structure cannot be superimposed on its mirror image (enantiomers or enantiomorphs) - the molecules are said to be *chiral* (chirality = handedness). In the next two sections we shall discuss geometric and optical isomerism in coordination compounds.

Geometric Isomerism

Geometric isomers differ in the spatial arrangement of the atoms within the same structural framework — the arrangement in a particular isomer is called a configuration. A pair of enantiomers is classified as the same geometric isomer. The occurrence of geometric isomerism is determined by the activation energy necessary for the interconversion. The staggered and eclipsed conformations of ethane undergo rapid interconversion even at very low temperatures. But the *cis* - and *trans* - forms of alkenes require a high activation energy for transformation of one form to another since rotation about a C = C bond is involved. So the two configurations persist unchanged for long at ordinary temperatures.

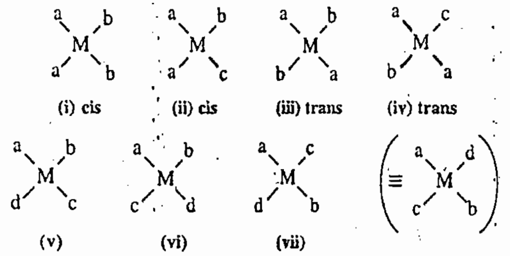
The terms *cis* - and *trans*-, meaning "on the same side" and "across" in Latin, were introduced by van't Hoff as early as 1874 in describing the geometric isomers of alkenes. The terms are still in use. The *E* (*entgegen*, opposite) and *Z* (*zusammen*, together) nomenclature is also used in organic chemistry.

We shall discuss geometric isomerism in complex compounds having coordination numbers four and six.

Coordination number 4

The geometries observed in this coordination number are square planar and tetrahedral. A regular tetrahedral species Ma_4, Ma_2b_2 or Mabcd (a, b, c, d = unidentate ligands) exists in only one geometric form. A square planar species of the type Ma_2bc or Ma_2b_2 can exist in cis– and trans– forms, while a planar complex of the type Mabcd may have three geometric forms :

	Tetrahedral	Square Planar
Ma_4	no isomer	no isomer
Ma_2b_2,Ma_2bc	"	two isomers for each, (i - iv)
Mabcd	"	three isomers, (v - vii)



(i) cis (ii) cis (iii) trans (iv) trans

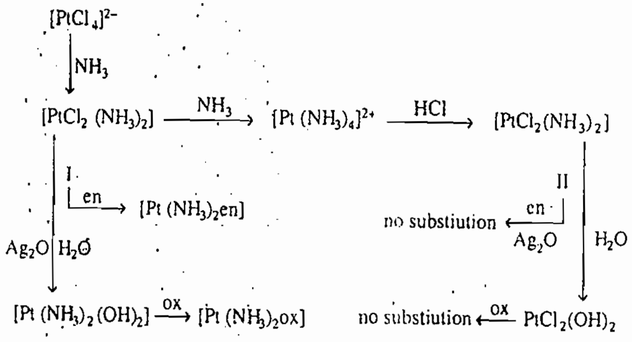
(v) (vi) (vii)

$[PtCl_2(NH_3)_2]$ exists in two isomeric forms, while three isomers are known for $[Pt(NO_2)(py)(NH_3)(NH_2OH)]NO_2$. This led Werner (1893) to conclude that the complexes were square planar. In fact, one can at best say that the complexes are not tetrahedral; if the plantinum atom were out of plane of the ligands at the apex of square pyramid, the same number of isomers would result. However, X-ray studies have confirmed that the above complexes of platinum are really square planar. Other physical methods used to differentiate between geometric isomers are measurement of dipole moment and vibrational spectroscopy. The *trans*-$[Pt(NH_3)_2Cl_2]$ has no dipole moment and shows a simpler vibrational spectrum than the *cis*- isomer. Similarly, the two square-planar isomers of $[Pt\ Br\ Cl(PR_3)_2]$ (PR_3 ≡ a trialkyl phosphine ligand) have different P-31 nmr spectra. The *trans*- compound shows a single ^{31}P group of lines but the *cis*- isomer shows two distinct ^{31}P resonances each similar to the single resonance region of the *trans*-isomer.

[**Sec. 26.4.4** *Stereo isomerism*]

The *cis*- and *trans*- isomers may be chemically distinguished by the fact that two unidentate ligands only in *cis*-position can be replaced by a bidentate ligand; bidentate ligands cannot span across the square plane to bridge two *trans*- positions.

The following scheme of interconversion among square planar complexes of platinum(II) may be illustrative



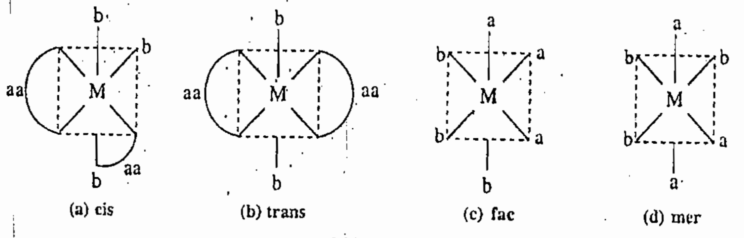
ox = oxalate

It is easily concluded that I is the *cis* isomer and II is the *trans* isomer.

However, when a bidentate ligand is replaced by two unidentate ligands, the product may or may not be *cis*; rearrangement may occur during the course of the reaction.

Coordination Number 6

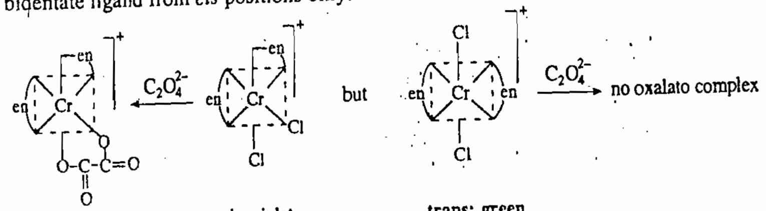
An octahedral complex of the type Ma_6 or Ma_5b exists in only one form but complexes of the type Ma_4b_2 or $M(aa)_2b_2$(aa = bidentate ligand) may have *cis* and *trans* - isomers (26-XXX a, b). For compounds of the type Ma_3b_3 also, two isomers are possible - (i) one in which the three a-groups are all adjacent at one face of the octahedron (facial isomer, 26-XXX c) or (ii) one in which the three a-groups occupy positions such that two are *trans* to each other (meridional isomer, 26-XXX d). $[Co(NH_3)_3(NO_2)_3]$ and $[Rh(py)_3Cl_3]$ provide examples of such isomers.



(a) cis (b) trans (c) fac (d) mer

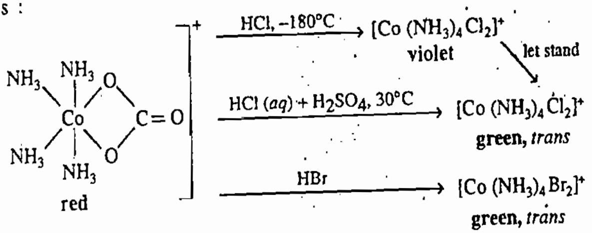
26-XXX

In this coordination number also, two unidentate ligands may be replaced by a bidentate ligand from *cis* positions only.



cis; violet trans; green

As explained in connection with C. N. 4, here also replacement of a bidentate group by two unidentate ligands does not guarantee a *cis* product, as exemplified in the following conversions :



Since the violet dichloro complex is nearly the same colour as the carbonato complex, it may be supposed to have *cis* - dichloro arrangement. Although in this particular case the assignment is correct, this is not always so as shown in other two reactions where the green complex (presumably *trans*) is formed directly. HBr directly gives the *trans*-substituted product since *cis*-occupancy of the larger bromine atoms is not favourable.

Only octahedral complexes of the type Ma_4b_2 (a, b = unidentate ligands) will yield two geometrical isomers- 1, 2 and 1, 6 in Figure 26.16. A planar hexagonal and trigonal prism would give rise to three isomers each for such complexes — 1, 2; 1, 3 and 1, 4 for planar and 1, 2; 1, 5 and 1, 6 for prism (Fig. 26.16). Werner concluded the octahedral arrangement of Co(III)-complexes from the isolation of two isomers for $[Co(NH_3)_4Cl_2]^+$ and similar compounds. Geometrical isomers differ in colour, solubility and reaction rates. Thus in the following *cis* and *trans* complexes of Co^{III}, rates of replacement of Cl^- by water is found to be higher for the *cis* - isomer (*k* at 25°C, min^{-1}).

cis - $[Co(en)_2Cl_2]^+$	$1{\cdot}5 \times 10^{-2}$	*trans* - $[Co(en)_2Cl_2]^+$	2×10^{-3}
cis - $[Co(en)_2(NO_2)Cl]^+$	7×10^{-3}	*trans* - $[Co(en)_2(NO_2)Cl]^+$	7×10^{-4}

Geometric isomers may be separated by simple crystallization techniques, by chromatography, or in certain cases by vacuum distillation.

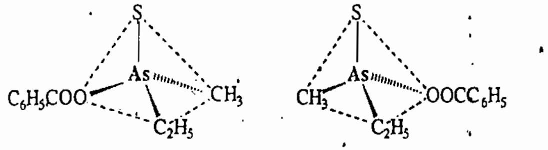
Optical Isomerism

A complex is optically active if its structure cannot be superimposed on its mirror image. This chiral property can be detected only by measuring devices which are themselves chiral. Interaction with plane polarized light is one such procedure. Ordinary light virbates in all directions perpendicular to its direction of propagation. When passed through a Nicol prism, the transmitted light vibrates in only one direction due to restrictions imposed by the atoms in the crystal. The plane in which the light now vibrates is called the plane of polarization of the light and the light is said to be plane polarized light.* When a beam of plane polarized light is passed through an optically active substance, the plane of polarization is changed. The extent of this change depends upon the wavlength of the light, the concentration of the optically active species along the path of light, the temperature, the nature of the solvent and the nature of the optically active compound. When other things are unchanged, the rotations caused by two enantiomers (mirror image isomers) are equal in magnitude but opposite in direction. The enantiomer which rotates the plane of plane polarized light to the right is given a '+' sign and the other one is given a '–' sign.

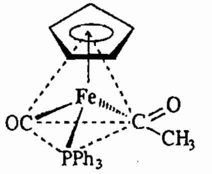
The variation of the angle of rotation with the wavelength of light used is known as optical rotatory dispersion (ORD).

The condition necessary for a molecule to exhibit optical isomerism is the absence of a rotation-reflection axis (S_n). An easy to judge criterion for optical activity, however, is the absence of a plane or a center of symmetry.

In organic chemistry, examples of optical activity involving a tetrahedral carbon atom are numerous. In case of inorganic complex compounds, much greater kinetic reactivity does not readily allow the resolution of tetrahedral complexes of the type Mabcd. Two optically active stereoisomers of the arsenic compound (26-XXXI a) have been resolved. A few other examples of Fe, Mn and Ti complexes, mostly, organometallic; are also known (26-XXXI b).

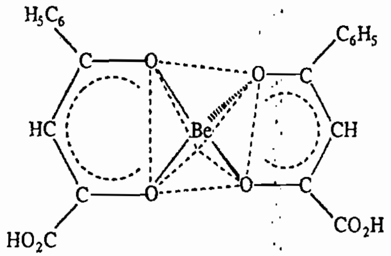


26-XXXI (a)



26-XXXI (b)

Tetrahedral complexes containing unsymmetrical chelate ligands are prepared relatively easily and some of them have been resolved, for example bis(benzoylacetonato) beryllium(II) and bis (benzoylpyruvato) beryllium(II) (26-XXXII). It may be observed that bis(acetylacetonato) beryllium(II) would not be optically active.



26-XXXII

Bis-(benzoylpyruvato)beryllium(II)

Other tetrahedral complexes of Be, B, Zn and Cu(II) have been resolved, often partially.

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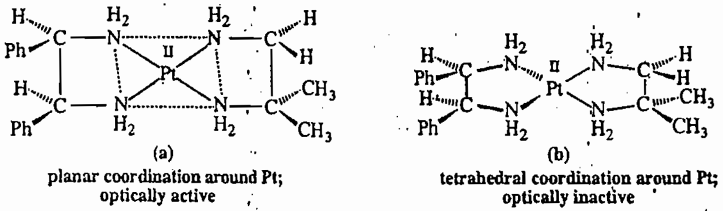
* This is a gross oversimplification. When a beam of plane polarized light is viewed along the direction of propagation, the electric vector (and also the magnetic vector) appears to be confined to a plane. Further clarification may be had from more advanced text-books.

Square planar complexes are generally not optically active since the molecular plane acts as a plane of symmetry. Mills and Quibell (1935) ingeniously prepared a square planar complex in which the plane of symmetry has been eliminated by careful choice of ligand : (*meso* - stilbene diamine)(isobutylenediamine) palladium(II) and platinum(II) complexes were resolved (26-XXXIII a).



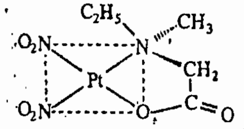
(a) planar coordination around Pt; optically active

(b) tetrahedral coordination around Pt; optically inactive

26-XXXIII

It may be noted that the complexes would not be optically active if the geometry around the metal were tetrahedral (26-XXXIII b). A mirror plane passes through the metal and N-atoms of isobutylenediamine.

Optical isomerism may also appear in square planar complexes having an asymmetric ligand, for example the compound dinitro(N-methyl-N-ethylglycinato) platinate (II) (Kuebler and Bailar, 26-XXXIV) is optically active due to the presence of the asymmetric nitrogen atom



26-XXXIV

Octahedral complexes offer larger class of optically active complexes. No complex with six different unidentate ligands (Mabcdef type) have been resolved. The two classes that have been most extensively studied are the tris-bidentate $M(L\text{-}L)_3$ and bis-bidentate $[M(L\text{-}L)_2X_2]$ or $[M(L\text{-}L)_2XY]$ complexes like $[Co(en)_3]^{3+}$, $[Cr(ox)_3]^{3-}$ or *cis* - $[Co(NH_3)Cl(en)_2]^{2+}$ ions.

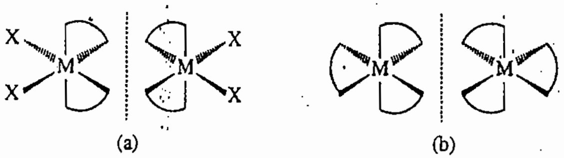


Fig. 26.20

Non-superimposable mirror images : (a) *cis*-MX_2(chelate)$_2$ and (b) M(chelate)$_3$.

"Purely inorganic" optically active compound

Werner succeeded in resolving a large series of complexes including Co(III), Cr(III), Fe(II) and Rh(III) with chelating ligands like ethylenediamine, oxalate and bipyridine. However, some of his critics tried to associate the optical isomerism of these complexes with the presence of carbon atom in the ligands. Werner then prepared an optically active complex compound having *no carbon atom* : tris [tetraammine-μ-dihydroxocobalt(III)]cobalt(III) was the first example of a "purely inorganic" optically active compound. In this compound, three bidentate $[Co(NH_3)_4(OH)_2]^+$ ions are arranged octahedrally around a central Co^{3+} ion (Fig. 26.21 a). Since non-carbon chelating agents are difficult to prepare, such examples are rare. Two other examples are *cis*-diaquabis(sulfamido)rhodate(III) (Fig. 26.21b) and $[Cr(HPO_4)_3]^{3-}$.

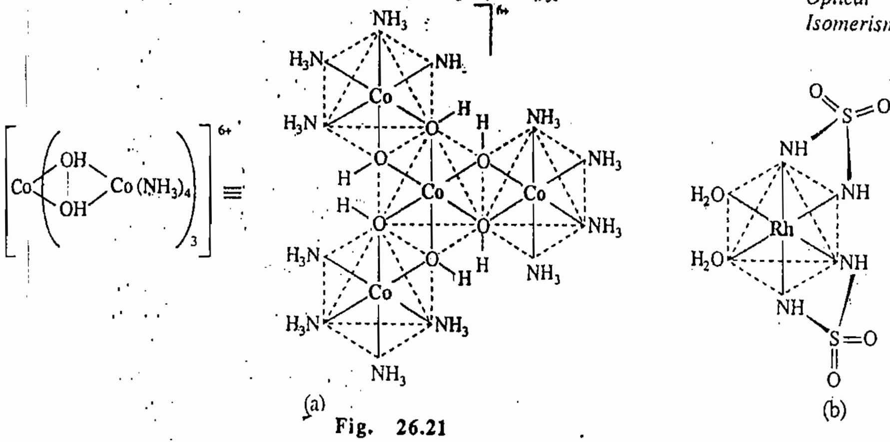


Fig. 26.21

Examples of "purely inorganic" optically active compounds :
(a) $[Co\{Co(NH_3)_4(OH)_2\}_3]^{6+}$ (b) cis-$[Rh(H_2O)_2\{SO_2(NH)_2\}_2]^-$.

However, the presence of chelating ligand is not indispensable for occurrence of optical isomerism. In Fig. 26.22 is shown the optical isomers of one geometrical isomer of $[Pt(NH_3)_2(NO_2)_2Cl_2]$.

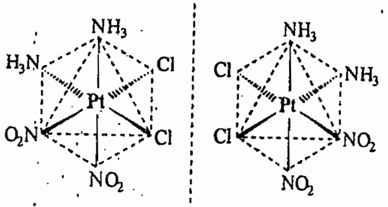
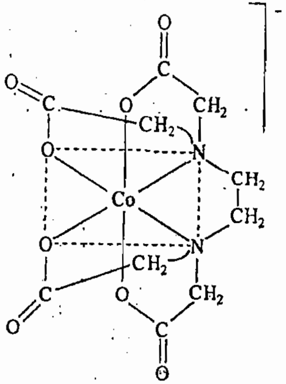


Fig. 26.22

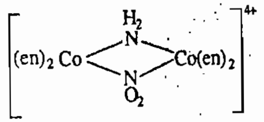
Optical isomers of $[Pt(NH_3)_2(NO_2)_2Cl_2]$.

Optical isomerism is also exhibited by octahedral complexes of sexidentate ligands, e.g. the $[Co(edta)]^-$ ion is chiral (26-XXXV).



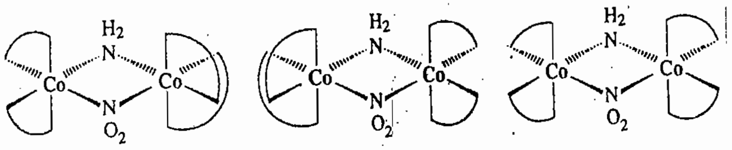
26-XXXV

Compounds containing more than one chiral center have also been studied. Werner himself separated the complex shown in 26-XXXVI into three isomers - a pair of optically active *dl* isomers and an internally compensated inactive isomer (*meso*) :



$$\left[(en)_2Co\overset{H_2}{\underset{O_2}{<\!N,N\!>}}Co(en)_2\right]^{4+}$$

26-XXXVI

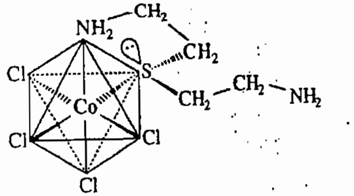


(a) (b) (c)

Fig 26.23

Three stereoisomers of the complex shown in 26-XXXVI;
a and b are mirror images of one another; c is the optically inactive *meso* form.

Optical isomerism arising from ligand dissymmetry is also known in octahedral complexes. The example shown in 26-XXXVII is interesting because here dissymmetry is induced around the sulphur as a result of coordination. The three bonds and the lone pair on S describe a tetrahedral geometry around the S atom. The compound has been resolved.

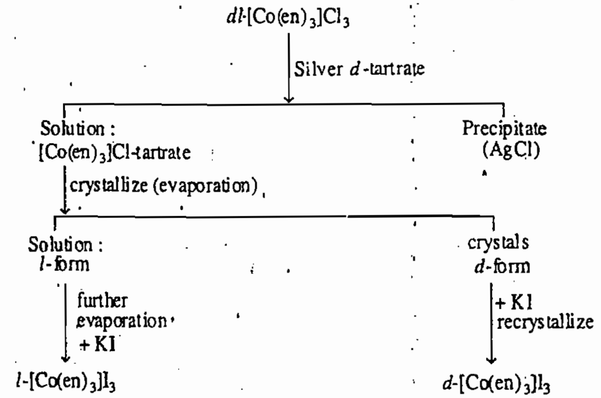


26-XXXVII

Resolution

Only in rare cases, the enantiomers of a complex compound form different visually recognizable crystals. Werner observed such behaviour with *cis* - $[Co(en)_2(NO_2)_2]^+$ salts. In most other cases, resolution of optical isomers involve interaction of the enantiomeric pair of the racemic mixture with some other chiral species. Thus, if a solution containing the isomers of $[Co(en)_2(NO_2)_2]^+$ is treated with potassium antimonyl(+)-tartrate, the [(–)-*cis*-$Co(en)_2(NO_2)_2$] [(+)-$SbOC_4H_4O_6$] combination which is only slightly soluble can be separated by crystallization, while the [(+)-*cis*-$Co(en)_2(NO_2)_2$] [(+)-$SbOC_4H_4O_6$] is left in solution. Similarly, (+)$[Co(en)_3]Cl$ [*d* - tartrate] crystallizes readily while the (–) complex forms much more soluble salt with *d*-tartrate. After resolution, the tartrate salts may be converted to chlorides by the action of concentrated HCl. Chiral anionic complexes like $[M^{III}(ox)_3]^{3-}$ may be resolved using an optically active cation such as those formed by bases strychnine or brucine. Resolved complex ions like $[Co(edta)]^-$, $[Co(en)_3]^{3+}$ may also be used as resolving agents.

Scheme for the resolution of *dl*-$[Co(en)_3]Cl_3$



In order to determine the absolute configuration of a chiral complex, the coordination entity is viewed along a threefold rotation axis of a regular octahedron (refer Fig. 26.17). For trischelate complexes, which have been most widely studied for optical activity, the ligands will appear as forming a helix. If the twist of the helix is to left (left hand screw, anticlockwise), it is now designated as Λ and if the twist of the helix is to right (right hand screw, clockwise), it is designated Δ. This is illustrated in Fig. 26.24 for $[Co(en)_3]^{3+}$.

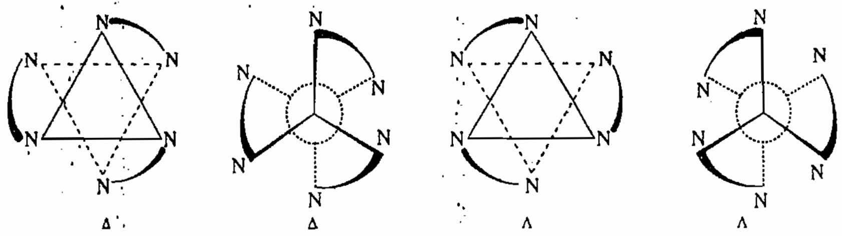


Fig. 26.24

Assignment of absolute configuration for [Co $(L\text{-}L)_3$]-type complexes.

(Note that the designations Δ and Λ are independent of the angle and direction of rotation of plane polarized light by the compound which changes with the wavelength of light.) It has been shown that the isomer which is (+) $[Co(en)_3]^{3+}$ at λ = 589 nm is the Δ isomer.

26.5 NOMENCLATURE OF COORDINATION COMPOUNDS

Main rules according to IUPAC recommendations, 1990 are summarized below :

26.5.1 Writing the Formula

(i) In writing the formula of a coordination species, the symbol of the central atom is written first.

(ii) This is followed by the ionic ligands and then by the neutral ligands.

Within each category, alphabetical order of the first letter (or next) in the formula of the ligands is followed.

(iii) Ligands containing carbon and hydrogen only are grouped under C.

For organic ligands containing heteroatoms, the position is determined by the alphabetical sequence of the heteroatom (for example N of C_5H_5N).

If two ligands are present with the same defining atom, one with fewer such atoms preceedes that with more. When the numbers of defining atoms are same, subsequent symbols are used to determine the sequence. Thus C_5H_5N preceedes NH_3 and $C_2H_8N_2$ preceedes $C_{10}H_8N_2$.

(iv) The entire coordination entity is enclosed with square brackets.

(v) Common abbreviations for ligands may be used. They should be lower case and enclosed in parenthesis.

A few examples will be illustrative :

$[Ru(NH_3)_5(N_2)]Cl_2$

$[PtBrCl(NO_2)NH_3]^-$

$[PtCl_2(C_5H_5N)NH_3]$

$[Al(OH)(H_2O)_5]^{2+}$

$K_4[Fe(^{14}CN)_6]$

26.5.2 Naming Mononuclear Coordination Compounds

(i) The central atom is named at the end in accordance with rule (iv) stated below.

(ii) This is preceeded by the names of ligands in alphabetical order.

Numerical prefixes (like di, tri- etc.) indicating the number of ligands are ignored. Thus, the position of dichloro is determined by the alphabet 'C' while diphenylphosphine is determined by '*d*' since this is the overall name of the ligand.

(iii) The prefixes di-, tri- etc. are replaced by bis-, tris- etc. (derived from ordinals) in complex expressions and in cases of probable ambiguity, e.g., bis(methylamine) to exclude dimethylamine).

(iv) All anionic coordination entities are ended with -ate; no distinguishing termination is used for cationic or neutral coordination entities.

The oxidation number of the central atom in roman numeral or arabic zero is indicated in parentheses after the name of the central atom (Stock number). Positive signs are not used before the oxidation numbers. No space is left between this number and the name of the central atom.

Alternatively, the net charge on the coordination entity may be included in parentheses in arabic numbers follwed by the charge sign (Ewens Bassett number). In this case also, no space is left after the name of the central atom.

Examples

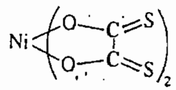
1. $K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III) potassium hexacyanoferrate(3–)
2. $[CoCl(H_2O)_2(NH_3)_3]Cl_2$	triamminediaquachlorocobalt(III) chloride triamminediaquachlorocobalt(2+) chloride
3. $[CoCl(NO_2)(NH_3)_4]Cl$	tetraamminechloronitrito-*N*-cobalt(III) chloride tetraamminechloronitrito-*N*-cobalt(1+) chloride
4. $[PtCl(NH_2CH_3)_2(NH_3)]Cl$	amminechlorobis(methylamine)platinum(II)chloride amminechlorobis(methylamine)platinum(1+) chloride
5. $[Ru(HSO_3)_2(NH_3)_4]$	tetraamminebis(hydrogensulfito)ruthenium(II)
6. $K_2[OsCl_5N]$	potassium pentachloronitridoosmate(VI) potassium pentachloronitridoosmate(2–)
7. $[Co(NH_2)_2(NH_3)_4]OCH_3$	diamidotetraamminecobalt(III) methoxide
8. $[CoN_3(NH_3)_5]SO_4$	pentaammineazidocobalt(III) sulfate
9. *cis*-$[PtCl_2(Ph_3P)_2]$	*cis*-dichlorobis(triphenylphosphine)platinum(II) *cis*-dichlorobis(triphenylphosphine)platinum
10. $[Pt(py)_4][PtCl_4]$	tetrakis(pyridine)platinum(II) tetrachloroplatinate(II) tetrakis(pyridine)platinum(2+) tetrachloroplatinate(2–)
11. $K[PtCl_3(C_2H_4)]$	potassium trichloro(η^2-ethene)platinate(II) potassium trichloroetheneplatinate(1–)
12. $[PtCl_2(C_2H_4)(NH_3)]$	amminedichloro(η^2-ethene)platinum(II)*

[* The symbol η with a numerical superscript (hapticity) indicates the number of ligating atoms in the ligand which bind to the metal atom.]

13. $Na_2[Fe(CN)_5NO]$	sodium pentacyanonitrosylferrate(2–)
14. $Na_4[Fe(CN)_5NOS]$	sodium pentacyano(nitrosylsulfido)ferrate(4–)
15. $K_3[Fe(CN)_5CO]$	potassium carbonylpentacyanoferrate(3–)

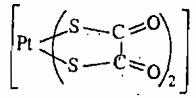
(v) Polydentate ligands with more than one donor site are specified by mentioning the ligating atoms in italicized symbols :

16.



bis (dithiooxalato-*O*, *O'*)nickel(II)

17.



bis(dithiooxalato-*S*, *S'*)platinum(II)

26.5.3 Polynuclear Complexes

Polynuclear complexes may be complicated enough to render their naming very difficult. The guidelines for such cases remain outside the scope of this book and may be had from the "red book" for IUPAC nomenclature. A few selected rules for relatively simpler cases are mentioned here.

Nomenclature for polynuclear complexes may be merely compositional nomenclature when it merely conveys the stoichiometric proportions of various moieties present. A better description is obtained from the structural nomenclature which attempts to specify the atom connectivities.

Bridging ligands are indicated by "μ-" before the ligand name and separated from rest of the ligands by hyphens. Multiplicative prefices are used when the bridging ligand occurs more than once (e.g., tri-μ-).

If the same ligand occurs as bridging as well as nonbridging, the bridging ligand is mentioned first (e.g., μ-chlorodichloro...... etc.).

[Sec. 26.5.2 *Nomenclature*]

When a bridging ligand joins two atoms, it is simply represented by 'μ-'; bridging between n atoms ($n > 2$) is shown by "μ_n-".

Metal-metal bonding may be indicated separately in parentheses after the name of the coordination entity before the ionic charge (Ewens Bassett No); the metals involved are shown within the parentheses by their italicized symbols.

When the symmetry of the entity permits, simpler names are used by multiplicative prefices.

18. $[(NH_3)_5Cr—OH—Cr(NH_3)_5]Cl_5$
    μ-hydroxo-bis(pentaamminechromium)(5+) chloride
19. $[Br_4ReReBr_4]^{2-}$
    bis(tetrabromorhenate)(*Re*—*Re*)(2–)
20. $[Mn_2(CO)_{10}]$
    bis(pentacarbonylmanganese)(*Mn*—*Mn*)
    or decacarbonyldimanganese(*Mn*—*Mn*)

Naming of unsymmetrical dinuclear coordination entities is complicated. The central atoms are numbered 1, 2 etc. according to certain priority sequence and the ligating atoms may be indicated by K, for example,

21. $(CO)_5Re—Co(CO)_4$
    nonacarbonyl-1K^5C2K^4C-cobaltrhenium(*Co*—*Re*).

26.5.4 Names of ligands

(i) Names of anionic ligands (both organic and inorganic) end in –o. The anion names are usually changed accordingly :

—ide ⟶ ido; —ite ⟶ ito; —ate ⟶ ato.

Exceptions are halides (halo), hydroxides (hydroxo), peroxides (peroxo) etc.

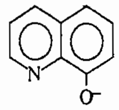
(ii) Names of inorganic anionic ligands containing numerical prefices (e.g. triphosphato) and the thio-, seleno-, and telluro- analogues of oxoanions having more than one oxygen atom (e.g. thiosulfato) are kept in enclosing mark.

(iii) Names of neutral and cationic ligands are used without modification and placed within enclosing mark except for aqua, ammine, carbonyl and nitrosyl.

Systematic names for some common ligands and their alternative names are given below :

Formula	Systematic Name	Alternative
H^- (D^-)	hydrido ([^{2}H] hydrido)	
H_2	dihydrogen	
F^- (Cl^- etc.)		fluoro (chloro etc.)
ClO_4^-	[tetraoxochlorato(1–)]	perchlorato
IO_6^{5-}	[hexaoxoiodato(5–)]	orthoperiodato
O^{2-}	oxido	oxo
S^{2-}	sulfido	thio
$(O_2)^{2-}$	[dioxido(2–)]	peroxo (peroxy)
$(O_2)^-$	[dioxido(1–)]	hyperoxo, superoxido
$(O_3)^-$	[trioxido(1–)]	ozonido
$(S_2)^{2-}$	[disulfido(2–)]	dithio
H_2O		aqua
OH^-	hydroxido	hydroxo, hydroxy
CH_3O^-	(methanolato)	methoxo
CO	(carbon monoxide)	carbonyl
CH_3COO^-	(ethanoato)	(acetato)
$C_2O_4^{2-}$	(ethanedioato)	(oxalato)
$S_2O_3^{2-}$	[trioxothiosulfato(2–)]	[thiosulfato(2–)]
SO_4^{2-}	[tetraoxosulfato(2–)]	[sulfato(2–)]
N_2	(dinitrogen)	
P_4	(tetraphosphorus)	
N^{3-}	(nitrido)	
NF_3	(trifluoroazane)	(nitrogen trifluoride)
NH_3	(azane)	ammine
NH_2^-	azanido	amido
CH_3NH_2	methanamine	(methylamine)
H_2NOH	(hydroxyazane)	(hydroxylamine)
NO_3^-	[trioxonitrato(1–)]	nitrato
NO_2^-	[dioxonitrato(1–)]	nitrito-*N*, nitrito-*O*, nitro
NO	(nitrogen monoxide)	nitrosyl

Organic ligands

Formula	Systematic name	Alternative
$H_2NCH_2CH_2NH_2$	1, 2-ethanediamine	(ethylenediamine)
$H_2NCH_2CH_2OH$	2-aminoethanol	(ethanolamine)
$CH_3COCHCOCH_3^-$	2, 4-pentanedionato	(acetylacetonato)
$CH_3C(NOH)C(NO)CH_3^-$	2, 3-butanedione dioximato	(dimethylglyoximato)
	8-quinolinolato	(8-hydroxyquinolinato) ('oxine' is not recommended)

SUMMARY

Complex (co-ordination) compound : A complex is said to have formed when a central atom attaches to it a number of ions or molecules to form a distinct entity in which the number of atoms directly linked to the central atom exceeds its normal covalency.

The groups bonded to the central atom are called ligands; they contain one or more donor atoms capable of donating a pair of electrons.

Werner's theory : Alfred Werner (1866-1919) was a pioneer in the systematic study of complex compounds. According to his theory, metals possess two types of valency—(i) primary or ionizable valency and (ii) secondary or nonionizable valency. The secondary valencies may also be satisfied by neutral molecules or ions and are directed in space in definite geometrical dispositions around the central metal atom. Werner predicted stereoisomerism among inorganic complex compounds and verified his theory by actually preparing a large number of geometrical and optical isomers.

Types of Ligands : Ligands are essentially Lewis bases which can coordinate to a metal through one or more atoms possessing non-bonding electron pairs. Ligands which coordinate only through one atom are called monodentate ligands. Ligands coordinating through two or more atoms are called didentate (bidnetate), tridentate etc. A ligand which shows different denticity is called a flexidentate ligand (e.g., edta, which may behave as a hexadentate, tetradentate or pentadentate ligand). Certain ligands can coordinate through either of two coordination sites (e.g., SCN^-); such ligands are called ambidentate ligands.

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Chelates : When a multidentate ligand coordinates to a metal ion from more than one donor site forming a ring with the metal, it is said to be a chelating ligand and the resulting compound is said to be a chelate complex. Ethylenediamine, $NH_2CH_2CH_2NH_2$, is a chelating ligand.

Chelating ligands having an anionic donor site, may simultaneously satisfy the secondary valency (co-ordination number) as well as the primary valency or charge on the metal ion. Such chelate complexes are also called inner metallic complexes.

Stability Constants (Formation Constants) : The equilibrium constants for each step of addition of a ligand to a metal ion are called the stepwise formation constants or stability constants. If the metal ion is simply represented by M (with proper charge) and L represents a neutral unidentate ligand, then

$$M + L \rightleftharpoons ML \qquad K_1 = [ML]/[M][L]$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = [ML_2]/[Ml][L]$$

and so on, where K_1, K_2,...... are the stepwise formation constants. One may also define the overall formation constant for a species ML_n as

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = [ML_n]/[M][L]^n$$

Clearly, $\beta_n = K_1K_2......K_n$.

In aqueous solution, each step of addition of a ligand L actually involves substitution of a coordinated water molecule from the aquated metal ion. In general, there is a slow and gradual decrease in the successive K_i-values.

The trend is determined by a number of factors like statistical factor, steric factor, thermodynamic factor etc.

The Chelate Effect : Chelate complexes are usually found to be more stable than comparable nonchelate complexes with same donor atoms. This extra stability, commonly referred to as the "chelate effect", arises mainly from the large increase in entropy consequent to the release of bound water molecules in the aquated metal ion.

Determination of the composition of a complex species in solution may be done by following any suitable variable physical property of the metal ligand system as a function of concentration of metal and ligand. The spectrophotometric method is most generally used.

In **Job's method** of continuous variation, any property of the solution is measured in a series of solutions having a *constant sum of the total concentration of metal and ligand.* In spectrophotometric method, light absorption is measured at the wavelength of maximum complex absorption and the absorbance is plotted against concentration. It can be shown that maximum absorbance will occur when ligand : metal ratio is equal to that in the complex.

Coordination numbers of metal ions in a complex range from 1 (very rare) to 12, among which C.N. 4 and 6 are most common. Four coordinated complexes may be either square planar or tetrahedral; six coordinated complexes are mostly octahedral but may also be trigonal prismatic.

Isomerism in coordination compounds may be of two general types—

(i) **Constitutional** or **structural isomerism** where two or more compounds with same empirical formula differ in bond connectivities. These may be of different types like ionization isomer, hydrate isomer etc.

(ii) **Stereoisomerism** in which the compounds have the same empirical formula and the same atom-to-atom link sequence but the atoms differ in their arrangement in space. These may be either geometrical or optical isomerism.

Linkage isomerism is a type of structural isomerism shown by ambidentate ligands which can coordinate to a metal ion through either of two ends, for example $[(NH_3)_5Co—NO_2]^{2+}$, the "nitro" complex (nitrito-*N*) and $[(NH_3)_5Co—ONO]^{2+}$ or the "nitrito" complex (nitrito-*O*).

EXERCISE

1. *Only two-thirds of the chlorine contained in a solution of complex $CoCl_3.5NH_3$ were precipitated instantaneously by $AgNO_3$ solution. The electrical conductivity of the solution of the complex showed the presence of three ions. No cobalt ions or free ammonia were detected in the solution.*

   Write the coordination structure of the compound. [Ans : $[CoCl(NH_3)_5]Cl_2$]

2. *Two complex salts A and B of cobalt are known with the empirical formula $CoBrSO_4.5NH_3$. A solution of A gives a precipitate with $BaCl_2$ but does not form a precipitate with $AgNO_3$. A solution of B, on the contrary, gives a precipitate with $AgNO_3$, but does not form a precipitate with $BaCl_2$. Write the coordination formulae of A and B and explain.*

3. *A complex of compositon $CrCl_3.5H_2O$ is known to contain six-coordinated chromium. Calculate the volume of 0.1 N solution of $AgNO_3$ required to precipitate instantly the chloride ions from 200 ml of a 0.01M solution of the complex salt.* [Ans. : 40 mL]

4. *0.319 g of the complex of compositon $CrCl_3.6H_2O$ is passed through a cation exchange resin. The acid liberated is eluted and titrated against 0.1 N NaOH. 35.6 mL of the alkali is required for complete neutralization. Suggest the formula of the complex.*

   [**Hint :** 1 mol complex ≡ 3 mol H^+].

5. *The instability constant of $[Ag(CN)_2]^-$ is 1×10^{-21}. Calculate the concentration of Ag^+ ion in a 0.05 M solution of $K[Ag(CN)_2]$ containing 0.01 M KCN.*

   [**Hint :** Dissociation of KCN may be considered complete. Hence $[CN^-] = 0.01$ mol L^{-1}. $[Ag(CN)_2^-] = 0.05$ mol L^{-1} assuming negligible dissociation.]

6. *A solution containing Cd^{2+} ions gives precipitate with alkali and also with H_2S (faint acid medium). When an alkali is added to a 0.05 M solution of $K_2[Cd(CN)_4]$ containing 0.1 M KCN, no precipitate is formed. When H_2S is passed through this solution, a yellow precipitate of CdS is obtained. Explain.*

   Solubility products : $Cd(OH)_2$ 4.5×10^{-15}; CdS 8×10^{-27}.

   Instability constant of $[Cd(CN)_4]^{2-} = 8 \times 10^{-18}$.

   [**Hint :** Final concentration of Cd^{2+} (3.9×10^{-15} mol L^{-1}). $[OH^-]$ required > 1 mol L^{-1}; $[S^{2-}]$ required > 2×10^{-12} mol L^{-1}.]

7. *Calculate the concentration of Ag^+ ion in a 0.1 M solution of $[Ag(NH_3)_2]NO_3$ containing an excess of 1 mol L^{-1} of NH_3. [Instability constant of $Ag(NH_3)_2^+ = 9.3 \times 10^{-8}$].*

   [Ans. : 9.3×10^{-9} mol L^{-1}]

8. *Will a silver halide precipitate if we add to one litre of a 0.1 M solution of $[Ag(NH_3)_2]NO_3$ containing 1 mol L^{-1} of ammonia (i) 10^{-5} mol of KBr (ii) 10^{-5} mol of KI?*

   $K_{inst} = 9.3 \times 10^{-8}$; $K_{sp}(AgBr) = 6 \times 10^{-13}$; $K_{sp}(AgI) = 1.1 \times 10^{-16}$.

   [Ans. : (i) No; (ii) Yes]

9. *How many grams of NaCl can be added to one litre of 0.08 M solution of $[Ag(NH_3)_2]NO_3$ containing 1 mol L^{-1} NH_3 before AgCl begins to precipitate?*

   $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ [Ans. : <1.4 g]

10. K_{inst} for $[Ag(NO_2)_2]^-$ and $[Ag(CN)_2]^-$ are 1.3×10^{-3} and 8×10^{-21} respectively. If C_1 and C_2 be the concentrations of Ag^+ ion in equimolar solutions of these two complexes respectively, then C_1 and C_2 will be related as

(i) $C_1 > C_2$ (ii) $C_1 = C_2$ (iii) $C_1 < C_2$. **[Ans. : (i)]**

11. Addition of KI to a solution of $[Ag(NH_3)_2]NO_3$ precipitates AgI but no precipitate of AgI is formed when KI is added to solution of $K[Ag(CN)_2]$ of same molar concentration as the ammine complex. If the instability constants of the two complexes be K_1 and K_2 respectively,

(a) $K_1 > K_2$ (b) $K_1 = K_2$ (c) $K_1 < K_2$. **[Ans. : (a)]**

12. The instability constants of $[Ag(NH_3)_2]^+$ and $[Cd(NH_3)_4]^{2+}$ are 9.3×10^{-8} and 7.6×10^{-8} respectively. In equimolar solutions of the two complexes containing 0.1 mol L^{-1} of NH_3,

(a) $C_{Ag^+} > C_{Cd^{2+}}$ (b) $C_{Ag^+} = C_{Cd^{2+}}$ (c) $C_{Ag^+} < C_{Cd^{2+}}$. **[Ans. : (c)]**

13. Compound A (mol. wt 600) forms two ions in solution. It contains 65% Pt, 23.6% Cl, 9.3% N and 2.0% H. Addition of silver nitrate to a solution of A does not give any precipitate immediately and no ammonia can be evolved from the solution.

Draw two possible isomers of the compound and identify the type of such isomers.

[At. wt. of Pt = 195]

14. (a) What are chelating, bridging and flexidentate ligands? Discuss with suitable examples.

(b) Suggest why a chelated complex is more stable than a similar nonchelated complex.

15. (a) Give one physical and one chemical method which could be used to distinguish between cis- and **trans-** isomers of a complex compound.

(b) Draw the streo-configurations of all possible isomers of the compound $Co(en)_2Cl_2Br$ (en = ethylenediamine.)

16. Potassium sulfocyanidopalladium(II) reacts with dipyridyl at –78°C to give a light orange solid A which when heated to 150°C gives a light yellow compound B. Both A and B give same elemental composition. Explain the phenomenon with equation.

17. Chromium(III) chloride forms three different hydrates of the same mole ratio Cr : Cl : H_2O = 1 : 3 : 6. A violet form does not lose water over concentrated H_2SO_4 and gives 3 equivalents of AgCl on treatment with $AgNO_3$. Two other forms, both green, lose 1 and 2 mol of H_2O over conc. H_2SO_4 and gives 2 and 1 equivalent of AgCl respectively with $AgNO_3$. Write down the coordination structures of the three isomeric complexes and explain the isomerism involved.

18. Briefly answer the following :

(a) A polydentate ligand may not use all its donor centres for complexation—comment.

(b) Inner complex salt formation depends on pH of a solution—explain.

(c) Show the possible coordination sites of the following ligands :

$C_2O_4^{2-}$, SCN^-, $S_2O_3^{2-}$, H_2NCH_2COOH

(d) Give one example each showing the use of chelating ligands in qualitative and quantitative analysis.

(e) State the stereochemistries of the following complexes (linear, tetrahedral etc.) with diagrams :

$VO(acac)_2$, $K_2[CoCl_4]$, $[Ag(NH_3)_2]Cl$ and $[Co(NH_3)_6]Br_3$.

(f) How would you show that the thiocyanate ion acts as an ambidentate ligand.

(g) Write down the structures of different isomeric forms of $[Cr(ox)_3]^{3-}$, ox = oxalate ion.

(h) The stability of $[Ni(en)_3]^{2+}$ is much greater than that of $[Ni(NH_3)_6]^{2+}$, although both contains Ni—N bonds. Explain.

19. Successive values of $\log K_i$ (30°C) for the $Ni^{2+} - NH_3$ system are

($\log_{10}$)	K_1	K_2	K_3	K_4	K_5	K_6
	2.67	2.12	1.61	1.07	0.63	–0.09

(i) Why do successive K_i values decrease?

(ii) What is the significance of the negative value of K_6?

(iii) What is the value of the cumulative stability constant β_3?

(iv) Which ionic species are actually involved in the equilibrium corresponding to K_3 in aqueous solution?

(v) What is the standard free energy change for the reaction

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$$

20. Values of $\log K_1$ for some dipositive metal ions are given below with corresponding ligands.

Ligand	Ca^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
8-hydroxyquinoline	3.3	6.8	8.0	9.1	9.9	12.6	8.5
ethylenediamine	—	2.7	4.3	5.9	7.7	10.7	5.9
acetylacetone	—	2.7	4.3	5.9	7.7	10.7	5.9
EDTA	10.7	13.6	14.3	16.2	18.6	18.8	16.3

(a) Identify the donor atoms in the ligands.

(b) Is there any general order of stability for these complexes?

(c) Is this order related to any property(s) of the metal ions?

[Hint : The Irving-Williams order :

$$Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}.$$

This order has been variously correlated with the reciprocal of the ionic radius, the ionization energy and also the electronegativity of the element. Ligand field stabilization is also important.]

21. (a) The formula $Co(NH_3)_5SO_4Cl$ could represent a sulfate and a chloride. Write the two possible structures and name them.

(b) How many isomers are possible for $[Co(NH_3)(OH)_2Cl_3]^{2-}$?

[Hint : (i) all Cl and OH cis; (ii) Two OH trans, two Cl trans; (iii) Two OH cis, two Cl trans.]

(c) The formula $Co(NH_3)_4CO_3Cl$ represents three compounds. Write their possible structures. How would you distinguish between the coordination isomers by (a) chemical tests (b) instrumental method?

[Hint : (i) and (ii) CO_3 (unidentate)-cis and trans with Cl. Net charge zero. (iii) CO_3 **bidentate,** Cl outside coordination sphere. Dintinguish by $AgNO_3$ solution/conductance study / **i.r. study].**

(d) Two isomers are obtained in the reaction

$$[CoCl_2(NH_3)_4]^+ + Cl^- \longrightarrow [CoCl_3(NH_3)_3] + NH_3$$

What is the likely configuration of the initial complex? Draw the probable structures of the two products.

[Ans. : *cis*. The products may be facial or meridional.]

(e) How will you distinguish between the following pairs of isomers by conductance study?

(i) $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][Co(NO_2)_6]$

(ii) $[Cr(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$

[Hint : (i) Different metals migrate to anode and cathode. (ii) 3-3 and 1-1 electrolyte].

22. *State the type(s) of isomerism possible and the actual isomers corresponding to the following*

(a) $Co(NH_3)_4Br_2NO_2$ (b) $[Co(en)_2Cl_2]^+$ (c) $[Co(en)_3]^{3+}$ (d) $Co(NH_3)_4ClBr_2$.

[Hint : (a) Geometric, coordination and linkage isomerism; (b) Geometric and optical isomerism (for the cis); (c) optical isomerism (d) Geometric and coordination isomerism.]

CHAPTER TWENTYSEVEN

COORDINATION COMPOUNDS–II

Bonding; Electronic and Magnetic Properties; Reactions

OBJECTIVES

27.1 Bonding in co-ordination compounds
  Effective atomic number [27.1.1]
  The valence bond theory [27.1.2]
  The crystal field theory [27.1.3]
  The molecular orbital approach [27.1.4]

27.2 Colour and electronic spectra
  Introduction [27.2.1]
  Ligand field spectra [27.2.2]
  Energy level diagram [27.2.3]
  Charge transfer spectra [27.2.4]

27.3 Magnetic properties
  Magnetic properties of electrons [27.3.1]
  Classification of substances according to magnetic properties [27.3.2]
  Magnetic susceptibility [27.3.3]
  Theoretical versus observed moments [27.3.4]
  Equilibrium between high-spin and low-spin states [27.3.5]

27.4 Reactions of co-ordination compounds
  Introduction [27.4.1]
  Substitution in tetrahedral complexes [27.4.2]
  Substitution in square planar complexes [27.4.3]
  Substitution reactions of octahedral complexes [27.4.4]
  Oxidation-reduction reactions [27.4.5]

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COORDINATION COMPOUNDS-II

27.1 BONDING IN COORDINATION COMPOUNDS

Werner forwarded his theory of complex compounds at a time when the structure of atoms was not clearly understood. Sidgwick (1927) first tried to explain the bonding in coordination compounds through donation of electron pairs from the ligand to the metal. This led to the idea of effective atomic number (EAN) : an element tends to acquire around it the same number of electrons as are present in the next inert gas (sec. 27.1.1). However, such one way donation of electrons by ligands would result in an unfavourable accumulation of negative charge on the metal. Pauling tackled this problem through the electroneutrality principle (sec. 27.1.2) and applied the idea of orbital hybridization to explain the geometry and magnetic properties of many complexes (VBT; sec 27.1.2).

However, the valence bond theory had many drawbacks; particularly, it could not explain the spectral properties of coordination compounds. The crystal field theory, first framed around 1933-36 by H. Bethe and van Vleck to account for certain physical properties of transition metal salts, was revived in 1950s to interpret the electronic spectra and certain thermodynamic and structural features of complex compounds (section 27.1.3). But the purely electrostatic approach with complete negligence of metal ligand bonding interaction was also subject to severe criticism. With some allowance for covalence, the theory works much better; it is then often called the adjusted crystal field theory (ACFT) or sometimes the ligand field theory (LFT).

The molecular orbital theory of bonding in complex compounds (MOT; sec. 27.1.4) was also initiated in 1930s. It gives a more systematic understanding of the bonding but quantitative work becomes more complicated than the other theories. However, in qualitative treatment also, the approach is quite satisfactory.

The bonding in coordination compounds do not involve any new bonding scheme which is fundamentally different from the ideas developed earlier for nontransition elements. In the MOT, the principles of orbital overlap giving rise to σ and π m.o.-s apply equally to the coordination compounds but necessary adustments have to be made for the *d*-orbitals of the transition elements with due regard to their highly directional character. In the CFT, the formation of a coordination compound may be treated in terms of purely electrostatic interaction between the metal and ligand; in this treatment also the directional character of the *d*-orbitals plays the key role.

Before passing to the VBT and CFT in more details, we shall briefly mention the effective atomic number rule.

27.1.1 Effective atomic number : The 18-electron rule

With the light nontransition elements, the octet rule appeared useful in understanding the valence of the elements. The "secondary valency" of transition elements mentioned by Werner may be similarly understood in terms of attaining the 18-electron configuration for a noble gas. Assuming that each metal-ligand bond is formed as a coordinate covalent bond by donation of a pair of electrons from the donor ligand atom to the metal, each transition metal may be supposed to reach a stable electron configuration same as a noble gas configuration. The metal thus attains the

same number of electrons as the atomic number of a noble gas ion; this corresponds to filling of $(n\text{-}1)d$, *ns* and *np* orbitals of the metal (5+1+3 = 9). The effective atomic number (EAN) of a metal is computed by counting the total electrons belonging to the metal (atom or ion) and adding the electrons received through coordination :

(i) $[Co(NH_3)_6]^{3+}$	Co^{3+}	:		24 electrons	(atomic no. = 27)
	$6NH_3$	: 6×2	=	12 electrons	
	Total		=	36 electrons	(atomic number of Kr.)
(ii) $[Fe(CN)_6]^{4-}$	Fe^{2+}	:		24 electrons	(atomic no. = 26)
	$6CN^-$	: 6×2	=	12 electrons	
	Total		=	36 electrons	
(iii) $Ni(CO)_4$	Ni (0)	:		28 electrons	(atomic no. = 28)
	4CO	: 4×2	=	8 electrons	
	Total		=	36 electrons	
(ii) $[Pt(NH_3)_6)]^{4+}$	Pt (IV)	:		74 electrons	(atomic no. = 78)
	$6NH_3$	: 6×2	=	12 electrons	
	Total		=	86 electrons	(atomic number of Rn)

As we shall shortly find, the EAN rule is an approximate guideline and there are many exceptions to it (so were there for the octet rule). The EAN rule is particularly useful for complexes of metals in low oxidtion numbers (≤ II). For complexes of metals having oxidation number greater than (or sometimes equal to) two, the EAN concept is only approximate.

It is obvious that the valence shell of the metal in complexes obeying EAN rule contain 18 electrons (for the $(n-1)$ *d*, *ns* and *np* orbitals) and hence the EAN rule is also known as the 18-electron rule. Roughly, the metal complexes may be classified into three categories according to their adherence to the 18-electron rule and these can be understood to a large extent from the bonding descriptions which we shall present in the next sections (MOT; section 27.1.4).

27.1.2 The valence bond theory

According to this theory, a coordination entity is formed as a result of coordinate covalent bond formation by electron pairs from ligands through overlap of appropriate atomic orbitals (usually hybrid orbitals) of the metal and the ligand. The extent of overlap provides a measure of the degree of covalence in the bonds while the coordination number and stereochemistry is determined by the nature of available orbitals, their directional nature in particular and also by size and charge effects. The following hypothetical sequence of steps may be supposed to lead to the complex formation :

(i) ionization of the metal atom to its appropriate oxidation state;

(ii) with the approach of ligands, rearrangement, where necessary, of the metal electrons within orbitals of similar energy to provide a set of empty orbitals to accommodate the ligand electrons;

(iii) hybridization of these empty metal orbitals to suit overlap with the approaching ligand orbitals;

(iv) overlap of the hybrid orbitals with ligand-orbitals containing lone pairs of electrons resulting in σ-bond formation.

The common coordination numbers with their associated hybrid orbitals and geometry are shown in Table 27.1.

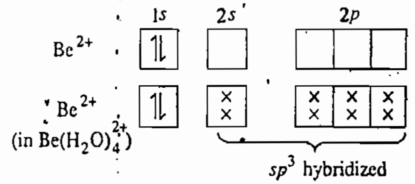
TABLE 27.1

Some hybridization schemes (σ-only) for complex compounds in common geometry

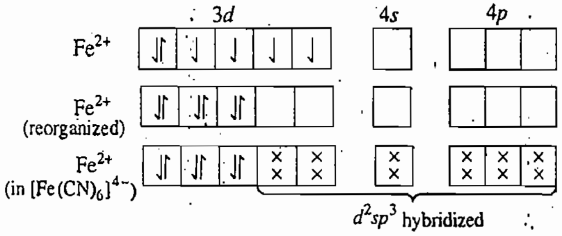
Coordination Number	Geometry	Hybridization	Examples
2	linear	$sp\ (s, p_z)$	$[Ag(NH_3)_2]^+$
3	trigonal planar	$sp^2\ (s, p_x, p_y)$,	$[Ag(PR_3)_3]^+$
4	tetrahedral	$sp^3\ (s, p_x, p_y, p_z)$	$[Be(H_2O)_4]^{2+}$
		$d^3s\ (d_{xy}, d_{yz}, d_{zx}, s)$	MnO_4^-
	square planar	$dsp^2\ (d_{x^2-y^2}, s, p_x, p_y)$	$[Ni(CN)_4]^{2-}$
5	trigonal bipyramid	$dsp^3\ (d_{z^2}, s, p_x, p_y, p_z)$	$[CuCl_5]^{3-}$
	square pyramid	$dsp^3\ (d_{x^2-y^2}, s, p_x, p_y, p_z)$	$[VO(acac)_2]$
6	octahedral	$d^2sp^3\ (d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_z)$	$[Co(NH_3)_6]^{3+}$
		sp^3d^2	$[CoF_6]^{3-}$
	trigonal prism	$d^2sp^3, (d_{xz}, d_{yz}, s, p_x, p_y, p_z)$	$[Mo(S_2C_2Ph_2)_3]$

The use of such hybrid orbitals in the formation of complex species according to VBT may be illustrated as follows—($\overset{\times}{\times}$ denotes an electron pair from ligands):

1. $[Be(H_2O)_4]^{2+}$: The Be^{2+} ion can use sp^3 hybrid orbitals (tetrahedral) to receive electron pairs from four water molecules :

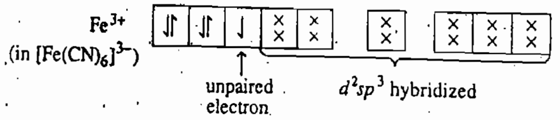


2. $[Fe(CN)_6]^{4-}$: The six $3d$ electrons in the Fe^{2+} ion are first paired up to provide vacant orbitals for d^2sp^3 hybridization; these are subsequently involved in σ-bond formation with six CN^- ions :

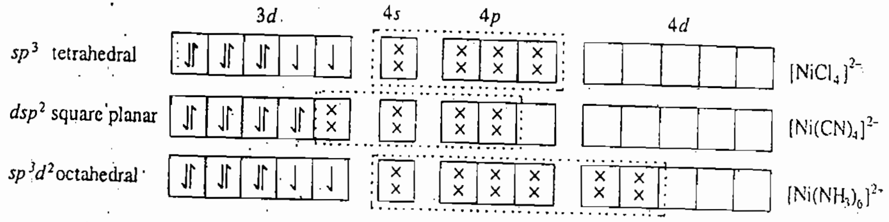


One expects that the complex species will be diamagnetic (see below) as it contains no unpaired electrons.

3. $[Fe(CN)_6]^{3-}$: Proceeding in the same manner as in the case of Fe^{2+} shown above, one observes that the complex should be paramagnetic with one unpaired electron



As we have seen in Table 27.1, many combinations between s, p and d orbitals are possible. The type of hybridization and the consequent spatial arrangement of the ligands depend on several factors like the number of d-electrons of the free metal ion, the nature of the ligand, its size etc. For instance, the Ni^{2+}ion (d^8) may adopt any of the following configurations



Magnetic properties

We shall defer our discussion on magnetic properties till the next section. Here we shall simply remember that substances with no unpaired electrons are called diamagnetic : they are repelled in a magnetic field. On the other hand, substances with one or more unpaired electrons are attracted towards a magnetic field and are said to be paramagnetic. An electron, a moving electric charge, gives rise to an electric current which produces an associated magnetic field. Thus, each unpaired electron in a molecule may be supposed to behave like a small bar magnet whose magnetic moment will interact with any externally applied magnetic field. The magnetic moments of spin-paired electrons cancel each other, hence only unpaired electrons give rise to paramagnetism.

Paramagnetism arises from both spin angular momentum and orbital angular momentum of the contributing electrons. However, in complexes of the first row transition metals, only spin-contribution becomes significant in most cases. The *spin-only* value of magnetic moment for a species with n unpaired electrons is given by the relation

$$\mu_{\text{spin-only}} = \sqrt{n(n+2)}\ \text{Bohr Magneton}\ (\mu_B).$$

Bohr Magneton (μ_B) is the unit of magnetic moment :

$$1\mu_B = eh/4\pi m = 9\cdot274\times10^{-24}\,\text{JT}^{-1}\ \text{(Joule per Tesla)}.$$

Such magnetic moments may also be determined experimentally from measurement of magnetic susceptibility (see later). Hence we can infer the number of unpaired electron(s) in a coordinated species and check the hybridization scheme proposed.

The spin-only magnetic moment for different number of unpaired electrons are as follows :

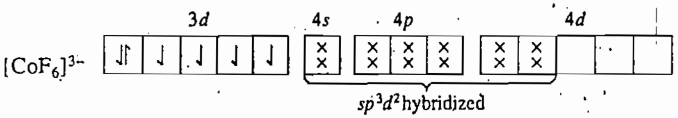
$$n = 1,\ \mu = \sqrt{3} = 1{\cdot}73 \text{ B.M.}$$

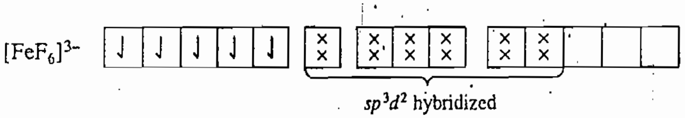
$$n = 2,\ \mu = \sqrt{8} = 2{\cdot}83 \text{ B.M.}$$

$$n = 3,\ \mu = \sqrt{15} = 3{\cdot}87 \text{ B.M. ... and so on.}$$

The observed magnetic moment, and hence the number of unpaired electrons in many complex species agree with that predicted by the valence bond theory. For example, $[Ti(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ both show magnetic moment corresponding to one unpaired electron; $[Fe(CN)_6]^{4-}$ and $[Co(NH_3)_6]^{3+}$ are both diamagnetic.

However, the experimental magnetic moments of some complexes like $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ correspond to the presence of 5 and 4 unpaired electrons respectively. Such complexes are then described as high-spin (or spin-free) complexes and their bonding is supposed to involve hybrid orbitals from 4*s*, 4*p* and 4*d* a.o.-s on the metal; the complexes are therefore also called *outer-orbital complexes*. Low-spin complexes like $[Fe(CN)_6]^{3-}$ are accordingly classed as *inner-orbital complexes* where the bonding involves "inner" 3*d* orbitals.





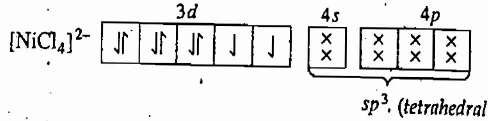
It may be noted that the electron distribution in the 3*d* orbitals of iron and cobalt in these complexes is the same as in the free gaseous ions Fe^{3+} and Co^{3+} respectively. In early valence bond treatment, these complexes were classed as "ionic" in contrast to the low-spin complexes like $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ which were called "covalent". The highly electronegative fluorine or oxygen atoms concentrate the bonding electrons near themselves and favour "ionic" or outer orbital bonding. The outer *d*-orbitals of the metal can still overlap due to their greater extension in space. Ligands in which the donor atom has low electronegativity can make stronger bonds with the inner *d*-orbitals. This also helps to establish π-bonding, as we shall find later. The various terminologies are still in use though the terms high-spin and low-spin are becoming most popular and unambiguous.

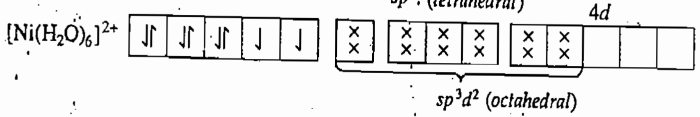
high-spin : outer orbital or ionic

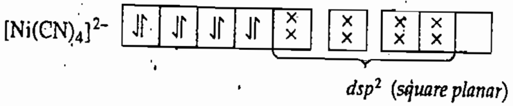
low-spin : inner orbital or covalent

The application of magnetic moment studies to interpret the nature of bonding in complex compounds was originally called "the magnetic criterion of bond type". From the number of unpaired electrons calculated from magnetic moments, one can suggest a suitable scheme of hybridization for the central metal atom or ion and predict the probable geometry of the complex. This is nicely illustrated by several complexes of nickel. Thus $[NiCl_4]^{2-}$ and $[Ni(H_2O)_6]^{2+}$ are both paramagnetic with two unpaired electrons while $[Ni(CN)_4]^{2-}$ is diamagnetic, showing that all electrons are paired in it. The electron configuration of the central metal in these complexes may then be described as follows :

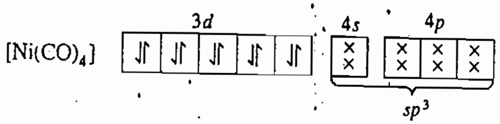
[Sec. 27.1.2 *Valence Bond Theory*]



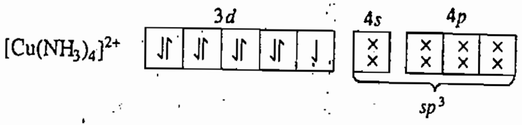




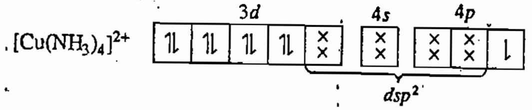
Nickel carbonyl, $[Ni(CO)_4]$, is a derivative of Ni(0); the compound is diamagnetic and the molecule is tetrahedral as expected from the VBT :



However, such "magnetic criterion" deduced from the valence bond theory does not work satisfactorily in some cases. For example, the so-called $[Cu(NH_3)_4]^{2+}$ ion is paramagnetic with one unpaired electron. The simple valence bond approach predicts the complex species to be tetrahedral corresponding to sp^3 hybridization of copper (II) :



However, the ion is actually square planar, which, according to VBT, ought to have involved dsp^2 hybrid orbitals. Pauling suggested that this might be possible through transfer of the lone 3*d* electron to the p_z orbital, followed by dsp_xp_y hybridization :



Magnetic criterion cannot distinguish between the two alternatives since both has one unpaired electron. However, this proposal is subject to strong criticism : if the last electron in Cu(II) were so labile, it would have been possible to obtain Cu(III) rather easily. Also, electron spin resonance (esr) data on several Cu(II) complexes established that the odd electron is in a 3*d* orbital, not in a 4*p* orbital.

At present, it has been established that the species is actually $[Cu(NH_3)_4(H_2O)_2]^{2+}$ with a strongly distorted octahedral structure in which the two axial water molecules are held at very large distances (see later).

The electroneutrality principle

Statement

The description of complex formation by σ-donation of ligand electrons to metals is likely to build up an unfavourable formal negative charge on the metal. Pauling tackled the situation by assuming that the electronic charges are distributed throughout the complex species to bring about virtual electrical neutrality on the atoms. His electroneutrality principle states that in a complex species the charge tends to get distributed in such a manner so that no atom in a complex has a resultant charge greater than about ± 1 electron; a complex would be most stable when the electronegativity of the ligand allows sharing of the electron pairs such that the metal achieves a condition of essentially zero net electrical charge. Pauling also suggested the possibility of "back-donation" of unused *d*-electron on metals to the ligands with the formation of double bonds as a secondary mode to establish electroneutrality (see later).

The distribution of electron charge over the complex species may be estimated from the per cent ionic characters of the bonds on the basis of the difference of electronegativity between linked atoms. The following examples will illustrate the application of the principle :

$$\begin{array}{lll} [Be(H_2O)_4]^{2+} & \text{Electronegativity of Be} & = 1.5 \\ & \underline{\text{Electronegativity of O} \;= 3.5} & \\ & \text{Difference} & = 2.0 \end{array}$$

∴ Percent ionic character (Ch. 7) = $18.(2)^{1.4} = 48$.

Hence the bonds are approximately 52% covalent. Hence the 4 oxygen atoms acutally donate a total of $4 \times 0.52 = 2.08$ valence electrons to the Be^{2+}.

So the net charge on beryllium is $-2.08 + 2 = -0.08$.

Correspondingly, each O-atom may be supposed to gain +0.52*e* charge for each Be-O link. Actually, this is partly neutralized by the H-atoms joined to them. The O—H bond is 29% ionic (from electronegativity difference = 3.5 – 2.1 = 1.4), Now, if the O-H bonds were 100% ionic, each H would donate one "full electron" to an adjacent O; since the O-H bonds are only 29% ionic, the O-atom receives in effect only 0.29*e* charge from each of two hydrogens, making a total of 0.58*e*. The "net charge" on each O is then $0.52e - 0.58e = -0.06e$.

The net charge on each hydrogen, as explained above, is +0.29*e*.

The results may now be summarized as :

$$\begin{array}{lll} & \text{Be :} & -0.08 \\ & 4\,O : 4 \times -0.06 & = -0.24 \\ & \underline{8\,H : 8 \times +0.29 = +2.32} & \\ [Be(H_2O)_4]^{2+} & \text{Total} & = +2.00 \end{array}$$

We infer that $[Be(H_2O)_4]^{2+}$ is likely to be a stable species since the effective charge distribution on the complex renders all atoms with very low net charge nearing "electroneutrality".

Corresponding calculation for $[Be(NH_3)_4]^{2+}$ shows that the species is not likely to be a stable one in view of the unfavourable charge distribution :

Electronegativity difference between Be & N :	1.50	Be	:	– 0.73
Per cent ionic character of Be-N bond :	31.75	4 N	:	+ 0.87
Per cent ionic character of N-H bond :	15.50	12 N	:	1.86
		Total	:	+ 2.00

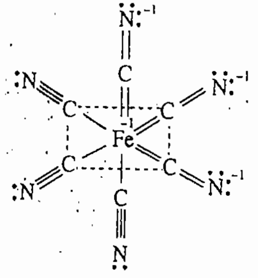
Similar calculations on the following species yield the results :

$[Be(H_2O)_6]^{2+}$		$[Al(H_2O)_6]^{3+}$		$[Al(NH_3)_6]^{3+}$	
Be :	– 1.12	Al :	– 0.12	Al :	– 1.08
6 O :	– 0.36	6 O :	– 0.36	6 N :	+ 1.20
12 H :	+ 3.48	12 H :	+ 3.48	18 H :	+ 2.88
Total :	+2.00	Total :	+3.00	Total :	+3.00

The high accumulation of charge on the metals in $[Be(H_2O)_6]^{2+}$ and $[Al(NH_3)_6]^{3+}$ suggest that these species are likely to be unstable. $[Al(H_2O)_6]^{3+}$, on the other hand, is likely to be stable since the Al-atom has only a very low effective electronic charge.

However, such straightcut estimates of electroneutrality does not work satisfactorily in all cases and further considerations become necessary. For example, Pauling suggested that the electrostatic stability of a complex may be aided by metal-ligand double bond formation. Thus, the $[Fe(CN)_6]^{4-}$ ion may be supposed to involve Fe—CN single bonds and Fe = CN double bonds which may resonate among several structures like 27-I.

The charge on Fe is now reduced to –1*e*, while in a structure involving six Fe—CN single bonds, the charge on the iron atom would have been –4*e*.



27-I

This structure may be regarded as resulting from resonance of each of the Fe-CN bonds among the following structures :

$Fe^{++}\!:(CN)^-$ $\quad$ $Fe^{+}\!:C\!::\!N\!:$ $\quad$ $Fe^{++}\overset{\times}{\underset{\times}{:}}C\!::\!\ddot{N}\!:^-$ $\quad$ ($\times \rightarrow e$ of Fe)

(a) $\quad$ (b) $\quad$ (c)

Thus, the apparent negative charge of –4*e* gained by the iron from Fe—CN single bonds (structure b, which now contributes only $^1/_3$ rd) is distributed among the six cyanide ligands.

Similar resonating structures were also suggested for complexes like $[Ni(CO)_4]$ where the donor ligand atom is of low electronegativity :

$\bar{N}i\!:\bar{C}\!:::\!O\!:^+$ $\quad$ $\bar{N}i : C^+\!::\!\ddot{O}\!:$ $\quad$ $Ni\overset{\times}{\underset{\times}{:}}C\!:\!:\ddot{O}\!:$

Such double bond formation does not change the shape of the $[Ni(CO)_4]$ molecule as this is determined by the spatial distribution of the hybrid orbitals used in forming σ-bond only. The idea of double bond formation was supported by bond distances : (i) The Ni—C distance (182 pm) is shorter in comparison to that expected for a Ni—C single bond (216 pm). (ii) The C—O distance is correspondingly greater than that in a triple bond.

Later, the idea of double bonds has been rationalized in terms of metal ligand π-bond formation. These will be mentioned later.

Limitations of the valence bond theory

Some of the major limitations of the valence bond theory (VBT) for coordination compounds are as follows :

(i) The VBT fails to explain satisfactorily the colours and characteristics of absorption spectra of complex compounds.

(ii) Though it explains the approximate magnetic moment of many complexes, many finer details like temperature-dependence of magnetic moment or deviation from spin-only values due to orbital contribution cannot be properly explained.

(iii) The theory fails to predict any distortion in the shapes of complexes from regular geometry; in practice, several complexes exhibit appreciable distortion of regular geometrical structures.

(iv) The relative stabilities of different structures and different coordination numbers are not explained by the theory. Thus Fe(III) forms both tetrahedral and octahedral complexes but Cr(III) forms only octahedral complexes.

(v) The classification of complexes as ionic or outer orbital and covalent or inner orbital is arbitrary. Thus [Fe(acac)$_3$] is paramagnetic, requiring an "ionic" description of bonding. But the complex is a highly volatile species soluble in organic solvents—properties contradictory to ionic species.

The observed acidity of aqua metal ions also do not follow directly from the ionic-covalent classification. We may expect that a species $[M(H_2O)_6]^{n+}$ would behave as a stronger acid when the M—O bond is more covalent. Among the complexes $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$, only $[Fe(H_2O)_6]^{3+}$ is outer orbital according to magnetic criterion, suggesting an "ionic" type of bonding. This is therefore expected to be a weaker acid than the other two which are inner orbital type and hence covalent. But the acidity trend of the complexes, as revealed by respective pK_a values, shows that the iron complex is actually a stronger acid than $[Cr(H_2O)_6]^{3+}$, while $[Co(H_2O)_6]^{3+}$ (also covalent) is the strongest among the three.

	$[Cr(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$
pK_a	3·8	2.2	0.7

It was also found that the $[Fe(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$ ions exchange with H_2O^{18} instantaneously while $[Cr(H_2O)_6]^{3+}$ does so only very slowly.

These behaviours are clearly inconsistent with Pauling's "ionic" and "covalent" classification.

(vi) The explanation offered in the VBT for many complexes of Cu(II) involving promotion of a 3*d* electron to a 4*p* orbital was unsatisfactory, as explained earlier.

(vii) The VBT failed to account for the differences in the observed rates of reactions of analogous metal complexes. For example, $[Mn(o\text{-}phen)_3]^{2+}$ dissociates instantaneously in acidic aqueous solutions but the corresponding Fe(II) complex dissociates at a much slower rate under identical conditions.

27.1.3 The crystal field theory (CFT)

The crystal field theory, first proposed by Hans Bethe in 1929 to explain the colour and magnetic properties of some solid crystalline salts of metals, was originally based on purely electrostatic interaction between a metal ion and the ligands. Though it was modified later to allow some covalent interaction (van Vleck, 1935), the application of the theory remained mostly confined to solid state physics. In 1950-s it was applied to interpret the electronic spectra of transition metal complexes. Theoretically, the crystal field theory is not an elegant theory of bonding in complex compounds (see limitations). Nevertheless, its apparent simplicity made it readily acceptable mostly as a "tool" in rationalizing certain features of complex compounds. We shall presently find that the same rationalizations are offered by the molecular orbital theory in a more satisfactory manner.

Later modifications of the crystal field theory are sometimes referred to as the Ligand field theory. But the label is now used in a much broader sense bridging the crude crystal field theory with the more sophisticated molecular orbital theory. We shall use the term in this broader sense in our interpretation of spectra and magnetic properties of complexes. Before that we shall briefly present the essentials of the CFT (in this section) and the MOT (next section).

The principal qualitative aspects of the crystal field theory (CFT) may be summarized as follows :

Salient features

(i) It is a hypothetical model in which the ligands are imagined to be point negative charges (either from the net negative charge on the ligand or from the negative end of the ligand dipole arising from the lone pair of electrons on its donor atom). The metal electrons, on the contrary, are allowed to maintain their wave mechanical identity; that is, they are supposed to occupy appropriate atomic orbitals of the metal.

(ii) The theory now considers only the electrostatic interaction between a metal and the ligands. This may be considered in two steps : (a) electrostatic attraction between the positive nucleus of the metal and the negatively charged electrons of the ligands (imagined as point charges); (b) electrostatic repulsion force between the electrons in the valence shell of the metal and the ligand electrons. Step (a) will result in an overall lowering in the energy of the system, making it stable. Step (b) will, however, slightly raise the energy of system the details of which are discussed below (see Fig. 27.3).

Though the CFT was first used to explain the properties of crystalline substances (hence the name), it can equally be applied to any other system in which the interacting particles have a regular arrangement, e.g., in an isolated complex species. The ligand electrons (assumed point charges) are assumed to constitute an electrostatic field around the metal ion, just as in ideal ionic crystals.

Let us consider the effect of this field on the energies of the metal orbitals. Since the *s* orbitals are spherically symmetrical, an electron in, for example, the metal 4s orbital is affected equally by the electrostatic field in all directions. Hence the energy of the 4*s* orbital is merely raised by the presence of the electrostatic field. But the case of the *p*, *d* or *f*, sets of orbitals are a bit different. When an atom is isolated, or is subjected to an electric field which is spherically symmetrical around the atom, the energy levels of the three *p*-orbitals are identical or degenerate; so also are the energies of *d*- or *f* orbitals. The prominent directional character of these orbitals, however, suggest that they will no longer remain degenerate in an unsymmetrical field.

Let us consider an atom strongly coordinated to two ligands along the ± z direction in a linear configuration. We expect that those orbitals of the central atom which lie along the z-axis (and therefore point towards the ligands) will be more affected than orbitals lying in other directions. (Mathematically, the energy function operator or Hamiltonian Operator (*H*) for such orbitals will be perturbed more by a change in the potential energy function. Such mathematical treatment is beyond our scope at present and we shall consider only the gross qualitative aspect of the situation). The z-directed orbitals will thus experience a stronger field of negative charges form the ligands and will be repelled more. The directional characters of the p- and d-orbitals tell us that an electron in the p_z or d_{z^2} orbital of the central atom will be repelled most, followed by the d_{xz} and d_{yz} orbitals to a somewhat less extent. This will destroy the degeneracy within the sets of p- and d-orbitals—the most affected ones will be energetically raised and electrons will try to avoid occupying them as far as practicable. The energies of the "non-z-orbitals" will be correspondingly lowered and there will be thus a splitting in the energies of these orbitals (Fig. 27.2).

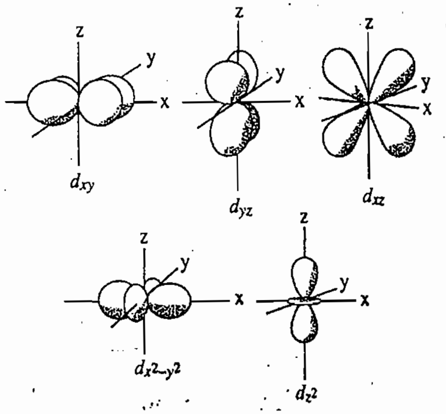


Fig. 27.1 : The five 3d orbitals.

The d_{z^2} orbital is acually a combination of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ i.e., it is $d_{2z^2-x^2-y^2}$.

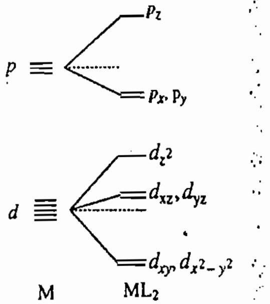


Fig. 27.2 : Splitting in a linear field.

Effect of ligands along the z-axis on the energy levels of the atom (in a spherically symmetric field of the average effect of the ligands).

The extent of such splitting will naturally depend on the strength of the field exerted by the ligands; this, in turn, will depend on the distance and intensity of attraction between the central atom and the ligands. Since the p-orbitals of a metal are usually full and equally populated, splitting of the p-orbitals will not have any net effect on the energy of the system. Hence the d-orbitals are the most affected in presence of the ligands. (Such effects will also be negligible for f-orbitals because the fields are too small, particularly with the 4f orbitals which are well shielded by the outer electrons. The 5f-orbitals give rise to larger splitting. In an octahedral field, the f-orbitals are expected to be split into three sets).

Next we consider how the d-orbitals are affected in other geometries, particularly in the octahedral environment of ligands which is most common among complex compounds.

Splitting of d-orbitals in an octahedral field

Let us consider a metal ion with ten d-electrons enclosed within a hollow sphere of radius equal to the metal-ligand distance in the complex; a charge of total quantity 12e (from the six ligands) is spread uniformly over the sphere. As explained before, the attraction between the central ion charge and the ligand charges or dipoles will first lower the energy of the system. The energy will be somewhat raised by repulsion of the electrons in the central ion (Fig. 27.3a). But the spherical symmetry of the environment tells us that the d-orbitals will still remain five-fold degenerate. The total energy of the system of metal ion and the charged sphere will have some definite value.

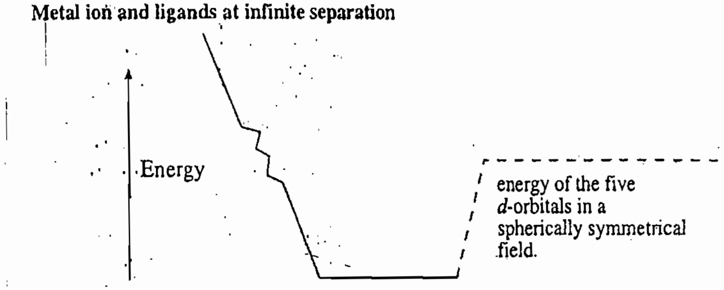


Fig. 27.3 (a)

The effect of a spherical field of 12e charges on the metal d-orbitals.

Now suppose the total charge of 12e on the surface of the sphere is redistributed as six separate point charges, each of magnitude 2e, at the six corners of a regular octahedron. This redistribution will not alter the total energy of the system but a secondary effect will come into play : all d-orbitals will not be affected to the same extent by this new arrangement of the charges.

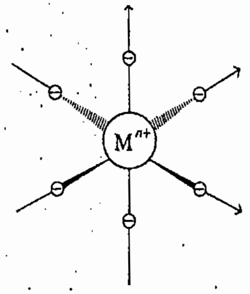


Fig. 27.3 (b)

Crystal-field model of an octahedral complex.

Referring to Fig. 27.3b, in which the cartesian axes are the four fold axes of the octahedron, and remembering the spatial distribution of the d-orbitals (Fig. 27.1), we expect that those d-orbitals whose lobes are directed along the axes will experience greater interaction from the point charges placed in these directions. These are the $d_{x^2-y^2}$ and d_{z^2} orbitals — the electrons in these orbitals will experience stronger repulsion from the point charges in the environment. In other words, the orbitals will be destabilized and their energy will be raised to some extent. But the remaining three d-orbitals, namely d_{xy}, d_{yz} and d_{zx} have their lobes in between the axes (45°) and will be less affected by the point charges in the octahedral environment; the electrons occupying them will be subject to less electrostatic repulsion. Since mere redistribution of the spherical charge cannot alter the total energy of the system, we are led to conclude that the energy of these latter three d-orbitals will be correspondingly lowered to keep the total energy of the system constant. Hence, the total increase in energy of the four electrons in $d_{x^2-y^2}$ and d_{z^2} should be equal to the total decrease in energy of the six electrons in d_{xy}, d_{yz} and d_{zx} orbitals (referring to the hypothetical spherical field). The splitting is thus said to conserve the barycenter or "center of gravity" of the orbitals. The idea is quite general and applies to any geometry.

The situation may now be generalized for any complex of the type ML_6 with six identical ligands in an octahedral environment around a central metal ion with any number of *d*-electrons. Our summary observation is that in the octahedral field of the ligands, imagined to be point charges, the degeneracy of the *d*-orbitals is lost : two of them, the $d_{x^2-y^2}$ and d_{z^2}, being pointed directly at the ligands, are raised in energy while the other three *d*-orbitals (d_{xy}, d_{yz}, d_{zx}) are lowered in energy. This splitting of the *d*-orbitals will also conserve the barycenter. The set of three lower energy degenerate orbitals are classed as t_{2g} while the two higher energy orbitals are labelled e_g set of orbitals from their symmetry considerations. The subscript '*g*' (for gerade) applies as the octahedral field is centrosymmetric.

The separation between the t_{2g} and e_g levels is conventionally represented by Δ_0 or $10Dq$. Conservation of "center of gravity", as explained just now, requires that the rise in energy of the e_g orbitals and the drop in energy of the t_{2g} orbitals will be in the ratio 6 : 4 (referred to the average energy of the orbitals in the hypothetical spherical field).

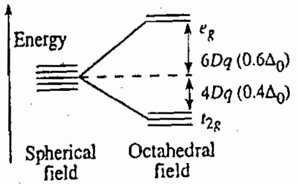


Fig. 27.4
Crystal field splitting in an octahedral field.

The terms *D* and *q* were introduced in the quantitative treatment of the crystal field theory while constructing the Hamiltonian operator appropriate to the system. The potential energy term and its effect on the *d*-wave functions are expressed conveniently using these two quantities which, in the octahedral field, have the values

$$D = \frac{35\,ze}{4a^5}\ ;\ q = \frac{2e\overline{r^4}}{105},$$

where *z* is the charge on the ligand; *e* is the charge of the electron; *a* is the metal-ligand distance and *r* is the distance of the electron from the nucleus. Experimental $10Dq$ values are obtained from electronic spectra (see later).

Crystal field stabilization energy

Let us consider a complex in which the metal has only one *d*-electron, for example the $[Ti(H_2O)_6]^{3+}$, which exists in aqueous solutions. In its ground state, the single *d*-electron will occupy the orbital of lowest available energy. The octahedral environment of the six H_2O ligands should split the *d*-orbitals into lower energy t_{2g} and higher energy e_g sets—and in its ground state, the electron occupies one of the t_{2g} orbitals (t_{2g}^1 configuration).

This will lower the energy of the electron by $4Dq$ or $0.4\ \Delta_0$ in comparison to that in a hypothetical spherical field of the ligands at the same distance. The complex may then be said to have gained crystal-field stabilization energy (CFSE) to the extent of $0.4\Delta_0$ or $4Dq$. The energy of the electron with reference to the barycenter will be $-0.4\Delta_0$ or $-4Dq$.

[Sec. 27.1.3 *Crystal Field Theory*]

The magnitude of Δ_0 in this case can be estimated from the observed spectrum of the complex. The single *d*-electron is expected to be promoted to the higher e_g level by absorption of energy equal to Δ_0 : $t_{2g}^1 e_g^0 \longrightarrow t_{2g}^0 e_g^1$ (Fig. 27.5).

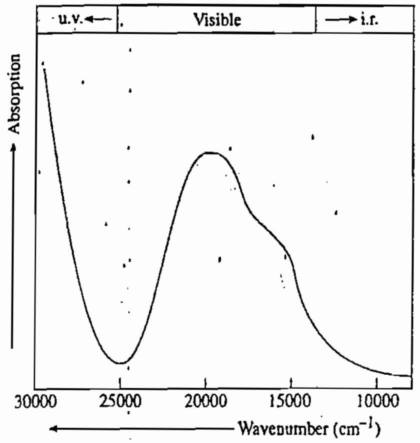


Fig. 27.5

The nature of absorption spectrum of $[Ti(H_2O)_6]^{3+}$ ion (visible region).

The absorption spectrum of the purple aqueous solution of $[Ti(H_2O)_6]^{3+}$ shows a maximum around 20,30000 m^{-1} (20,300 cm^{-1}),

i.e., $\frac{1}{\lambda} = 20,30000\ m^{-1}$.

$$\therefore E = h\nu = \frac{hc}{\lambda} = 4 \cdot 035 \times 10^{-19}\ J$$

$$\equiv 243\ kJ\ mol^{-1}.$$

The magnitude of Δ_0 in $[Ti(H_2O)_6]^{3+}$ corresponds to 243 kJ mol^{-1}. For $[VCl_6]^{2-}$, also d^1, an absorption maxima occurs at about 15400 cm^{-1}, which corresponds to Δ_0 = 184 kJ mol^{-1}; we shall consider details of these spectra in later sections.

Next let us consider the crystal field stabilization energy in complexes with more than one *d*-electron. Up to three *d*-electrons, the orbital occupancy of electrons and corresponding CFSE are readily arrived at :

$d^2 : t_{2g}^2$ $\quad 0 \cdot 8\ \Delta_0 \quad (8Dq) \qquad d^3 : t_{2g}^3 \quad 1.2\ \Delta_0 \quad (12Dq)$

With a d^4 complex, the fourth *d*-electron may either (i) doubly occupy a t_{2g} orbital at the cost of the pairing energy *p* or (ii) enter one of the e_g orbitals at the cost of destablization by an amount $10Dq$ (Δ_0). The actual configuration adopted will correspond to lowest energy of the system :

$d^4 \quad 10Dq > p : t_{2g}^4 \qquad CFSE = 16Dq - p$

$\quad\ \ 10Dq < p : t_{2g}^3 e_g^1 \qquad CFSE = 12Dq - 6Dq$

In the first case ($\Delta_0 > p$), the complex has only two unpaired electrons and is said to be a *low-spin complex* while in the second case ($\Delta_0 < p$), the complex has four unpaired electrons; it is said to be a *high-spin complex*. Strong ligand fields cause greater splitting, making Δ_0 high. Hence low-spin complexes are also referred to as strong-field complexes while high-spin complexes are called weak-field complexes.

The CFSE for configurations $d^1 - d^{10}$ ions in strong and weak octahedral fields are computed below. (There will be no splitting of the *d*-orbitals in a d^0 case).

TABLE 27.2

Crystal Field Stabilization Energy for Octahedral Complexes*

Configuration	Strong field (low spin)		Weak field (high spin)	
d^1	t_{2g}^1	$4Dq$	t_{2g}^1	$4Dq$
d^2	t_{2g}^2	$8Dq$	t_{2g}^2	$8Dq$
d^3	t_{2g}^3	$12Dq$	t_{2g}^3	$12Dq$
d^4	t_{2g}^4	$16Dq-p$	$t_{2g}^3e_g^1$	$6Dq$
d^5	t_{2g}^5	$20Dq-2p$	$t_{2g}^3e_g^2$	0
d^6	t_{2g}^6	$24Dq-2p$	$t_{2g}^4e_g^2$	$4Dq$
d^7	$t_{2g}^6e_g^1$	$18Dq-p$	$t_{2g}^5e_g^2$	$8Dq$
d^8	$t_{2g}^6e_g^2$	$12Dq$	$t_{2g}^6e_g^2$	$12Dq$
d^9	$t_{2g}^6e_g^3$	$6Dq$	$t_{2g}^6e_g^3$	$6Dq$
d^{10}	$t_{2g}^6e_g^4$	0	$t_{2g}^6e_g^4$	0

* Note : In terms of Dq. But Dq for strong field is higher than Dq for weak field. This should be kept in mind while comparing the stability gained in passing from one configuration to another for d^4-d^7 ions.

The pairing energy may be ignored for many practical purposes. Here it has been computed by taking into account the number of unpaired electrons present in the free ion. For example, a d^6 metal ion already contained one pair of electrons in a d-orbital. The extra destabilization in a t_{2g}^6 configuration therefore comes from two more paired electrons. However, the "pairing energy" also includes a major contribution from the loss of exchange energy when electrons with parallel spins are forced to adopt antiparallel spins.

The CFSE's comprise only about 2% to 10% of the total binding energy of a given complex and hence are not the main source of binding energy in a complex. However, the CFSE's may be important in explaining many properties of complex species, as we shall encounter soon.

Splitting of d-orbitals in tetrahedral complexes

In order to correlate the spatial distribution of d-orbitals in a cartesian system with the electrostatic interaction arising in a tetrahedral complex, let us first visualize the tetrahedral structure as being related to a cube. As shown in Fig. 27.6(a), a tetrahedral structure results when diagonally opposite corners of the top and bottom faces of a cube are joined to its centre. The C_4 axes of the cube (or octahedron) coincide with the C_2 axes of the tetrahedron. These two-fold symmetry axes bisecting the six edges are chosen as the coordinate axes.

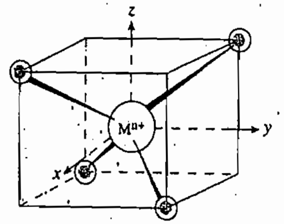


Fig. 27.6 (a)

Four opposite corners of a cube describe a tetrahedron.

The d_{xy}, d_{yz} and d_{zx} orbitals have lobes that can be imagined to intersect the edges of the cubes at a distance equal to half a cube edge away from a ligand position; the lobes of d_{z^2} and $d_{x^2-y^2}$ orbitals intersect the cube faces at a distance equal to half a face diagonal away from a ligand position.

Reference to the cartesian system of coordinates and the d-orbitals now tells us that none of the orbitals are pointed directly at the ligand charges. However, the d_{xy}, d_{yz} and d_{zx} set of orbitals point more closely to the ligands and will be somewhat destabilized; the $d_{x^2-y^2}$ and d_{z^2} orbitals, being farther away, will be relatively stabilized to maintain the barycenter of the average energy of the d-orbitals in a hypothetical spherical field of these four ligands. The nature of splitting is shown in Fig. 27.6(b).

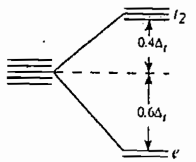


Fig. 27.6(b)

Nature of splitting in a tetrahedral field.

The lower-energy $d_{x^2-y^2}$ and d_{z^2} orbitals are now labelled e_2 and the higher energy d_{xy}, d_{yz}, d_{zx} orbitals are now labelled t_2; the subscript g does not apply in the tetrahedral case as the tetrahedron does not possess a centre of symmetry.

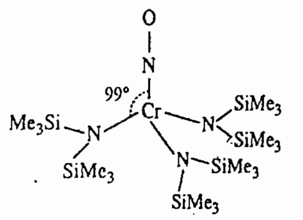
The separation between t_2 and e levels (Δ_{tet}) in the tetrahedral case is much less than that in the corresponding octahedral field. If the same ligands operate on the same metal ion at the same distance, we expect that the electrostatic effect of four point charges will be $\frac{2}{3}$ rd of that produced by six point charges. Again, none of the metal-ligand interactions in a tetrahedral complex are "straight forward". Detailed calculations now show that

$$\Delta_{tet} = \frac{4}{9}\Delta_{oct} = \frac{4}{9}\cdot 10Dq_{oct}$$

for the same metal ion and same ligands at same metal-ligand distances. In general terms, the magnitude of splitting for a tetrahedral complex is nearly half that for the corresponding octahedral complex. Tetrahedral complexes thus gain lower CFSE compared to octahedral complexes. This is supported by the absorption spectra of VCl_4

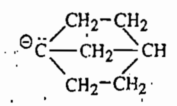
and VCl_6^{2-}. Though VCl_4 has significant covalence, one may treat it by the CFT as a tetrahedral complex of V(IV), d^1 system. The ground state configuration would then be $e^1t_2^0$. Absorption of light results in the electronic transition $e \rightarrow t_2$. If this is related to the broad absorption band of VCl_4 centered around 8000 cm^{-1}, Δ_{tet} for VCl_4 should be equal to 8000 cm^{-1}. This is nearly half the value of Δ_{oct} observed with VCl_6^{2-} (15400 cm^{-1}).

Since tetrahedral complexes are marked by lower crystal field splittings, the energy separation is usually lower than the pairing energy. Hence the complexes are mostly high spin. However, $[Cr\{N(SiMe_3)_2\}_3NO]$ (Me = methyl) is a low-spin complex with a distorted tetrahedral structure; it contains Cr(II) (d^4) coordinated by NO^+ and three $\overline{N}(SiMe_3)_2$. Tetrakis(1-norbornyl)cobalt(IV) is also a low-spin tetrahedral complex of cobalt(IV).



(a)

Skeleton of $[Cr\{N(SiMe_3)_2\}_3NO]$.



(b)

The 1-norbornyl anion (bicyclo[2.2.1]hept-1-yl).

27-II

Since tetrahedral complexes are not favoured by large CFSE, they are adopted only when the ligands are large or other stereochemistry is not favoured by high gain of CFSE.

Orbital splittings in fields of other symmetries

In order to find the nature of *d*-orbital splitting in other stereochemical environments, we can apply the same ideas of electrostatics and symmetry that we used in octahedral and tetrahedral cases.

Square planar complexes

The crystal field splitting diagram for the square planar case may be obtained in either of two ways. (i) We can gradually remove the two trans-axial ligands from an octahedral complex to infinity or (ii) we can start with the square planar arrangement. As the ligands along the *z*-axis in an octahedral complex are removed, the *d*-orbitals having a *z*-component will be subject to less electrostatic repulsion from the ligands. Hence the energies of d_{z^2}, d_{xz} and d_{yz} will be lowered. There will be corresponding increase in the energies of other orbitals, conserving the barycenter (Fig. 27.7).

In the limiting square planar complex with ligands in the *xy* plane, we can readily conclude that the $d_{x^2-y^2}$ orbital will be highest in energy as its lobes point directly at the ligands. The d_{xy} orbital, lying in the same plane, should be the second highest in energy. The d_{z^2} orbital appears next in energy but in some cases it may lie below the d_{xz}, d_{yz} orbitals.

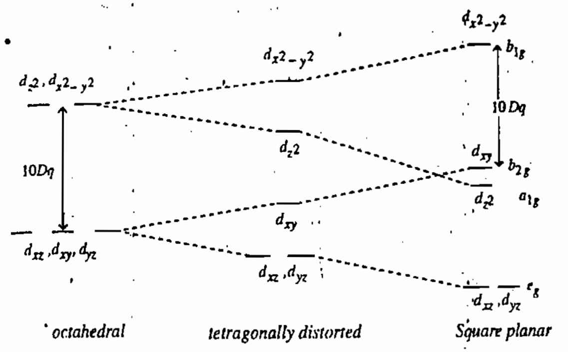


Fig. 27.7

The effect of gradual removal of the z-ligands in an octahedral complex.

Q. 27.1 *The difference in energy between the $d_{x^2-y^2}$ and d_{xy} orbitals in a square planar field is identical to the difference between the same orbitals in the octahedral field. Comment.*

Hint : We have imagined the formation of a square planar complex from an octahedral one by elongation of the z-ligands. As these ligands are further removed, the effect will be the same on the two orbitals on the *xy* plane. When the z-ligands are completely detached, the $d_{x^2-y^2}$ and d_{xy} orbitals will maintain the same difference of energy as before since both have been equally raised.

Relative energies of different *d*-orbitals in the square planar complex have been calculated as follows (in units of *Dq*).

d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}, d_{yz}
−4·28	12·28	2·28	−5·14

It may be observed that square planar complexes are marked by high crystal field stabilization energies. The only splitting large enough to give rise to spin pairing is that between $d_{x^2-y^2}$ and d_{z^2}. The CFSE for various d^n configurations in strong field are given in Table 27.3.

TABLE 27.3

CFSE (strong field) for square planar complexes (in units of *Dq*)

d^1	e_g^1	5·14	d^6	$e_g^4a_{1g}^1b_{2g}^1$	22·56 − *p*
d^2	e_g^2	10·28	d^7	$e_g^4a_{1g}^2b_{2g}^1$	26·84 − *p*
d^3	$e_g^2a_{1g}^1$	14·56	d^8	$e_g^4a_{1g}^2b_{2g}^2$	24·56 − *p*
d^4	$e_g^2a_{1g}^1b_{2g}^1$	12·28	d^9	$e_g^4a_{1g}^2b_{2g}^2b_{1g}^1$	12·28
d^5	$e_g^3a_{1g}^1b_{2g}^1$	17·42 − *p*	d^{10}	$e_g^4a_{1g}^2b_{2g}^2b_{1g}^2$	0

Metal ions with d^8 configurations form square planar complexes which are favoured by high CFSE. A strong ligand field raises the energy of the $d_{x^2-y^2}$ orbital which eventually remains unoccupied. The orbitals lowered in energy become occupied. Some common examples of square planar complexes of d^8 metal ions are $[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$, $[AuCl_4]^-$, $[Ag(OH)_4]^-$ and $[Pt(NH_3)_4]^{2+}$.

Crystal Field Splitting in TBP and Square Pyramid geometry

Qualitative crystal-field splitting diagrams for 5-coordinate trigonal bipyramid and square pyramid geometries are shown in Fig. 27.8.

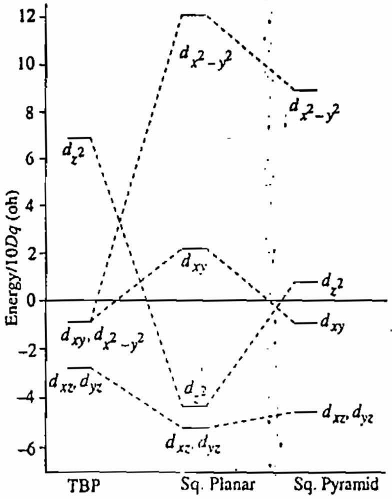


Fig. 27.8

Comparative crystal field splitting in TBP, Sq. Planar and Sq. Pyramid cases.

Energies in $10Dq$. (Pyramid base lies in the xy plane).

Q. 27.2 *Draw a qualitative crystal field splitting diagram in a cubic environment of ligands by reference to a tetrahedral field.*

Solution : (See Fig. 27.9). The tetrahedral field was derived from a cubic field in which ligands are missing from alternate corners of the cube. With the same reference frame of coordinates, the pattern of splitting in a cubic field will be the same as in a tetrahedral field. But the magnitude of Δ_c will be twice as great as Δ_{tet}. As the cubic field is centrosymmetric, the subscript 'g' is included in the terms for the two sets of orbitals. With the same metal ion and same ligands at same distances,

$$\Delta_{cubic} = 2\Delta_{tet} = 2 \times \frac{4}{9}\ \Delta_0 = 0{\cdot}889\ \Delta_0.$$

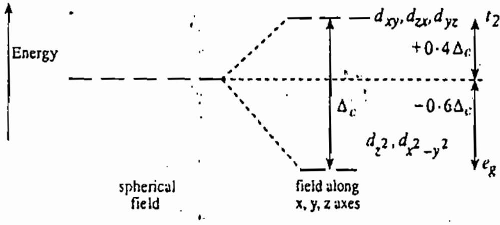


Fig. 27.9 : Splitting of d-orbitals in a cubic crystal field.

In units of Dq $(10Dq = \Delta_0)$; the relative energies of various orbitals are $d_{z^2}, d_{x^2-y^2}$: $-5{\cdot}34$; d_{xy}, d_{yz}, d_{zx} : $+ 3{\cdot}56$.

Note : It is obvious that a d^4 metal ion (e_g^4) will have the highest CFSE in such a field.

Factors affecting the magnitude of Δ

Certain generalizations can be made from the magnitudes of Δ determined from spectral studies on various complexes. Some typical values for a few octahedral complexes are given in Table 27.4.

TABLE 27.4

Values of Δ (kK)* for some octahedral complexes

		$6F^-$	$6H_2O$	$6NH_3$	$6CN^-$
d^3	Cr^{3+}	15·06	17·4	21·5	26·6
d^5	Mn^{2+}	7·75	8·5	—	~ 30
	Fe^{3+}	13·35	14·0	—	35
d^6	Fe^{2+}	—	10·4	—	32·2
	Co^{3+}	13·1	20·7	22·9	32
d^8	Ni^{2+}	7·3	8·5	11·0	—

* 1kK (kilo Kayser) = 1000 cm^{-1} = 10^5 m^{-1} ≡ 11·97 kJ mol^{-1}.

1. For a given ligand, Δ_0 does not vary much along the metal ions in first transition series in the same oxidation state. Thus Δ_0 for hexaaqua complexes of Mn^{2+} and Ni^{2+} have nearly same values.

2. For a given ligand, Δ_0 increases with the oxidation state of the metal. The hexaaqua complex of Fe^{3+} has a much higher value of Δ_0 than has the Fe^{2+} complex.

3. For a given ligand and same stereochemistry, the magnitude of Δ_0 increases by about 30% to 50% on passing from the 1st transition series to the 2nd transition series and again by about the same amount from the 2nd transition series to the 3rd transition series, that is

$$3d < 4d < 5d$$

For example, Δ_0 for the three hexaammines increases as $[Co(NH_3)_6]^{3+}$: 23,000 cm^{-1}; $[Rh(NH_3)_6]^{3+}$: 34,000 cm^{-1}; $[Ir(NH_3)_6]^{3+}$: 41,000 cm^{-1}. Higher effective nuclear charge and greater spatial distribution of the larger d-orbitals are mainly responsible for this change.

4. For a given ligand and stereochemistry, the metal ions can be arranged according to increasing order of Δ_0 (see Table 27.5) :

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$$

This is a spectrochemical series of the metal ions—the magnitude of Δ_0 generally increases with the charge on the metal which results in increased metal-ligand interaction.

Spectro-chemical series

Similarly, a spectrochemical series of the ligands may be written by arranging them in the increasing order of their Δ-value or field strength in a given geometry. It is not possible to form the entire series by studying complexes with a single metal ion; the series has been made by overlapping different sequences obtained from spectroscopic studies. It has been so named because the original order for ligands X was determined from spectral shifts for complexes such as $[Co(NH_3)_5X]^{n+}$. The order of common ligands according to their increasing ligand field strength is

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < CH_3CO_2^- < C_2O_4^{2-},\ O^{2-} < H_2O <$$
$$NCS^- < py \sim NH_3 < en < dipy \sim o\text{-phen} < NO_2^- < CN^- < CO.$$

However, it is not possible to interpret the series from electrostatic effects alone. For example, neutral water molecules offer a stronger ligand field than the negatively charged hydroxyl ion. Also, H_2O has a greater dipole moment than NH_3; but the latter causes a greater crystal field splitting. Similarly, many neutral ligands occupy the extreme right region of the series. We shall find that the sequence in the spectrochemical series is explained satisfactorily in the m.o. theory.

The spectrochemical series for ligands is useful in a semiquantitative way—the ligands cyanide and CO are known as strong-field ligands while the halides are weak field ligands. Ligands such as water and ammonia are said to produce medium field strengths. If one knows the position of the absorption maxima in the complex of a metal with any ligand, one can approximately predict the position (or region) of the band for analogous complexes of this metal with other ligands. Similarly, if a metal forms a low-spin complex with say, ethylenediamine, it will form low-spin complexes with ligands farther right to it in the series, that is, bipyridyl or cyanide ions.

Jörgensen suggested a method of estimating the approximate Δ_0 for an octahedral complex from two independent factors arising from the ligand and the metal :

$$\Delta_0 = f \cdot g$$

f describes the field strength of the ligand relative to water ($f = 1$). The value of f usually lies in the range 0.7 to 1.7; g depends upon the nature of the metal and may have values ranging from 8000 to 36,000 cm^{-1} (Table 27.5).

TABLE 27.5

Some f and g values

Ligand	f	Metal	g (in kK)
Br^-	0·72	Mn (II)	8·0
Cl^-	0·78	Ni (II)	8·7
oxalato	0·99	Co (II)	9·0
H_2O	1·00	Fe (III)	14·0
py	1·23	Cr (III)	17·4
NH_3	1·25	Co (III)	18·2
en	1·28	Ir (III)	32.0
CN^-	1·70	Pt (IV)	36.0

Applications of the crystal field theory

The crystal field theory can be applied to explain certain spectral, magnetic, thermodynamic and structural properties of coordination compounds.

Spectral properties : The colour and spectra of the complexes in the visible and ultraviolet region may be correlated to transition of electrons between the split groups of d-orbitals. We have already applied this to the purple solution of $[Ti(H_2O)_6]^{3+}$. Details of colour and spectra will be discussed separately later in this chapter.

Magnetic properties : The crystal field theory also helps us to explain the observed paramagnetism and diamagnetism of complex compounds in terms of ground state distribution of the metal d-electrons among the energetically discriminated groups of d-orbitals. We have seen (Table 27.2) how the ground state electron distribution for various d^n ions in octahedral field gives rise to various number of unpaired electrons. For d^1, d^2, d^3, d^8, d^9 and d^{10} configurations, the electrons can be distributed among the t_{2g} and e_g levels in only one way (Fig. 27.10). The calculated spin-only magnetic moment from the number of unpaired electrons for these configurations are also shown.

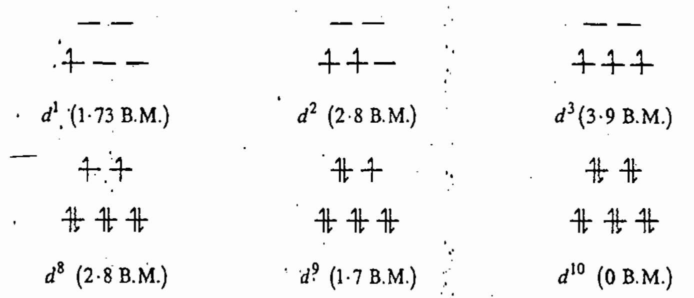


Fig. 27.10 : Electron occupancy in CFT.

Ground state electron occupancy of d^1, d^2, d^3, d^8, d^9 and d^{10} configurations in octahedral complexes. Expected spin-only magnetic moments are given in parentheses.

Weak field
$p > \Delta_0$
"high spin"

The remaining d^n configurations, that is, d^4, d^5, d^6 and d^7 present two alternative electron distributions depending upon the relative magnitudes of the crystal-field splitting parameter Δ_0 and the pairing energy p. We have seen (Table 27.2) that in complexes with small crystal field splitting (*weak field* complexes), the magnitude of Δ_0 may be less than the pairing energy (p) of an electron in the t_{2g} level, giving rise to *high spin* or *spin-free* complexes with maximum number of unpaired electrons. In complexes with large value of Δ_0 (*strong field*, $\Delta_0 > p$), electrons pair up as far as practicable in the t_{2g} level, giving rise to *low-spin* or *spin-paired* complexes. The *spin-only* magnetic moment calculated for each type (see VBT) from the number of unpaired electrons in different d^n ions is shown in Table 27.6.

TABLE 27.6

Calculated spin-only magnetic moment (B.M.) for octahedral complexes of d^4, d^5, d^6 and d^7 ions

High Spin

Configuration	Distribution t_{2g}	Distribution e_g	No. of unpaired electrons	μ (B.M.)
d^4	↑ ↑ ↑	↑	4	4·9
d^5	↑ ↑ ↑	↑ ↑	5	5·9
d^6	↑↓ ↑ ↑	↑ ↑	4	4·9
d^7	↑↓ ↑↓ ↑	↑ ↑	3	3·9

Low Spin

Configuration	Distribution t_{2g}	Distribution e_g	No. of unpaired electrons	μ (B.M.)
d^4	↑↓ ↑ ↑		2	2·8
d^5	↑↓ ↑↓ ↑		1	1·7
d^6	↑↓ ↑↓ ↑↓		0	0
d^7	↑↓ ↑↓ ↑↓	↑	1	1·7

The experimental magnetic moments of complexes of d^1 to d^9 metal ions show good agreement with the spin-only value calculated on the basis of above distributions.

The existence of two separate classes of complexes are distinctly shown by the following examples

			$\mu_{calculated}$	$\mu_{experimental}$
High spin	$[CoF_6]^{3-}$	$t_{2g}^4e_g^2$	4·9 B.M.	4·3 B.M.
	$[FeF_6]^{3-}$	$t_{2g}^3e_g^2$	5·9 B.M.	5·9 B.M.
Low spin	$[Co(NH_3)_6]^{3+}$	t_{2g}^6	0	0
	$[Fe(CN)_6]^{3-}$	t_{2g}^5	1·7 B.M.	2·4 B.M.

Q. 27.3 *What is the probable electron configuration of an octahedral complex of Co(II) whose experimental magnetic moment is 4·0 B.M.?*

Hint : Co(II) is a d^7 species. The high-spin configuration $t_{2g}^5e_g^2$ has three unpaired electrons with calculated spin-only magnetic moment 3·9 B.M.

Note : In this and many other cases, e.g., the $[Fe(CN)_6]^{3-}$ ion mentioned before, observed magnetic moments often deviate significantly from the spin-only value. This is mainly due to orbital contribution which will be discussed later in this chapter.

Thermodynamic properties : The effect of crystal field stabilization energy appears most prominent when related to the enthalpy of formation of many complexes. Since values of Δ lie in the region 10 kK to 30 kK (Table 27.4), it follows that CFSE-s will lie in the range 5-40 kK, that is 60-480 kJ mol^{-1}. Clearly these amounts of energy are not insignificant. We shall see their role in some cases.

(i) **Ionic radii of M^{2+}/M^{3+} ions,** (M = 3*d* series metal)

Proceeding along the transition metal series, one might expect that the radii of ions should show a steady decrease with increase in effective nuclear charge. The actual values show fluctuations as evident from the crystal radii given in Table 27.7. When plotted against the number of *d*-electrons, these give a typical two humped curve (Fig. 27.11). The radius of a metal ion is determined by the proximity to which it may be approached by surrounding ions or ligands. In a strong octahedral environment, the metal electrons will gradually populate the t_{2g} level. Since these orbitals do not lie directly along the path of approaching ligands, the ligands can approach the metal ion closer. In other words, the size of the metal ion shows a steady decrease until the t_{2g}^6 configuration is reached. As the next electron enters an e_g level, it is placed at an orbital directed at the ligands. Repulsion causes an increase in the effective radius of the metal ion. This explains the hump.

TABLE 27.7

Crystallographic radii (pm) for 1st transition series metal ions

(C.N. 6; low-spin values given in parentheses)

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
M^{2+}	114	—	100	93	94	97	92	88·5	83	87
						(81)	(75)	(79)		
M^{3+}	—	88·5	81	78	75·5	78·5	78·5	75	74	—
						(72)	(69)	(68·5)	(70)	

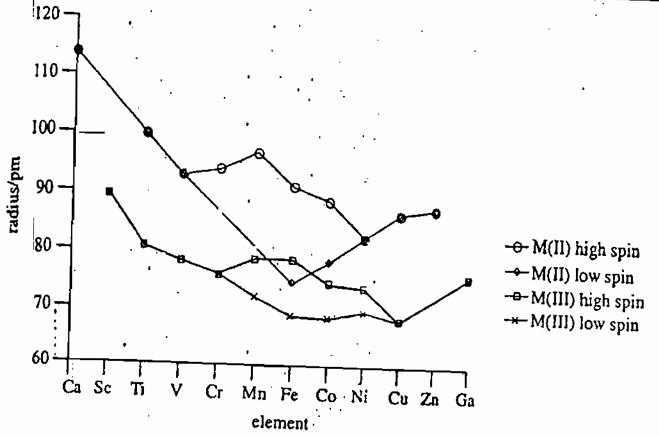


Fig. 27.11

Ionic radii of M^{2+} and M^{3+} ions.

In a weak octahedral field, an electron enters an e_g level as soon as the t_{2g} level has three electrons. Consequently the size of the ion increases at d^4 and d^5; the size decreases again when electrons occupy the t_{2g} level (d^6 – d^8 configurations). Ions with d^9 and d^{10} configurations again show an increase in size corresponding to population of the e_g level.

(ii) **Lattice energy of metal halides**

The lattice energies of divalent halides MX_2 (M = Ca — Zn) may be calculated by using the Born-Landé equation. On electrostatic considerations alone, one expects that the ionic radii of M^{2+} ions should gradually decrease along the series Ca^{2+}—Zn^{2+} and the corresponding lattice energies of MX_2 should smoothly increase. This expectation holds for CaX_2, MnX_2, and ZnX_2 (Fig. 27.12), where the metal ions are d^0, d^5 or d^{10}. In other cases, the experimental lattice energies form a double humped curve. This can be

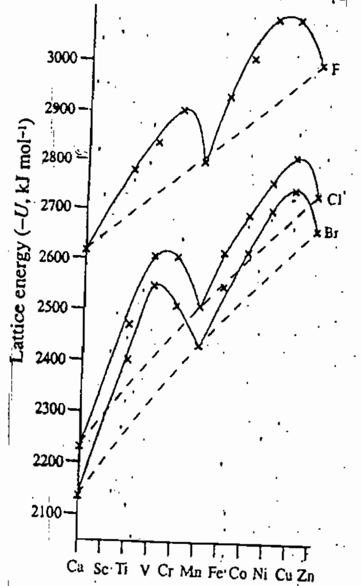


Fig. 27.12

Lattice energies of MX_2 type dihalides (M = Ca – Zn).

explained on the basis of CFSE calculated for the solid halides assuming an octahedral environment of the halides around the metal ions. The halide ions provide a weak ligand field in which the lower energy t_{2g} level is occupied first in ions with configurations d^1, d^2 and d^3. The additional CFSE gained in this manner explains the steady rise of lattice energy above the theoretical value. With d^4 and d^5 metal ions, occupancy of the e_g level lowers the CFSE and also increases the effective size of the ion; the lattice energy decreases (in magnitude). The same pattern is repeated for the ions with d^6 - d^{10} configurations. Unfortunately the correlation remains essentially qualitative because of the high uncertainties in experimental results.

(iii) Enthalpy of hydration of transition metal ions

Heats of hydration of divalent metal ions of the first transition series are related to the process

$$M^{2+}(g) + H_2O\,(excess) \longrightarrow [M(H_2O)_6]^{2+}(aq)$$

Although this enthalpy change should be measured at infinite dilution (or extrapolated), the metal ion may be assumed to remain octahedrally coordinated by six water molecules in the first neighbourhood. Hence we may relate this enthalpy of hydration to the enthalpy of formation of their hexaaquo complexes. If the ratio of charge to radius were the only factor affecting the bonding in such complexes, we would expect that the heats of hydration should increase steadily from Ca^{2+} to Zn^{2+} with expected decrease in radius. The actual values, however form a doubly humped curve as shown in Fig. 27.13. The shape of the curve again matches with our expectation for additional CFSE gained in the weak octahedral field of H_2O by the ions except d^0, d^5 and d^{10} cases. When the estimated CFSE is subtracted from the experimental values a smooth curve with upward slope is obtained.

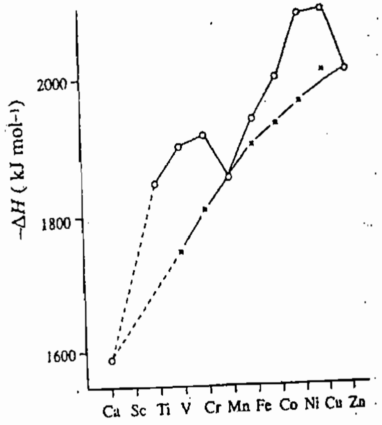


Fig. 27.13 Hydration energies (−Δ*H*) of divalent metal ions;

o : experimental values

• : values corrected for CFSE.

(iv) Structure of mineral spinels

The spinel structure is typical for a large number of ternary oxides and sulfides of the general stoichiometry AB_2X_4 where X = O or S. A is usually a cation of charge +2 and B a cation of charge +3 but other combinations are also known, as shown below:

Charge of A	Charge of B	Example
(i) 2+	3+	$MgAl_2O_4$
(ii) 4+	2+	$TiMg_2O_4$, $ZrCu_2S_4$
(iii) 6+	1+	Na_2WO_4 *(distorted)*

[Sec. 27.1.3 *CFT—applications*]

As evident from the stoichiometry, one type of cation (cation B in category i and ii) is twice as abundant as the other. The overall structure consists of a cubic close packing of the anions giving rise to both tetrahedral and octahedral holes. *n* close-packed anions generate *n* octahedral holes and 2*n* tetrahedral holes; among these, the A cations normally occupy one-eighth of the tetrahedral sites and the B cations occupy half of the octahedral holes. The distribution of A and B cations in the *normal* spinel structure may be represented as $A^{tet}B_2^{oh}X_4$ where the superscripts denote the coordination geometry of the ions.

However, in some spinels, the coordination geometry of A and B cations are reversed — the A cations displace half of the B cations from their octahedral sites, the displaced B cations now enter the vacated tetrahedral sites. This is usually referred to as the *inverse* spinel structure. The coordination geometries in normal and inverse spinels may be summarised as

Normal spinel	Inverse spinel
$A^{tet}B_2^{oh}X_4$	$B^{tet}(AB)^{oh}X_4$

Lattice energy considerations provide some rationalization for the normal spinel structure : the B-cations with higher charge provide greater lattice energy when placed in an octahedral environment (coordination no. 6) than in a tetrahedral environment (coordination no 4).

The adoption of inverse spinel structure by some minerals may result from a number of factors like charge and size of the ions. For spinels containing transition metal ions, relative gain of crystal field stabilization energy for one structure over another may be a dominant factor.

The B-cations, with higher charge, are usually smaller in size than the A-cations. Side by side, the tetrahedral holes are smaller than the octahedral holes. This may prompt half of the smaller B-cations to occupy tetrahedral holes giving rise to the inverse structure if the loss in lattice energy is not too high.

In oxide spinels containing transition metal ions, the CFSE may become an additional factor in determining the ultimate structure. The oxide ion is a moderately weak field ligand giving the spinels high spin occupancy of the metal *d*-orbitals with maximum number of parallel spins.

Some spinels with inverse structure are the iron (III) oxide spinels like AFe_2O_4 where A may be Co^{2+}, Ni^{2+} or Cu^{2+}. The gain of CFSE by transfer of the A^{2+} ions from tetrahedral to octahedral coordinations in the moderately weak ligand field of oxide ions seems to be the determining factor in these cases; the transfer of Fe^{3+} (d^5) ion from weak octahedral field to tetrahedral field makes little loss of CFSE. Let us take the case of $NiFe_2O_4$.

Ni^{2+} octahedral $t_{2g}^{6}e_g^{2}$ CFSE = $1.2\Delta_0$

Ni^{2+} tetrahedral $e^4t_2^4$ CFSE = $0{\cdot}8\,\Delta_t \approx 0{\cdot}36\,\Delta_0$

Thus, the system will gain in CFSE if Ni^{2+} ions occupy octahedral sites rather than tetrahedral holes. Displacement of the Fe^{3+} ions from the octahedral holes does not make any loss or gain in CFSE (d^5 : $t_{2g}^{3}e_g^{2}$ or $e^4t_2^3$).

$NiAl_2O_4$ also has an inverse spinel structure since only Ni^{2+} ions are ligand field stabilized in an octahedral site.

The difference between the CFSE for octahedral and tetrahedral cases is the excess octahedral site stabilization energy (OSSE). OSSE values for some first row transition metal ions are given below (converted to kJ mol⁻¹).

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}
0	17	31	86	64	29	54	158	95	0

The high preference of Cr^{3+} for octahedral sites reinforces the lattice energy factor for the normal spinel structure, as is found in $MgCr_2O_4$.

Q. 27.4 *$CuFe_2O_4$ has an inverse spinel structure but $ZnFe_2O_4$ has the normal spinel structure. Comment.*

Hint : Zn^{2+} is a d^{10} ion; no gain in CFSE if transferred to octahedral holes.

Q. 27.5 *Magnetite, Fe_3O_4, may be looked upon as a mixed valence oxide : $FeFe_2O_4$. Do you expect it to adopt the normal spinel structure from CFSE considerations?*

Hint : Fe^{2+} (d^6) will have higher CFSE in octahedral environment than in a tetrahedral environment. Fe^{3+} (d^5) has zero CFSE in both tetrahedral and octahedral fields. Hence the structure expected is inverse spinel.

Q. 27.6 *Both Mn_3O_4 and Co_3O_4 are mixed valence oxides with normal spinel structure. Comment.*

Hint : In $Mn^{II}Mn_2^{III}O_4$., Mn^{II} is d^5, CFSE is zero in both tetrahedral and octahedral environments. Mn^{3+} (d^4) has a site preference for octahedral field.

In $Co^{II}Co_2^{III}O_4$. Co^{2+} is d^7, offering some preference for octahedral sites over tetrahedral. However, this is not sufficient to displace the Co^{3+} ions from their octahedral environment where the CFSE is high because of its low spin t_{2g}^6 configuration. If the structure were to invert, half of the Co^{3+} ions would be forced to tetrahedral sites where they will be high spin, making a tremendous loss of CFSE.

Spinels containing ions with magnetic moments exhibit interesting magnetic properties like ferromagnetism and antiferromagnetism because the ions are close enough to interact mutually (see later).

(v) Trend in formation constants

We have noted earlier that the formation constants of complexes of divalent metal ions from Mn^{2+} to Zn^{2+} with nitrogen donor ligands follow the general trend :

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}.$$

This order is sometimes called the Irving-Williams order. There may be certain exceptions to this order arising from spin-pairing effects in strong crystal fields, but the general order of the stability constants are consistent with crystal field stabilization.

Complexation equilibria with nitrogen donor ligands in aqueous solution may be represented as (N = nitrogen donor ligand)

$$[M(H_2O)_6]^{2+} + N \rightleftharpoons [M(H_2O)_5N]^{2+} + H_2O \text{ ...and so on.}$$

Since the N-donor ligands lie higher in the spectrochemical series, the substituted complexes will have higher CFSE than the aqua complexes. For Mn^{2+} (d^5 weak), there is no CFSE and hence the substitution process does not result in any extra crystal field stabilization. This is again true for Zn^{2+} (d^{10}). The intermediate ions (d^6 - d^9) offer varying amount of additional CFSE according to the number of t_{2g} and e_g electrons. This effect of CFSE controls the enthalpy term (ΔH). If we reasonably assume that the entropy change in complex formation remains essentially same for all ions, the ΔG^0 and hence K-values of complex formation will be determined by the enthalpy term :

$$RT\ln K = -\Delta G^0 = -\Delta H^0 + T\Delta S^0$$

(vi) Preferred geometry : octahedral vs tetrahedral coordination.

The common geometries found in complex compounds are tetrahedral, square planar and octahedral. Unless opposed by severe steric or electronic factors, the octahedral coordination, using the largest number of available sigma bonding orbitals on the metal, is the most stable one. As we have already seen, such complexes are also favoured by higher CFSE than tetrahedral complexes. However, certain metal ions in the first transition series

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exhibit a greater tendency than others to form tetrahedral complexes. The relative stabilities of octahedral and tetrahedral complexes of a metal naturally depend upon several factors in addition to CFSE. However, if we compare such trends in a series of ions where all other factors contributing to ΔH^0 vary uniformly, the effect of the difference between the CFSE's may be appreciated to some extent.

[Sec. 27.1.3
*CFT—
J-T distortion*]

CFSE in both tetrahedral and octahedral fields may be expressed in terms of Δ_{oct} (using the relation $\Delta_{tet} = \frac{4}{9}\Delta_{oct}$). Thus, for a d^1 ion in tetrahedral field (e^1), the CFSE is $\frac{3}{5}\Delta_{tet} = \frac{3}{5} \times \frac{4}{9}\Delta_0 = 0{\cdot}266\,\Delta_0$. The values of CFSE thus obtained for all the d^0 to d^{10} configurations may be similarly calculated. These are plotted against the number of d-electrons together with the CFSE values of high spin octahedral complexes in Fig. 27.14.

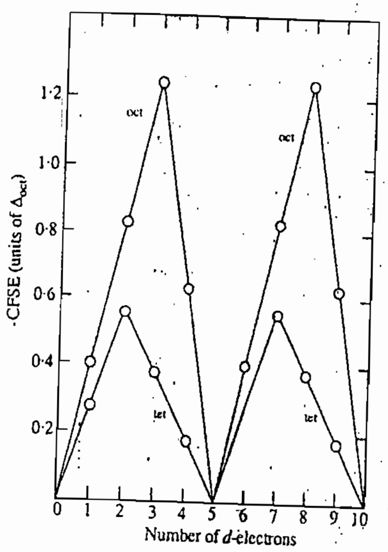


Fig. 24.14

CFSE for d^0—d^{10} (high spin) ions in octahedral and tetrahedral fields.

It appears that the d^3 and d^8 (high spin) configurations will gain high CFSE on passing from tetrahedral to octahedral coordination. Indeed, Cr(III) (d^3) and Ni(II) (d^8) show strong preference for octahedral coordination over tetrahedral. In fact, tetrahedral chromium(III) complexes are virtually unknown.

The d^4 and d^9 configurations are next to gain a higher CFSE by adopting octahedral coordination, for example Mn(III) and Cu(II). However, these configurations gain further stabilization through distortion (see later).

Ions with d^1, d^2, d^6 and d^7 configurations will gain little additional CFSE on passing from tetrahedral to octahedral coordination. Hence, these ions may be expected to form many tetrahedral complexes. Thus V(III) (d^2), unlike Cr(III), forms tetrahedral VX_4^- species (X = Cl, Br, I); Co(II) (d^7), unlike Ni(II) (d^8), similarly forms a large number of tetrahedral complexes with both neutral and anionic ligands.

d^0, d^5 (high spin) and d^{10} configurations have no crystal field stabilization either in tetrahedral or octahedral environment.

Distortion from perfect symmetry : The Jahn Teller effect

We have seen how the degeneracy of the five d-orbitals is removed in a crystal field to provide greater stability by way of crystal field stabilization energy. Further removal of the degeneracy of the d-orbitals can sometimes result in additional stabilization of the system. This involves distortion of the complex from perfectly symmetric geometries like the regular octahedral in case of six-coordinate complexes. Certain electron configurations facilitate such distortions. For example, consider an octahedral high spin d^4 complex having $t_{2g}^3e_g^1$ distribution of electrons. In a regular octahedral environment, the e_g level is doubly degenerate : the electron can occupy either the $d_{x^2-y^2}$ or d_{z^2} orbital. If the e_g level is split as a consequence of some distortion in the regular geometry, the electron will now occupy the lower energy state and get further stabilized. A rigorous and generalized statement of this situation was made by Jahn and Teller in 1937 in a theorem :

Any nonlinear molecule in a degenerate electronic state will undergo distortion to remove the degeneracy and to lower the energy.

The theorem only tells us when a distortion is most likely to be expected; but it does not tell us anything about the direction or magnitude of distortion. But it requires that if the undistorted system has a center of symmetry, this will be maintained in the equilibrium configuration after distortion. Examples of Jahn-Teller distortions are common among systems with unsymmetrically filled e_g level :

d^4 *(high spin)* : CrF_2, MnF_3

d^7 *(low spin)* : $NaNiO_2$

d^9 : $CuCl_2$, CuF_2, K_2CuF_4

The structure of the $[Cu(H_2O)_6]^{2+}$ ion in the perchlorate salt is shown below. The unusually long axial Cu-O distances are noteworthy. Since the ion still retains a four-fold axis of symmetry, the distortion is referred to as *tetragonal distortion.* The $[Ni(H_2O)_6]^{2+}$ ion, in contrast, has a symmetric octahedral distribution of the ligands.

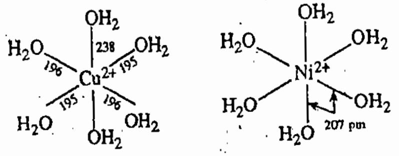


Fig. 27.15

J-T distortion in octahedral Cu(II).

Tetragonally distorted octahedral structure of $[Cu(H_2O)_6]^{2+}$ in $[Cu(H_2O)_6][ClO_4]_2$ and the symmetric octahedral structure of $[Ni(H_2O)_6]^{2+}$ in $[NH_4]_2[Ni(H_2O)_6][SO_4]_2$.

We may use simple physical reasoning to appreciate Jahn-Teller distortion with the $[Cu(H_2O)_6]^{2+}$ ion example. In an octahedral field, the d^9 ion has an electron distribution $t_{2g}^6e_g^3$. Since the e_g levels are degenerate, we may have two alternative ways of filling them :

Case 1 : $d_{x^2-y^2}^1d_{z^2}^2$: The ligands along the x and y axes will be less screened from the electrostatic attraction of Cu^{2+} ion than the two ligands on the z-axis. Hence the four ligands in the xy-plane will be drawn more closely to the cation than the other two on the z-axis. This gives rise to a tetragonal distortion of the octahedron which is elongated along the z-axis (z-out).

Case 2 : $d_{x^2-y^2}^2d_{z^2}^1$: The four ligands in the xy-plane will be more screened from the electrostatic attraction of the Cu^{2+} ion than the two ligands on the z-axis. Hence, the two axial ligands will be drawn more closely than the other four and we shall get a tetragonally distorted octahedron with a contraction along the z-axis (z-in).

These two situations are illustrated in Fig. 27.16.

For copper (II) compounds, most experimental data indicate an elongated octahedron with two long and four short distances, as shown earlier for $[Cu(H_2O)_6]^{2+}$ ion.

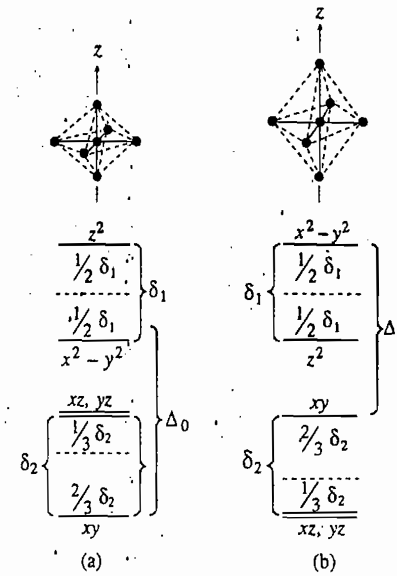


Fig. 27.16

Consequence of Jahn-Teller distortion in an octahedral complex : (a) z-in and (b) z-out situation. Drawing not to scale. $\delta_2 < \delta_1 << \Delta_0$.

An examination of Fig. 27.16 reveals that distortion (either z-in or z-out) results in a lower energy for the system, that is, causes stabilization. The *centre of gravity* rule holds for the tetragonal splitting and the system gains a net stabilization equal to $\frac{1}{2}\delta_1$. There is no net change in energy for the t_{2g} electrons.

Following the same line of argument, we expect J-T distortion in complexes of metal ions having unsymmetrical electron distribution in e_g or the t_{2g} level. Since the e_g group of orbitals lie directly along the lines of approach of the ligands in an octahedral field, the distortion is much pronounced with unsymmetrical electron occupancy in the e_g level. Thus, we also expect pronounced J-T distortion with ions of the following configurations (in addition to the $t_{2g}^6e_g^3$ configuration discussed above).

$t_{2g}^3e_g^1$: high-spin Cr(II) and Mn(III);

$t_{2g}^6e_g^1$: low-spin Co(II) and Ni(III);

Except with low spin Co(II), there are ample evidences to confirm the expected distortion. Indeed, some Cu(II) compounds undergo such a high amount of distortion that the coordination around the metal appears virtually square planar, as in the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

We should also expect J-T distortions when an octahedral complex has 1, 2, 4 or 5 electrons in the t_{2g} level. Since these orbitals are not oriented directly along the lines of approach of the ligands, the splitting of these orbitals consequent to distortion would be naturally very small and difficult to detect. Referring to Fig. 27.16, we expect a t_{2g}^1 species to be stabilized by $\delta_2/3$ on elongation along one axis; flattening along one axis would cause stabilization by $2\delta_2/3$. Similar reasoning leads us to expect distortion by elongation in case of t_{2g}^2 configuration (stabilization = $2\delta_2/3$) and distortion by flattening in the t_{2g}^5 case.

Since the energy difference involved is very small, there is little experimental evidence to confirm such distortions owing to partially filled t_{2g} configurations. However, the Jahn-Teller theorem applies to excited states as well. When the first excited state of any species has partially filled e_g level, we expect much greater J-T distortion. Such effects are readily observed in the electronic spectra, as we have already seen in the case of $[Ti(H_2O)_6]^{3+}$ ion. The ground state of the ion suggests a distorted octahedral structure with the single electron occupying the d_{xy} orbital, the z-in distortion providing more stabilization than the z-out distortion. The excited state being also susceptible to distortion, we expect two transitions :

$$d_{xy} \rightarrow d_{x^2-y^2};\ d_{xy} \rightarrow d_{z^2}$$

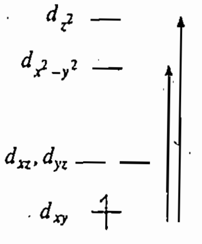


Fig. 27.17 The two transitions expected in a d^1 metal complex consequent to J-T distortion.

The transition $d_{xy} \rightarrow d_{yz},\ d_{zx}$ will not be observed in the visible spectrum; the very small energy gap should drive it to the i.r. region of the spectrum. The broad shoulder in the spectrum of $[Ti(H_2O)_6]^{3+}$ is in fact a superposition of two overlapping bands, one at around 17,000 cm^{-1} and the other at about 20,000 cm^{-1}. Similar broadenings of visible absorption bands are observed in the case of d^6 high spin ions $[Fe(H_2O)_6]^{2+}$ and $[CoF_6]^{3-}$; both $t_{2g}^4 e_g^2$. They become J-T sensitive in the first excited state $(t_{2g}^3 e_g^3)$ (Fig. 27.18).

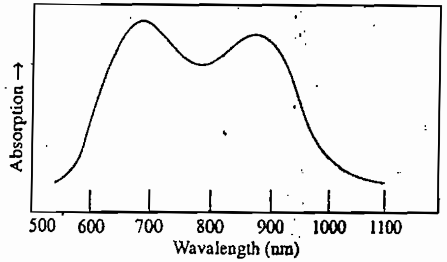


Fig. 27.18 The nature of absorption spectrum of $[CoF_6]^{3-}$ (not to scale).

Splitting due to J-T distortion of the excited state $(t_{2g}^3 e_g^3)$ is clearly reflected.

Tetrahedral complexes are also expected to undergo J-T distortion with d^3, d^4, d^8 and d^9 configurations where the t_2 orbitals are partially filled :

d^3 $(e^2t_2^1)$ and d^8 $(e^4t_2^4)$: elongation

d^4 $(e^2t_2^2)$ and d^9 $(e^4t_2^5)$: flattening

In d^3 and d^8 configurations one t_2 orbital has an additional electron than the other two; this will provide better screening of the nuclear charge of the metal, ultimatly resulting in a greater M-L distance i.e., elongation. In d^4 and d^9 configurations, one t_2 orbital has one electron less than the others and hence we expect contraction or flattening of the regular tetrahedral geometry. In keeping with these expectations, the $[CuCl_4]^{2-}$ ion has a flattened tetrahedral structure while $[NiCr_2O_4]$ has an elongated tetrahedral coordination.

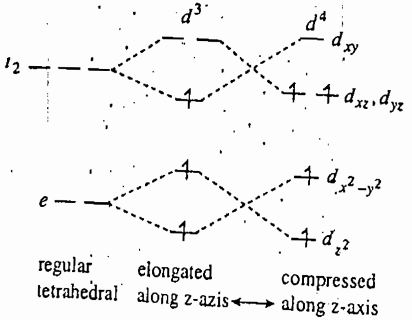


Fig. 27.19 **Jahn-Teller distortion in tetrahedral complexes of d^3 and d^4 metal ions.**

d^8 metal ions will behave in the same manner as d^3 and d^9 metal ions will follow the pattern in d^4.

Static and Dynamic J-T effect

Examples of Jahn-Teller distortion cited above are sometimes called *static Jahn-Teller effect*; the distortion is manifested in measurable differences in bond lengths and other properties of the system, be at room temperature or at low temperature. In contrast, there are many systems for which we expect J-T distortion but the system behaves as though it were symmetric. In these cases, the distortion in the structure may be supposed to oscillate very quickly at random among the available symmetry axes of the complex; if this oscillation is more rapid than any physical measurement can follow, a time-average symmetry is indicated. Such effects have been called *dynamic Jahn-Teller effect*. Thus the $[Cu(H_2O)_6]^{2+}$ ion in a host crystal of $[Zn(H_2O)_6]SiF_6$ gives an epr (electron paramagnetic resonance) spectrum suggesting a regular octahedral geometry. When cooled to 20K, the interchange of the distortion axis becomes slow and each cation is shown to be tetragonally distorted along one of three mutually perpendicular axes. The $[Cu(NO_2)_6]^{4-}$ ion also shows static and dynamic J-T distortion in salts $K_2M[Cu(NO_2)_6]$ where M = Ca, Sr, Ba and Pb.

Jahn-Teller distortion in chelate complexes

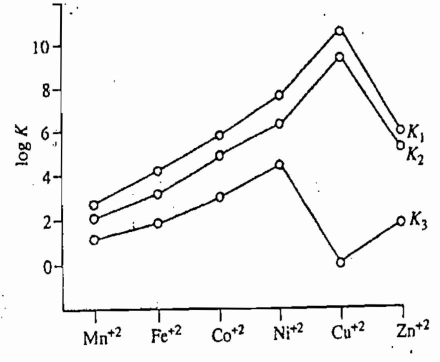
In chelated compounds or ions susceptible to J-T distortion, the effective span between coordinating atoms may oppose elongation and the consequent distortion of the complex. Let us consider the following steps of complexation by ethylenediamine (en; log K values at 30°C) :

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4en]^{2+} + 2H_2O \qquad \log K_1 = 10.72$$

$$[Cu(H_2O)_4en]^{2+} + en \rightleftharpoons [Cu(H_2O)_2en_2]^{2+} + 2H_2O \qquad \log K_2 = 9.31$$

$$[Cu(H_2O)_2en_2]^{2+} + en \rightleftharpoons [Cuen_3]^{2+} + 2H_2O \qquad \log K_3 = -0.90$$

The abrupt drop in the value of log K_3 is unusual (Fig. 27.20); it suggests that the trischelate is extremely unstable. This may be related to the strain developed in the complex when it tends to elongate the axial bonds due to Jahn-Teller effect. This causes stretching of the ethylenediamine molecules joining axial positions with equatorial positions in the coordination octahedron, thereby straining the molecule. The effective span or distance between the coordinating atoms in the ligand are often referred to as the "bite" of the ligand.

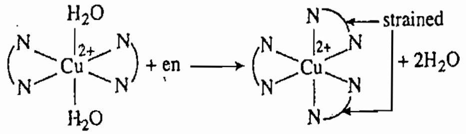


(a)

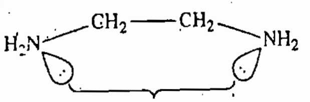
Fig. 27.20

(a) Stepwise formation constants (30°C) for ethylenediamine complexes of M^{2+} (M = Mn – Zn).

K_1 and K_2 show an uniform upward trend upto Cu^{2+}, but K_3 shows an opposite trend.



(b) The strain developed in the trischelate on tetragonal distortion.



(c) "bite" of the ethylenediamine molecule.

The tris-chelate [$Mn^{III}(acac)_3$] was long considered an exception to this generalization as its structure was found undistorted. Recently it has been established that this compound is also distorted as per expectation. However, if favoured otherwise, trischelates without J-T distortion may be formed by foregoing the extra stabilization due to distortion, e.g., [$Cu^{II}(OMPA)_3$]$^{2+}$ (OMPA = octamethyl pyrophosphoramide). Trischelates with tetragonal distortion are also known, e.g., [Cu(dipy)(hfacac)$_2$] (hfacac = hexafluoroacetylacetonato).

Review

The crystal field theory provides an easy to grasp description of complex formation. The chief merits of the theory are :

(i) it permits qualitative and quantitative interpretation of the electronic spectra of complexes (section 27. 2);

(ii) the theory explains the variation of magnetic moment with temperature and some other details of magnetic properties;

Merits and Demerits

(iii) the stereochemistry of complexes find a reasonable interpretation;

(iv) certain thermodynamic as well as kinetic aspects of complexes can be explained by the CFT;

In spite of these apparent merits, the theory is not theoretically sound. Its chief demerits are

(i) the CFT considers only electrostatic interaction between the metal and the ligands, but even then it does not attempt to consider the ligands in a realistic manner as a distribution of negative charge over some finite space (say a sphere with a positive charge located at the center).

(ii) the central assumption of purely electrostatic interaction between the metal ion and ligands can never be strictly true — there is always the likelihood that the metal and the ligands will mix their orbitals at least to some extent. Several experimental evidences piled up to show that this is true (see later).

(iii) the theory considers ligand electrons as localized point charges while the metal *d*-electrons are associated with their *d*-orbital wave functions, i.e., these are considered in wave mechanical terms. This is certainly a blend of self-contradicatory ideas.

(iv) the theory does not explain charge transfer bands and the intensities of absorption bands in *d-d* transition.

(v) π-bonding cannot be explained though it is very common in many complexes.

(vi) the relative positions of many ligands in the spectrochemical series cannot be explained, e.g., OH^- vs. H_2O.

A later modification of the theory to include some metal-ligand orbital overlap, also called the Adjusted Crystal Field Theory (ACFT) and sometimes the Ligand Field Theory (LFT), worked fairly for most complexes of metals in their normal oxidation states where the orbital overlap is really found to be small. The modification for orbital overlap are introduced in the parameters of interelectronic interactions like spin-orbit coupling constant and inter-electron repulsion parameters. However, the basic approach of the electrostatic model is still retained and thus the objections raised against the fundamental tenets of the approach are not fully eliminated.

The molecular orbital approach, which provides the most statisfactory description of metal-ligand interaction in complexes, has now been developed extensively with the availability of powerful computers. It has also been possible to apply the molecular orbital concept in a qualitative manner which helps the non-specialised freshers to appreciate the superiority of the approach over others. In the next section we shall briefly discuss some evidences of metal-ligand overlap; a simplified overview of the m.o. approach will then follow.

27.1.4 The molecular orbital approach

Evidences for metal-ligand orbital overlap

The nephelauxetic effect

An indirect, but convincing evidence for metal-ligand orbital overlap is obtained from the Nephelauxetic effect. In the interpretation of electronic spectra of complexes by the CFT (section 27.2), the separation between various Russel-Saunders states are found to depend upon certain inter-electron repulsion parameters. These parameters (see Racah parameters) are found to have lower values in complexes—nearly 70% of the corresponding values in free ions. Such decrease in interelectron repulsion in complexes suggests wider separation between the *d*-electrons, as if the *d*-orbital electron clouds have "expanded" to some extent. The effect is thus called the *Nephelauxetic effect* (Greek for cloud expanding), which is a consequence of overlap between the metal and ligand orbitals forming larger molecular orbitals. Hence ligands with greater ability to delocalize metal electrons exhibit higher nephelauxetic effect.

In fact, it is found that the Racah repulsion parameter B decreases in magnitude (as determined by spectral studies, see section 27.2.2) with increasing delocalization. A reduced value of B thus implies greater covalence in the metal-ligand bond. Ligands can be arranged in order of decreasing value of the ratio β, where

$$\beta = \frac{B \text{ in complex}}{B \text{ in free ion}}$$

The resulting series of ligands represent increasing order of delocalization or covalence in the metal-ligand bond. The series, which is more or less independent of the metal ion, is called the *nephelauxetic series* :

β : $F^- > H_2O > ...., Cl^- \approx CN^- > Br^- > S^{2-} \approx I^-$

Covalence : $F^- < H_2O <<< .... < Br^- < S^{2-} \approx I^-$

Hard ionic ligands such as the fluoride ion have β values close to unity, suggesting that the complexes formed by them are mostly ionic. The more covalently bonding ligands like the iodide ion have β-values as low as 0·3.

It is also possible to draw up a nephelauxetic series of metal ions with a particular ligand. Greater polarizing power of the metal ion implies greater covalence in the metal-ligand bond and hence a lower value of β. An approximate series is

$$Mn^{2+} \approx V^{2+} > Ni^{2+} \approx Co^{2+} > Mo^{3+} > Cr^{3+} > Fe^{3+} > Co^{3+} > Pt^{4+} \approx Mn^{4+}$$

Electron paramagnetic resonance (EPR)

This provides a direct support to the idea of metal-ligand orbital overlap in complexes. If we think of the electron classically as a small magnet, the behaviour of molecules (or ions) containing one or more unpaired electrons when placed in a magnetic field may be understood from the behaviour of a small magnet in the field of a larger one. When the field of the small magnet is lined up with that of the larger one, the potential energy of the system increases; the potential energy decreases in the opposite alignment. Thus a molecule containing one unpaired electron in an S state ($L = 0$) will lose the spin degeneracy in presence of a magnetic field and the electron will have different energies in its two states corresponding to two M_s values $+\frac{1}{2}$ and $-\frac{1}{2}$. Resonant energy in the form of electromagnetic radiation may be supplied to induce transition of the electron from one energy state to the other and can be detected spectroscopically. We expect a single absorption for this transition when the electron does not interact with another electron or with the magnetic nuclei. However, the actual spectrum of many d-metal complexes shows a hyperfine structure, that is, a number of subbands. This has been explained by assuming overlap of the metal d-orbitals (which contain the unpaired electron) with ligand orbitals; the nuclear magnetic moments of the ligand nuclei affect the energy levels of the metal electron. This indicates partial delocalization of the metal electron into ligand orbitals.

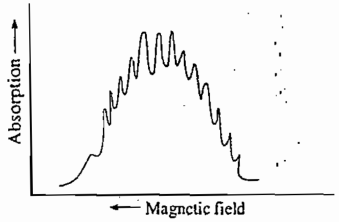


Fig. 27.21

The nature of hyperfine structure of the EPR spectrum of $[IrCl_6]^{2-}$.

Nuclear Magnetic Resonance spectra (NMR) are also indicative of metal ligand orbital overlap in complexes. Owing to such overlap, unpaired electron(s) on metals influence the nuclear resonances of all atoms in ligands. This is reflected in a shift in the resonance frequency from a typical diamagnetic environment. As an example, the resonance frequency of the ring proton in $[V(acac)_3]$ shows considerable shift from its position in $[Al(acac)_3]$. This is explained by assuming that the spin density of the unpaired electrons in vanadium(III) are delocalized into the π-electron cloud of the ring and eventually into the 1s orbital of the hydrogen atom. Al(III) is diamagnetic.

The molecular orbital approach

The molecular orbital approach to coordination compounds starts with the idea of symmetry permitted overlap between atomic orbitals on metals and appropriate ligand group orbitals (actually the terminal atom symmetry orbtials or TASO-s, as they are called). Molecular orbitals are formed by the LCAO approach and electrons from the metal ion and the ligands are assigned to these m.o.-s, filling the lowest energy level first. We shall illustrate the approach through a pictorial description of the molecular orbital energy level diagram for an octahedral complex.

A. Complexes involving only σ-bonding

Let us first consider an octahedral complex ML_6 involving metal-ligand σ-bonding only.

We first pick out the valence shell atomic orbitals of the metal suitable for bonding. If M is a metal of the first transition series, the metal orbitals are :

(a)	3s and 3p :	filled, low energy and radially contracted; hence ineffective for overlap with ligand orbitals.
(b)	five 3d :	partially filled and fairly diffuse; strong directional character suggests symmetry matched overlap.
(c)	one 4s and	empty, somewhat higher energy than the 3d and fairly diffuse;
	three 4p :	may be involved in bonding in appropriate cases.

Excluding the 3s and 3p orbitals which may be considered as part of the core, we are now left with nine metal orbitals. Choosing the cartesian axes as the fourfold symmetry axes of the octahedron, we find that out of the nine metal orbitals mentioned above, six have their lobes projected along the corners of the octahedron : these are

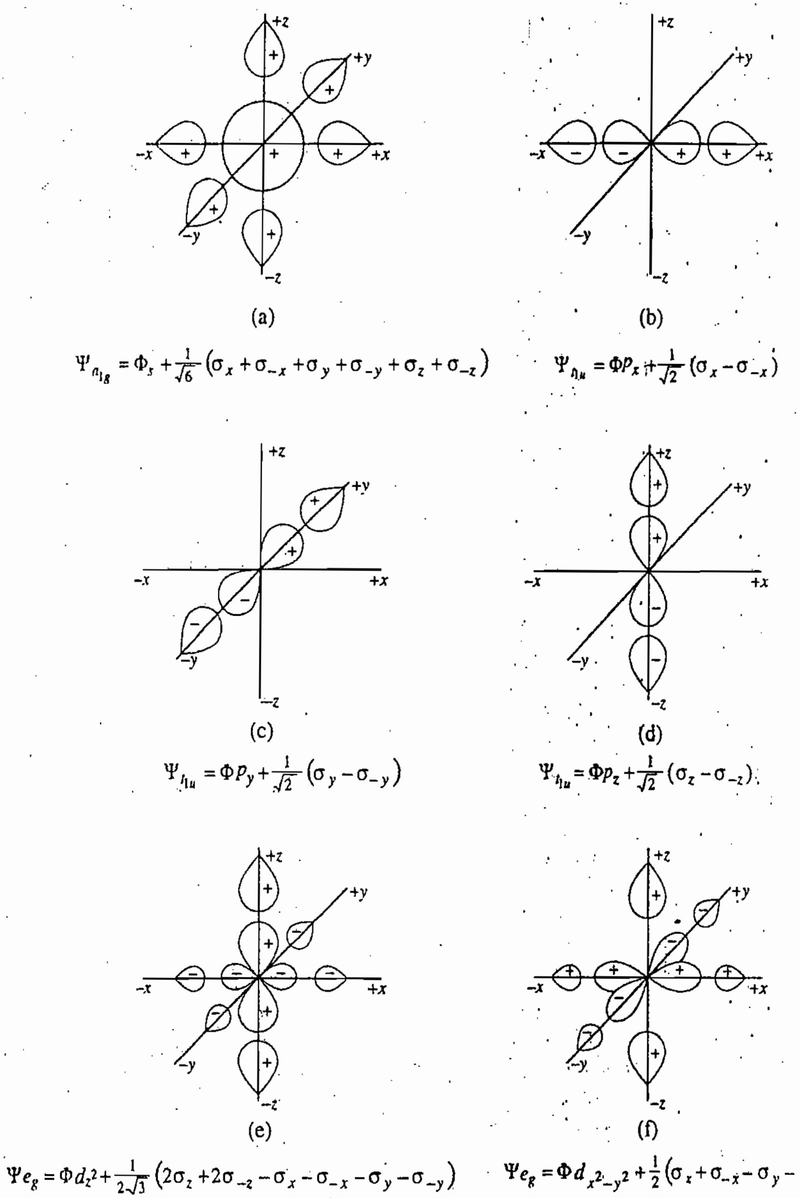
$3d_{x^2-y^2}$, $3d_{z^2}$, 4s (spherically symmetrical), $4p_x$, $4p_y$ and $4p_z$ (total = six).

Only these orbitals are suitable for σ-bonding with matching orbitals of the ligands. The remaining three orbitals, $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$ have their lobes lying between the cartesian axes and hence are not suitable for σ-bonding. The six σ-bonding metal orbitals are now classified according to their symmetry classes as follows :

4s	: a_{1g}	a single orbital that is totally symmetrical.
$3d_{x^2-y^2}$, $3d_{z^2}$	: e_g	a pair of orbitals that are equivalent except for their spatial orientations.
$4p_x$, $4p_y$, $4p_z$	: t_{1u}	a set of three orbitals that are equivalent except for their spatial orientation.

'g' and 'u' represent, as before, whether the orbitals are centrosymmetric (gerade) or noncentrosymmetric (ungerade).

We shall now consider the σ-bonding orbitals from ligands. Of course, these will vary from ligand to ligand, but in most cases they will be composed of s and p atomic orbitals; they can be represented by lobes as in Fig. 27.22. The linear combinations of



(a) $\Psi_{a_{1g}} = \Phi_s + \frac{1}{\sqrt{6}}\left(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}\right)$

(b) $\Psi_{t_{1u}} = \Phi p_x + \frac{1}{\sqrt{2}}\left(\sigma_x - \sigma_{-x}\right)$

(c) $\Psi_{t_{1u}} = \Phi p_y + \frac{1}{\sqrt{2}}\left(\sigma_y - \sigma_{-y}\right)$

(d) $\Psi_{t_{1u}} = \Phi p_z + \frac{1}{\sqrt{2}}\left(\sigma_z - \sigma_{-z}\right)$

(e) $\Psi e_g = \Phi d_{z^2} + \frac{1}{2\sqrt{3}}\left(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$

(f) $\Psi e_g = \Phi d_{x^2-y^2} + \frac{1}{2}\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$

Fig. 27.22

σ overlap in an octahedral complex.

ligand σ-orbitals suitable for bonding with the three symmetry classes of metal orbital (denoted by Φ) are expressed algebraically as normalized linear combination of individual ligand σ-orbitals. Thus the linear combination of ligand σ-orbitals that has

the same symmetry as the metal $d_{x^2-y^2}$ orbital (e_g) has a plus sign in the +*x* and −*x* directions and a minus sign in the +*y* and −*y* directions. This gives us the ligand group orbital (LGO) having the combination $\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$. The combinations for other matching LGO-s are found similarly and shown in Fig. 27.22 with respective normalizing constants. The d_{z^2} orbital is actually a superposition of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals, i.e., it may be thought of as a shorthand notation for $d_{2z^2-x^2-y^2}$. This explains the expression for its LGO.

We are now in the final step to construct an m.o. energy level diagram for the complex ML_6. For the transition metals, the most usual order of energies of metal orbitals is $nd < (n+1)s < (n+1)p$ that is, $3d < 4s < 4p$ for first row transition metals. For most ligands, for example H_2O, NH_3 or F^-, the ligand σ-orbitals are lower in energy than the metal valence orbitals. Again, for each combination of metal and ligand orbitals, there will be a lower energy bonding molecular orbital and a higher energy antibonding molecular orbital. To a first approximation, the bonding and antibonding m.o.-s lie equidistant from the mean of the energies of the combining orbitals. The t_{2g} orbitals on the metal $\left(d_{xy}, d_{yz}, d_{zx}\right)$ remain unchanged in energy as they are nonbonding in a σ-only bonding description. The resulting molecular orbital energy level diagram is shown in Fig. 27.23.

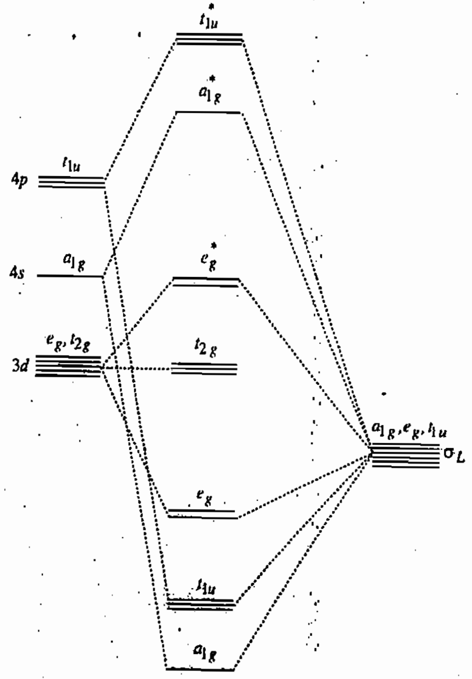


Fig. 27.23

M.O. energy level diagram for an ML_6 type octahedral complex involving σ-bonding only.

The diagram is qualitative and even the ordering of the energy levels is not certain. However, we may make the following observations on it.

(i) The six bonding m.o.-s (three t_{1u}, two e_g and one a_{1g}) are closer in energy to the low energy ligand orbitals; hence these m.o.-s are expected to have greater ligand character. Electrons occupying these bonding m.o.-s will have somewhat greater probability of being associated with the ligands than with the metal. This, in turn, implies some polarity in the metal-ligand bond.

(ii) The antibonding m.o.-s are expected to resemble the metal orbitals more to which they are close in energy.

(iii) Any electron in the nonbonding t_{2g} orbital will have only metal character in absence of π-bonding.

(iv) One may expect that overlap of the metal 4*s* and 4*p* atomic orbitals with the ligand orbitals will be better than the overlap of 3*d* orbitals. This is shown by the relatively small displacement of e_g and e_g^* m.o.-s (arising from metal 3*d* orbitals) from their barycenter. In contrast, the a_{1g} and t_{1u} m.o.-s arising from metal 4*s* and 4*p* orbitals are the lowest in energy. This is not unusual since the large and diffuse *d*-orbitals cannot make quantitatively good overlap.

(v) The central part of the diagram consisting of the t_{2g} and e_g^* m.o.-s correspond to the t_{2g} and e_g level in the crystal field theory where they were considered as pure metal orbitals. Here also, the orbitals have greater metal character.

Let us now see how simple magnetic and spectroscopic properties of complexes may be explained by using this m.o.-diagram. If we consider a d^1 metal ion, e.g., $[Ti(H_2O)_6]^{3+}$, we have to place a total of 13 electrons (1 from the metal and 6 × 2 = 12 from the ligands) into the m.o. energy levels. The occupancy will be

$$a_{1g}^2\, t_{1u}^6\, e_g^4\, t_{2g}^1$$

The single unpaired electron in the t_{2g} level accounts for the paramagnetism of the complex ($\mu \approx 1.7$ B.M.).

For complexes of metal ions with 2 or 3 *d* electrons, the highest occupied m.o. will have the configuration t_{2g}^2 (2 unpaired electrons) and t_{2g}^3 (3 unpaired electrons) respectively. A d^4 metal ion gives rise to a choice between the two alternative electron configurations :

$$t_{2g}^4 \text{ or } t_{2g}^3 e_g^{*1}.$$

Obviously the actual configuration is determined by the relative magnitudes of the energy gap between t_{2g} and e_g^* and the pairing energy. The energy gap thus corresponds to the crystal field splitting or 10*Dq* in an octahedral field in the crystal field theory. Two possible electron configurations are also expected for complexes of metal ions with configurations d^4, d^5, d^6 or d^7. Thus, the high-spin (spin-free) and low-spin (spin-paired) complexes of cobalt(III) may be described in terms of the m.o. electron distributions as :

Co^{3+} (ground state) : $[Ar]\,3d^6$

$[Co(NH_3)_6]^{3+}$ (low-spin) : $a_{1g}^2\, t_{1u}^6\, e_g^4\, t_{2g}^6$

$[CoF_6]^{3-}$ (high-spin) : $a_{1g}^2\, t_{1u}^6\, e_g^4\, t_{2g}^4\, e_g^{*2}$

Such descriptions, which fit the observed magnetic moment of the complexes, are based on the assumption that in case of F^- as ligand, the separation between t_{2g} and e_g^* is much less than in the case of NH_3 as ligand. The reason behind this will be taken up shortly (see π-bonding).

The electronic spectra of complexes may be similarly explained from the molecular orbital energy level diagram. For a d^1 metal complex like $[Ti(H_2O)_6]^{3+}$, the ground state electron configuration is t_{2g}^1 and the first excited state corresponds to $t_{2g}^0\, e_g^{*1}$. Hence the complex is expected to absorb electro-magnetic radiation of frequency ν where $\Delta = h\nu$, Δ being the separation between the t_{2g} and e_g^* levels. The measured absorption maxima at 20,100 cm^{-1} gives an estimated value of Δ equal to 240·64 kJ mol^{-1}. For many electron systems, however, discussion of spectra requires the use of spectroscopic states. This will be discussed separately in the next section.

B. Effect of pi-bonding

So far we have considered the metal-ligand bond as a pure σ-interaction. However, in many complexes, the bonding also involves π-interaction; the extent of this is determined by the symmetry of the orbitals as well as the match in size and energy of the orbitals.

In π-bonds, a nodal surface plane passes through the internuclear axis and the electron clouds are distributed symmetrically on the two sides of this plane. Hence the metal and ligand orbitals which are perpendicular to the internuclear axis can take part in π-bond formation (subject to match in size and energy). Such π-bonding may involve π-donor effects as well as π-acceptor effects. Examples will be found soon.

In an octahedral complex of the transition metals, the t_{2g} and t_{1u} metal orbitals (d_{xy}, d_{yz}, d_{zx}; p_x, p_y, p_z) are capable of π-bond formation; but the *p*-orbitals naturally prefer to form stronger σ-bonds. The t_{2g} metal orbitals (nonbonding in a σ-description) form π-bonds with LGO-s of matching symmetry. These ligand π-orbitals may be simple *p*π orbitals as in R_3P and arsines, or molecular orbitals of a polyatomic ligand as in CO, CN^- etc. We begin with simple *p*-orbitals.

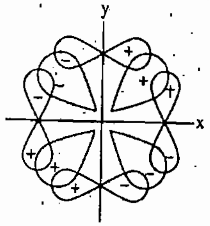


Fig. 27.24

π-overlap of the d_{xy} metal orbital (t_{2g}) with ligand p-orbitals.

The d_{yz} and d_{zx} orbitals will behave similarly.

The effect of such π-interaction on the final energy level diagram depends mainly upon two factors : (i) the relative energies of ligand π-orbitals and the metal t_{2g} orbitals and (ii) whether the ligand π-orbitals are filled or empty. Two distinct cases may be considered :

(i) Ligands possess filled π-orbitals of lower energy

The complex $[CoF_6]^{3-}$ is an example of this category. It is convenient to regard a halide ligand (X^-) to use its *sp* hybrid orbitals in bonding. One *sp* hybrid orbital is used in the M-X σ-donor bond. The other hybrid, located on the other side of M-X interaction, plays further effective part in bonding. The lone pairs of electrons on the halogen atoms occupy p_x and p_y orbitals (if internuclear axis lies along z). The filled p_x and p_y orbitals are of the correct symmetry to interact with the metal t_{2g} orbitals. Since the halogens are more electronegative, the filled p orbitals will be at a lower energy than the corresponding metal $3d$ orbitals. A bonding and an antibonding combination of the π-type will result (Fig. 27.25). The bonding π-m.o.-s will more closely resemble the halide p-orbitals. Conversely the upper antibonding orbitals are closer in energy to the metal t_{2g} orbitals and so are largely metal based. Effectively the metal t_{2g} orbitals are slightly pushed up in energy. The electrons in the p-orbitals of the ligands occupy the lower bonding set of m.o.-s and the highest occupied m.o. is located in the t_{2g}^* and e_g^* m.o.-s, depending upon the number of metal electrons. Δ_0 now corresponds to the new separation between t_{2g}^* and e_g^* level, which is lower than that in the σ-only description. The interaction of the two sets of orbitals corresponds to a partial transfer of electron density from ligand p-orbitals to the metal; hence the ligands are called π-donor ligands.

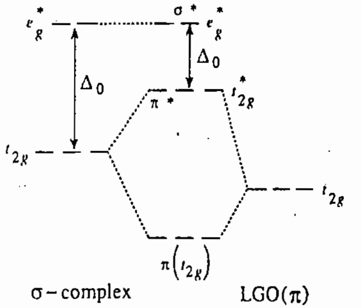


Fig. 27.25

Effect of π-bonding on the m.o. energy level diagram when the ligands possess filled π-orbital of low energy.

Note : Such π-bonding interactions help us to rationalize the relative positions of certain ligands in the spectrochemical series. The greater the π-donor capacity of the ligand, the more will be the destabilization of the t_{2g}^* level and the less will be the magnitude of Δ_0. The effect is shown for the halide ions in Fig. 27.26.

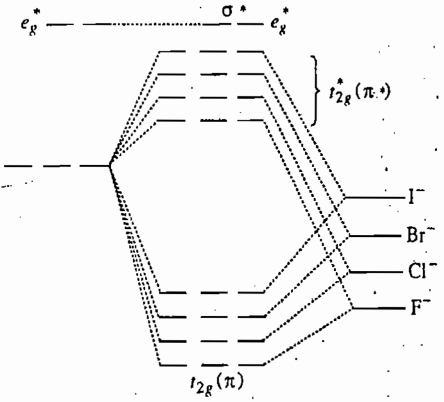


Fig. 27.26

Effect of π-bonding by different halide ions on the m.o. energy level.

Q. 27.7 *Explain why OH^- is a weaker-field ligand than H_2O.*

Hint : Refer to π-bonding energy level diagram. OH^- is a stronger π-donor than H_2O; π-donation reduces the magnitude of Δ_0.

[Sec. 27.1.4 *The M.O. approach*]

Except fluoride, the halide ions possess empty d-orbitals which may also participate in π-bonding with metals. However, such interaction would effectively tend to increase Δ_0. But the halide ions appear at the weak end of the spectrochemical series, implying that such interactions are less important than π-bonding from the filled p-orbitals.

(ii) Ligands possess empty π-orbitals of higher energy than metal t_{2g} orbitals

Phosphines, arsines, carbon monoxide etc. belong to this category. These ligands possess vacant orbitals with the correct symmetry to enter π-interaction with the metal t_{2g} orbitals. These are therefore called π-acceptor ligands or π-acid ligands (Lewis acid). In fact, these are σ-Lewis base and π-Lewis acid ligands.

Carbon monoxide is an excellent example of such π-acceptor ligands. In forming a metal carbonyl, the HOMO of CO, localized near the carbon atomic orbitals in energy, will first form a C→M σ-donor bond. The LUMO on CO, the π*-m.o.-s are fully vacant and possess the correct symmetry for π-interaction with metal t_{2g} orbitals.

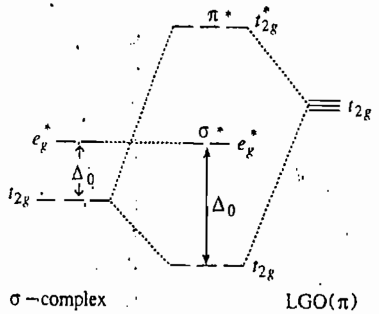


Fig. 27.27

Effect of the π-interaction on the m.o. energy level diagram in an octahedral complex.

The bonding t_{2g} π-orbitals are now closer in energy to the metal t_{2g} orbitals. Since the ligand π^* m.o. level is vacant, the electrons in the metal t_{2g} (nb) orbital are now assigned to the t_{2g} (π) m.o., whereby they get somewhat stabilized. Δ_0 now corresponds to the separation between t_{2g} (π) and the e_g^* level, which is higher than in a σ-only description. The net effect of a π-acceptor ligand is therefore to increase the separation Δ_0.

Such π-bonding helps to remove electron density accumulated on the metal (from σ-donation by ligands) and thus stabilizes lower oxidation states of metals. However, the net effect is always the result of a competition between σ-donation and π-acceptance in the metal-ligand interaction and the order of energy levels in the final m.o. diagram may be changed if the energies of metal orbitals are greatly changed, for example, if we pass from a normal oxidation state of the metal to one which is unusually high or low.

Note : σ*-orbitals on ligands may also serve as π-acceptors. Phosphines, for example, were supposed to use empty pure d-orbitals as π-acceptors. But they may also accept π-electron density into low-lying σ* orbitals or into some hybrid involving σ* and $3d$ orbitals. Complexes of dihydrogen (H_2) are supposed to involve donation from the σ-m.o. of H_2 and back donation from metal into the σ* m.o. of H_2.

Molecular orbital energy levels for other geometries

Symmetry considerations similar to those applied for octahedral complexes may be adopted for other geometries to establish a qualitative m.o. energy level diagram.

Tetrahedral Complex

For a tetrahedral ML_4 type complex (T_d symmetry), the nine metal orbitals may be classified according to their symmetry as

s : a_1

p : t_2 Note that the subscript 'g' has been dropped since the

$d_{z^2}, d_{x^2-y^2}$: e system becomes non-centrosymmetric.

d_{xy}, d_{yz}, d_{zx} : t_2

The ligand orbitals may be combined to form a set of three LGO-s (t_2) and one orbital of a_1 symmetry. The e orbitals of the metal cannot enter σ-interaction with the LGO-s and remain nonbonding (in absence of π-bonding). The metal t_2 orbitals (both p and d) can be combined with the t_2 LGO-s to give three sets of σ-m.o.-s : three bonding (t_2), three strongly antibonding (t_2^*) and three slightly antibonding (t_2^*). The a_1 metal orbital and the a_1 LGO-s similarly give rise to one bonding and one antibonding m.o. For a complex such as $[NiCl_4]^{2-}$, the electron count comes to 16 (8 from Ni, 2 from each Cl). The slightly anti-bonding t_2^* m.o. will now contain four electrons among which two will be unpaired. Δ_t corresponds to the separation between the e (non-bonding) and the t_2^* orbitals just above. The central portion of the m.o. diagram thus resembles the description in CFT.

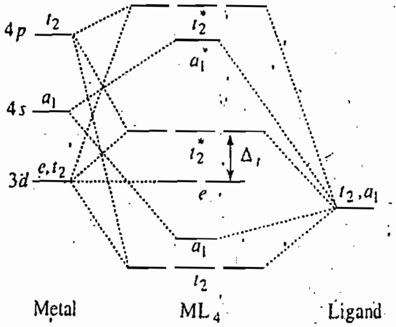


Fig. 27.28
M.O. energy level diagram in tetrahedral ML4 type complex (σ-bonding only).

Square Planar

In a complex with square planar geometry in the xy plane, having four identical ligands oriented along the x and y axes (D_{4h} symmetry), the σ-orbitals of a metal are those directed along the x and y axes, including the spherical s and the d_{z^2} which has its collar around the xy plane. Thus we have the following metal orbitals with their symmetry labels :

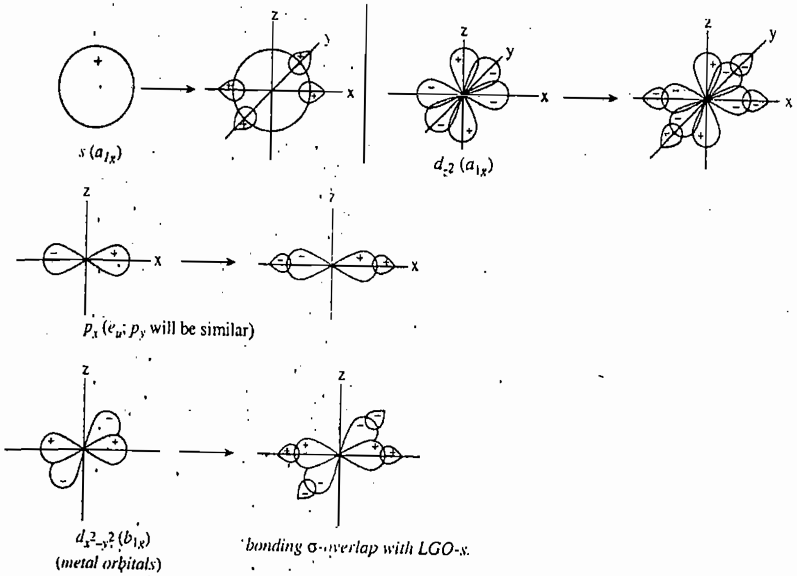
s : a_{1g}

p_x, p_y : e_u p_z : a_{2u}

d_{z^2} : a_{1g} d_{xz}, d_{yz} : e_g

d_{xy} : b_{2g} $d_{x^2-y^2}$: b_{1g}

The a_{2u}, e_g and the b_{2g} metal orbitals do not make any net σ-overlap in the xy plane and remain nonbonding in a σ-only system. The four ligands give rise to LGO-s of a_{1g}, b_{1g} and e_u symmetry which interact with metal orbitals of the same symmetry (Fig. 27.29 a). The resulting σ-m.o. diagram is like one shown in Fig. 27.29b.



$s(a_{1g})$ $d_{z^2}(a_{1g})$

$p_x(e_u; p_y$ will be similar)

$d_{x^2-y^2}(b_{1g})$
(metal orbitals)

bonding σ-overlap with LGO-s.

Fig. 27.29 (a)
The metal orbitals and their bonding σ-overlap in a square planar complex.

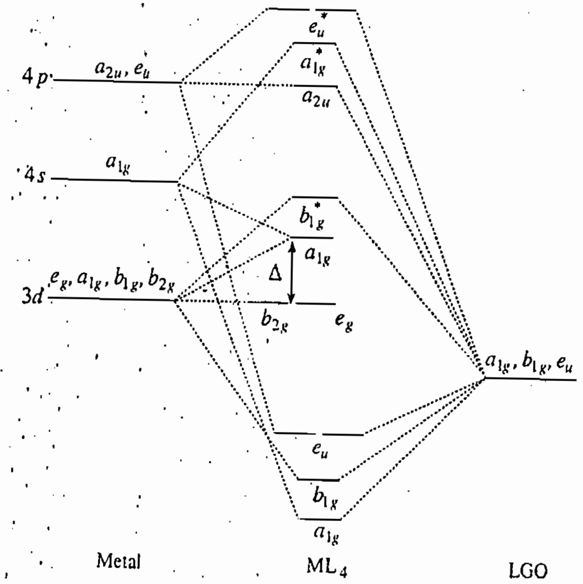


Fig. 27.29 (b)
σ-only m.o. energy level diagram for a square planar complex.

For complexes of a d^8 metal ion, the four ligands contribute eight electrons, making a total of sixteen. These may be assigned just to fill all the bonding m.o.-s; any additional electron will have to be accommodated in the anti-bonding molecular orbitals. Thus we may infer that square planar complexes will be most stable when the metal has eight d-electrons; fewer electrons will leave vacancy in some of the bonding m.o.-s, diminishing the stability.

Q. 27.8 *Indicate the metal orbitals which may take part in π-interaction with ligands lying along the x and y axes in a square planar arrangement around the metal atom.*

Hint : The metal orbitals with π-symmetry which may overlap with LGO's parallel to the C_4 axis are p_z, d_{xz} and d_{yz}.

In the xy plane, p_x, p_y and d_{xy} metal orbitals may also form π-bonds. But the p_x and p_y orbitals are primarily involved in σ-bonding where they undergo much better overlap.

Q. 27.9 *Sketch probable π-overlap of p_x, p_y and p_z and d_{xy} metal orbitals in a square planar complex. (See Fig. 27.30 for hint).*

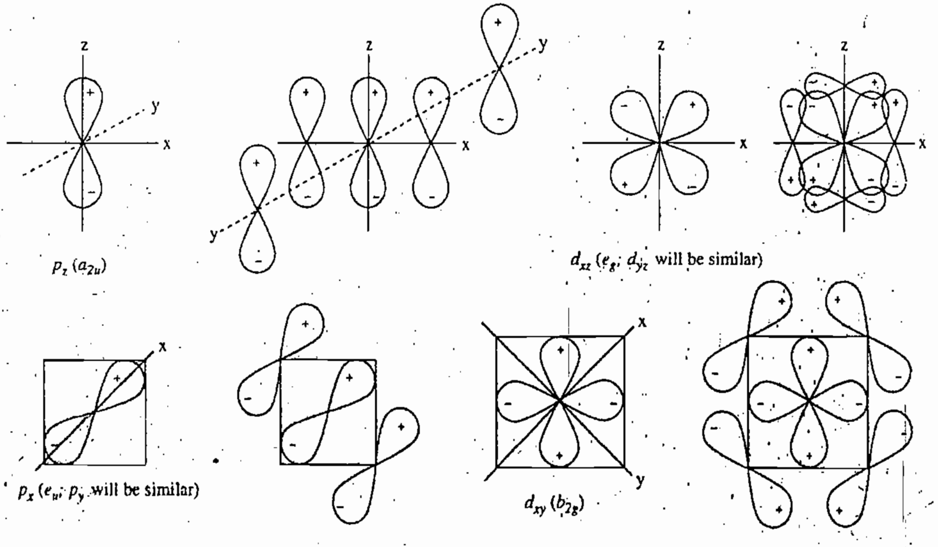


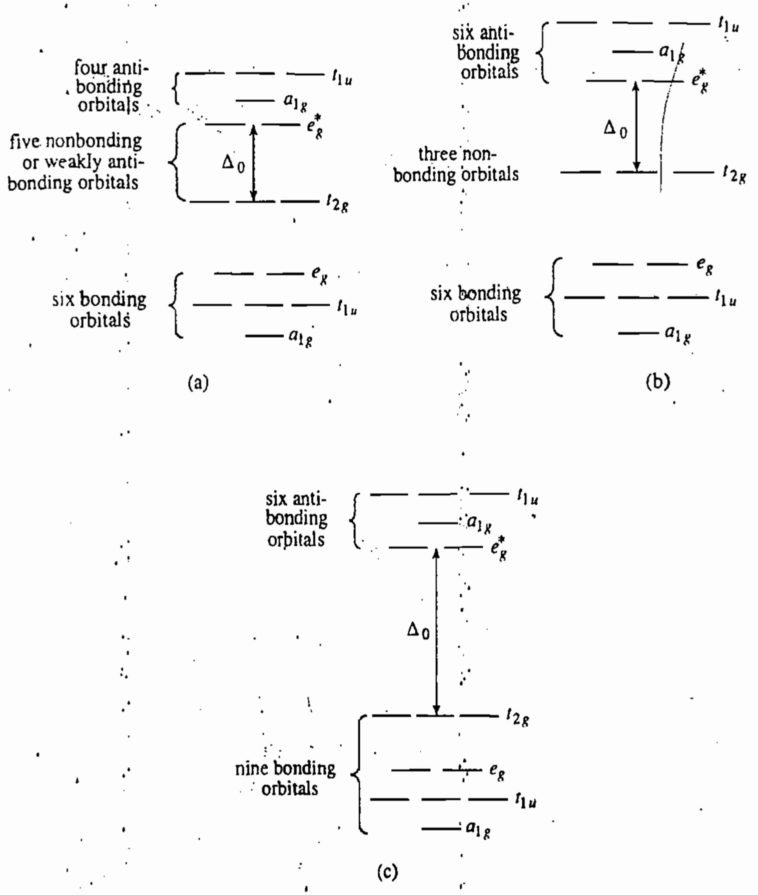
Fig. 27.30
Sketch of probable π-overlap in a square planar complex.

Looking back at the 18-electron rule

At this stage, we recall that the empirical 18-electron rule holds for many complexes while deviations from it are also not uncommon. We may rationalize the formal valence electron count by classifying the ligands into three categories and the gross m.o. energy level diagram applicable to their complexes.

(i) **Ligands are weak σ-donors with weak π-interaction** (Fig. 27.31a)

We expect this behaviour among ligands with small Δ_0. Weak σ-bonding implies that the bonding m.o.-s are not very low in energy, nor are the antibonding orbitals very high in energy. Since they are not far above the non-bonding t_{2g} m.o., Δ_0 will be small (27.31 a).



(a)

(b)

(c)

Fig. 27.31
The central sections of the energy level diagrams for the three types of ligand set.

There are six low energy m.o.-s which can be occupied by the ligand electrons (6 × 2). The five intermediate energy levels will be occupied according to the metal ion involved. A total of eighteen electrons (twelve from ligand and six from metal) will exactly fill upto the nonbonding t_{2g} m.o. But placing an electron in the antibonding e_g^* level does not involve much loss in energy since the energy separation is not high. As such, complexes of such ligands do not show any inclination to the 18-electron rule—there may be any number from 12-22 valence electrons.

First row transition elements in low or medium oxidation states, in their complexes with ligands which are not strongly back-bonding, belong to this category : the number of valence electrons of the metal in the complex range from 12 to 22 as they can freely occupy the nonbonding t_{2g} and weakly antibonding e_g^* molecular orbitals. For example :

Complex	No. of *d*-electrons provided by the metal	No. of electrons provided by the ligand	Total
$[TiF_6]^{2-}$	0	6 × 2 = 12	12
$[VCl_6]^{2-}$	1	6 × 2 = 12	13
$[Fe(H_2O)_6]^{3+}$	5	6 × 2 = 12	17
$[Fe(H_2O)_6]^{2+}$	6	6 × 2 = 12	18
$[Co(H_2O)_6]^{2+}$	7	6 × 2 = 12	19
$[Ni(en)_3]^{2+}$	8	3 × 4 = 12	20
$[Cu(NH_3)_6]^{2+}$	9	6 × 2 = 12	21
$[Zn(NH_3)_6]^{2+}$	10	6 × 2 = 12	22

$[Mn^{III}(CN)_6]^{3-}$, although low-spin (high Δ_0), also does not follow the 18-*e* rule (Mn^{III} : 4; $6CN^-$: 12; total 16).

(ii) **Ligands are strong σ-donor with weak π-interaction** (Fig. 27.31b)

Strong σ-bonding implies that the bonding m.o.-s are significantly lowered in energy. Correspondingly, the antibonding m.o.-s will be raised higher in energy and the separation t_{2g} (non-bonding) — e_g^* (antibonding) will be high, making Δ_0 large (27.30 b). The six lower bonding m.o.-s can hold twelve electrons while the t_{2g} orbitals can have six more electrons — accounting for a total of eighteen electrons for the complex. Any additional electron will substantially destabilize the system since the e_g^* m.o. is much higher in energy. Hence complexes in this category will be most stable when they contain a total of 12 to 18 valence electrons.

Complexes having high Δ_0 value of the ligands which are not strongly back bonding include mostly transition metals of the second and third row where the Δ_0 value is considerably higher. For example,

Complex	No. of *d*-electrons provided by metal	Total no. of valence electrons on metal account
$[ZrF_6]^{2-}$	0	12
$[WCl_6]^-$	1	13
$[TeF_6]^{2-}$	3	15
$[PtF_6]^-$	4	16
$[PtF_6]^-$	5	17
$[PtF_6]^{2-}$	6	18
$[PtCl_4]^{2-}$	8	16

(iii) **Ligands are strong σ-donors with strong π-interaction** (Fig. 27.31c)

These ligands are both strong σ-donors and good π-acceptors. The e_g level is raised to a high position owing to strong σ-donor property; at the same time, strong π-interaction lowers the t_{2g} orbitals to a great extent. The molecular orbitals of the system now clearly fall into two categories - the strongly bonding lower levels and strongly antibonding higher levels (Fig. 27.30c); there are no intermediate energy levels. The nine lower levels are completely filled by eighteen electrons and the complexes particularly follow the 18-electron rule. Octahedral complexes of d^6 transition metal ions are good examples, e.g., $[Cr(CO)_6]$, $[Co(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$. Some more examples are :

Complex	No. of *d*-electrons provided by metal	Total no. of valence electrons on metal account
$[V(CO)_6]^-$	6	18
$[Ni(CN)_5]^{3-}$	8	18
$[Fe(CO)_5]$	8	18
$[CH_3Co(CO)_4]$	9	18
$[Co(CO)_4]^-$	10	18

To summarize, strongly back bonding ligands stabilize the complex as π-interaction removes a substantial part of the electron density built on the metal through σ-bonding. When the ligands are weakly back-bonding, the complexes are usually 16-electron rather than 18-electron :

Complex	No. of *d*-electrons provided by metal	Total no. of valence electrons on metal
$[AuCl_4]^-$	8	16
$[PdCl_4]^{2-}$	8	16
$[Ni(CN)_4]^{2-}$	8	16
$[Mn(CN)_6]^{3-}$	4	16
$[Ni(dmg)_2]$	8	16

Thus the 18-electron rule serves as a valuable guide in rationalizing the structure and bonding of complexes with strong back-bonding, as in the carbonyls and organometallics and may also be extended to the rapidly growing field of polyhedral metal cluster compounds. However, space does not permit a thorough discussion of the last named category in this section. Examples of other types are :

(i) $[Cr(CO)_6]$
Cr (0) : 6 valence electrons
6 CO : 12 valence electrons
Total : 18

(ii) $[Mn_2(CO)_{10}]$ The Mn-Mn bond effectively adds one electron to the valence shell of each Mn.
Mn (0) : 7
5 CO : 10
Mn—Mn : 1
Total : 18

(iii) $[Mn(CO)_5]^-$

Mn(–I)	:	8
5 CO	:	10
Total	:	18

(iv) $[CH_3Mn(CO)_5]$ The CH_3 group essentially donates one electron to Mn :

Mn(0)	:	7
CH_3—	:	1
5 CO	:	10
Total	:	18

Alternatively, we may count the electrons on the basis of a complex of Mn(1) and CH_3^- :

Mn(1)	:	6
5 CO	:	10
CH_3^-	:	2
Total	:	18

(v) $[Fe_2(CO)_9]$ The bridge CO groups effectively contributes one electron to each Fe atom, so does the Fe - Fe bond.

Fe(0)	:	8
3 terminal CO	:	6
3 bridge CO	:	3
Fe-Fe	:	1
Total	:	18

(vi) $[Fe(C_5H_5)_2]$ This may be looked upon as a complex of Fe(II) with $C_5H_5^-$ (cyclopentadienide) ions, each having six-electrons or as a complex of Fe(0) with two C_5H_5 groups (5 electrons) :

Fe(II)	:	6	Fe (0)	:	8
$2C_5H_5^-$	:	12	$2C_5H_5$	:	10
Total	:	18	Total	:	18

(vii) $[Cr(C_6H_6)_2]$

Cr (0)	:	6
$2C_6H_6$	:	12
Total	:	18

(viii) $[(\eta^7-C_7H_7)\ Mo(CO)_3]^+$ The cyclo-heptatrienium cation, $C_7H_7^+$, is a planar aromatic system contributing 6 electrons to the metal :

Mo (0)	:	6
$C_7H_7^+$	:	6
3 CO	:	6
		18

There are many examples where compounds not following the 18-electron rule are readily converted to compounds conforming to this rule :

(i) $[V(CO)_6]$ is a 17 electron species (5 + 12), but gets easily reduced to $[V(CO)_6]^-$.

(ii) $[Fe(C_5H_5)_2]^+$ is also a 17-electron species which gets reduced to $Fe(C_5H_5)_2$.

Discussion

The qualitative approach to the molecular orbital theory of complex compounds helps us to explain their magnetic and spectral properties, stereochemistry, stability and related properties in the same manner as we have done earlier in connection with the crystal field theory. In MOT, the separation between the t_{2g} and e_g^* m.o.-s correspond to the crystal field splitting (Δ_0 or 10*Dq*). However, in MOT, this appears as a natural consequence of the symmetry-permitted overlap of the metal and ligand orbitals and we do not require to assume any idealized electrostatic interaction as in the CFT. Without π-bonding, the results of the MO treatment are more or less the same as in the crystal field theory. But the MOT has the additional capacity to consider metal ligand π-bonding which enables it to interpret certain more aspects of the situation : for example the relative position of the ligands in the spectrochemical series. For many complexes of metals in their normal oxidation states, the extent of overlap between metal and ligand orbitals is small and the adjusted crystal field theory or the ligand field theory works quite well. But in complexes involving extensive covalent bonding, the MOT is certainly more desirable. The approach is also useful for interpretation of spectra involving higher energy levels such as the charge transfer spectra.

27.2 COLOUR AND ELECTRONIC SPECTRA

One important characteristic of the transition metal compounds is the wide range of colours they exhibit. Such colours are associated with absorption of electromagnetic radiation in the visible region. Attempts to understand the process of such light absorption by molecules have provided valuable support to the theories of bonding in complex compounds.

27.2.1 Introduction

The spectra of the electromagnetic radiation emitted, absorbed or scattered by matter are studied in spectroscopy. Each quantum of energy absorbed or emitted by a substance corresponds to an alteration of energy due to some single atomic event or molecular process. The region of electromagnetic radiation associated with various processes are summarized in Table 27.8.

TABLE 27.8

Range of electromagnetic radiation associated with different atomic and molecular processes

Spectral region	wavelength (m)	wave number (m^{-1})	Process
(i) Gamma-radiation	10^{-12}	10^{12}	nuclear reactions
(ii) X-rays	10^{-11}-10^{-9}	10^{9}-10^{11}	quantum transitions of inner electrons in atoms or molecules
(iii) U.V. and visible light	10^{-8}-10^{-6}	10^{6}-10^{8}	quantum transitions of outer electrons
(iv) near infra-red radiations	10^{-5}	10^{5}	atom oscillation in molecules (bond vibration)
(v) far-infrared radiation	10^{-4}	10^{4}	molecular rotation
(vi) radio-frequency radiations	10^{-3}-1	10^{3}-1	spin-transitions of electrons
	10-10^{3}	0·1-10^{-3}	spin-transitions of nuclei

Our discussion in this section will be limited to electronic spectra in the uv and visible region.

The energy corresponding to each transition may be readily obtained from the relation

$$E = h\nu = h\,c/\lambda$$

The energy change per mol is obtained by multiplying with N, the Avogadro number.

However, spectroscopists often refer to the wavenumber $(1/\lambda)$ as such. The cm^{-1} is a common unit, though kilo kaisers (kK) are also in much use :

$$1\ kK\ molecule^{-1} = 1000\ cm^{-1}\ molecule^{-1} \equiv hc \times 1000\ cm^{-1}\ molecule^{-1}$$

$$= 6{\cdot}626 \times 10^{-34} Js \times 2{\cdot}9979 \times 10^{8}\ ms^{-1} \times 1000\ cm^{-1} \times 100\ cm\ m^{-1}\ molecule^{-1}$$

$$= 1{\cdot}9864 \times 10^{-20}\ J\ molecule^{-1} \equiv 11{\cdot}962\ kJ\ mol^{-1}.$$

Q. 27.10 *The visible region spreads approximately over radiation in the wavelength range 700-400 nm. Calculate the corresponding energy in kJ mol*$^{-1}$.

Hint : $E = N\,hc/\lambda$. [170·9 – 299·1 kJ mol^{-1}]

Visible light consists of radiation in the wavelength range 720-400 nm with the gross perceivable colour divisions shown in Fig. 27.32. When a compound has an absorption band in one of these regions, the compound shows the complementary colour. Thus, an aqueous solution of copper sulphate absorbs radiation in the orange region and appears blue while in a solution of potassium dichromate the situation is exactly reversed. This is also obtained from the "artist's wheel" shown in Fig. 27.33

wave length (nm)	400	420	490	530	590	640	720
energy (1000 cm^{-1} or kK)	25·0	23·0	20·0	18·9	17	15·6	13·9
kJ mol^{-1}	299	285	244	226	203	187	166
COLOUR	VIOLET	BLUE	GREEN	YELLOW	ORANGE	RED	
COMPLEMENTARY COLOUR	yellow green	yellow-orange	purple	indigo	blue	blue-green	

Fig. 27.32 : Main colours in the visible region. 1kK = 1000 cm^{-1} ≡ 11·962 kJ mol^{-1}

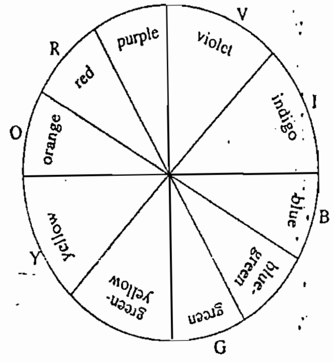


Fig. 27.33 : The "artist's wheel".

The wheel is divided into ten regions — Blue-green, Green-yellow, Purple and the seven colours in VIBGYOR. The absorption band is diametrically opposite to the observed colour.

Do yourself :
Prepare separately 0.1*M* solutions of cobalt(II) sulfate (purple) and nickel(II) sulfate (green).
Mix the two solutions in equal volumes and observe the colour change.

A complex compound may absorb light in the uv and visible region for a variety of reasons. Accordingly, electronic spectra may be broadly classified as follows :

1. *d-d* spectra or ligand field spectra :

These arise from transition of electrons between orbitals that have predominant metal *d*-orbital character. We shall discuss the salient features of such spectra in the following section.

2. Charge-transfer spectra :

Such spectra consist of intense bands arising from transfer of electron from a molecular orbital centered mainly on ligand(s) to an m.o. centered mainly on the metal or vice versa. Such transitions are associated with the intense colour observed in CrO_4^{2-}, MnO_4^-, prussian blue etc.

Besides, there are two other important types of electronic spectra.

3. Ligand spectra :

These arise due to characteristic absorptions by the ligands themselves which normally lie in the uv region. These bands persist in the spectra of complexes formed by these ligands but may be somewhat modified. Three principal types of ligand absorptions are usually encountered :

(i) **n-σ* transition :** Non-bonding electrons lying above filled σ-bonding m.o.-s give rise to such transitions as are found in water, alcohols, amines and haloalkanes. Such absorption bands in the uv region limit the use of such compounds as solvents for spectral study. Thus, it is often difficult to balance spectrosopic cells with water above 50,000 cm^{-1} or with chloroform above 40,000 cm^{-1} because of the presence of intense absorption bands by these solvents.

(ii) **n-π* transition :** Such transitions arise in ligands in which nonbonding electrons are present in m.o.-s lying above σ and π-bonding m.o.-s and the lowest unoccupied m.o. is the π* level. Compounds containing the $>C=O$ group are common examples of this type. n - π* transitions usually fall in the uv region. The next transition is π-π*, occurring above 50,000 cm^{-1}, a region called the vacuum ultraviolet.

(iii) **π-π* transition :** Such transitions occur in molecules in which the HOMO is a π-bonding orbital and the LUMO is a π*-m.o., as in olefins, dienes and aromatic systems.

More than one type of these bands may be shown by some ligands. For example, pyridine shows both n - π* and π - π* transitions. When the ligands form complexes, their absorption bands do not change significantly and may be identified from their typical shapes.

4. Counter-ion spectra :

Such spectra arise from absorption in the uv or visible region by common counterions usually present with an ionic complex species. The common anions Cl^-, SO_4^{2-} and ClO_4^- do not absorb radiation in the visible or uv regions but oxo-anions like NO_2^- and NO_3^- have intense absorption bands in the ultraviolet.

27.2.2 Ligand Field Spectra (*d-d* spectra)

An aqueous solution of copper(II) sulphate looks blue because it absorbs in the **orange region of the visible spectrum.** Now we desire to know "light" of which **particular frequencies are absorbed** by the solution and to what extent. This is achieved by a spectrophotometer, a layout plan of which is shown in Fig. 27.34.

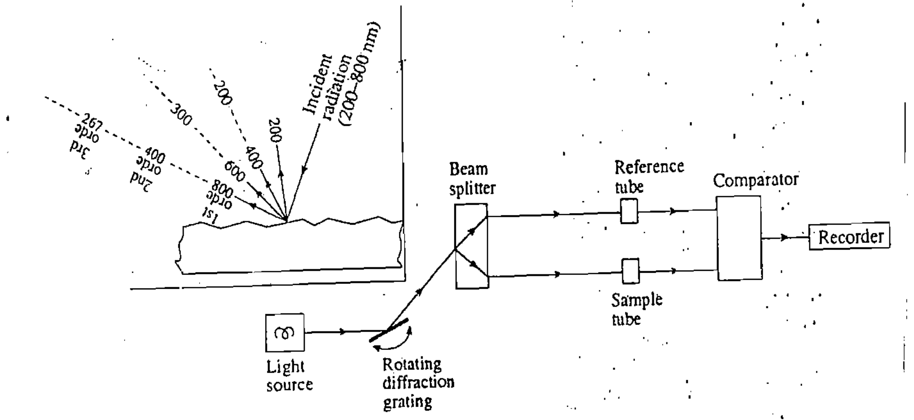


Fig. 27.34 : Layout of a uv — visible spectrophotometer.

A tungsten/iodine lamp is used as source for the visible region. A discharge through D_2 or Xe in quartz may be used for the near uv. Inset : A diffraction grating.

In the spectrophotometer, white light is first split up into its component frequencies by means of a diffraction grating. A diffraction grating consists of glass or ceramic plate on which very fine grooves (~ 1000 nm apart, comparable to the wavelength of visible light) are cut in specific designs and covered with a coating of aluminium. Constructive interference between the waves reflected from the groove surfaces occurs at specific angles depending on the frequency of the light. By slowly rotating the grating, light of any particular frequency may be allowed to pass through a slit into the beam splitter. After focussing, one beam is allowed to pass through the sample tube (containing, say, the copper(II) solution) and the other beam is passed through a reference tube (containing, in this case, water). The intensity of the beams coming out from the two tubes are compared by an electronic device and a final signal is sent to the pen recorder on the moving chart paper. The chart paper, calibrated in wavelengths, is moved in conjunction with the diffraction grating so that the position of the pen recorder shows the absorbance for the various wavelengths. The higher the pen moves up the chart paper, the greater is the absorption for light of that wavelength. A typical spectrum of an aqueous solution of copper(II) sulphate is shown in Fig. 27.35.

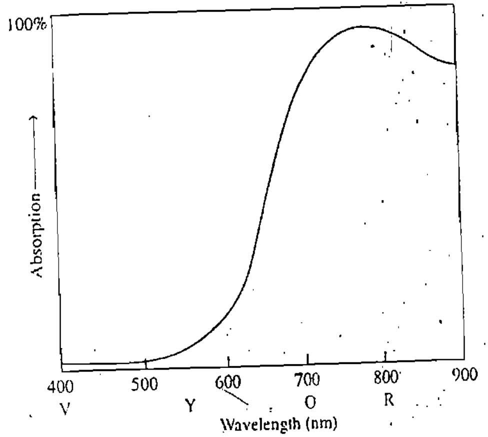
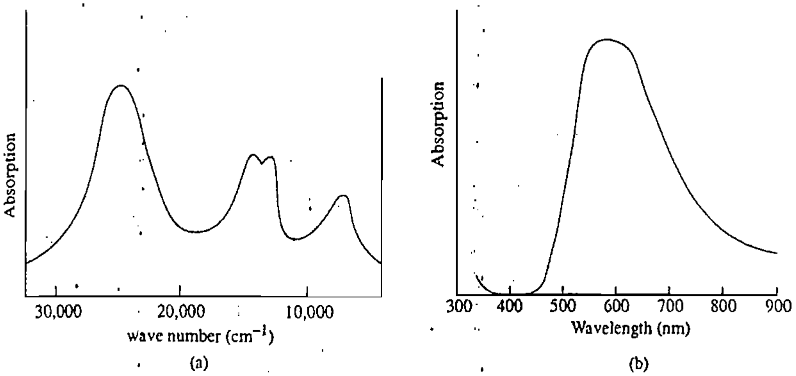


Fig. 27.35 : Visible spectrum of copper(II) sulphate solution.

Light in range 580-900 nm is strongly absorbed; this corresponds to the yellow (Y), orange (O) and red (R) region of the spectrum. Absorption in the range 340-580 nm is almost negligible, causing the solution to appear blue.

Q. 27.10. *Fig. 27.36 shows two visible spectra : (a) a solution of nickel (II) sulphate (b) a solution of Cu(II) sulphate with excess ammonia. What colour is expected for each of the solutions?*



(a)

(b)

Fig. 27.36

Visible spectrum of (a) Ni(II) sulphate, aquo and (b) Cu(II), aqueous ammonia.

Hint : (a) The complex absorbs in three regions : the strongest band lies around 25,000 cm^{-1}, the blue region; one band is centered around 14,000 cm^{-1} (red region); the third band appears in near infrared and will not affect the colour observed. Absorption is minimum in the green region (~ 20,000 cm^{-1}). The solution is (yellowish) green.

(b) Strong absorption is indicated above 450 nm. Thus only the blue region of the spectrum is transmitted.

We observe that the precise nature of the spectra are not quite simple. There are several features to be noted, for example the intensities and widths of the bands, their positions and so on. To understand these, we have to understand the nature of energy levels within the complex which are involved in the electronic transitions. Before we do so, we would like to have a few more words about the intensities of various electronic transitions.

The intensities of spectral lines

In Figures 27.35 and 27.36 we have plotted the percent absorption of incident radiation against different wave numbers/wavelengths. In fact light absorption by a solution depends also on the concentration and length of the sample traversed. Students experience this when they compare the colour intensities of 0·1 *N* and 0·05 *N* solutions of potassium dichromate in laboratory work. Also, the colour of the same solution appears lighter in a burette than that in a volumetric flask where the light travels a longer distance through the solution before reaching our eye. All these facts are in accord with the **Beer-Lambert law** which may be expressed in the following form

$$\log \frac{I}{I_0} = -\varepsilon c l$$

where I_0 = intensity of the incident radiation (of a particular wavelength);
I = intensity of the emerging radiation (of the same wavelength);
c = molar concentration of the absorbing species;
l = path-length which the radiation traverses through the solution;
ε = molar absorption coefficient (formerly called the *extinction coefficient*)

The ratio I/I_0 is called the **transmittance** T, so that we can also write

$$\log T = -\varepsilon c l$$

$\varepsilon c l$ is called the **absorbance** A (formerly optical density) of the solution. Both A and T are dimensionless while ε has the dimension [concentration]$^{-1}$ [length]$^{-1}$; it is commonly expressed in L mol^{-1} cm^{-1} (dm^3 mol^{-1} cm^{-1}).

Writing 1L = 1000 cm^3 at once gives 1 L mol^{-1}cm^{-1} = 1 cm^2 mmol^{-1}. ε is thus a molar cross-section for absorption. The higher the value of ε, the more is the absorbance.

Selection Rules

When concentrated ammonia solution is added in excess to an aqueous solution of copper(II) sulphate, the light blue colour of the solution becomes more intense. Similarly, when concentrated HCl is added to a solution of iron(III) prior to reduction with Sn(II), the solution turns deep brown. In marked contrast to these observations, some transition metal compounds have extremely faint colour. For example a solution containing Mn(II)-salts appears almost colourless although the complex ion $[Mn(H_2O)_6]^{2+}$, with $t_{2g}^3 e_g^2$ distribution of electrons, has scopes for electronic transition.

Here we face another reality of electronic transitions — they are subject to certain "selection rules". We came across such a selection rule in connection with atomic spectra : $\Delta l = \pm 1$ for a transition to be allowed. The underlying sense of this selection rule is that an electron will interact with the electric field of a light wave only when it is able to move in the same direction as the field. In other words, there should be a change in dipole moment associated with the migration of the electron charge. A transition from 1*s* to 2*s* does not create any dipole, there is only spherical migration of charge (Fig. 27.37 a) as both the orbitals favour no direction more than another. Hence such a transition is "forbidden". But a transition of an electron from 1*s* to 2*p* orbital has an associated dipole character with it since the 2*p* orbital is not spherically symmetrical (Fig. 27.37 b). In order that an electron moves from 1*s* to a $2p_z$ orbital (say), the electric field of the exciting radiation must be in the *z*-direction. The $1s \to 2p$ transition is thus "allowed".

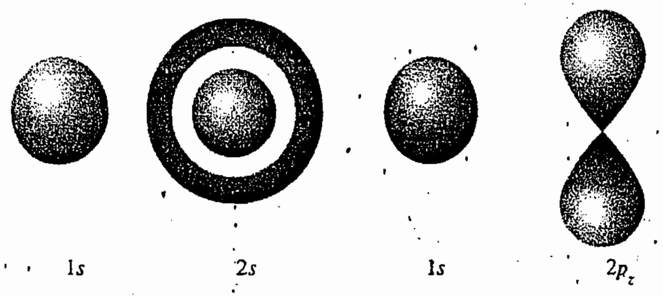


Fig. 27.37 : The selection rule.

(a) Electron transition between 1*s* and 2*s* orbitals is forbidden (b) transition between 1*s* and 2*p* orbitals allowed (signs of wave functions not shown).

Selection rules for the *d-d* spectra of transition metal complexes have been framed on a similar basis. Here also, the idea of an electric dipole transition* appears very satisfactory : a molecule absorbs or creates a photon only when it possesses a dipole oscillating at the frequency of the photon, at least transiently. This implies that the concerned electronic transition should give rise to a dipolar charge distribution. Quantum mechanically, this is expressed in terms of a transition dipole moment which is determined by the extent of charge redistribution. The intensity of a transition is proportional to the square of this transition dipole moment.

[Sec. 27.2.2 *d-d spectra*]

From detailed theoretical consideration of transition moment it has been possible to frame two important selection rules for *d-d* transition :

(i) *LaPorté or Orbital selection rule* : In a centrosymmetric environment an allowed transition must involve orbitals having different symmetry properties with respect to inversion, i.e., gerade (*g*) to ungerade (*u*) transitions or vice versa are only allowed. Since *d* orbitals are *g*-type, a *d-d* transition is $g \to g$ and hence forbidden. Similarly *f - f* transitions would also be forbidden.

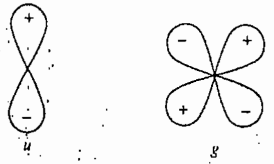


Fig. 27.38 : LaPorté selection rule

$g \to u$, $u \to g$: allowed; $g \to g$, $u \to u$: forbidden.

The selection rule may also be stated in terms of parity : transitions are allowed only between states of opposite parity.

Parity refers to the behaviour of a wave function toward inversion of the space coordinates through the origin i.e., when x is replaced by $-x$, y by $-y$ and z by $-z$.

If, $\psi(x, y, z) = \psi(-x, -y, -z)$,

ψ is said to have an even parity (*g*, gerade). cos x is a function of even parity '*g*', since $\cos x = \cos(-x)$.

If $\psi(x, y, z) = -\psi(-x, -y, -z)$, ψ is said to have odd parity (*u*, ungerade). sin x is such a function since $\sin x = -\sin(-x)$. The *p* - atomic orbitals are *u* - type, while the *s* or *d* atomic orbitals are *g* type.

If we write $\psi(x, y, z) = P\,\psi(-x, -y, -z)$, P will have a value +1 for even (*g*) parity and –1 for odd (*u*) parity. Thus P is also a quantum number characterizing ψ.

Accordingly, $g \to u$ or $u \to g$ transitions are LaPorté allowed while $g \to g$ or $u \to u$ transitions are LaPorté forbidden. This is equivalent to saying that allowed transitions for an electron will be accompanied by $\Delta L = \pm 1$; $d \to p$, $s \to p$ transitions are allowed but $d \to d$ or $s \to d$ transitions are not.

If a complex has no center of inversion e.g., a tetrahedral one, the LaPorté rule does not apply. In such complexes, LaPorté allowed transitions have high molar absorption coefficient (Table 27.9).

In tetrahedral complexes, the *e*-set of *d*-orbitals remain non-bonding when π-bonding is ignored. These *d*-orbitals, therefore, retain their *g*-character. On the other hand, the higher energy t_2-set of *d*-orbitals makes π-bonding with the ligand *p*-orbitals and hence acquire some *u* character. Hence transitions of the type $e^* \to t_2$ occur with greater probability. This is why tetrahedral complexes have absorption bands which are nearly 100 times as intense as those of similar octahedral complexes.

(Now try to explain your observation on adding concentrated HCl to dilute aqueous Fe(III) solution. Consult your teacher).

The LaPorté rule may be relaxed or it may not strictly apply in certain cases permitting some "*d-d*" transition ($\varepsilon \simeq 5 - 100$; Table 27.9).

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* Other modes of transition, viz. magnetic dipole and electric quadrupole transitions have a very much lower probability of occurrence.

The reasons for such relaxation will be mentioned in the next few paragraphs.

(ii) *Spin selection rule* : It states that transition may occur only between two energy states which have the same spin multiplicity. This means transitions resulting in a change in the total number of unpaired electrons are spin-forbidden. Since spin-multiplicity depends upon S, for a spin-allowed transition $\Delta S = 0$. Transitions for which $\Delta S \neq 0$ are spin-forbidden. The manganous ion (d^5) in an octahedral field (weak) will have the distribution $t_{2g}^3e_g^2$. Since both e_g orbitals are occupied, an electron from the t_{2g} level cannot be excited without spin reversal, i.e., $\Delta S \neq 0$. Hence such transitions would be spin-forbidden and hence extremely weak. Like the LaPorté rule, the spin-selection rule is also relaxed in many cases. These are discussed below.

Relaxation of the selection rules

The LaPorté selection rule may be relaxed in octahedral complexes if the centre of symmetry is eliminated by some means. For example, if the molecule vibrates asymmetrically (Fig. 27.39), the centre of inversion will be destroyed. There may be, for example, a number of normal modes of vibration which are antisymmetric with respect to the center of inversion. These vibrations are therefore u-type vibrations. Now, the vibrational transitions which are of much lower energy than the electronic transitions may be mixed up with each electronic transition. Such mixing of vibrational and electronic parts of the wave function is known as *vibronic coupling*. As a consequence, the ground term may become mixed with a g-type vibration and the excited term with a u-type vibration. Hence the so-called $g \rightarrow g$ transition becomes partly $g \rightarrow u$ and therefore permissible. Also, mixing of p and d orbitals can occur to some extent due to distortion of the perfect centrosymmetric environment and transition becomes allowed between d-orbitals having different p-character. In the molecular orbital description of bonding, such d-p mixing appears directly as a consequence of covalence involving metal d- and ligand p-orbitals.

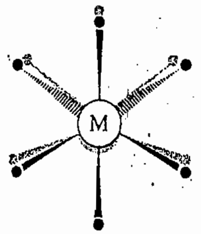


Fig. 27.39 : Asymmetric vibration in an octahedral complex.

The spin selection rule breaks down because the definite S values are arrived at only through the Russel-Saunders coupling scheme which holds only approximately. Actually, the spin and orbital angular momentum get always mixed through so-called spin-orbit coupling (see later). This gives states of same total angular momentum with partial orbital and spin contributions. Thus, the spin function cannot be completely separated to give well-defined S values as arrived at through the Russel-Saunders scheme. The effect becomes very prominent with heavier transition metals of the second and third transition series — spin-forbidden transitions are more common among the complexes of these elements.

Some typical values for molar absorption coefficients for the different types of forbidden and relaxed transitions are given in the next page.

TABLE 27.9

Molar absorption coefficients for a few transition metal complexes

Complex	Typical Transition	Class	Typical value of ε (L mole^{-1} cm^{-1})
$[Mn(H_2O)_6]^{2+}$	$d \rightarrow d$ with change of multiplicity	spin forbidden, LaPorté forbidden	0·1
$[Ti(H_2O)_6]^{3+}$	$d \rightarrow d$ with no change of multiplicity	spin allowed, LaPorté forbidden	10
$[CoCl_4]^{2-}$	$d \rightarrow dp$, no change of multiplicity	spin allowed, LaPorté "partly allowed".	5×10^2
$[TiCl_6]^{2-}$	Charge transfer	spin allowed, LaPorté allowed	10^4

Intensity stealing

There is another phenomenon called *intensity stealing* which causes a marked gain in intensity of absorption in ligand field transitions occurring close to charge-transfer bands (section 27.2.4). It is likely that the electronic wave function of the forbidden excited term gets mixed with the wave functions of the allowed charge transfer states; the probability of electron transitions to the excited state thereby increases significantly. The degree of mixing depends upon the energy separation between the ground state wave function and the odd excited state. For this reason, crystal field transitions generally increase in intensity on moving into the blue region of wave length, where they can couple with higher energy wave functions.

Bandwidth

Transition from one energy state (E_1) to another (E_2) is expected to give rise to a sharp line corresponding to a definite frequency ν equal to $(E_2 - E_1)/h$. This follows from the *Franck-Condon principle* : electronic transitions in molecules take place so rapidly that the nuclei, because of their ~~large mass,~~ may be considered to remain stationary. In reality, such sharp lines are rather exception in electronic spectra — instead one commonly finds broad bands of halfwidths of the order of 500 - 2000 cm^{-1}. A large number of factors may be held responsible for such broadening of bands, the principal ones being the accompanying vibrational excitations, the occurrence of Jahn-Teller effect and spin-orbit coupling effect.

(i) Vibration results in a fluctuation of the metal-ligand distance in complexes. Since Dq is inversely proportional to the 5-th power of this distance, the magnitude of Δ_0 $(10Dq)$ changes very sensitively with such changes due to vibration. Accordingly, the energy separation between the states of transition does not have a fixed value — rather it spreads over a range of energies corresponding to different values of Δ_0 resulting from bond vibration. Since fewer vibrational levels are occupied at low temperatures and the probability of transition is reduced, such broadening effects may be partly overcome in spectral measurements at lower temperature.

(ii) We have already discussed broadening due to Jahn-Teller effect in $[Ti(H_2O)_6]^{3+}$ and other species. When the ligands in a complex species are not identical, the ligand field strength will vary in different directions, thereby lowering the symmetry compared to a complex with all ligands identical. This effect may also lead to broadening and splitting of absorption bands.

(iii) We shall see that spin-orbit coupling results in a splitting of terms into energy states separated by multiples of λ, the spin-orbit coupling coefficient. Such coupling is therefore expected to broaden or even split the absorption bands into fine structure. In the first row transition series, the value of λ is small [except Cu(II)] and may give rise to broadening of upto 1000 cm^{-1}. In the later transition series and in lanthanides, such coupling becomes more notable. Usually, the fine structure due to spin-orbit coupling is blurred by vibrational broadening.

Free ion terms : Russell-Saunders states

We have discussed earlier (Chapter 3) how the angular momenta of the individual electrons in an atom may be combined or coupled to give a total angular momentum for the whole atom (Russel-Saunders coupling or L-S coupling). A single electron configuration may thus represent a number of different energy states of the atom. This helps us to understand to what other states an atom may jump by absorption or emission of radiation.

As already mentioned, in the Russel-Saunders coupling scheme electrostatic interactions between electrons dominate and the magnetic interactions between the intrinsic magnetic moments of the electrons (and the fields created by their orbital motion) are thought of as small perturbations. This description holds well for light atoms, (say up to atomic number 30) and may be used successfully for the first transition series elements. For heavy atoms, a different scheme, called *j-j* coupling, provides better description.

The main steps in finding the states actually represented by a particular electron configuration according to the Russel-Saunders scheme are recapitulated below :

(i) Individual spin angular momenta of the electrons (s_i) combine to give a resultant spin angular momentum $S = \sum s_i$ (or, $M_S = \sum m_s$).

S is obtained by coupling the spin quantum numbers for the separate electrons according to

$$S = (s_1 + s_2), (s_1 + s_2 - 1), \ldots\ldots, (s_1 - s_2)$$

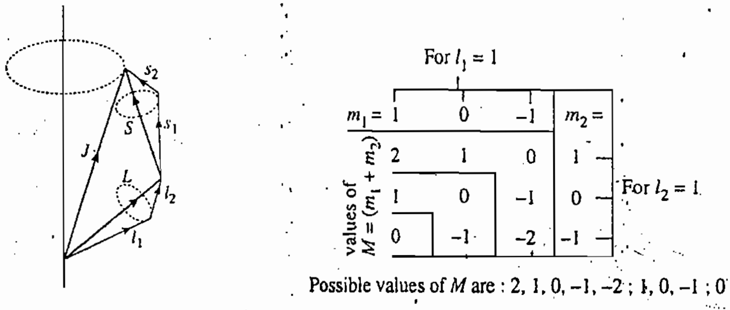
Thus for two electrons, $S = 0$ or $(\pm)1$. For four electrons, S may have values ± 2 $(\uparrow\uparrow\uparrow\uparrow$ or $\downarrow\downarrow\downarrow\downarrow)$; ± 1 $(\uparrow\uparrow\uparrow\downarrow$ or $\downarrow\downarrow\downarrow\uparrow)$ or 0 $(\downarrow\downarrow\uparrow\uparrow)$.

(ii) Individual orbital angular momenta of the electrons (l_i) combine vectorially to give a resultant orbital angular momentum $L = \sum l_i$.

As explained before (Chapter 3), the vector addition of l-values is conveniently achieved by adding the m_l values (see Fig. 27.40). For two electrons with orbital angular momenta l_1 and l_2, L may have values

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots\ldots, (l_1 - l_2).$$

(iii) L and S couple together to give a total resultant angular momentum J. J is also quantized, and can take the values $(L + S)$, $(L + S - 1)$,......, $(L - S)$.



Possible values of M are : 2, 1, 0, −1, −2 ; 1, 0, −1 ; 0

Fig. 27.40

Schematic representation of Russel-Saunders coupling.

Information about these various states arising from L, S and J are expressed by the term symbols

$${}^{2S+1}L_J \quad [(2S+1) = \text{spin multiplicity}]$$

The value of the quantum number L is expressed by letters S, P, D etc, corresponding to the numbers :

L =	0	1	2	3	4	5	6 ...
symbol =	*S*	*P*	*D*	*F*	*G*	*H*	*I* ...

Terms of *d*-electron systems

(i) d^1 : We have only one electron. Hence

$$L = l = 2; \quad S = s = \tfrac{1}{2} \text{ or } 2S + 1 = 2$$

For $L = 2$, we use the letter D; hence the term will be ${}^2D$. The J values are $(L + S)$ and $(L - S)$ i.e., $\frac{5}{2}$ and $\frac{3}{2}$.

(ii) d^2 : For two d-electrons, L may have values 4, 3, 2, 1 and 0 corresponding to G, F, D, P and S terms respectively. S may be either 0 or ±1. Corresponding $(2S + 1)$ values are 1 and 3. Remembering Pauli exclusion principle, the allowed terms are ${}^3P$, ${}^3F$, ${}^1S$, ${}^1D$ and ${}^1G$.

Now we may apply Hund's rules to select the lowest-energy or ground term :

1. The most stable state has the highest spin-multiplicity [maximum value of $(2S + 1)$; in this case it is 3, i.e. a triplet state].

2. For a group of terms with the same spin multiplicity, the largest value of L (highest orbital multiplicity) corresponds to the lowest energy state i.e., in this case ${}^3F < {}^3P < {}^1G < {}^1D < {}^1S$.

The effect of Russel-Saunders coupling for a d^2 ion is shown in Fig. 27.41.

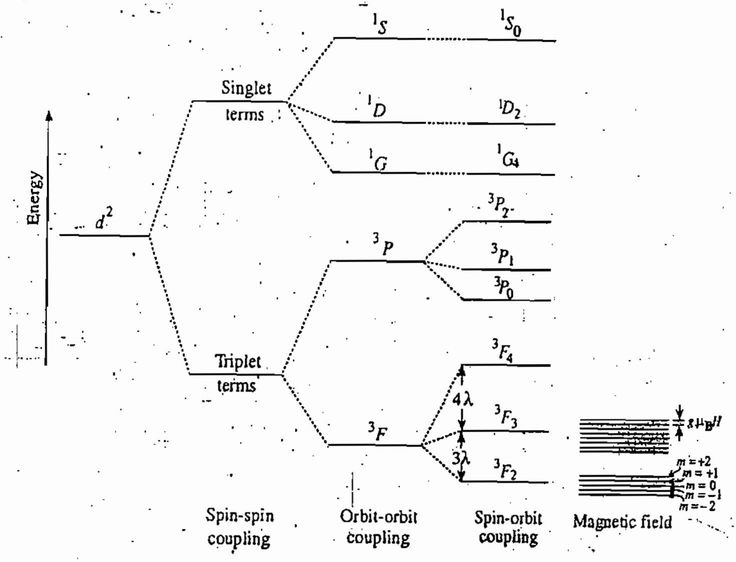


Fig. 27.41

Russel-Saunders or LS coupling on a d^2 ion (Energy separations are not to scale).

Separation between the levels with J values J and $(J+1)$ is given by $(J+1)\lambda$ where λ is called the spin-orbit coupling constant.

Under the influence of an external magnetic field, the energy levels are further split into $2J+1$ equally spaced levels; these correspond to the number of m_l values. These values are $-J \ldots 0 \ldots +J$, each separated by an amount $g\mu_B H$ where g is known as the Landé splitting factor, μ_B is the Bohr magneton and H is the strength of the applied magnetic field. g is related to L, S and J by the Landé formula.

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

The Ground Term

The ground term arising from each d^n configuration may be readily identified by remembering that this has the highest spin-multiplicity and hence the maximum number of unpaired electrons with their spins parallel. Since there are five degenerate d-orbitals, spin pairing does not occur upto d^5 configuration. The multiplicities of the ground terms from d^1 to d^9 are thus

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
2	3	4	5	6	5	4	3	2

The maximum value of M_L corresponding to this arrangement and obeying the Pauli exclusion principle may now be readily found out: The results are summarized in Table 27.10.

TABLE 27.10

Ground terms for d^n configurations

Configuration	Example	m_l					M_L	S	Ground Term
		2	1	0	−1	−2			
d^1	Ti^{3+}	↑					2	$\frac{1}{2}$	$^2D_{3/2}$
d^2	V^{3+}	↑	↑				3	1	$^3F_2$
d^3	Cr^{3+}	↑	↑	↑			3	$\frac{3}{2}$	$^4F_{3/2}$
d^4	Cr^{2+}	↑	↑	↑	↑		2	2	$^5D_0$
d^5	Mn^{2+}	↑	↑	↑	↑	↑	0	$\frac{5}{2}$	$^6S_0$
d^6	Fe^{2+}	⥮	↑	↑	↑	↑	2	2	$^5D_4$
d^7	Co^{2+}	⥮	⥮	↑	↑	↑	3	$\frac{3}{2}$	$^4F_{9/2}$
d^8	Ni^{2+}	⥮	⥮	⥮	↑	↑	3	1	$^3F_4$
d^9	Cu^{2+}	⥮	⥮	⥮	⥮	↑	2	$\frac{1}{2}$	$^2D_{5/2}$

Besides the ground term, there may be other terms arising from a given d^n configuration, as exemplified in the case of d^2. The various terms arising from d^1-d^9 configurations are given in Table 27.11. These represent the allowed Russel-Saunders states for equivalent d-electrons. In accordance with the hole formalism (section 3.6) d^n and d^{10-n} configurations give rise to the same term.

TABLE 27.11

Terms arising from various d^n configurations

Configurations	Terms*
d^1, d^9	^2D
d^2, d^8	$^3F, {}^3P, {}^1G, {}^1D, {}^1S$
d^3, d^7	$^4F, {}^4P, {}^2H, {}^2G, {}^2F, {}^2D(2), {}^2P$
d^4, d^6	$^5D, {}^3H, {}^3G, {}^3F(2), {}^3D, {}^3P(2), {}^1I, {}^1G(2), {}^1F, {}^1D(2), {}^1S(2).$
d^5	$^6S, {}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G(2), {}^2F(2), {}^2D(3), {}^2P, {}^2S.$

*Numbers 2, 3 etc. in parentheses denote the number of times the term occurs.

The energy separation between the various terms are determined mainly by inter-electron repulsions. The separations are conveniently described in terms of parameters called **Racah parameters,** which are linear combinations of relevant Slater integrals. The parameters are actually determined from spectral data. The energy of each term originating from a given electron configuration may be expressed as the linear combination of three Racah parameters A, B and C. For example, energies (E) for different terms arising from the d^2 configuration are

$$\begin{aligned} {}^1S &= A+14B+7C \\ {}^1G &= A+4B+2C \\ {}^1D &= A-3B+2C \\ {}^3P &= A+7B \\ {}^3F &= A-8B. \end{aligned}$$

The difference in energy between states are given by B and C only; for states with same spin multiplicity, the difference is given by B only. Here, separation between ^3F and ^3P is equal to $15B$. This also holds for V^{2+} (d^3) for which

separation between ^4F and ^4P terms $= 15B$

separation between ^4F and ^2G terms $= 4B + 3C$

Since complex formation reduces interelectron repulsion, the values of B and C in complexes are much lower than the free ion values. Usually, the former are ~70% of the respective free ion values in the first transition series. Ions of the first transition series have a C/B ratio of about 4, with B lying around 1000 cm^{-1}.

Q. 27.11 *Find the ground term in each case : (a) a free ion with $3d^9$ configuration; (b) a set of terms $^5D, {}^3F, {}^3P, {}^2I$; (c) a set of terms $^3F, {}^3P, {}^1P, {}^2D$.*

Hint : (a) eight electrons are paired, hence largest value of $S = \frac{1}{2}$, $2S + 1 = 2$. Largest value of $M_L = 2$, i.e., a D term. Hence the ground term is ^2D.

(b). The ground term has highest multiplicity, hence it is ^5D.

(c) The highest multiplicity is 3, but there are two triplet terms ^3F and ^3P. The ^3F term has greater L value and hence will be the ground term.

Terms arising in ligand fields

So far we have considered the terms arising from various d^n configurations of a free ion. We next try to understand how these terms are affected when the ion is placed in the field of ligands. Two situations may be considered :

(i) *Weak-field case* : Here the effect of the crystal-field is smaller in comparison to interelectron repulsion. We can first derive the terms for the free ion and then introduce the effect of the crystal field on them (perturbation, as it is called). In effect, the ligand field may lift the degeneracy of the energy states (and hence the terms) and a number of component terms will be introduced.

(ii) *Strong field case* : Here electron pairing may significantly alter the situation and hence the crystal field becomes more important than interelectron repulsions. So it would be more appropriate to consider the crystal-field splitting first and then to make necessary adjustments for interelectronic repulsions.

We shall first confine ourselves to the discussion of weak field cases.

Let us first attempt to understand the nature of splitting of the free-ion ground terms on a physical basis. In an octahedral field, the *d*-orbitals are split into a lower group of triply degenerate t_{2g} orbitals and a higher group of doubly degenerate e_g orbitals. For a d^1 metal ion, the ground configuration is t_{2g}^1 : this implies that the single electron can occupy either of the three degenerate t_{2g} orbitals — an orbital degeneracy of 3. This gives the ground T_{2g} term. In the excited state, this single *d*-electron can occupy either of the two upper e_g orbitals — implying an orbital degeneracy of 2, corresponding to an E_g term (Fig. 27.42).

Spectroscopic labels for split components

The labels for split components of various electron configurations in a particular field are derived from group theory and are used to express as much possible about the degeneracy and the symmetry in this field. The capital letters *T*, *E* etc. (Mulliken symbols) signify the orbital degeneracy. *T* denotes three-fold degeneracy, *E* denotes two-fold degeneracy. *A* or *B* are used to signify orbitally non-degenerate states. *A* relates to a wave function symmetric with respect to rotation by $2\pi/n$ degrees about the *n*-fold principal symmetry axis while *B* is antisymmetric. (The letters actually refer to the dimension of an irreducible represenation in group theory.)

The superscripts 3, 2 etc. (e.g., ^3T, ^2E) denote the spin multiplicity of the term. The numericals in subscripts e.g., T_2, A_1, etc. are also derived from group theory. When used with the symbol *A* (or *B*), the subscripts 1 and 2 denote that the wave function is symmetric or antisymmetric respectively either with respect to a 2-fold rotational axis perpendicular to the principal axis, or to a plane of symmetry including the principal axis. When used with *E* and *T* terms, the subscripts 1 and 2 are derived from more detailed considerations which are beyond the scope of this treatment. We shall use them merely as labels. The subscripts *g* and *u* represent, as before, gerade (or even) and ungerade (or odd) wave functions respectively. If the wave function does not change sign on inversion about a center it is *g*, otherwise it is *u*. These labels are relevant only for systems with an inversion center, e.g., a regular octahedron but are redundant for systems without a center of inversion, e.g., a tetrahedron.

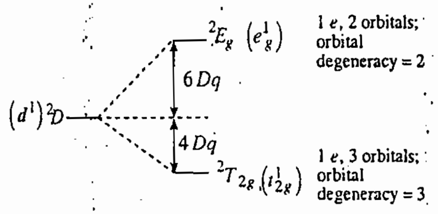


Fig. 27.42

Splitting of the free-ion *D*-term for d^1-ion in an octahedral field.
Electron configurations are shown in bracket.

[Sec. 27.2.2 *d-d Spectra*]

The behaviour of a d^9 -ion may be similarly understood if we remember the hole formalism : the ground state configuration is $t_{2g}^6e_g^3$, with a "hole" in the upper e_g-level. Since the hole can occupy either of the two e_g levels, the degeneracy is 2, giving rise to an *E*-term in the ground state. Excitation of an electron from the t_{2g} level to this hole amounts to creation of a new "hole" in the t_{2g} level. This can be placed in any of the three t_{2g} orbitals, hence an orbital degeneracy of 3. So the excited $t_{2g}^5e_g^4$ configuration corresponds to a *T*-term, 10 *Dq* higher in energy than the ground *E*-term. Thus, the d^9-ion will have a splitting pattern which would be the inverse of the d^1 - case.

We may similarly work out the terms arising from various d^n configurations in cubic fields — cubic, octahedral or tetrahedral. These may also be arrived at from group theoretical approach. The terms arising from different free ion terms are listed in Table 27.12. As usual, the subscript '*g*' should be added to centrosymmetric environments.

TABLE 27.12

Terms arising from d^n configurations in cubic crystal fields

Free ion term	Terms arising in crystal field
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$

Note : 1. It can be readily seen that the orbital multiplicity of the free ion term is retained in the aggregate of the component terms. Thus, an *F* term ($L = 3$, orbital multiplicity $= 7$) splits into one singlet (A_2) and two triplet (T_1 and T_2) terms, maintaining a total orbital degeneracy of $(1 + 3 + 3)$ or 7.

2. *S* and *P* states are not split in the cubic field. The *S*-state of the free ion can be mentally correlated to the *s* atomic orbital which is spherically symmetrical and does not split in the crystal field. Hence the *S* term gives rise to the term A_1. Likewise, the *p* atomic orbitals are also unaffected in a cubic field and the *P* term gives a triplet term, T_1.

Following the same line of approach as with the *D*-term, we may try to understand the splitting of the free ion *F* term (for d^2 configuration) in an octahedral field. The ground-state (t_{2g}^2) has an orbital degeneracy 3 ($2e$ in 3 orbitals) corresponding to the $^3T_{1g}$ term.

Now we consider the possible excited states :

(i) only one electron may be excited to either of the two e_g orbitals - giving the configuration $t_{2g}^1e_g^1$. The t_{2g}-electron can occupy any one of the three t_{2g} orbitals with equal probability—hence the degeneracy is 3. The e_g-electron can occupy any one of the two e_g - orbitals, implying two fold degeneracy. Hence the total probability is $3 \times 2 = 6$.

(ii) both the t_{2g} - electrons may be excited to the e_g level. Two electrons can occupy the two orbitals in only one way (with $M_s = 1$) and hence the degeneracy is 1.

Sum of orbital degeneracy of the ground state plus the excited states now equals $3 + 6 + 1 = 10$.

But the free ion F-term alone accounts for an orbital degeneracy of only 7 ($L = 3$; $2 \times 3 + 1 = 7$). The balance is adjusted by taking into account the upper P-term ($L = 1$; multiplicity = 3) which does not split and gives rise to a T-term. In fact, both $^3T_2(F)$ and $^3T_1(P)$ correspond to the electron distribution $t_{2g}^1 e_g^1$ described earlier and account for the total degeneracy of six.

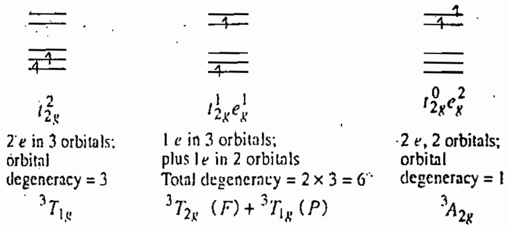


Fig. 27.43 (a)
Electron distribution in ground and excited states of a d^2 ion ($M_s = 1$) in an octahedral field.

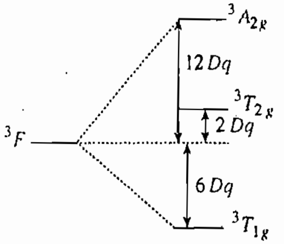


Fig. 27.43 (b)
Splitting of free ion F-term for d^2 ion in octahedral field.

The splitting of the free-ion F-term in the octahedral field is shown in Fig. 27.43.

Similar correlations between free ion terms and the terms arising therefrom can be made in other cases too. Our next task will be to correlate these split terms with observed electronic spectra of appropriate complexes.

27.2.3 Energy level diagram (Orgel diagram; Tanabe-Sugano diagram)

We have seen (Table 27.12) how the ground state terms for various d^n configurations are split in a ligand field. Now we shall discuss how the energy-separation between these terms are altered with increasing ligand field. Such diagrams are termed **Orgel diagrams** after their originator.

d^1 and d^9 cases :

First we consider the case of a d^1 ion in an octahedral field (Fig. 27.44 a). As the ligand field increases, separation between the $^2T_{2g}$ and ^2E_g levels also increases. The observed maximum in the absorption spectrum of $[Ti(H_2O)_6]^{3+}$ may now be assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition. This is spin-allowed and LaPorté forbidden, with $\varepsilon \approx 6$ L mol^{-1} cm^{-1}. In this case the value of $10Dq$ can be directly calculated from the value of the peak, 20,100 cm^{-1}.

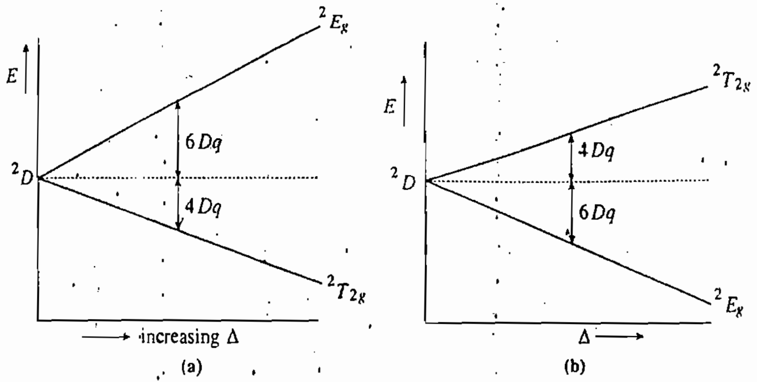


Fig. 27.44
Energy of $^2T_{2g}$ and ^2E_g levels with increasing value of $10Dq$ for (a) d^1 and (b) d^9 (octahedral field).

We have seen that the d^9-ion in an octahedral field can be considered by the hole formalism (or by thinking a d^{10} core with one positron) to give the inverse pattern of splitting. Hence the transition in a d^9 ion would be the reciprocal of that for d^1, as shown in Fig. 27.44 (b).

Now we may combine Figures 27.44 (a) and (b) in a single diagram 27.45 with the free-ion term ^2D at the origin which corresponds to zero crystal field level. The left side, which is reciprocal of the right side, refers to d^9 ions and the right side refers to d^1 ions, both in octahedral fields.

If we now think of a tetrahedral ligand field, we find that the same free-ion term ^2D gives rise to a lower E term and an upper T_2 - term (the subscript g is dropped as the tetrahedral complex is non-centrosymmetric). Hence the energy level diagram of a d^1 ion in a tetrahedral field will be the reverse of the d^1 octahedral situation (Fig. 27.44 a). The spectra of tetrahedral d^1 complexes are thus expected to show a band corresponding to the transition $^2E \longrightarrow {}^2T_2$. This will be qualitatively similar to that for a d^9 octahedral complex. From the relation $\Delta_{tet} = 4/9\ \Delta_{oct}$, we expect the band at a much lower energy than the corresponding octahedral complex.

We may generalize our finding as follows :

(i) Octahedral d^n configurations and tetrahedral d^{10-n} configurations give rise to similar type of splitting.

(ii) Octahedral d^n configurations show splitting patterns which are inverse of those for octahedral d^{10-n}.

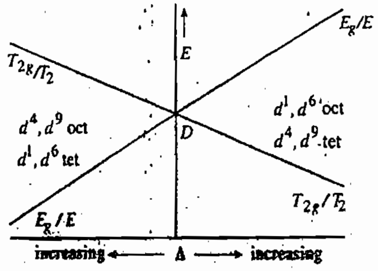


Fig. 27.45
Combined energy level diagram for free-ion ground term D.

d^4, d^6 cases :

Now we may try to correlate other configurations to the energy level diagram for d^1 and d^9. Let us first consider a high spin d^6 configuration in an octahedral field. We assign one electron to each of five orbitals in the t_{2g} and e_g level. The sixth electron should be in one of the t_{2g} orbitals with opposite spin. According to the spin-selection rule, transitions with reversal of spin are formally forbidden; hence we may neglect any transition of the first five electrons (with parallel spin). So we expect the only transition band arising from excitation of the "sixth" electron with antiparallel spin from its t_{2g} level to the upper e_g level. The free-ion term for d^6 configuration is again D, same as that for d^1, though the spin-multiplicity is different ($S = 2, 2S + 1 = 5$). So we infer that the energy level diagram for d^6 octahedral (high spin) will resemble that for d^1 octahedral case. The diagram will be the same as shown in Fig. 27.45 except that the central free ion term will be ^5D instead of ^2D.

Applying the hole formalism, we can now extend our logic to the high spin d^4 configuration. We conclude that the ^5D term should follow the same pattern as d^9 octahedral. Again in tetrahedral cases, d^6 will resemble d^4 octahedral and d^4 will resemble d^6 octahedral.

Thus Fig. 27.45 (ignoring the spin-multiplicity) may be taken as the overall qualitative representation of the effect of ligand field on :

(i) d^1, d^6 octahedral (high-spin) and d^4, d^9 tetrahedral by the right-hand side of the origin and (ii) d^4, d^9 octahedral (high-spin) and d^1, d^6 tetrahedral by the left-hand side of the origin.

For all these cases, there exists only one state above the ground state separated by ΔE, so that we expect only one transition occurring at a position in the spectrum corresponding to ΔE.

As we have noted earlier, the spectrum of $[Ti(H_2O)_6]^{3+}$ shows a broad band with a peak around 20,100 cm^{-1} which we can now assign to the $^2T_{2g} \rightarrow {}^2E_g$ transition. The broad peak is actually due to pronounced Jahn-Teller effect in the excited state, giving two closely spaced absorption bands. Similarly, octahedral Cu(II) complexes may be expected to produce a single absorption band in the visible spectrum corresponding to the $^2E_g \rightarrow {}^2T_{2g}$ transition. Here again, Jahn-Teller distortion is considerably greater than that in the d^1 case and overlap of several bands gives rise to a broad band. For $[Cu(H_2O)_6]^{2+}$ this broad band has a long tail into the near infrared.

Q. 27.12 *The spectrum of $[Ti(H_2O)_6]^{3+}$ shows an absorption maximum at 20,000 cm^{-1}. Calculate Δ_0 in kJ mol^{-1} and eV.* **[Ans. : 239 kJ mol^{-1}; 2.48 eV]**

Q. 27.13 *According to Jorgensen's rule of average environment, the position of the peak in a complex $[TiX_3L_3]$ will be midway between that for $[TiL_6]^{3+}$ and $[TiX_6]^{3-}$ provided all three complexes have the same stereochemistry. Calculate Δ_0 for $[Ti(CH_3COCH_3)_6]^{3+}$ from the following absorption peaks :*

$TiCl_3$, $3CH_3COCH_3$: 15400 cm^{-1} $[TiCl_6]^{3-}$: 12,750 cm^{-1}.

Solution : Δ_0 for $TiCl_3$, $3CH_3COCH_3$ should be half the sum of Δ_0 for $[TiCl_6]^{3-}$ and $[Ti(CH_3COCH_3)_6]$. If the latter is Δ_0', then $15400 = \frac{1}{2}(12750 + \Delta_0')$ or, $\Delta_0' = 18{,}000$ cm^{-1}.

Q. 27.14 *Consider a hypothetical ion D^+ containing a single positron (e^+) in its d - subshell.*

(i) Would the ground state of the ion be degenerate?

(ii) What would be the degeneracy of the ion in an octahedral field of six equal positive dipoles?

Hint : (i) 5-fold degenerate; (ii) 3-fold degenerate.

[Sec. 27.2.3 *Orgel diagram*]

d^2 case :

The Orgel diagram is shown in Fig. 27.46. It appears from the diagram that the $^3T_{1g}$ state arising from the ^3F term is the ground state in all field strengths. The ^3P ground term does not split in the ligand field and gives rise to another higher $^3T_{1g}$ term. The two $^3T_{1g}$ terms are labelled $^3T_{1g}$ (F) and $^3T_{1g}$ (P) according to their origin. Transitions from $^3T_{1g}$ (F) to the singlet states will be spin-forbidden and hence unimportant. Hence there will be three triplet states above the ground state : $^3T_{2g}$, $^3T_{1g}$ and $^3A_{2g}$. This leads us to expect that the spectrum of a d^2 complex (octahedral) should contain three bands.

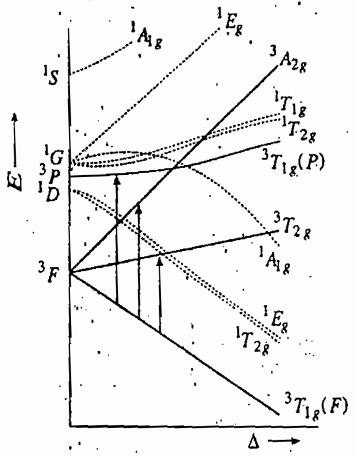


Fig. 27.46

Orgel diagram for a d^2 ion in octahedral ligand field. Dotted lines represent spin-singlet states (spin-paired).

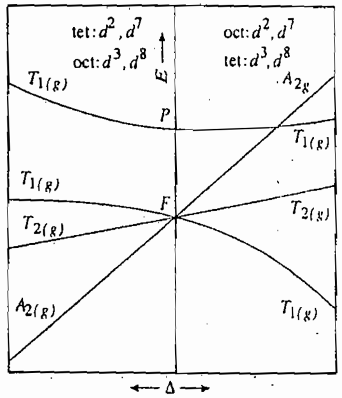


Fig. 27.47

Energy level diagram for d^2, d^3, d^7 and d^8 ions in tetrahedral and octahedral fields.

Energies of the various states after splitting relative to the ground state are obtained theoretically as follows :

$$^3T_{1g}(F) : E_1 = -3Dq + 7.5B - \tfrac{1}{2}[100Dq^2 + 225B^2 + 180BDq]^{1/2}$$

$$^3T_{2g}(F) : E_2 = 2Dq$$

$$^3T_{1g}(P) : E_3 = -3Dq + 7.5B + \tfrac{1}{2}[100Dq^2 + 225B^2 + 180BDq]^{1/2}$$

$$^3A_{2g} \quad : E_4 = 12Dq$$

The wave numbers for the three spin allowed transitions are now given as

$$\bar{\nu}_1 : {}^3T_{1g}(F) - {}^3T_{2g}(F) = E_2 - E_1$$

$$\bar{\nu}_2 : {}^3T_{1g}(F) - {}^3T_{1g}(P) = E_3 - E_1$$

$$\bar{\nu}_3 : {}^3T_{1g}(F) - {}^3A_{2g}(F) = E_4 - E_1$$

We note, $10Dq = E_4 - E_2$. Thus $10Dq$ is obtained by $\bar{\nu}_3 - \bar{\nu}_1$. Unfortunately, the third band cannot always be located. Rather, its position is located from a knowledge of $10Dq$ (see note to Fig. 27.48).

The splitting of ^3F and ^3P free ion terms are shown in Fig. 27.47. The dependence of energy level on ligand field is somewhat modified owing to mutual interaction between the levels derived from ^3F and ^3P — we find the levels to curve away from each other as the ligand field increases. This interaction depends on the Racah parameter B; it is less marked for the ^3F line as it is lowest in energy in d^2 octahedral case.

The divergent nature of T_{1g} (F) and T_{1g} (P) lines with increasing Δ illustrates the **non-crossing rule** : if two states of the same symmetry approach each other as a parameter is changed (here the increasing ligand field), they do not cross each other but bend apart from one another.

From this diagram also, we expect three spin-allowed transitions from the ground T_{1g} (F) state to the three upper states. The spectrum of an octahedral d^2 complex is thus expected to show three bands (Fig. 27.48).

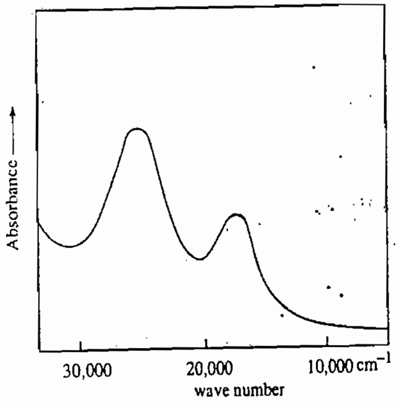


Fig. 27.48
The electronic spectrum of $[V(H_2O)_6]^{3+}$ (perchlorate).

It shows the general features for a d^2 ion expected from Fig. 27.46 and 27.47. There are only two low intensity bands in the visible and near uv region. High intensity charge-transfer bands are observed in shorter uv region but no other bands are observed at lower energies in the visible range. The two bands may be assigned to the two spin-allowed transitions

$^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ $\quad \bar{\nu}_1 = 17{,}250 \text{cm}^{-1}$

$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ $\quad \bar{\nu}_2 = 25{,}000 \text{cm}^{-1}$

The position of ν_3 corresponding to the transition $^3T_{1g}(F) \longrightarrow {}^3A_{2g}$ may be estimated by assuming that the Racah parameter B for the free ion (860 cm^{-1}) has the same value in the complex. We may now draw Fig. 27.46 with ^3P —^3F separation equal to 15B. Next we select the value of Dq which fits the observed ratio of ν_1 to ν_2. A vertical line drawn at the point will cut the $^3A_{2g}$ level giving an estimate of ν_3. However, the method is only an approximate one; it can be improved by treating B as a variable parameter (see Tanabe-Sugano diagram).

More involved calculations give an estimate of ν_3 at 35700 cm^{-1} but the transition is not observable with $[V(H_2O)_6]^{3+}$ owing to strong charge transfer absorption in this region.

In a tetrahedral complex, as we have seen before, the same states will be involved with an inversion; the left hand side of Fig. 27.47 shows the gross nature of the energy level diagram.

d^8 case :

As we have correlated the d^9-configuration with d^1, the d^8-configuration may be similarly correlated with the d^2. We conclude, by the same arguments as applied before, that the spectral behaviour of d^8 octahedral (high-spin) will be the inverse of d^2 octahedral, represented by the left-hand side of the energy-level diagram in Fig. 27.47. The spectrum of $[Ni(H_2O)_6]^{2+}$ (Fig. 27.36a) shows three bands which is typical for many octahedral nickel(II) complexes (Table 27.13). The involved transitions are shown in Fig. 27.49.

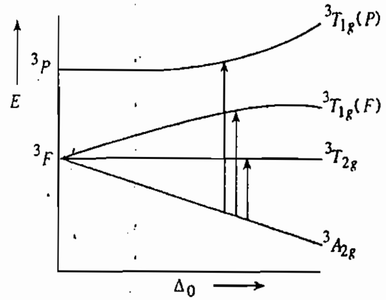


Fig. 27.49
Simplified Orgel diagram for d^8 ion.

10Dq is given by the lowest energy transition ($^3A_{2g} \longrightarrow {}^3T_{2g}$) (see Fig. 27.46 for d^2-case. The situation is exactly reversed here).

This is also true for d^3 (oct) and d^2, d^7 (tet).

TABLE 27.13

Band positions (cm^{-1}) in the electronic spectra of some octahedral complexes of Ni(II)

Complex	$^3A_{2g} \longrightarrow {}^3T_{2g}$	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
$[Ni(H_2O)_6]^{2+}$	8,500	13,800	25,300
$[Ni(NH_3)_6]^{2+}$	10,750	17,500	28,200
$[Ni(en)_3]^{2+}$	11,200	18,350	29,000
$[Ni(bipy)_3]^{2+}$	12,650	19,200	obscure

As Δ_0 increases, the bands move towards the uv region.

The behaviour of d^8 tetrahedral complexes will again follow the right hand side of the energy level diagram in Fig. 27.47, similar to d^2 octahedral.

Since tetrahedral complexes do not have any center of symmetry, we expect more intense absorption bands than with octahedral complexes. Again, the splitting in tetrahedral fields being smaller than that in an octahedral field, separation between the terms will be given by Dq-regions closer to the origin in Figure 27.47. Hence the transitions will involve much lower energy difference than in the octahedral case. In fact, in many cases the lowest energy transition cannot be located as it falls in the infra-red region.

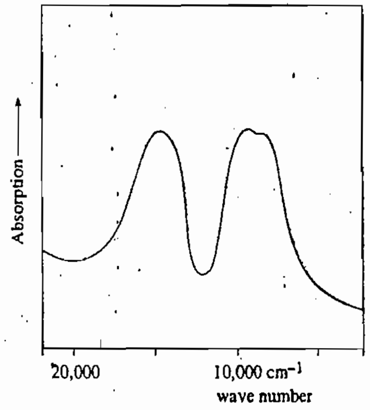


Fig. 27.50
Electronic spectrum of $[VCl_4]^-$, typical for a d^2 tetrahedral complex.

Two absorption bands are seen :

$^3A_2 \longrightarrow {}^3T_1(F)$: 8900 cm^{-1}

$^3A_2 \longrightarrow {}^3T_1(P)$: 15,000 cm^{-1}

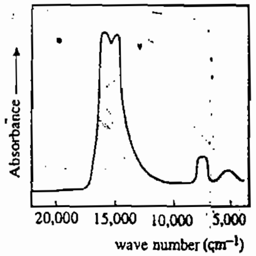


Fig. 27:51

Electronic spectrum of $[NiCl_4]^{2-}$ typical for a d^8 tetrahedral complex. The three bands correspond to the transitions :

$^3T_1 \longrightarrow {}^3T_2$: 4,000 cm^{-1}

$^3T_1 \longrightarrow {}^3A_2$: 7,500 cm^{-1}

$^3T_1 \longrightarrow {}^3T_1$ (P) : 15,000 cm^{-1}

Strong absorption ($\varepsilon \simeq 10^2$ L mol^{-1} cm^{-1}) in the red part of visible region makes such complexes intense blue. The band around 8000 cm^{-1} is considerably weaker while the lowest energy transition is not very often observed. Spin-forbidden transitions to levels derived from free ion ^1D and ^1G terms sometimes give rise to weak bands on either side of the 15,000 cm^{-1} band.

d^3, d^7 :

Both these configurations result in ^4F and ^4P free ion terms together with several other doublet terms. By applying the same arguments as we did previously for the energy level diagram in Fig. 27.45 (for d^1, d^4, d^6 and d^9 configurations), we can conclude that the qualitative nature of the energy level diagram for d^3 and d^7 will be the same as for d^2 and d^8 configurations. d^3-tetrahedral and d^7-octahedral (high spin) will be represented on the right hand side of the energy level diagram while d^3 octahedral and d^7 tetrahedral will follow the left side of the diagram. In both cases, we again expect three spin-allowed transitions.

The gross features of the spectrum of a d^3 ion is illustrated in Fig. 27.52 for $[Cr(NH_3)_6]^{3+}$ in aqueous solution.

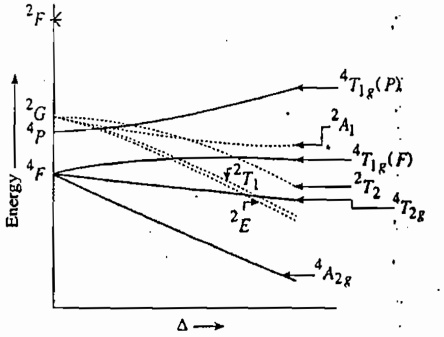


Fig. 27.52 (a)

(a) **Simplified energy level diagram for d^3 octahedral.** Three spin-allowed transitions are expected for the transitions $^4A_{2g} \to {}^4T_{2g}$, $^4A_{2g} \to {}^4T_{1g}(F)$ and $^4A_{2g} \to {}^4T_{1g}(P)$. The last band is often obscured by CT bands (see Fig. 27.52 b).

The doublet states arising from the higher ^2G term (……) play a key role in ruby lasers (see below).

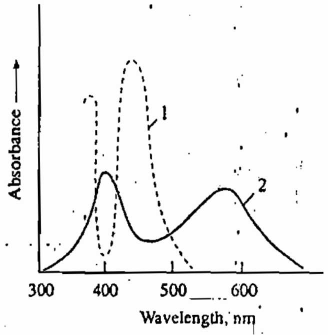


Fig. 27.52 (b)

Absorption spectra of $[Cr(NH_3)_6]^{3+}$ (1) and $[Cr(H_2O)_6]^{3+}$ (2).

[Sec. 27.2.3 *Orgel diagram*]

Ruby Laser

Ruby contains Cr^{III} ions embedded in α-Al_2O_3 where the oxide ions provide a nearly distorted octahedral field. When a large single crystal of ruby is exposed to light of appropriate frequency to excite the Cr^{III} to the $^4T_2$ (*F*) state, it does not return to the ground state. Instead the energy is lost to the crystal lattice by vibrational modes and by some intricate balance of energy the chromium(III) is taken to the ^2E and $^2T_1$ states arising from the higher ^2G free ion term (Fig. 27.52 a). Return to the ground state is now accompanied by simulated emission of monochromatic radiation in phase with the stimulating radiation. This principle is used in *Ruby lasers*.

The electronic spectra of cobalt(II) complexes (Fig. 27.53) may be taken as an illustration for d^7 ions.

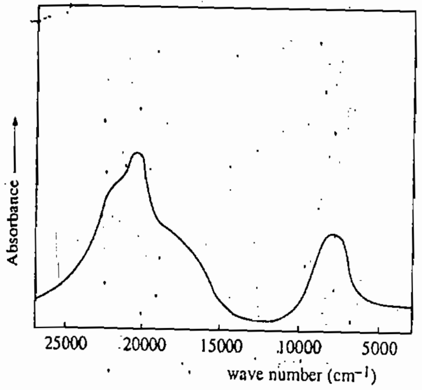


Fig. 27.53

Gross features of the spectrum of $[Co(H_2O)_6]^{2+}$.

The pale pink solution shows weak (ε = 10 L mol^{-1} cm^{-1}) multiple absorption bands.

The lowest-energy band at 8000 cm^{-1} coresponds to the transition $^4T_{1g} \longrightarrow {}^4T_{2g}$. Assignment of other bands appear difficult due to poor resolution; also the $^4A_{2g}$ and $^4T_{1g}$ (*P*) states are close to the center of the diagram in the weak ligand field. The following bands are commonly assigned :

16,000 cm^{-1} $^4T_1 \longrightarrow {}^4A_{2g}$

19,400 cm^{-1} $^4T_{1g} \longrightarrow {}^4T_{1g}$ (*P*)

The shoulder at ~ 21,600 cm^{-1} has been attributed to spin-orbit coupling effects or to transition to doublet states.

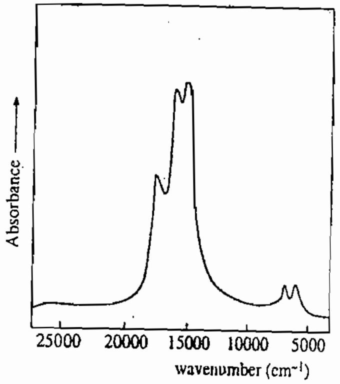


Fig. 27.54

Gross features of the electronic spectrum of $CoCl_4^{2-}$.

The complex is intensely blue, as seen from the high value of ε (600 L mol^{-1} cm^{-1}). The lowest energy band lies in the infrared region. Other two bands are

5,800 cm^{-1} $^4A_2 \longrightarrow {}^4T_1$ (*F*)

15,000 cm^{-1} $^4A_2 \longrightarrow {}^4T_1$ (*P*)

(The $^4A_2 \longrightarrow {}^4T_2$ transition is thus expected to occur around 3300 cm^{-1}).

The fine structure of the bands may originate from several factors, the important ones being spin-orbit coupling and transitions to doublet states.

d^5 :

In a d^5 ion in octahedral (high spin) field, all d-orbitals are singly occupied and no spin allowed transition is expected. The ^6S ground term does not split in an octahedral field and gives rise to only one term, $^6A_{1g}$. There are four excited states involving only one spin reversal. In O_h and T_d ligand field these states split into a total of ten states whose energy variation with ligand field is shown in Fig. 27.55.

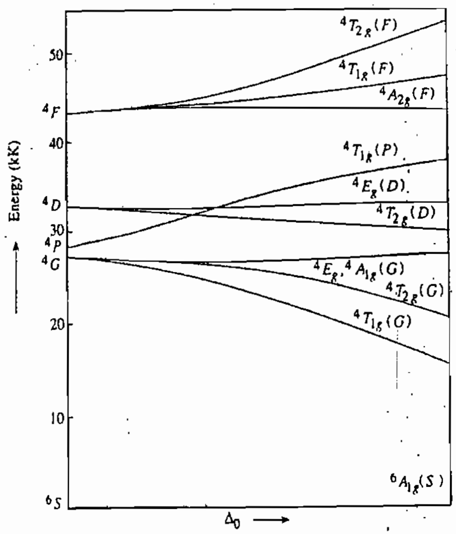


Fig. 27.55
Orgel diagram for d^5 octahedral (high spin).
The ^6S state of the free ion and the $^6A_{1g}$ term arising out of it lie on the abscissa. Note that the energies of the $^4A_{1g}$, ^4E_g (G), ^4E_g (D) and $^4A_{2g}$ (F) terms do not vary with the field strength.

In absence of charge transfer absorption, d^5 complexes are expected to be very faintly coloured as we find in pale pink manganese(II) salts or pale violet ferric alum. The electronic spectrum of $[Mn(H_2O)_6]^{2+}$ in perchlorate media is shown in Fig. 27.56.

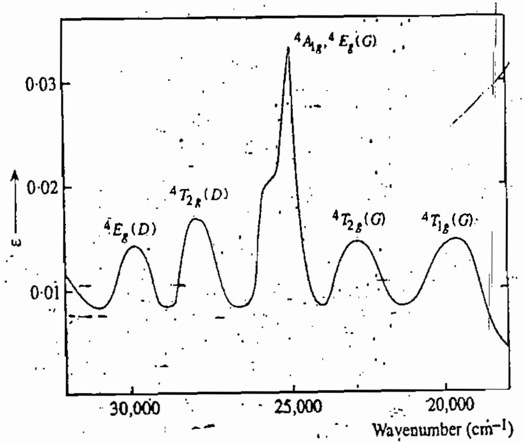


Fig. 27.56
Gross nature of the electronic spectrum of $[Mn(H_2O)_6]^{2+}$.

The bands are very weak and relatively sharp (in contrast to spin-allowed bands observed earlier which are always broad). Spin forbidden bands may be both broad or sharp.

The bands have been assigned as follows :

18,900 cm⁻¹	$^6A_{1g} \to {}^4T_{1g}$ (G)
23,100 cm⁻¹	$^6A_{1g} \to {}^4T_{2g}$ (G)
24,970, 25,300 cm⁻¹	$^6A_{1g} \to {}^4E_g, {}^4A_{1g}$ (G)
28,000 cm⁻¹	$^6A_{1g} \to {}^4T_{2g}$ (D)
29,700 cm⁻¹	$^6A_{1g} \to {}^4E_g$ (D)

The sharpness of the bands may be correlated with the slope of the state in the energy level diagram. The ligand field strength 10Dq varies about some mean value during the vibration of a complex. When a transition involves two energy states whose difference does not depend upon the ligand field strength, such vibrations will not significantly affect the bands and we expect a sharp absorption band. The transition energy varies during vibration when the upper state has a slope (Fig. 27.55; the ground $^6A_{1g}$ state has zero slope). Thus transitions to ^4E_g, $^4A_{1g}$ (G), $^4T_{2g}$ (D) and ^4E_g (D) states give sharp bands.

We may summarize our findings about the electronic spectra of transition metal complexes as follows :

d^1, d^4, d^6, d^9 (Oh or Td) :	A single band is expected. This corresponds to Δ_o or Δ_t.
d^2, d^3, d^7, d^8 (Oh or Td) :	Three bands are expected. For d^3, d^8 (Oh) and d^2, d^7 (Td), the lowest energy transition gives Δ_o or Δ_t. For d^3, d^8 (Td) or d^2d^7 (Oh), separation between the first and the third band gives Δ_o or Δ_t.
d^5 :	Large number of sharp bands of low intensity are observed.

Modification of the Orgel diagram

In Orgel diagrams we have considered only weak-field cases and the states of highest multiplicity. It is also possible to include states of lower multiplicity in the diagram when it is found that for d^4, d^5, d^6 and d^7 configurations, the energy of the low spin state gradually decreases as the strength of the ligand field increases. Eventually the low-spin state becomes the ground term beyond a certain value of the ligand field. The actual treatments of d^4, d^5 and d^7 systems are quite complex and beyond the scope of this text. The low-spin d^6 case is briefly discussed below.

The ground state for a low-spin octahedral d^6 metal ion is t_{2g}^6. Since all three orbitals are full, only one arrangement is possible and the ground configuration is $^1A_{1g}$. The first excited configuration will be $t_{2g}^5 e_g^1$. We may consider the t_{2g}-level as containing a hole; this may occur in any of the three orbitals, giving rise to a probability of 3. Corresponding to each assignment of the hole, the e_g-electron may be placed in either of two orbitals, giving rise to a total probability of 3 × 2 = 6; this is the sum of two triplet terms $^1T_{1g}$ and $^1T_{2g}$. Thus we expect two absorption bands corresponding to transitions to these excited states. Since the magnitude of 10Dq in low-spin complexes is high, transitions to still higher excited states (involving promotion of two or more electrons) will fall among the charge transfer transition in uv region. The modified Orgel diagram for $d^6(O_h)$ also suggests two spin-allowed transitions from the $^1A_{1g}$ (Fig. 27.57 a) to $^1T_{1g}$ and $^1T_{2g}$.

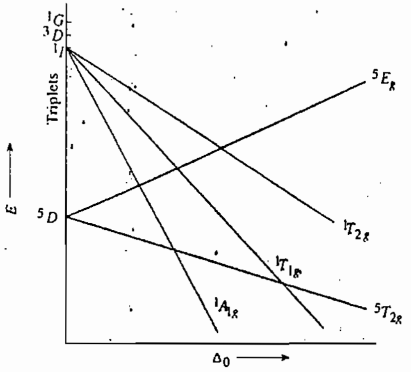


Fig. 27.57 (a)
Modification of Orgel diagram for d^6 octahedral configuration to include the singlet states arising from free ion ^1I term.

At low field strength, ground term is $^5T_{2g}$ but as field strength increases the $^1A_{1g}$ term decreases sharply in energy and after a certain point (10Dq = P), becomes the ground term.

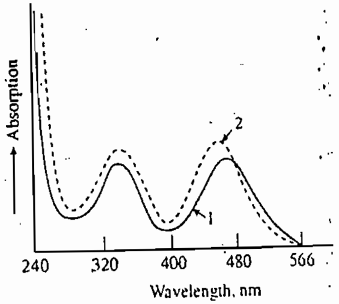


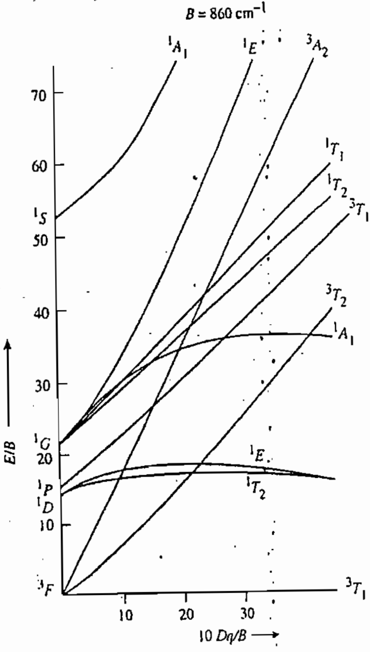
Fig. 27.57 (b)

Absorption spectra of [Co(NH$_3$)$_6$]$^{3+}$ (1) and [Coen$_3$]$^{3+}$ (2) in aqueous solution.

The peaks correspond to spin, allowed transitions from the ^1A ground state.

Tanabe-Sugano diagrams

The Orgel diagram is more or less qualitative in nature and suitable for weak field cases only. In such diagrams (e.g. Fig. 27.55), the energies of different states are plotted in absolute units; so each diagram applies only to a particular system in which the separations between free ion terms match with those in the diagram. These difficulties have been largely eliminated by quantitative calculations for various field strengths using group theory and construction of appropriate diagrams. Among these, the Tanabe-Sugano diagram is most widely used. The salient features of the diagram are : (i) It is a diagram showing the energy of different states at various field strengths, including low-spin terms. (ii) The state energies and 10*Dq* are both expressed in units of the Racah parameter *B*. *B* has different values for different isoelectronic ions, which are shown at the top of each diagram. Since energies are plotted in units of *B*, one Tanabe-Sugano diagram may be used for all members of an isoelectronic group. (iii) The zero of energy for any particular d^n ion is taken to be the energy of the ground state. The horizontal axis represents the energy of the ground state regardless of the ligand field strength; energies of higher states are plotted against the energy of the ground state. (iv) Since $C = 4B$, energies of terms depending on both *B* and *C* can also be plotted on the same diagram.



We shall give a brief introduction to these diagrams with a d^2 ion as an example (Fig. 27.58).

Fig. 27.58

Simplified Tanabe-Sugano diagram for [V(H$_2$O)$_6$]$^{3+}$, a d^2 ion.

As noted earlier (Fig. 27.48), the electronic spectrum of [V(H$_2$O)$_6$]$^{3+}$ shows two weak absorption bands out of three spin-allowed transitions :

$$\nu_1 = 17{,}800\ \text{cm}^{-1}\ (\varepsilon = 3{\cdot}5\ \text{L mol}^{-1}\ \text{cm}^{-1});$$

$$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$$

$$\nu_2 = 25{,}700\ \text{cm}^{-1}\ (\varepsilon = 6{\cdot}6\ \text{L mol}^{-1}\ \text{cm}^{-1});$$

$$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P).$$

Next we may scan the Tanabe-Sugano diagram for d^2 to obtain a suitable value of 10*Dq*/*B* which best matches the observed ratio of $\nu_1 : \nu_2$. This is found to occur around 10*Dq*/*B* equal to 29. Conversion now gives *B* = 630 cm^{-1} for [V(H$_2$O)$_6$]$^{3+}$ while the free ion value of *B* was 860 cm^{-1}. The value of *B* for the aquocomplex is thus only 73% of the free ion value.

[Sec. 27.2.3 *Tanabe-Sugano diagram*]

Spectrum of Ni(II) (d^8)

The spectrum of [Ni(H$_2$O)$_6$]$^{2+}$ shows three bands (Fig. 27.36a) corresponding to ΔE = 8,500, 13,800 and 25,300 cm^{-1} (Table 27.13). The lowest transition at 8,500 cm^{-1} should correspond to 10*Dq*. The free ion value of *B* for Ni(II) is 1080 cm^{-1}. If we assume that the value of *B* in the complex is approximately 80% of the free ion value, we have *B* (complex) = 0·8 × 1080 cm^{-1} = 864 cm^{-1}. We now locate on the abscissa of the Tanabe-Sugano diagram for 10*Dq*/*B* = 8500/864 = 9.83. This corresponds to *E*/*B* values of about 18 and 29, giving transition energies 15,500 and 25,000 cm^{-1} respectively. The agreement with experiment is satisfactory.

Spectra of Co^{3+} (d^6)

A simplified Tanabe-Sugano diagram for a d^6 ion showing only singlet and quintet states are shown in Fig. 27.59. The free ion ground-term ^5D is split in the octahedral ligand field into $^5T_{2g}$ and ^5E_g states. The $^5T_{2g}$ state forms the ground state up to $Dq = 2B$; thereafter the $^1A_{1g}$ state (arising from free ion ^1I; see Fig. 27.57) becomes the ground state. All the states show discontinuity at $Dq/B = 2$ (shown by a vertical line). For ligand field strengths below this line, high-spin complexes are formed while at higher field strength, low-spin complexes are formed. Since the cross-over ligand field strength is not high, most octahedral Co(III) complexes including [Co(H$_2$O)$_6$]$^{3+}$ have diamagnetic ground states. Very few, like [CoF$_6$]$^{3-}$ and [Co(H$_2$O)$_3$F$_3$] are paramagnetic with four unpaired electrons.

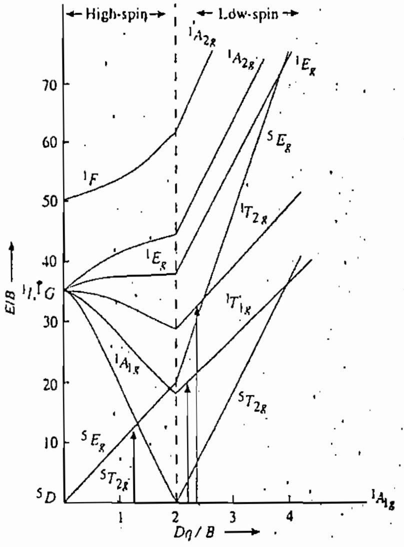


Fig. 27.59

Simplified Tanabe-Sugano diagram for d^6 (Co^{3+}) in octahedral field.

High-spin complexes are expected to show a single absorption peak corresponding to the transition $^5T_{2g} \rightarrow {}^5E_g$ (shown by arrow). Indeed, the deep blue complex [CoF$_6$]$^{3-}$ shows a single peak at 13,000 cm^{-1}.

Low-spin regular octahedral complexes like [Co(en)$_3$]$^{3+}$ show two absorption bands corresponding to transitions from $^1A_{1g}$ to $^1T_{1g}$ and $^1T_{2g}$.

Note : Since the above energy level-diagrams are derived from symmetry properties of the system, they apply only to *regular* octahedral complexes like [Co(en)$_3$]$^{3+}$ or [CoL$_6$]$^{3+}$. Thus, complexes of the type CoX$_4$Y$_2$ having lower symmetry are marked by further splitting of the $^1T_{1g}$ level, depending upon the separation of X and Y in the spectrochemical series. The extent of this splitting is much greater for the *trans*-isomer than for the *cis*-isomer

(Fig. 27.60). Again, the cis isomer shows somewhat stronger absorption as it lacks symmetry.

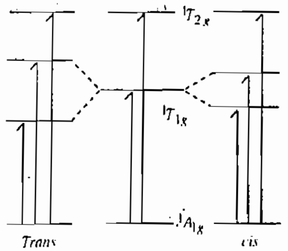


Fig. 27.60 Schematic representation of electronic transition in $[(Co(en)_3]^{3+}$ regular octahedral (center) and *cis* and *trans* $[Co(en)_2F_2]^+$. Note the number and proximity of the bands.

Q. 27.15 *Fig. 27.61 shows a simplified version of the Tanabe-Sugano diagram for the d^3 configuration. Predict the position of the first two spin-allowed transitions in the spectrum of $[Cr(H_2O)_6]^{3+}$ ion ($10Dq = 17{,}400\ cm^{-1}$; $B = 918\ cm^{-1}$.*

Hint.: Cr^{3+} (d^3) has the free-ion ground term ^4F which splits into $^4A_2$, $^4T_2$ and $^4T_1$ terms in the octahedral field as shown in the diagram. The $^4A_2$ term is the ground term and the first two spin-allowed transitions will be to $^4T_2$ and $^4T_1$ level.

$$\Delta_0/B = 17{,}400/918 \simeq 19$$

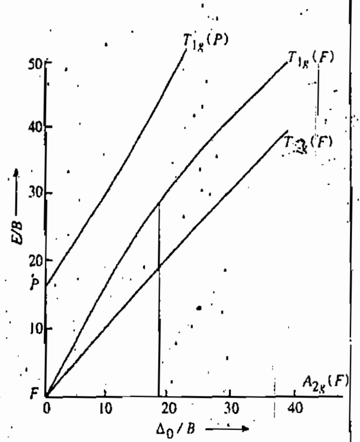


Fig. 27.61 Tanabe-Sugano Diagram for d^3 (simplified)

A vertical line drawn at $x = 19$ cuts the $^4T_2$ line at $y = 19$ and the $^4T_1$ line at $y = 28.5$. Since the y - axis is also plotted in terms of E/B, we have

$$E\left({}^4A_2 \to {}^4T_2\right) = 19 \times B = 19 \times 918\ \text{cm}^{-1}$$
$$= 17442\ \text{cm}^{-1}$$
$$E\left({}^4A_2 \to {}^4T_1\right) = 28 \cdot 5 \times B = 28 \cdot 5 \times 918\ \text{cm}^{-1}$$
$$= 26{,}163\ \text{cm}^{-1}$$

[Actually there are three spin-allowed bands at 17,400, 24,500 and 37,700 cm^{-1}. Values calculated above are higher because we have taken the free ion value for B. Also, accuracy of the method depends on the accuracy of the T-S diagram. Here we have used only an approximate diagram.]

27.2.4 Charge transfer spectra

A charge transfer transition is an electronic transition between orbitals which are centered on different atoms. In the ***d-d*** transitions discussed earlier, electrons are redistributed in orbitals which are primarily based on the metal. The ground and excited states of the complex thus have nearly the same charge distribution. Charge transfer transitions involve movement of electrons from orbitals which have basically ligand character to orbitals which have essentially metal character or vice versa. Besides there may be also metal to metal charge transfer involving two different-oxidation states of a metal (see later). In such transitions, the charge distribution in the excited state differs considerably from that in the ground state and may be crudely supposed to be equivalent to an effective transfer of charge from one part of the molecule to another; hence these are known as *charge-transfer* (CT) *transitions* and the bands arising from such charge transfer are called charge transfer bands.

[Sec. 27.2.4 *Charge-transfer spectra*]

Most charge-transfer transitions do not flout selection rule of any kind, that is, they are $g \leftrightarrow u$ transitions with $\Delta S = 0$. Hence, they give rise to intense bands with extinction coefficients of the order of $10^3 - 10^4$. (However, there may be some weak CT bands arising from forbidden transitions but they are often covered by the strong CT bands). CT bands are usually high energy transitions and often lie in the uv region and blue end of the visible spectrum. The spectrum of $[Ti(H_2O)_6]^{3+}$ (Fig. 27.5) shows the "edge" of a CT band in the uv region. Such bands occur in many other complexes in addition to usual *d-d* transitions, and because they are many times stronger than the ligand-field bands (of *d-d* transitions), they may obscure the ligand field spectra in the neighbouring region. Charge transfer bands also account for the strong colours of many d^0 and d^{10} species like CrO_4^{2-}, MnO_4^- and HgI_2.

Three main types of charge-transfer transitions are important.

(i) ***Ligand-to-metal (L → M) transitions.***

Ligand to metal charge transfer is common among both octahedral and tetrahedral complexes. Transfer of electron charge from ligand to metal is tantamount to reduction of the metal and hence such transitions take place with lower energy as the metal becomes more easily reducible (oxidizing) and the ligand gets readily oxidizable. L → M CT bands are common in the spectra of complexes in which the ligands have filled π-orbitals, for example the halo complexes. The intense colours associated with many compounds involve L→M charge transfer, for example CdS (yellow) : $S^{2-}(\pi) \to Cd^{2+}(5s)$; HgS (red) : $S^{2-}(\pi) \to Hg^{2+}(6s)$.

A simplified molecular orbital energy level diagram for an octahedral MX_6^{n-} complex (X^- = a halide ion) is shown in Fig. 27.62.

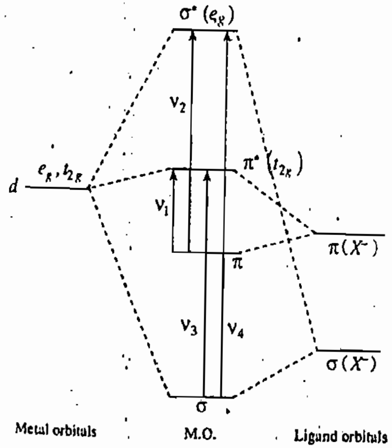


Fig. 27.62 Simplified m.o. diagram showing charge transfer transitions in an octahedral MX_6^{n-} complex.

Four transitions are expected; in order of increasing energy, these are :

$\pi \longrightarrow \pi^*(t_{2g})$ ν_1
$\pi \longrightarrow \sigma^*(e_g)$ ν_2
$\sigma \longrightarrow \pi^*(t_{2g})$ ν_3
$\sigma \longrightarrow \sigma^*(e_g)$ ν_4

(ν_3 and ν_4 are rarely observed).

Each of the transitions shown will be actually composite in nature since the excited configuration (and sometimes also the ground configuration) gives rise to several different states with similar but not identical energy. In spite of this and other complications, it is possible to mark certain general features of such charge-transfer spectra.

(i) Since the π and π^* orbitals involved in the lowest energy transition are largely non-bonding in character, their energies will not fluctuate noticeably with change in M – L distance as the ligands vibrate. Hence such transitions are expected to give a relatively narrow band.

(ii) No question of $\pi \rightarrow \pi^*$ transition arises when the π^* level is filled with metal electrons, as in the case of d^6 metal ions (remember that the π-m.o. is occupied by ligand electrons in the complexes under consideration). In such cases the $\pi \rightarrow \sigma^*$ transition will give the lowest CT band, as in $[PtBr_6]^{2-}$ and $[PtI_6]^{2-}$. Such transitions take place from a mainly non-bonding orbital to an antibonding one and hence their energy varies noticeably with change in M – L distance accompanying vibration. Hence the bands are broad.

(iii) ν_1 and ν_2 for some hexahalo complexes are given in Table 27.14.

TABLE 27.14

CT bands of some hexahalo complexes (cm^{-1})

Complex	$\nu_1, \pi \rightarrow \pi^*$ (t_{2g})	$\nu_2, \pi \rightarrow \sigma^*$ (e_g)
$[TiCl_6]^{2-}$	31,850	42,500
$[TiBr_6]^{2-}$	25,200	36,500
$[ZrCl_6]^{2-}$	42,400	
$[ZrBr_6]^{2-}$	38,900	
$[VCl_6]^{2-}$	21,400	

It appears that for a given metal ion both ν_1 and ν_2 decreases from the chloro to the bromo complex, as expected from greater oxidizable character of bromide.

The energy of the $\pi \rightarrow \pi^*$ (t_{2g}) transition also decreases in the order $[ZrCl_6]^{2-} > [TiCl_6]^{2-} > [VCl_6]^{2-}$. This is also consistent with the increasing ease of reduction of the metal ions, in other words, with increasing oxidizing power of the metal ion. Vanadium(IV) is so highly oxidizing toward bromide that the complex $[VBr_6]^{2-}$ has not been prepared.

Combination of oxidizing cations with reducing ligands (good electron donors) may give rise to CT bands from low energy absorption in the visible region, resulting in intense colours as in the complexes of Fe(III) with phenol and thiocyanate.

Strong L ⟶ M charge transfer bands are also observed in tetrahedral complexes like NiX_4^{2-}, CoX_4^{2-} and MnX_4^{2-} as well as complexes of d^{10} metal ions HgX_4^{2-} ($X = Cl^-, Br^-, I^-$). In the tetrahedral complexes of formula MO_4^{n-} (M = first row transition metal), the observed colours arise from O ⟶ M charge transfers. Since the metal is in a high oxidation state, the population in the d-orbital is low or zero, providing acceptor orbitals of low energy. The CT bands then correspond to promotion of an oxygen lone pair electron into a low-lying vacant e_g orbital on the metal.

The energies of the LMCT bands again follow the trend expected from the position of the metals in the electro-chemical series : the most easily reducible ions show the lowest energy transitions. This is shown by the gradual decrease of ν_1 with increasing oxidation number of the metal along the series.

$$\underset{\text{white}}{VO_4^{3-}} > \underset{\text{yellow}}{CrO_4^{2-}} > \underset{\text{purple}}{MnO_4^-}$$

(ii) *Metal-to-ligand (M ⟶ L) charge transfer*

Metal to ligand charge transfer takes place when the ligands possess low-lying vacant orbitals and the metal can provide filled orbitals at a higher level than the highest filled m.o. of ligands. As expected, readily oxidizable metals with ligands which are readily reducible offer the most favourable combination for studying such M ⟶ L charge transfer. Pyridine, 2, 2′-dipyridyl, 1, 10 - phenanthroline, CO, CN^- etc ligands have vacant π^* orbitals which can give rise to such CT bands.

[Sec. 27.3.1 *Magnetic Properties*]

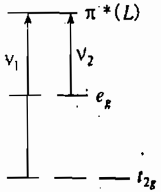


Fig. 27.63

M ⟶ L CT : a simplified representation.

	ν_1	ν_2 cm^{-1}
$Cr(CO)_6$	35,800	44,500
$Mo(CO)_6$	35,000	43,000

(iii) *Metal-metal charge transfer*

"Intravalence" charge transfer can take place in compounds containing a metal in two different oxidation states. Such charge transfers are associated with intense colours of some mixed valence compounds e.g. Prussian blue, $Fe_4^{III}[Fe^{II}(CN)_6]$; molybdenum blue (contains Mo^{IV} to Mo^{VI} in MoO_3) and $Cs_2Au^IAu^{III}Cl_6$ (black gold). In this last compound intravalence electron transfer occurs between $[Au^{III}Cl_4]^-$ and $[AuCl_2]^-$ ions.

Optical electronegativity

The energy of charge transfer transition between ligand to metal orbitals (L → M CT) may be related to some assigned property of the filled ligand π-orbitals and the metal t_{2g} orbitals (these ultimately become the π^* m.o. in the complex). This property has been called the *optical electronegativity* of ligand (λ_L) and metal (λ_M). It is possible to express the wave number of LMCT as

$$\bar{\nu} = C(\lambda_L - \lambda_M)$$

when $C = 30{,}000\ cm^{-1}$ gives values of λ_L and λ_M comparable to the Pauling scale. For metal to ligand charge transfers ending in an e_g orbital, Δ_0 has to be added to the energy calculated from the above equation.

The idea of optical electronegativity is somewhat arbitrary, but it helps to express the variation in the positions of LMCT bands. Some typical values are given below :

Metal	Cr^{III} (oh)	Co^{III} (oh, l.s.)	Ni^{II} (Td)	Co^{II} (Td)
λ_M	1·9	2·3	2	1·9

Ligand	F^-	Cl^-	Br^-	I^-	NH_3
λ_L	σ : 4·4	3·4	3·3	3·0	3·3
	π : 3·9	3·0	2·8	2·5	—

27.3 MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

27.3.1 Magnetic properties of the electron

We know that an electric charge in motion gives rise to magnetic effects. The magnetic effect arising from the nucleons are about one-thousandth time weaker than the magnetic effect produced by electrons. Hence only the latter influence the bulk magnetic properties of substances. (Magnetic effect due to nucleons may be studied in specially designed experiments like the nuclear magnetic resonance studies). First we shall see how the spin and orbital angular momenta of electrons give rise to magnetic moments.

A magnetic dipole μ experiences a torque τ in a magnetic field of flux density B given by

$$\tau = \mu B \sin\theta ......(\theta = \text{angle between } \mu \text{ and } B)$$

It is convenient to set a reference configuration of zero potential energy $(V_m = 0)$ when $\theta = 90°$, i.e., μ is perpendicular to B. The potential energy at any other orientation of μ may now be calculated by the external work necessary to rotate the dipole from $\theta = 90°$ to any angle θ:

$$V_m = \int_{90°}^{\theta} \tau d\theta = \mu B \int_{90°}^{\theta} \sin\theta \, d\theta$$

$$= -\mu B \cos\theta \qquad ......(27.1)$$

Clearly, the potential energy is minimum when $\theta = 0°$ $(V_m = -\mu B)$ i.e., μ is pointed in the same direction as B. This is why a magnetic dipole tends to align itself with an external magnetic field.

An electron gives rise to magnetic moments as a consequence of its orbital and spin angular momentum. The vector addition of such moments may be accomplished in the classical representation of the electron as a charged particle and its orbital angular momentum and the consequent magnetic moment may be calculated on this basis. Quantum mechanics also yields analogous results for the magnetic moment due to orbital motion and these are also supported by experimental facts like the Zeemann effect and the Stern-Gerlach experiment.

First we consider the magnetic moment of an electron arising from its orbital motion. We recall that the magnetic moment of a current loop is given by

$$\mu = IA,$$

where I is the current and A is the area of the loop. If an electron moves in a circular orbit of radius r, the area A is equal to πr^2. If the electron, with charge $-e$, makes ν revolutions per second, the current I will be equal to $-e\nu$. Therefore,

$$\mu = -e\pi r^2 \nu$$

The linear velocity (V) of the electron is $2\pi\nu r$ and so its angular momentum L is

$$L = mVr = mr \cdot 2\pi\nu r$$
$$= 2\pi\nu m r^2.$$

It we now substitute $\pi r^2 \nu$ $(= L/2m)$ in the above expression for μ, we get

$$\text{electron magnetic moment (orbital)}: \mu = -\frac{e}{2m} L \qquad ......(27.2)$$

We can also substitute the quantum mechanical expression for angular momentum L (instead of mvr):

$$L = \sqrt{l(l+1)}\frac{h}{2\pi}; \quad \mu = -\frac{e}{2m}\sqrt{l(l+1)}\frac{h}{2\pi} \qquad ......(27.3)$$

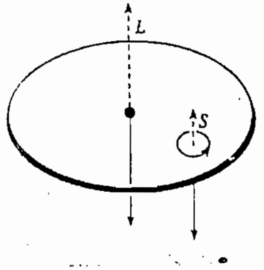


Fig. 27.64

Magnetic moments (solid line) due to orbital and spin angular momenta of an electron are directed opposite to the direction of the orbital angular momentum vector (L) and spin angular momentum vector (S) (broken lines).

$e/2m$ is called the *gyromagnetic ratio* (or *magnetogyric ratio*). We observe that the magnetic moment is proportional to the angular momentum vector. The minus sign, a consequence of the negative charge of the electron, implies that μ and L will act in opposite directions (Fig. 27.64). We can also write

Orbital magnetic moment $\mu = \gamma_e \cdot L$ where $\gamma_e = -e/2m$ stands for the magnetogyric ratio.

We know (Chapter 3) that l, m_l and L are related as

$$m_l = \sqrt{l(l+1)}\cos\theta \qquad L = \sqrt{l(l+1)}\hbar$$

where $\hbar = h/2\pi$ and θ is the angle between L and the Z-axis taken as reference. Combining, one gets

$$L = \frac{m_l}{\cos\theta}\hbar.$$

Now, from eqution 27.1, putting $\mu = (-le/2m)L$, the magnetic potential energy V_m is

$$V_m = \frac{e}{2m} LB \cos\theta \qquad ......(27.4)$$

Substitution of L now gives

$$V_m = \frac{e}{2m} m_l . \hbar . B = \left(\frac{e\hbar}{2m}\right) B m_l \qquad ......(27.5)$$

The quantity $\frac{e\hbar}{2m}$ is called the *Bohr magneton* (μ_B) and regarded as an elementary unit of magnetism.

Bohr magneton : $\mu_B = \frac{e\hbar}{2m} = \frac{eh}{4\pi m} = 9 \cdot 274 \times 10^{-24}\,\text{JT}^{-1}$ (joule per tesla).

The spin has no classical analogy, but the existence of spin magnetic moment has been confirmed by the Stern-Gerlach experiment. An estimate of the magnetic moment associated with the spin motion can also be made from the observed separation of peaks corresponding to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

The spin angular momentum S due to electron spin is given by the spin quantum number s

$$S = \sqrt{s(s+1)}\hbar$$

By analogy with equation 27.2 or 27.3, we might expect the spin magnetic moment to be given by

$$\mu_{spin} = -\frac{e}{2m} S$$

But experiments (like the Stern-Gerlach experiment) show that the spin magnetic moment of the electron is nearly twice this value, that is the gyromagnetic ratio characteristic of electron spin is nearly twice that characteristic for orbital magnetic moment. Taking this ratio as 2, the spin magnetic moment becomes

$$\mu_{spin} = -\frac{e}{m} S$$

The component S_z of the spin angular momentum of an electron along a magnetic field directed along the z-axis is given by the spin magnetic quantum number m_s $(= \pm\frac{1}{2})$:

$$S_z = m_s . \hbar$$

Hence the possible components of μ_{spin} along the Z-axis are limited to the values

$$\mu_{spin(z)} = \pm\frac{e\hbar}{2m} \qquad \ldots\ldots(27.6)$$

The magnitude is equal to the Bohr magneton.

The spin magnetic moment of the electron has been estimated with great precision from modern experiments like electron spin resonance (esr) studies. It is possible to write

$$\mu_{spin} = g.\gamma.S, \qquad g = 2\cdot0023193$$

g is called the g-factor of the electron and γ is the gyromagnetic ratio mentioned earlier ($-e/2m$). Dirac's theory of the electron gives a value of g = 2.0; the remaining part (0·0023...) arises due to electromagnetic fluctuation in the vacuum surrounding the electron — a concept understood by quantum electrodynamics.

The g value of an electron may differ from the free electron value when an applied magnetic field induces orbital motions producing an extra magnetic field with which the electron spin will interact. In the first transition series metal ions and large organic radicals, such deviation is almost negligible. For the later transition metal ions and f-block elements, the g-value differs appreciably from the value for free electron.

In a bulk substance, the magnetic contributions from individual electrons combine to produce a net effect. Before we proceed to understand how these net effects are estimated, we shall get some idea of the different types of magnetic properties observed in bulk. Primarily, this is done by observing the behaviour of substances when placed in an external magnetic field and substances are classified as diamagnetic, paramagnetic etc. The associated magnetic properties are called diamagnetism, paramagnetism and so on.

27.3.2 Classification of substances according to magnetic properties

(i) ***Diamagnetism*** : Diamagnetism is the characteristic ascribed to substances which are repelled by a magnetic field. This property is common to all forms of matter and is caused by the presence of closed shells of electrons. In such closed shells, the spin and orbital moments of individual electrons balance one another, leaving no net magnetic moment. In an external magnetic field, these atoms or molecules gain an induced moment proportional to the strength of the field. A law in physics called Lenz's law states that such induced fields will always oppose the parent field. In fact, this induced magnetic moment does not influence the spins of the electrons which are paired; but the planes of the orbits are slightly altered and a net orbital moment acts in opposition to the applied magnetic field. As a consequence of this opposition, diamagnetic substances are repelled in a magnetic field.

Diamagnetism is independent of temperature and the effect is much weaker than paramagnetism, a property associated with the presence of unpaired electrons.

The magnetic permeability P, which is the ratio of the density of lines of force within a body (placed in a magnetic field) to the density of lines in vacuum, is less than 1 for diamagnetic substances. (Fig. 27.65 a).

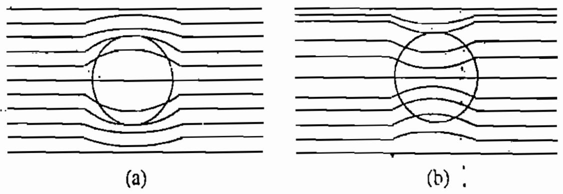

(a) (b)

Fig. 27.65
Change in lines of force in presence of (a) diamagnetic and (b) paramagnetic substances.

(ii) ***Paramagnetism*** : It is the property of substances which are attracted in a magnetic field with a force proportional to the product of field strength and field gradient. Paramagnetism derives from the spin and orbital angular momenta of electrons. When all the electrons in a molecule are paired, their spin and orbital angular momenta cancel each other. Hence paramagnetism occurs only in substances with unpaired electrons. Another kind of weak paramagnetism may occur in certain substances without any unpaired electron which is known as temperature independent paramagnetism (see later).

Paramagnetism varies inversely with temperature (see later). The permeability of paramagnetic substances is much greater than unity, that is, they draw more lines of force through them than normally pass through the same space in vacuum (Fig. 27.65 b).

When the individual paramagnetic centres in a substance are sufficiently apart so that there is practically no further interaction between neighbouring centres, the substance is said to be *magnetically dilute*. $[Ni(H_2O)_6]Cl_2$ is an example of a magnetically dilute substance. In such substances, the paramagnetic centres (Ni^{2+} in this example) are separated from one another by several diamagnetic species, for example the water molecules in the hydrated nickel ion. On the other hand, in a *magnetically concentrated* substance, the individual magnetic centres are sufficiently close to allow further magnetic interaction. In $Cu_2(CH_3COO)_4.2H_2O$ (see later), the unpaired electrons on the two copper atoms interact with each other. In metals, the paramagnetic centres are close together sufficiently to interact with one another. Interaction may also occur when the paramagnetic centres are separated only by an atom or monatomic ion that may transmit magnetic interactions. Such interactions may give rise to other types of magnetic behaviour known as ferromagnetism and antiferromagnetism.

(iii) ***Ferromagnetism, Antiferromagnetism and Ferrimagnetism***

Ferromagnetism is actually greatly enhanced paramagnetism due to close alignment of magnetic dipoles in the same direction, for example in the metallic lattice of iron at temperatures upto 768°C. Above this temperautre, thermal agitation overcomes the aligning tendency and normal paramagnetism follows. As we shall see in the next sections, this temperature is called the Curie temperature. Ferromagnetic substances have their permeability very much greater than unity. CrO_2 used in magnetic tapes (T_c = 386 K) is ferromagnetic.

Antiferromagnetism arises when the magnetic moments at neighbouring centres are aligned in opposite directions, that is they are antiparallel below a certain temperature (the Néel temperature, see later). MnO is antiferromagnetic below 118 K.

Ferrimagnetism is shown by substances in which the individual magnetic moments are systematically aligned so as to oppose others but giving rise to some finite resultant magnetic moment. Fe_3O_4 is ferrimagnetic. It has the inverse spinel structure — half of the Fe(III) occupying tetrahedral sites and the Fe(II) with other half of Fe(III) occupying octahedral sites. In the magnetically ordered phase, magnetic moments of all octahedral sites are aligned in one direction and those on the tetrahedral sites in the opposite. Thus the moments of Fe(III) in octahedral sites cancel those of Fe(III) in tetrahedral sites. The observed net moment corresponds to that from Fe(II) only. Complex superexchange interaction (see later) also occurs in the lattice.

The alignment of individual magnetic moments in paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic substances are schematically represented in Fig. 27.66.

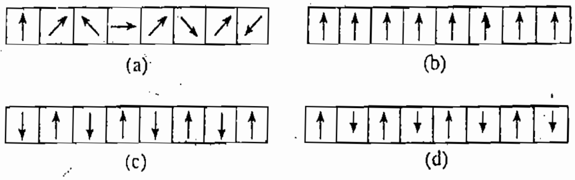


Fig. 27.66 Alignment of individual magnetic dipoles in (a) paramagnetic (b) ferromagnetic (c) antiferromagnetic and (d) ferrimagnetic substances.

The variation of these magnetic behaviour with temperature will be mentioned in the next section.

27.3.3 Magnetic susceptibility

When a material is placed in a magnetic field of strength H, the magnetic flux density (density of magnetic lines of force passing through the medium) B is given by

$$B = \mu H.$$

where μ is the *permeability* of the medium. The permeability of vacuum is a fundamental constant, μ_0 (see units, vol-I) :

$$\mu_0 = 4\pi \times 10^{-7}\ \text{JC}^{-2}\text{m}^{-1}\text{s}^{2}\ (= \text{kg m s}^{-2}\,\text{A}^{-2})$$

The SI unit of magnetic flux is weber (Wb; kg $\text{m}^2\text{s}^{-2}\text{A}^{-1}$); magnetic flux density is expressed in tesla (T; kg $\text{s}^{-2}\ \text{A}^{-1}$).

The *relative permeability* μ_r of a substance is the ratio of its permeability μ to μ_0

$$\mu_r = \frac{\mu}{\mu_0} \quad \text{(dimensionless)}$$

The magnetic susceptibility χ of a substance is now defined by the relation :

$$\chi = \mu_r - 1$$

χ is called the *volume magnetic susceptibility* of the substance. It also has no dimension.

One may also arrive at the volume magnetic susceptibility from the idea of *magnetization* (M, the analogue of the electric polarization P) which is the magnetic dipole moment per unit volume induced by a magnetic field. M is proportional to the strength of the magnetic field H, so that

$$M = \chi H \quad \text{or} \quad \chi = M/H$$

where χ is the volume magnetic susceptibility and is the ratio between the magnetic dipole moment per unit volume (M) to the field strength H. The magnetic flux density B is related to the strength of the field H and the magnetization M as

$$B = \mu_0(H + M) = \mu_0(1 + \chi)H$$

For substances with $\chi > 0, M$ adds to H, and hence the flux density increases. Such substances are called paramagnetic.

When $\chi < 0$, M opposes H and the flux density decreases in presence of the substances. As we have seen earlier, such substances are termed diamagnetic.

The contribution to magnetization primarily arises from two sources :

(1) a molecule with a permanent magnetic dipole moment of magnitude μ contributes an amount proportional to $\mu^2/3kT$ (this μ is different from the permeability);

(2) the applied field also induces a magnetic moment proportional to the magnetizability ξ of the molecules. If there are n molecules per unit volume, it is possible to write

$$\chi = n\mu_0\left(\xi + \frac{\mu^2}{3kT}\right).$$

The contribution by Avogadro number of molecules may be obtained by multiplying both sides by the molar volume V_m ($= M/\rho$, M = molar mass). Since nV_m is equal to N, the Avogadro number, we get

$$\chi V_m = \frac{\chi M}{\rho} = N\mu_0\left(\xi + \frac{\mu^2}{3kT}\right)$$

$\chi V_m = \chi M/\rho$ is called the molar magnetic susceptibility, χ_M

$$\chi_M = \chi\frac{M\ \text{Kg mol}^{-1}}{\rho\ \text{kg m}^{-3}} = \frac{\chi M}{\rho}\ \text{m}^3\ \text{mol}^{-1}.$$

Soon we shall find how the measurement of volume susceptibility and therefrom the molar susceptibility can be used to deduce the effective magnetic moment of a paramagnetic molecule.

Temperature dependence of paramagnetism; Curie's Law

Pierre Curie studied the paramagnetic susceptibilities of various substances at different temperatures and obtained a general relationship :

$$\chi_M = \frac{C}{T}$$

where T is the absolute temperature and C is a constant characteristic of the substance. This is known as the Curie constant. The above relation expresses *Curie's law* which states that paramagnetic susceptibilities depend inversely on the absolute temperature of the substance.

The relation suggests that any plot of $1/\chi_M$ vs T for a substance at different temperatures should give a straight line passing through the origin. This is found to hold approximately for many substances but in a large number of cases we have straight lines which cuts the T-axis at other points (Fig. 27.67).

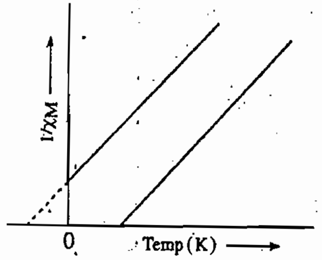


Fig. 27.67 **Idealized plot of $1/\chi_M$ vs T.**

The lines may be represented by slightly modifying the original relationship of Curie, i.e. writing

$$\chi_M = \frac{C}{T - \theta}$$

where θ is the temperature at which the straight line ($1/\chi_M$ vs T) cuts the T-axis. θ is known as the Weiss constant and the relation expresses the **Curie-Weiss law**.

We can rewrite the relation

$$\chi_M = N\mu_0\left(\xi + \frac{\mu^2}{3kT}\right) \quad \text{as,} \quad \chi_M = A + \frac{C}{T},$$

where $A = N\mu_0\xi$ and $C = N\mu_0\mu^2/3k$.

For many practical purposes, it is convenient to neglect ξ and write

$$\chi_M = \frac{N\mu^2\mu_0}{3kT}.$$

Comparison with Curie's law gives

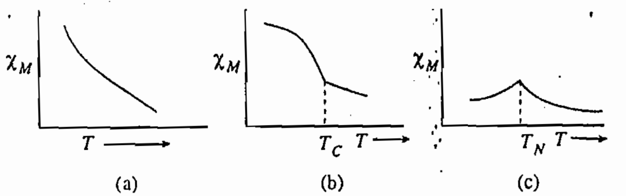
$$C = \chi_M T = N\mu^2\mu_0 / 3k \quad \therefore \mu = \sqrt{3k/N\mu_0}\ \sqrt{\chi_M T}$$

In the above theoretical treatment, it has been assumed that the individual atomic dipoles are completely independent. If we think that the orientations of each dipole is also influenced by the orientation of other dipoles in its neighbourhood, it becomes possible to derive the Curie-Weiss law and therefrom to write

$$\mu = \text{constant}.\sqrt{\chi_M(T-\theta)}\ .$$

The Weiss constant θ now accounts for the inter-dipole interaction.

The temperature dependence of the magnetic susceptibility of paramagnetic, ferromagnetic and antiferromagnetic materials is shown in Fig. 27.68.



(a) (b) (c)

Fig. 27.68 **Temperature-dependence of magnetic susceptibility for (a) paramagnetic (b) ferromagnetic and (c) antiferromagnetic substances (idealized).** (See below for explanation of T_c and T_N).

We have already discussed how thermal agitation in paramagnetic substances oppose the alignment of individual magnetic dipoles, resulting in a decrease in susceptibility with increase in temperature (27.68a).

In a ferromagnetic material, a transition takes place at lower temperature when all the individual magnetic moments align, and there is a sharp rise in susceptibility with decrease in temperature. The temperature of this transition is known as the *Curie temperature*, T_C (Fig. 27.68 b). Above the Curie temperature, thermal agitation is again sufficient to overcome the tendency to alignment and normal paramagnetic behaviour is observed. Below the Curie point, the tendency to alignment dominates and the molar susceptibility is higher than expected on the basis of magnetic dipoles acting independent of one another.

In case of antiferromagnetic substances, the individual magnetic dipoles tend to align themselves so as to cancel out one another. Below the *Neel temperature* (T_N), such alignment causes a lowering of susceptibility while above T_N, thermal agitation becomes sufficient to randomize such orientations and the substances show normal paramagnetism (Fig. 27.68c).

Temperature independent paramagnetism (TIP)

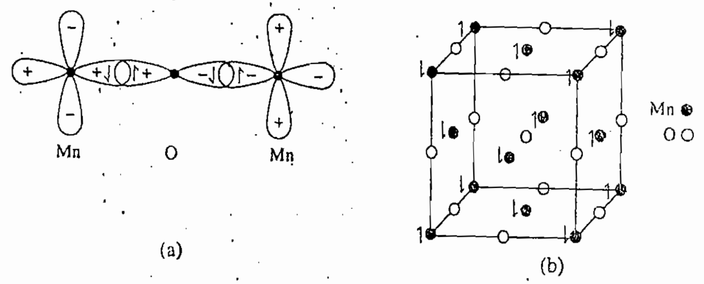
This is a kind of weak paramagnetic behaviour independent of temperature which is shown by certain substances with or without any unpaired electron. Such behaviour does not orginate from any permanent magnetic dipole in the species in its normal state. The paramagnetism is induced when the substance is placed in a magnetic field which can effect a change in the ground state of the atom or ion. The higher energy excited states caused by the field (see later) can mix with the ground state and current can be stimulated by movement of the electrons to otherwise unoccupied higher energy orbitals. Such orbital paramagnetism gives rise to temperature independent paramagnetism (TIP). Since the substance has no permanent magnetic dipoles, the influence of thermal agitation on their alignment does not exist and hence the paramagnetism is temperature independent. Systems with low-lying excited states show such TIP, e.g. the chromate and permanganate ions, CrO_4^{2-} and MnO_4^-, both d^0. For accurate work, measured susceptibilities are corrected for TIP where involved.

[Sec. 27.3.3 *Magnetic Susceptibility*]

Superexchange

So far we have considered bulk magnetic properties of substances in terms of dipole-dipole interactions between the individual atomic (or ionic) magnetic moments. But the observed ferromagnetic, ferrimagnetic and antiferromagnetic properties suggest that the interaction may be actually more intensive than simple dipole-dipole interactions. In such cases the individual magnetic dipoles are supposed to interact by a mechanism called *superexchange*. This involves coupling of magnetic dipoles through electrons of intervening ligands.

MnO provides a good example of such superexchange. The Mn^{2+} ion has five d-electrons with high spin configuration, $t_{2g}^3 e_g^2$. In the rock salt structure adopted by the oxide, the e_g orbitals can overlap with the p-orbitals of oxygen along each of the cell axes. An unpaired electron occupying an e_g orbital can thereby align in antiparallel spin with an electron in the p-orbital of the oxide ion. The other electron in the p-orbital of the oxygen is necessarily of opposite spin; this can, in turn, form an antiparallel combination with an e_g electron in the next manganese ion (Fig. 27.69 a). This chain of interaction can run throughout the entire structure producing alternating spin orientations on all neighbouring Mn^{2+} ions. The strength of such superexchange interactions at temperatures below 122K (Néel temperature) make MnO antiferromagnetic (Fig. 27.69 b). Above this temperature, thermal agitation overcomes the energy of interaction between the unpaired electrons; the electrons on adjacent Mn^{2+} ions are now randomly oriented.



(a) (b)

Fig. 27.69

(a) Schematic representation of superexchange in MnO.

(b) Antiferromagnetic ordering in MnO crystal below 122K.

Such interactions also operate in other molecular complexes with two ligand-bridged metal atoms. Thus copper(II) formate tetrahydrate shows a room temperature paramagnetic moment which is much below the normal value (1·67 B.M vs 1·73 B.M. at 290K). The Cu — Cu distances in the crystal are also too large to suggest any Cu—Cu bond formation. The reduction in magnetic moment has been ascribed to a superexchange mechanism involving π-interaction between $3d$ orbitals of Cu(II) and π-orbitals of the bridging formate ions. In higher Cu(II) alkanoates, shorter Cu-Cu distances suggest Cu—Cu δ-bond formation, but superexchange may still play an additional role in quenching magnetic moments.

Determination of Susceptibility

Methods for measuring magnetic susceptibilities are based on measuring the force exerted on a substance when placed in an inhomogeneous magnetic field. This foree, proportional to the paramagnetism of the substance, tends to draw the substance toward the more intense part of the field. We shall discuss only the outline of the simplest and most widely used method, the Gouy method.

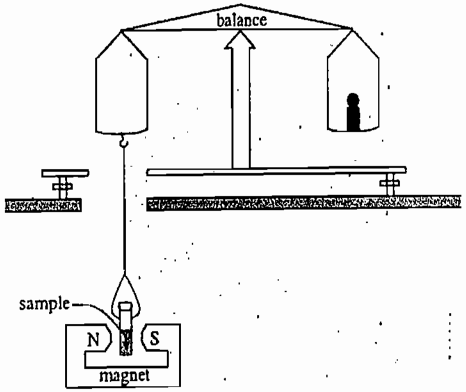


Fig. 27.70 Lay-out plan for a Gouy balance.

In the Gouy method (Fig. 27.70), the experimental compound, in the form of finely divided solid or in solution is taken in a long, narrow tube of uniform cross-section A and suspended by a fine thread from one pan of a precision balance. One end of the tube lies in the field of a powerful magnet and the other end in the earth's magnetic field only. The weight of the sample is determined accurately (i) in absence of any mgnetic field and (ii) in presence of a strong magnetic field. (Usually an electromagnet is used, and the magnetic field may be applied very conveniently as and when necessary).

The force F acting on the sample in the magnetic field is given by

$$F = \frac{1}{2\mu_0}(\chi - \chi_{\text{air}})\left(H_2^2 - H_1^2\right)A$$

where
χ = volume susceptibility of the sample
χ_{air} = volume susceptibility of air
H_2 = strength of the applied magnetic field
H_1 = strength of earth's magnetic field
A = cross-sectional area of tube
μ_0 = permeability of free space

In presence of the magnetic field, paramagnetic materials are drawn towards the magnetic field and hence show an apparent increase in weight.

Diamagnetic materials will be repelled away from the field owing to the small magnetic moment induced by the external field; hence they will show an apparent decrease in weight in presence of the magnetic field.

For a complex with unpaired electrons, the observed increase in weight in the magnetic field is the net sum of the paramagnetic effect of the metal ion and diamagnetic effect of the ligands and other ions present. Necessary corrections are introduced to obtain the paramagnetic susceptibility of the metal ion (see below).

If Δm is the observed increase in weight of the sample, the additional force F acting on it in the magnetic field will be equal to $\Delta m.g$ (g = acceleration due to gravity). Hence, one may write

$$\Delta mg = \frac{1}{2\mu_0}(\chi - \chi_{air})\cdot A\cdot\left(H_2^2 - H_1^2\right)$$

$$\text{or,}\quad \chi = \chi_{air} + \frac{2\Delta m\cdot g\mu_0}{A\cdot\left(H_2^2 - H_1^2\right)}$$

χ_{air} is known ($3{\cdot}64 \times 10^{-13}$).

The magnetic field strength and the cross-sectional area of the sample tube are calibrated using a substance of known susceptibility, e.g., Hg[Co(NCS)$_4$] ($\chi_M = 206.6\times10^{-12}\,\text{m}^3$ mol^{-1} at 293 K). The value of χ for the unknown sample is then obtained by direct substitution in the above expression. The molar susceptibility χ_M is calculated as

$$\chi_M = \frac{\chi M}{\rho},\quad M = \text{molar mass},\ \rho = \text{density}$$

This χ_M is now subjected to corrections for diamagnetism (and temperature independent paramagnetism in appropriate cases). The diamagnetic correction is computed by adding relevant values for the atoms, ions and multiple bonds :

$$\chi_{\text{diamag}} = \sum\chi_{\text{atom}} + \sum\chi_{\text{multiple bond}}$$

Tables of diamagnetic corrections are available. Some values are given in Table 27.15.

The corrected paramagnetic susceptibility is obtained by subtracting the diamagnetic correction (and TIP) :

$$\chi_M^{Corr} = \chi_M(\text{measured}) - \chi(\text{diamagnetic})$$

TABLE 27.15

Diamagnetic corrections to χ_M (mol^{-1} m^3 × 10^{10})

Species	Correction (× 10^{10})	Species	Correction
NH_4^+	+ 1·67	F^-	+ 1·14
Hg^{2+}	+ 5·02	Cl^-	+ 2·94
Fe^{2+}	+ 1·61	Br^-	+ 4·35
Cu^{2+}	+ 1·61	NO_3^-	+ 2·37
Co^{2+}	+ 1·61	SO_4^{2-}	+ 5·03
Ni^{2+}	+ 1·61	water	+ 1·63
		dipyridyl	+ 13·2
		phenanthroline	+ 16·1

Magnetic susceptibilities of solids can hardly be determined by the Gouy method with a precision better than 1% mainly due to (i) anisotropy of the crystals and (ii) non-uniformity of packing. The errors are largely minimised by grinding the sample to fine powder.

The method can also be modified for measurement in solutions. Magnetic susceptibility in solution can also be determined with good sensitivity (and varying temperature) by NMR method. A modern technique of determining susceptibility makes use of a superconducting quantum interfering device (SQUID).

Paramagnetic moment from magnetic susceptibility

The *effective paramagnetic moment*, μ_{eff} of a substance can be calculated from its measured magnetic susceptibility according to the relation

$$\mu_{eff} = \sqrt{\frac{\chi M}{\rho}\cdot\frac{3kT}{N\mu_0}}\,,\quad \text{A m}^2\left(\text{or JT}^{-1}\right)$$

$$= \sqrt{\chi_M\cdot\frac{3kT}{N\mu_0}}\quad \text{A m}^2\left(\text{or JT}^{-1}\right)$$

Since 1 Bohr magneton (μ_B) = $9{\cdot}274 \times 10^{-24}$ JT^{-1},

$$\mu_{eff} = \sqrt{\chi_M\cdot\frac{3kT}{N\mu_0}}\cdot\frac{1}{9\cdot27\times10^{-24}}\mu_B.$$

$$= 797{\cdot}6\sqrt{\chi_M T}\,\mu_B.$$

$$\sqrt{3k/N\mu_0} = \sqrt{\frac{3\times 1\cdot 3805\times 10^{-23}\,\mathrm{JK^{-1}}}{6\cdot 023\times 10^{23}\,\mathrm{mol^{-1}}\times 4\times 3\cdot 142\times 10^{-7}\ \mathrm{kg\,ms^{-2}A^{-2}}}}$$

$$= 7\cdot 3967\times 10^{-21}\left(\frac{\mathrm{kg\,m^2\ s^{-2}\ k^{-1}}}{\mathrm{mol^{-1}\ kg\,m\,s^{-2}A^{-2}}}\right)^{\frac{1}{2}}$$

$$= 7\cdot 3967\times 10^{-21}\ \mathrm{m^{\frac{1}{2}}\ mol^{\frac{1}{2}}\ K^{-\frac{1}{2}}A.}$$

To convert to Bohr magneton units, we divide by

$$1BM(\mu_B) = 9\cdot 274\times 10^{-24}\,\mathrm{JT^{-1}}\quad(\text{or, Am}^2)$$

$$\therefore\ \mu_{eff} = \frac{7\cdot 3967\times 10^{-21}}{9\cdot 274\times 10^{-24}}\ \frac{\mathrm{m^{\frac{1}{2}}\ mol^{\frac{1}{2}}\ K^{-\frac{1}{2}}\ A}}{\mathrm{kg\,m^2\ s^{-2}\ kg^{-1}\ s^2\ A}}\ \sqrt{\chi_M T}$$

$$= 797\cdot 5755\ \mathrm{m^{-\frac{3}{2}}\ mol^{\frac{1}{2}}\ K^{-\frac{1}{2}}}\ \sqrt{\chi_M T}\cdot\mu_B.$$

Q. 27.16 *Powdered $(NH_4)_2Co(SO_4)_2$, $6H_2O$ (density = $1{\cdot}92\times 10^3$ kg m^{-3}) has χ at 293 K* = $6{\cdot}70\times 10^{-4}$. *Calculate*

(i) $\chi_M\left(=\chi\cdot\frac{M}{\rho}\right)$ *uncorrected, (ii)* χ_M *corrected, (iii)* μ_{eff}. *Use data in Table 27.15.*

Solution :

(i) Putting $M = 0{\cdot}395$ kg mol^{-1}, χ_M (uncorrected) =

$$\frac{\chi M}{\rho} = \frac{6\cdot 70\times 10^{-4}\times 0\cdot 395\ \mathrm{kg\ mol^{-1}}}{1\cdot 92\times 10^3\ \mathrm{kg\ m^{-3}}} = 1\cdot 38\times 10^{-7}\ \mathrm{mol^{-1}\cdot m^3}$$

(ii) Diamagnetic correction for two NH_4^+, one Co^{2+}, two SO_4^{2-} and six H_2O :

$$= (2\times 1\cdot 67 + 1\cdot 61 + 2\times 5\cdot 03 + 6\times 1\cdot 63)\times 10^{-10}\ \mathrm{mol^{-1}\ m^3}$$

$$= +24\cdot 79\times 10^{-10}\ \mathrm{mol^{-1}\ m^3} = 0\cdot 025\times 10^{-7}\ \mathrm{mol^{-1}\ m^3}$$

$$\therefore\ \chi_M\ (\text{corrected}) = (1\cdot 38 + 0\cdot 025)\times 10^{-7}\ \mathrm{mol^{-1}\ m^3}$$

$$= 1\cdot 405\times 10^{-7}\ \mathrm{mol^{-1}m^3}.$$

(iii) $$\mu_{eff} = \sqrt{\frac{\chi_M^{corr}T\times 3k}{N\mu_0}}$$

$$= \sqrt{\frac{1\cdot 405\times 10^{-7}\ \mathrm{mol^{-1}m^3}\times 293\ \mathrm{K}\times 3\times 1\cdot 38\times 10^{-23}\,\mathrm{JK^{-1}}}{6\cdot 02\times 10^{23}\ \mathrm{mol^{-1}}\times 4\times 3\cdot 142\times 10^{-7}\ \mathrm{kg\ m\ s^{-2}\ A^{-2}}}}$$

$$= 4\cdot 75\times 10^{-23}\ \mathrm{JT^{-1}}\ (\mathrm{Am^2})$$

$$= 5\cdot 12\mu_B.$$

[We may also use the direct relation established before :

$$\mu_{eff} = 797\cdot 57\sqrt{\chi_M^{corr}T}\ \mu_B$$

$$= 797\cdot 57\times\sqrt{1\cdot 405\times 10^{-7}\times 293}\ \mu_B = 5\cdot 12\ \mu_B.\ ]$$

(See In-chapter Q. 27.17 for discussion)

27.3.4 Theoretical vs observed moments

Orbital contribution

We have already seen how the spin and orbital motion of an electron gives rise to permanent magnetic moment. The magnetic moment of a free atom or ion may be similarly calculated by using the resultant of spin and orbital angular momentum quantum numbers L, S and J :

$$\mu_{eff} = g\sqrt{J(J+1)}\mu_B$$

where g is known as the Lande' splitting factor and is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Now let us look back at Fig. 27.41 where the splitting of spectral terms arising from various coupling schemes was illustrated for a d^2 ion. We note that spin-orbit coupling separates the terms with different J values in multiples of λ, the spin orbit coupling constant. The value of λ thus determines the energy gaps between successive states with different J values. For light atoms, λ is small, ranging from a fraction of a cm^{-1} to a few hundred only. Hence the separation between the states becomes comparable to the thermal energy kT available around room temperature—approximately 200 cm^{-1} at 300 K. In fact for most metal ions in the first transition series spin-orbit coupling may be practically ignored; the spin and orbital angular momenta of the electrons now interact independently with an external magnetic field. In such cases, quantum mechanics gives the effective magnetic moment as

$$\mu_{eff} = \mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}\,\mu_B$$

In practice, experimental results help us simplify the situation still more : for many of the first transition series metal ions, notably those in the first half of the series, the orbital contribution may be ignored. The magnetic moment is then determined only by the spin angular momentum of the electrons :

$$\mu_{eff} = \mu_{spin\text{-}only} = \sqrt{4S(S+1)}\,\mu_B$$

This is the *spin-only formula* of magnetic moment mentioned earlier. For an ion with n unpaired electrons, $S = n/2$ and hence

$$\mu_{spin\text{-}only} = \sqrt{n(n+2)}\,\mu_B$$

The observed magnetic moments of complex compounds of the first transition series often agree quite satisfactorily with the spin-only formula (Table 27.16). When significant deviations are observed, the orbital contribution to magnetic moment must be important.

If an electron is to have orbital angular momentum, it must effectively rotate about the axis referred to for the orbital rotation. This requires that the orbital occupied by the electron should transform to an exactly equivalent and degenerate orbital by rotation. In a free atom or ion (having d electrons) an electron in the $d_{x^2-y^2}$ orbital is transferred into the d_{xy} orbital by 45° rotation about the z-axis. Hence this electron contributes $\pm 2(h/2\pi)$ units of orbital angular momentum about the z-axis. Similarly the d_{xz} orbital is transformed into the equivalent d_{yz} orbital by 90° rotation about the z-axis; so an electron in this orbital will contribute $\pm 1(h/2\pi)$ units of angular momentum about the z-axis. An electron in a d_{z^2} orbital contributes zero angular momentum about the z-axis.

In a ligand field (other than spherical), the degeneracy of the d-orbitals are partly destroyed. In an octahedral field, the t_{2g} group of orbitals are still rotationally related to one another. For example, the d_{xz} orbital rotated about the z-axis by 90° produces the d_{yz} orbital. During such rotation the electron in this orbital is partly orbiting around the nucleus. Thus an electron in a t_{2g} orbital is expected to contribute orbital angular momentum (see below). But the e_g orbitals $\left(d_{x^2-y^2} \text{ and } d_{z^2}\right)$ cannot be interconverted by rotation about any axis. Hence an electron in an e_g group of orbitals cannot contribute any orbital angular momentum.

However, electrons in t_{2g} orbitals may not always contribute orbital angular momentum. Consider an ion having d^3 configuration - in an octahedral field the distribution will be t_{2g}^3, each of the three t_{2g} orbitals containing one electron with spins parallel. Now an electron in the d_{xz} orbital cannot be placed in the d_{yz} orbital by rotation since the d_{yz} orbital already contains an electron of the same spin. Similar argument applies to an ion with t_{2g}^6 electron distribution in an octahedral field. From similar considerations, ions with the following occupancy of t_{2g} level are expected to make orbital contributions in an octahedral complex :

High spin : $d^1,\ d^2,\ d^6,\ d^7;\ \left(t_{2g}^1,\ t_{2g}^2,\ t_{2g}^4e_g^2,\ t_{2g}^5e_g^2\right)$

Low spin : $d^4,\ d^5;\ \left(t_{2g}^4,\ t_{2g}^5\right)$

Tetrahedral complexes can be treated in the same way — here the e level is occupied first and the complexes are mostly high spin. Hence the configurations likely to make orbital contribution are :

$$d^3,\ d^4,\ d^8,\ d^9;\ \left(e^2t_2^1,\ e^2t_2^2,\ e^4t_2^4,\ e^4t_2^5\right)$$

Thus a comparison of observed and estimated spin-only value of magnetic moment will suggest if there is any orbital contribution; this helps to distinguish between the two stereochemistries.

Now let us look at the ground terms of the ions with d^1 to d^9 configurations in octahedral and tetrahedral fields (Table 27.10). As explained above, we can classify them into two categories — those for which orbital contribution to magnetic moment is expected and those for which no orbital contribution is expected.

No orbital contribution are thus expected for the following electron distributions :

Octahedral			Tetrahedral		
d^3	t_{2g}^3	$^4A_{2g}$	d^1	e^1	^2E
d^4	$t_{2g}^3e_g^1$	^5E_g	d^2	e^2	$^3A_2$
d^5(*h.s.*)	$t_{2g}^3e_g^2$	$^6A_{1g}$	d^5	$e^2t_2^3$	$^6A_1$
d^6(l.s.)	t_{2g}^6	$^1A_{1g}$	d^6	$e^3t_2^3$	^5E
d^7(l.s.)	$t_{2g}^6e_g^1$	^2E_g	d^7	$e^4t_2^3$	$^4A_2$
d^8	$t_{2g}^6e_g^2$	$^3A_{2g}$			
d^9	$t_{2g}^6e_g^3$	^2E_g			

We observe that these are the configurations with ground terms

A_1 (arising from free-ion S term).
E (arising from free ion D term).
A_2 (arising from free ion F term).

Ions with 1, 2, 4 or 5 t_{2g} electrons, all of which have T ground terms, should have some residual orbital contributions. We shall consider them separately. First let us consider some magnetic moments for ions with A and E ground terms.

TABLE 27.16

Magnetic moments for some octahedral and tetrahedral complexes with A and E ground terms.

Compound	electron distribution	Stereo chemistry	spin-only moment	observed moment	
				80K	300K
VCl_4	$d^1\,(e^1)$	Td	1·73	1·6	1·6
K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$	$d^3\left(t_{2g}^3\right)$	Oh	3·87	3·8	3·8
$CrSO_4$, $6H_2O$	$d^4\left(t_{2g}^3e_g^1\right)$	Oh	4·90	4·8	4·8
K_2SO_4, $MnSO_4$, $6H_2O$	$d^5\left(t_{2g}^3e_g^2\right)$	Oh	5·92	5·9	5·9
Cs_2CoCl_4	$d^7\left(e^4t_2^3\right)$	Td	3·87	4·5	4·6
$(NH_4)_2SO_4$, $NiSO_4$, $6H_2O$	$d^8\left(t_{2g}^6e_g^2\right)$	Oh	2·83	3·3	3·3
$(NH_4)_2SO_4$, $CuSO_4$, $6H_2O$	$d^9\left(t_{2g}^6e_g^3\right)$	Oh	1·73	1·9	1·9

The table presents magnetic data at two temperatures, showing that μ_{eff} in these compounds do not change remarkably with temperature.

Though the results are mostly in agreement with the spin-only formula, some deviations are noteworthy. This has been explained by spin-orbit coupling; in the ligand field the terms of same multiplicity are not perfectly separated according to their different orbital angular momenta. Some higher T-term (which can make orbital contribution) gets mixed up with the ground term of same multiplicity - thus the ground term acquires some orbital contribution.

For the d^5 ions (Mn^{2+}), the spin multiplicity is 6, but there is no higher T-term of this multiplicity. So the A_1 ground term gets no contribution from higher terms — and no orbital contribution results. The value of μ_{eff} for Mn(II) complexes thus corresponds to the spin-only formula.

A_2 (from free ion F) and E (from free ion D) ground terms have a higher T term of the same multiplicity. For example in Ni^{2+} (octahedral), the electron configuration $t_{2g}^6e_g^2$ gives rise to the singlet $^3A_{2g}$ (Fig. 27.49); the first excited state $\left(t_{2g}^5e_g^3\right)$ corresponds to the triplet $^3T_{2g}$ and the second excited state $\left(t_{2g}^4e_g^4\right)$ to the triplet term $^3T_{1g}$. Both these excited states are capable of making orbital contribution. The separation between the $^3T_{2g}$ and $^3A_{2g}$ depends upon the magnitude of $10Dq$. Hence, a small value of $10Dq$ will place these terms sufficiently close so that they may partly mix to make some orbital contribution. Co^{II} (d^7) in a tetrahedral field similarly has a $^4A_2$ ground state and a $^4T_2$ first excited state which can easily mix (Δ tetrahedral is smaller than Δ octahedral) to make orbital contribution. Theoretically, the observed effective magnetic moment can be fitted to the spin-only value by the relation

$$\mu_{eff} = \mu_{spin-only}\left(1 - \alpha\frac{\lambda}{\Delta}\right)$$

where α is a constant depending upon the spectroscopic ground state of the concerned d^n configuration.

For S state (d^5); $\alpha = 0$;
For D state (d^1, d^4, d^6, d^9) : $\alpha = 2$
For F state (d^2, d^3, d^7, d^8) : $\alpha = 4$.

In the cases considered above α has a value equal to 2 for an E term and 4 for an A_2 term. λ is the spin-orbit coupling constant; its value is positive for d-shells less than half-filled and negative for d-shells more than half-filled. Some typical values are given in Table 27.17.

TABLE 27.17

Values of λ, the spin-orbit coupling constant and $\alpha\lambda$ for some ions

Metal ion	Symmetry	Ground term	λ(cm^{-1})	$\alpha\lambda$ (cm^{-1})
V^{4+} (d^1)	Td	^2E	250	500
Cr^{3+} (d^3)	Oh	$^4A_{2g}$	92	368
Cr^{2+} (d^4)	Oh	^5E_g	58	116
Fe^{2+} (d^6)	Td	^5E	−100	−200
Co^{2+} (d^7)	Td	$^4A_2$	−172	−688
Co^{2+} (d^7)	Oh	^2E_g	−515	−1030
Ni^{2+} (d^8)	Oh	$^3A_{2g}$	−315	−1260
Cu^{2+} (d^9)	Oh	^2E_g	−830	−1660

Since α and $10Dq$ are positive quantities, magnetic moments should be greater or less than μ-spin-only depending upon the sign of λ. Thus, for $CoCl_4^{2-}$, Δ = 3100 cm^{-1} gives

$$\mu = 3.87\left(1 - \frac{-688}{3100}\right)\mu_B = 4.73\mu_B$$

This is in fair agreement with the observed value of 4.5 – 4.6 μ_B.

K_2Pb [$Co(NO_2)_6$], an octahedral low-spin complex of Co(II) has $\mu = 1.8$ μ_B which is also consistent with the above formula

$$\mu = 1{\cdot}73 \times \left(1 + \frac{1030}{12000}\right) = 1{\cdot}87\mu_B$$

d^1, d^3 and d^4 ions like V^{4+}, Cr^{3+} or Cr^{2+} have a positive value of λ; hence their effective magnetic moments are less than their spin-only values.

The difference in energy between the ground term and the higher term that is mixed is usually of the order of 10,000 cm^{-1}; this is much higher than the magnitude of kT around room temperature — about 200 cm^{-1} only. As a consequence this spin-orbit contribution to the moment does not depend significantly on temperature.

[Sec. 27.3.4 *Orbital contribution*]

Again, orbital contribution decreases as the degeneracy of the d-orbitals is lifted. Hence, lower symmetry of a complex implies diminished orbital contribution and hence a magnetic moment close to the spin-only value.

The deviation of Fe(II) and Co(II) from spin-only value appears greatest since both of them possess some unquenched orbital contribution in addition to the contribution from spin-orbit coupling (see in-chapter Q 27.17).

Complexes with T-ground terms

We have mentioned earlier that ions with T ground terms make orbital contribution to their magnetic moment. Spin-orbit coupling splits the T terms into energy levels with separations usually of the order of kT. Hence the occupancy of the various levels arising in a magnetic field will be largely influenced by temperature and the magnetic moment is expected to show significant temperature dependence. In fact, study of magnetic moment at different temperatures may be used as a crierion for distinguishing the two types of ground terms and deducing the stereochemistry of a complex. Only for d^5 ions, the same type of ground term is associated with both tetrahedral and octahedral geometries.

Magnetic moments of some complexes with T ground terms are given in Table 27.18. In all cases except V(III), the room temperature moments are higher than the spin-only formula in line with our expectation from orbital contribution. The extent of such orbital contribution may be understood if one knows the extent of splitting between the various levels. However, a detailed discussion of the topic is beyond the scope of the present treatment.

TABLE 27.18

Some representative magnetic moments for complexes with T ground terms

	Compound	Geometry	μ_{eff} (μ_B)		
			spin-only value	observed value	
				80K	300K
d^1	Cs_2VCl_6	Oh	1·73	1·4	1·8
d^2	$(NH_4)_2SO_4$, $V_2(SO_4)_3$, $24H_2O$	Oh	2·83	2·7	2·7
d^4	K_3 [$Mn(CN)_6$]	Oh	2·83	3·1	3·2
d^5	K_3 [$Fe(CN)_6$]	Oh	1·73	2·2	2·4
d^6	$(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$	Oh	4·90	5·4	5·5
d^7	$(NH_4)_2SO_4$, $CoSO_4$, $6H_2O$	Oh	3·87	4·6	5·1
d^8	$(Et_4N)_2NiCl_4$	Td	2·83	3·2	3·8

Several factors may be responsible for the observed discrepancy in case of V(III) : (i) partial delocalization of metal electrons over the ligand orbitals giving rise to covalence; when an electron is removed from the metal to the ligands, it no longer contributes to orbital angular momentum around the metal nucleus. (ii) The V^{3+} ion (d^2) is susceptible to Jahn-Teller distortion. Deviation from perfect cubic symmetry splits the ground T term into an A term (singlet) and an E term (doublet). We have already seen that an A or E term does not make orbital contribution to magnetic moment. The separation between these two levels is commonly of the order of a few hundred cm^{-1} — much smaller than the average magnitude of $10Dq$. However, such small splitting of ground terms can be followed from magnetic studies and used to detect small distortions.

Q. 27.17 *High spin octahedral complexes of Co(II) have magnetic moments much higher than the spin-only value for 3 electrons (4·8 - 5·2 B.M. vs 3·88 B.M.); in contrast, low-spin octahedral complexes of Co(II) have magnetic moments which are only slightly higher than the spin-only value for 1 electron (1·8 - 1·9 B.M. vs 1·73 B.M.). Comment.*

Hint : In high-spin octahedral complexes, the ground state electron population $t_{2g}^5 e_g^2$ permits orbital contribution to the magnetic moment. In addition to this unquenched orbital moment, spin-orbit coupling occurs by mixing of the first excited state $\left(t_{2g}^4 e_g^3\right)$ with the ground state.

In low-spin octahedral complexes, the ground state configuration $t_{2g}^6 e_g^1$ is not competent to make any direct orbital contribution. The observed values are slightly high due to spin-orbit coupling involving the first excited state.

Q. 27.18 *In high-spin octahedral as well as in tetrahedral complexes, Co(II) contains three unpaired electrons. But the magnetic moments of its octahedral complexes are much higher (4.8 - 5.2 B.M.) in comparison to the tetrahedral ones (4·2 - 4·8 B.M.). Comment.*

Hint : Octahedral — see Q. 27.17. In tetrahedral complexes, the ground state configuration $e^4 t_2^3$ does not allow orbital contribution to spin-magnetic moment. The slightly high values of μ arise out of spin-orbit coupling involving higher levels like $e^3 t_2^4$ and $e^4 t_2^2 4p^1$.

Q. 27.19 *Magnetic moments observed for tetrahedral CoX_4^{2-} complexes are :*

X^-	=	SCN^-	Cl^-	Br^-	I^-
μ (B.M.)	=	4·4	4·6	4·7	4·8

Comment.

Hint : The observed moments are higher than spin-only values due to spin-orbit coupling.

$$\mu = \mu_{spin-only}\left(1 - \frac{\alpha\lambda}{\Delta}\right)$$

$\alpha\lambda / \Delta$ increases as the magnitude of Δ decreases from SCN^- to I^- and this actually increases μ since λ is negative (d^7, more than half-filled).

27.3.5 Equilibrium between high-spin and low-spin states

In certain cases the same metal ion and ligand combination may form both high-spin and low-spin complexes in the same stereochemistry; these two forms may coexist in equilibrium, often greatly influenced by temperature. Besides, certain complexes may also exist as an equilibrium of two stereochemical forms which differ in the number of unpaired electrons and hence the spin states. We shall discuss both these types of equilibrium in brief.

(a) ***Thermal equilibrium between spin states : high-spin—low-spin cross-over***

We have seen that metal ions with 4 — 7 *d*-electrons may give rise to high-spin or low-spin octahedral complexes depending on whether the magnitude of the ligand field splitting (10*Dq*) is lower or greater than the mean pairing energy (*P*) :

$$10Dq > P : \text{low-spin}; \quad 10Dq < P : \text{high-spin}$$

Hence, there exists a critical value of 10*Dq* (≈ *P*) around which the high and low-spin states will have about the same energy. This critical value is sometimes referred to as the *high-spin low-spin cross-over point*.

If we have a ligand whose field is close to this cross-over point, its complex might be able to coexist in measurable amounts of both forms at equilibrium. Further, if the separation of energy between the two spin-states is of the order of *kT*, the position of equilibrium will be greatly influenced by temperature (Fig. 27.71).

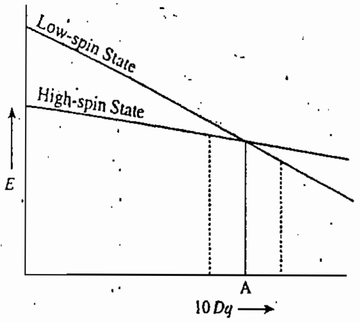


Fig. 27.71

Qualitative nature of the variation of energies of high-spin and low-spin states for octahedral complexes of d^4, d^6 and d^7 metal ions.

The slopes of the two lines will depend upon the relative energies of the two states (compared to the free ion) as determined by 10*Dq* and *P* :

	high-spin	low-spin
d^4 :	$-6Dq$	$-16Dq + P$
d^6 :	$-4Dq$	$-24Dq + 2P$
d^7 :	$-8Dq$	$-18Dq + P$

For d^5 metal ions, the relative energy of the high-spin state will be zero and hence independent of 10*Dq*.

The point A represents the high-spin—low-spin cross over point where $10Dq = P$. On the left of A, the high-spin state is more stable; on the right of A, low-spin state will be more stable.

In a limited range of 10*Dq* around the point A (shown by dotted lines) where $10Dq \approx P$ and the actual values do not differ by more than 2000 cm^{-1}, the two spin-states may exist in equilibrium with each other. These are then said to be *spin-isomers* and the phenomenon is called *spin-isomerism*.

An example of such high-spin low-spin equilibrium in solution is provided by the iron(II) complexes (d^6) $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, (phen = 1, 10-phenanthroline).

Spin-state	No. of unpaired electron	Spin-multiplicity	Term symbol
Low-spin, t_{2g}^6	0	1	$^1A_1$
High-spin, $t_{2g}^4 e_g^2$	4	5	$^5T_2$

The nature of variation of the magnetic moments of these complexes with temperature is shown in Fig. 27.72.

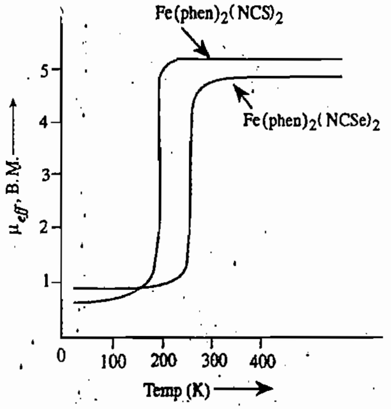


Fig. 27.72

Nature of variation of magnetic moment with temperature for $Fe(phen)_2X_2$ (X = NCS, NCSe).

At room temperature, both the complexes exist in the high-spin $^5T_2$ ground state — the measured magnetic moments are found to be higher than the spin-only value. But μ_{eff} drops suddenly as the temperature is lowered—$Fe(phen)_2(NCS)_2$ shows μ_{eff}<1 B.M. below 174 K. The ground state of the complex is now $^1A_{1g}$.

Tris-dialkyldithiocarbamatoiron(III) complexes $[Fe(S_2CNR_2)_3]$ also present such an equilibrium in benzene solution in the monomeric form. At low temperatures, μ_{eff} tends towards a value of about 2.1 B.M., which may be correlated to the low-spin t_{2g}^5 configuration of Fe(III) ($^2T_{2g}$ state). As temperature is increased, μ_{eff} slowly increases to about 4 B.M. or higher at room temperature. It shows that as temperature increases, more molecules are present in the high-spin $^6A_{1g}$ state through gain of thermal energy. Since RT varies from about 70 cm^{-1} mol^{-1} at 100K to about 200 cm^{-1} mol^{-1} at 300K, we expect such behaviour for all complexes where the high-spin and low-spin states differ in energy by about 50-250 cm^{-1}. Since all the molecules cannot be thermally excited to populate the upper level, the limiting value of μ_{eff} will be below that for a pure high-spin complex.

Bis-(2, 6-pyridinedialdehydehydrazone)cobalt(II) iodide (d^7) provides another example of such spin-state equilibrium. The complex shows a moment of 1.9 B.M. at 80K which slowly increases to 3.7 B.M. at 337 K.

(b) ***Structural equilibrium between spin-states***

When a metal ion and a ligand form complexes in different stereochemistries which differ only slightly in their energy, the complex may readily switch over from one stereochemistry to another by a slight change of the conditions. If the two structures contain different number of unpaired electrons, the magnetic properties of the complex will also change accordingly. Many complexes of Ni(II) exhibit this behaviour and were previously described as "anomalous". The three main types of structural equilibria shown by complexes of Ni(II) are as follows :

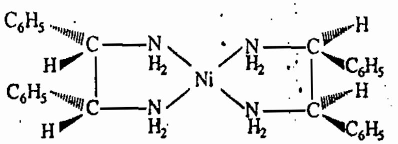
(i) ***Octahedral-square planar equilibrium in solution***

Many diamagnetic square planar complexes of Ni(II) add one or two additional ligands according to the following equilibrium :

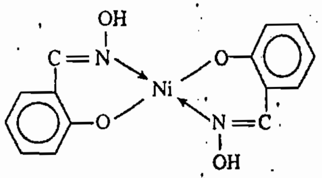
$$NiL_4 + L' \rightleftharpoons NiL_4L'$$

$$NiL_4L' + L' \rightleftharpoons NiL_4L'_2 \ (trans)$$

Only the five-coordinate species is formed when L = L′ = CN$^-$; but in most cases high-spin paramagnetic octahedral complexes are formed, specially with good donor solvents like H_2O, C_2H_5OH, pyridine etc. The *Lifschitz salts* provide a classic example of such square-octahedral equilibrium. These Ni(II) complexes of substituted ethylenediamines (specially the stilbenediamines, 27-III) were sometimes obtained in a blue paramagnetic form and some other times in a yellow diamagnetic form; temperature, anion, solvent etc. factors influenced the form that was obtained.



27-III



27-IV

It is now established that in most cases the blue paramagnetic form corresponds to the octahedral complex formed by addition of two trans ligands to the yellow diamagnetic square planar complex; these additional ligands may be provided by solvent molecules, water molecules or anions present.

Other diamagnetic, square complexes are also known to behave similarly, e.g. $Ni(py)_4(ClO_4)_2$ exists in two forms :

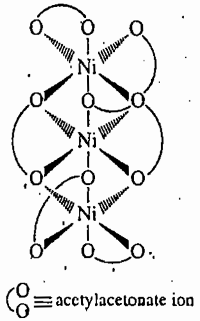
$[Ni(py)_4]^{2+} (ClO_4)_2$	$[Ni(py)_4(ClO_4)_2]$
yellow, diamagnetic;	*blue, paramagnetic*
square planar	octahedral (trans)

Q. 27.20 *Colourless crystals of diamagnetic nickel (II) salicylaldoximate (27-IV) form a green paramagnetic solution when dissolved in pyridine. Explain.*

[Sec. 27.3.5 *High Spin-Low Spin*]

In most of the cases cited above, the octahedral complex shows paramagnetism corresponding to the presence of two unpaired electrons. However, in some cases, solutions of the square planar complex show only a fraction of the paramagnetism expected from a full-fledged octahedral complex.

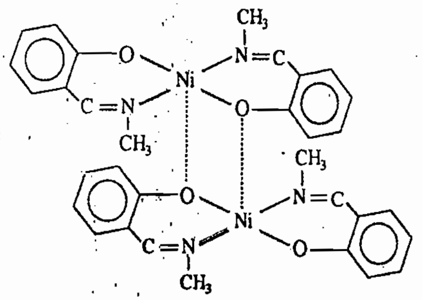
(ii) ***Monomer-polymer equilibria*** **:** Some four coordinate nickel(II) complexes associate or polymerize to provide an effective five - or six coordination around the metal. In this process, the red, diamagnetic square planar compounds change to blue paramagnetic polymers present in an equilibrium mixture; the equilibrium depends markedly upon temperature and concentration. In some cases, the polymer is so stable that the monomeric species can be observed only at high temperatures.



27-V

Bis-acetylacetonatonickel(II) exists as a stable trimer (27-V) in which nickel atoms attain octahedral coordination; the monomer can be detected around 200°C in a non-coordinating solvent. But trimerization becomes difficult when the methyl groups in acetylacetone are replaced by bulky groups like $(CH_3)_3C$—, in which case the monomer predominates. Groups of intermediate bulk give rise to an equilibrium between the monomeric and trimeric forms dependent upon temperature and concentration.

N-methylsalicycaldiminato complexes of nickel(II) in $CHCl_3$ or C_6H_6 show an equilibrium between the diamagnetic monomer and the paramagnetic dimer with 5-coordinate high-spin Ni(II) (27-VI).



27-VI

(iii) ***Square-tetrahedral equilibrium*** **:** Complexes of nickel(II) of the type NiL_2X_2 may have either square planar or tetrahedral structures depending on the nature of the ligand. When L is triphenylphosphine, the complexes are tetrahedral; when L = trialkylphosphine, the complexes are square planar. When L is a mixed alkylaryl phosphine, the complexes may exist in solution in an equilibrium mixture of both square planar and tetrahedral forms. Sometimes it is also possible to isolate two crystalline forms - one red and diamagnetic; the other green and paramagnetic with two unpaired electrons. The solid square complex $[NiBr_2(i\text{-}PrPPh_2)_2]$ is stable at 0°C but isomerizes to the tetrahedral form in about one day at 250°C. $[NiBr_2(PhCH_2.PPh_2)_2]$ has been isolated in a red form (diamagnetic) and a green form (μ = 2.7 B.M. at room temperature). X-ray analysis shows that the green form contains nickel in both square and tetrahedral environment corresponding to the formula NiL_2Br_2 (*square*). $2NiL_2Br_2$ (*tetrahedral*) where L = $PhCH_2.PPh_2$.

27.4 REACTIONS OF COORDINATION COMPOUNDS

This section provides a brief exposure to the vast, complicated, and yet amazing field of reaction mechanism of transition metal complexes. Valuable mechanistic information may be gathered from the study of reaction kinetics, a detailed discussion of which is beyond the scope of the present text. We shall restrict ourselves only to the general conclusions arrived at for the main reaction types.

27.4.1 Introduction

Inert and labile complexes

A wide range of reaction rates is found for different varieties of metal complexes; some react very rapidly while others react very slowly. The lability of a complex may be associated with the rapidity with which a complex undergoes substitution of one or more ligands by other ligands. Lability (and inertness) is thus a kinetic property and different from thermodynamic instability (or stability). As an example, the following reaction is highly favoured thermodynamically, as shown by the large value of the equilibrium constant

$$[Co(NH_3)_6]^{3+} + 6H_2O + 6H^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+; \quad K \simeq 10^{25}$$

Yet the hexaammine complex can be kept for months in strongly acid medium at room temperature without noticeable decomposition, showing that the complex is kinetically inert toward substitution. Side by side, the thermodynamically stable species, $[Ni(CN)_4]^{2-}$ ($\beta = 10^{22}$), undergoes very rapid exchange of its coordinated cyanide ligands with excess CN^- ions in solutions, as is seen by using isotopically labelled CN^-.

Complexes entering reactions with half-lives longer than one minute may be classified formally as inert. Their kinetics may be easily studied by so called static methods like change in pH, absorbance in uv and visible region etc. Kinetics of reactions of labile complexes are studied by fast techniques like flow methods and relaxation methods (see Chapter 15, section 15.3).

The existence of a relationship between lability and electronic structure of a complex was first pointed out by H. Taube (1952). In a simple qualitative approach, we expect that in an octahedral complex with electrons in the antibonding e_g^* orbitals, the ligands will be relatively weakly bound and hence may be displaced easily. This leads us to infer that all high spin d^4, d^5, d^6 complexes as well as complexes with d^7, d^8, d^9 and d^{10} configurations should be labile. Again, when a complex has less than three d-electrons, it will have one or two t_{2g} orbitals vacant; the metal can now be approached by another ligand along the directions of these vacant t_{2g} orbitals with relatively less electrostatic repulsion. This implies that a substitution reaction via a seven-coordinate activated complex (associative or *A* mechanism, section 15.3.3) will be favoured for such configurations, making the complex labile. Some examples of labile and inert octahedral complexes for various d-configurations (Table 27.19) illustrate this simple generalization.

TABLE 27.19

Few labile and inert octahedral complexes for various *d*-configurations

Labile		*Inert*	
***d*-configuration**	**Example**	***d*-configuration**	**Example**
d^0	$[Ca(edta)]^{2-}$, $[TiCl_6]^{2-}$	d^3	$[V(H_2O)_6]^{2+}$
d^1	$[Ti(H_2O)_6]^{3+}$, $[VO(H_2O)_5]^{2+}$	d^4 (low-spin)	$[Cr(CN)_6]^{4-}$, $[Mn(CN)_6]^{4-}$
d^2	$[V(phen)_3]^{3+}$	d^5 (low-spin)	$[Mn(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$
d^4 (high-spin)	$[Cr(H_2O)_6]^{2+}$	d^6 (low-spin)	$[Fe(CN)_6]^{4-}$, $[Co(en)_2(H_2O)_2]^{3+}$
d^5 (high-spin)	$[Mn(H_2O)_6]^{2+}$		
d^6 (high-spin)	$[Fe(H_2O)_6]^{2+}$		
d^7	$[Co(NH_3)_6]^{2+}$		
d^8	$[Ni(en)_3]^{2+}$		
d^9	$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

Nucleophilicity

We have seen that strengths of Lewis bases may be compared from the relative magnitudes of equilibrium constants of acid-base reactions. In any ligand substitution reaction which proceeds through an associative mechanism it is possible to set up a scale for the affinity of different ligands (= Lewis bases) for metal sites (= Lewis acid or nucleus) from the *rates* of substitution reactions by the ligands. This order is expressed by ***nucleophilicity*** (nucleophile = nucleus loving) of the ligands. Relative nucleophilicity of a given ligand L with respect to a reference standard ligand L^0 is given by the ratio of their rates of substitution on a chosen metal center (at a given oxidation state and stereochemistry). If L replaces L^0 from the coordination sphere of the metal, L is said to have a higher rate of substitution.

$$\text{nucleophilicity of L} = \frac{\text{Rate of substitution by L on } ML_n^{x+}}{\text{Rate of substitution by } L^0 \text{ on } ML_n^{x+}}$$

Classification of reactions

Four general classes of reactions are important for a metal complex in a given geometry. These are

(i) *Substitution* : replacement of one coordinated ligand by another ligand.

(ii) *Isomerization* : *cis-trans* and racemization.

(iii) *Electron transfer* : change in oxidation state of the metal.

(iv) *Activation of ligands* : attack at a ligand.

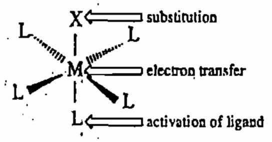


Fig. 27.73

Reaction sites at a transition metal complex.

These three main types may be combined to describe other varieties of reactions.

Mechanisms of reactions

We have had a brief introduction to different types of substitution mechanisms, namely dissociative (*D*), associative (*A*) and interchange (*I*) (Section 15.3.3). These processes may be said to constitute the ***stoichiometric mechanism*** or the sequence of elementary steps involved in a substitution reaction. These steps should be consistent with observed rate laws. The *intimate mechanism* of a reaction concerns the details of the formation of the activated complex.

The three types of stoichiometric mechanism for ligand substitution reactions may be represented on reaction profiles as shown in Figures 27.74—27.76.

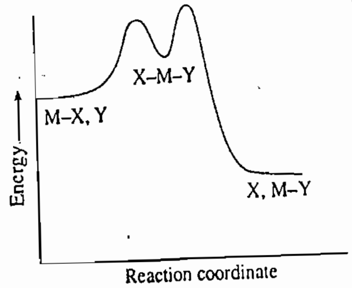


Fig. 27.74

Reaction profile for associative or *A* mechanism for substitution reaction.

$$M-X+Y \longrightarrow Y-M-X \longrightarrow M-Y+X$$

The entering group binds to the reaction center before any bond weakening of the leaving group takes place. The reaction profile consists of a single intermediate and two transition states, one for the formation and one for the decomposition of the intermediate. Usually the energy barrier to the decomposition of the intermediate is the larger one.

Example : $[Ni(CN)_4]^{2-} + \overset{*}{C}N^- \longrightarrow [Ni(CN)_4(\overset{*}{C}N)]^{3-}$

$$[Ni(CN)_4(\overset{*}{C}N)]^{3-} \longrightarrow [Ni(CN)_3(\overset{*}{C}N)]^{2-} + CN^-$$

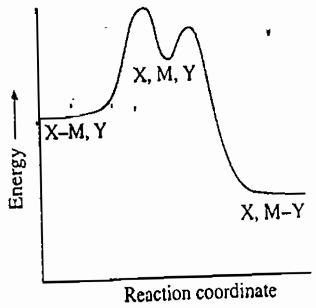


Fig. 27.75

Reaction profile for dissociative or *D* mechanism.

$$\underset{\substack{\uparrow \\ Y}}{M-X} \longrightarrow M+X \longrightarrow M-Y$$

Leaving group has left the reaction center before any interaction with the incoming group. This reaction profile also consists of a single intermediate and two transition states. The intermediate has a lower coordination number of the metal than either the reactant or the product. The energy barrier to the formation of the intermediate is larger.

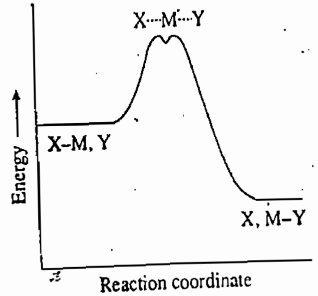


Fig. 27.76

Reaction profile for an interchange (*I*) mechanism.

$$M-X+Y \longrightarrow Y \ldots M \ldots X \longrightarrow M-Y+X$$

The leaving and entering groups exchange in a single step by forming an activated complex but not a true intermediate. As the entering group approaches the metal center, the outgoing group responds in a concerted manner and progressively leaves the site; eventually the incoming group becomes tightly bound and the leaving group is fully dissociated. The reaction profile has a single transition state.

[Sec. 27.4.1 *Classification of reactions*]

In reality, there may be all possible variation of mechanisms from *A* through *I* to *D* processes. Such processes may be formally assigned an I_a or I_d mechanism. In the I_a mechanism, the outgoing group is reluctant to leave its hold on the metal with the approach of the entering group and retains its attachment right upto the time when the incoming group gets completely bound to the metal site. The reverse is the case in the I_d mechanism; the leaving group is very sensitive to the approach of the new ligand and practically loses its hold even before the incoming group is tightly bound.

When an intermediate survives sufficiently long and attains a concentration detectable, it is relatively easy to distinguish between a *D* or *A* mechanism.

The rate of a reaction is affected by changes in certain physical conditions like temperature, pressure, solvent etc. It is also affected by variation in structural and electronic factors like the overall charge on the complex, steric crowding at the reaction center, nature of the leaving and entering groups, nature of the central metal ion etc. Important mechanistic conclusion may be drawn if such variations in rate can be experimentally followed in a suitably designed system.

For example, suppose in a substitution reaction the rate for the formation of the activated complex is found to be independent of the nature of the entering group (say Y), but dependent on the nature of the leaving group (say X). This implies that the reaction is largely controlled by the rate at which the metal-X bond breaks, indicative of a dissociative (*D*) intimate mechanism. If, on the other hand, the rate of a reaction depends upon the identity of Y, it may be concluded that formation of the M—Y bond is important in reaching the activated state and the process involves an associative (*A*) intimate mechanism.

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are determined from the variation of rate constant with temperature (section 15.3). These parameters, if known for elementary steps in a reaction mechanism may provide us with important mechanistic information. For example, a negative $\Delta S^{\ddagger}$ indicates an associative mechanism. An associative mechanism results in a net decrease in the number of chemical species and hence is accompanied by a negative $\Delta S^{\ddagger}$. A dissociative process causes $\Delta S^{\ddagger}$ to increase. However, in ascertaining such values of $\Delta S^{\ddagger}$, allowance must be made for the ordering (or disordering) of the solvent molecules (polar) around the activated complex, a process called *electrostriction*. If the formation of the activated complex is accompanied by a net increase in charge, say by union of two ions of like charge, the solvent molecules will be more ordered around the complex, lowering the entropy. If two oppositely charged species unite to form the activated complex, the overall charge will be reduced causing the release of bound solvent molecules, thereby increasing the entropy. Such solvent effects on $\Delta S^{\ddagger}$ have to be corrected before proper assignment of intimate mechanism.

The change of volume in the formation of an activated complex has also received considerable attention in the study of reaction mechanism. The *molar volume of activation* $\Delta V^{\ddagger}$ is the difference in molar volume between the initial reactant and the activated complex. It is related to the effect of pressure on the rate constant according to the relation

$$\frac{d\ln k}{dP} = -\frac{\Delta V^{\ddagger}}{RT}$$

Since the volume of any species in solution also changes when its extent of solvation changes, the volume of activation actually consists of two parts :

(i) the intrinsic volume change on going from the reactant to the activated complex, $\Delta V^{\ddagger}_{int}$;

(ii) the volume change associated with solvation effects, $\Delta V^{\ddagger}_{sol}$;

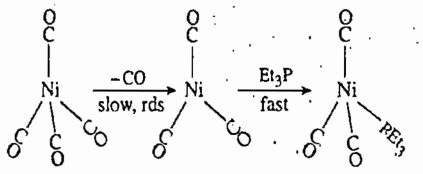
$\Delta V^{\ddagger}_{int}$ relates the changes in bond lengths and geometry upon reaching the transition state and hence is one of the most important parameters for mechanistic studies. The effect of solvation may be minimized by taking reactions in which the total charge remains unchanged. In a process of dissociation, a ligand leaves the primary coordination sphere of the metal, and we expect the volume of activation to increase ($\Delta V^{\ddagger} > 0$). In an associative process, binding of an additional ligand into the coordination site is expected to make $\Delta V^{\ddagger} < 0$. Study of reaction rates under high pressure has been used with advantage to evaluate $\Delta V^{\ddagger}$ and hence understand the intimate mechanism of many reactions.

27.4.2 *Substitution at tetrahedral complexes*

Substitution reactions at coordinatively saturated tetrahedral complexes with a formal 18-*e* count like $Ni(CO)_4$ or $Ni(CO)_2(PR_3)_2$ follow a simple first order kinetics

$$\text{rate} = k_1[ML_4]$$

The rate does not depend on the concentration and nature of the ligand, suggesting a dissociative or *D* mechanism, e.g.

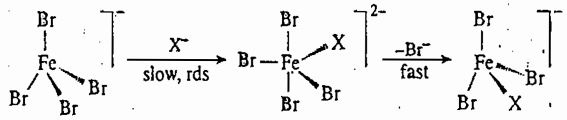


The proposed *D* mechanism is supported by the value of $\Delta V^{\ddagger}$ + 8 $\text{cm}^3\,\text{mol}^{-1}$.

In contrast, complexes with fewer than 18 electrons usually show a second order kinetics in substitution. Thus, $FeBr_4^-$ (13 *e* species) undergoes halide exchange in which the rate depends both on the concentrations of the complex and the halide (X^-).

$$\text{rate} = k_1\,[FeBr_4^-]\,[X^-]$$

A similar rate dependence has been observed in the phosphine exchange of $[CoBr_2(PPh_3)_2]$, a 15-*e* species. An associative or *A* mechanism is thus suggested for both these reactions :

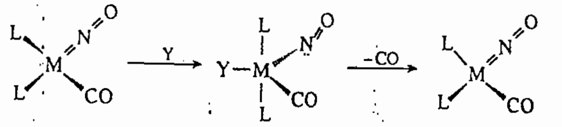


Large negative values for the entropy of activation $\Delta S^{\ddagger}$ of these reactions lend support to the associative mechanism.

However, the 18-electron complexes $[Co(CO)_3(NO)]$ and $[Fe(CO)_2(NO)_2]$ do not react by the expected dissociative route, as shown by the dependence of the reaction rates on both the concentration and nature of the attacking ligand. As we have mentioned earlier, this behaviour is characteristic of an associative (*A*) mechanism. Here the nitrosyl group may act in two ways (see nitrosyl complexes) :

(i) effectively as a 3-electron donor, first transferring an electron to the metal to form NO^+. The M—N—O moiety in such complexes is linear.

(ii) effectively as an 1-electron donor as NO^-, resulting in a bent M—N—O arrangement. In the second mode the metal becomes coordinatively unsaturated, transfer of an electron pair to the nitric oxide giving rise to a 16-electron species. This may now react in an associative mechanism with the incoming nucleophile.



The activation energy required in the process is low as expected for an A process.

Temperature has a pronounced effect on the course adopted by a reaction. Thus both $Ni(CO)_4$ and $Ni(CO)_3N_2$ are isoelectronic 18-electron species. While the former reacts via a purely dissociative route at ordinary temperature, the latter shows a combination of both associative and dissociative pathways at – 160°C (liquid krypton). In fact, the relative magnitudes of the activation energies for these two processes are highly sensitive to changes in temperature but they do not respond equally to temperature change.

27.4.3 Substitution at square planar complexes

Square planar complexes are formed by various metal ions, typically by Pt(II), Pd(II), Au(III) and Rh(I). Platinum was largely available in Russia and its complexes were found to be moderately inert. These factors helped kinetic investigation of a wide range of platinum(II) complexes by Russian chemists.

Available kinetic data on substitution at square planar complexes in solution fit most satisfactorily into an associative mechanistic model. The typical kinetic features of such reactions are

(i) a two-term rate law :

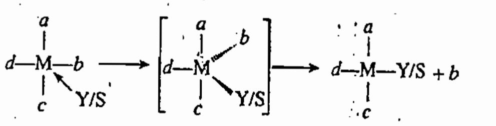
$$\text{rate} = \{k_1 + k_2[Y]\}\ \ [\text{complex}]$$

where Y is the incoming ligand.

(ii) strong dependence of rate on the nature of the incoming nucleophile, the leaving ligand and even the non-leaving ('spectator') ligands.

(iii) a dramatically strong rate enhancing effect of the ligand trans to the leaving group, specially in complexes of Pt(II). Such kinetic effect of the 'trans-ligand' in a square planar substitution is called the "trans effect".

The associative path most reasonably leads us to expect a five-coordinate activated complex, or even a five-coordinate intermediate involving the attacking nucleophile (Y) or the solvent (S); this is the nucleophile for the k_1-path.



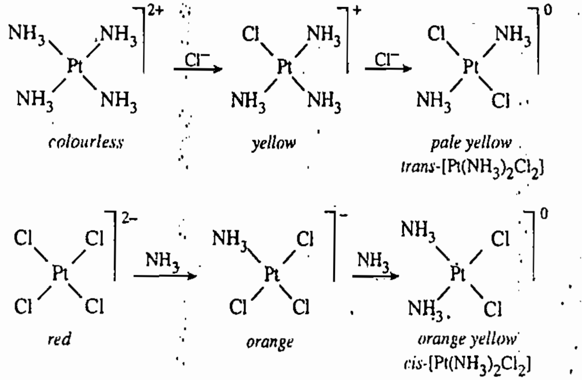
The nucleophile Y/S approaches the metal center along a path of minimum steric interference, for example along a line perpendicular to the plane of the four ligands. Now the leaving group gradually weakens its attachment to the metal and bends away from the plane of the other three ligands (the *trans* ligand *d* and the *cis* ligands *a* and *c*). Thus the trigonal bipyramid intermediate always contains the attacking group, the leaving group and the group originally *trans* to it. The groups that were originally *cis* to the leaving group now occupy the axial positions. With the departure of the leaving group, the attacking group adjusts itself into the plane of the other three groups. This is consistent with the observation that most substitution reactions of square planar complexes take place with retention of stereochemistry.

The Trans-effect

The principle of trans-effect was first established by Chernyaev (1926) from observations on substitution reactions at platinum(II). He observed that certain ligands facilitate the substitution of the ligand that is in a position *trans* to them and it is possible to arrange different ligands in a series according to this ability :

$$H_2O < H_3N < OH^- < Cl^- < Br^- < SCN^-; I^- < NO_2^- < H^-, PR_3 < C_2H_4, CO, CN^-$$

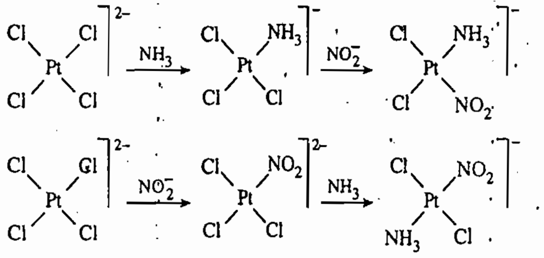
The formation of *cis-* and *trans-* $[Pt(NH_3)_2Cl_2]$ illustrates this effect :



In both the cases, the greater *trans*-directing power of Cl^- over NH_3 determines the geometry of the final product in the second step of replacement : the chloride ions trans to each other are more labile than the chloride ion trans to NH_3. Hence these are replaced first. As we shall presently see, this *trans* effect arises primarily from greater rate of substitution at the *trans* position and hence is also called the *kinetic trans effect*. Some ligands may also weaken the bond between the metal and a ligand in a *trans* position — this thermodynamic effect is called *trans influence.*

The *trans* effect can be used to synthesize a variety of isomers :

(i) *Preparation of cis- and trans-* $[Pt(NH_3)(NO_2)Cl_2]$.

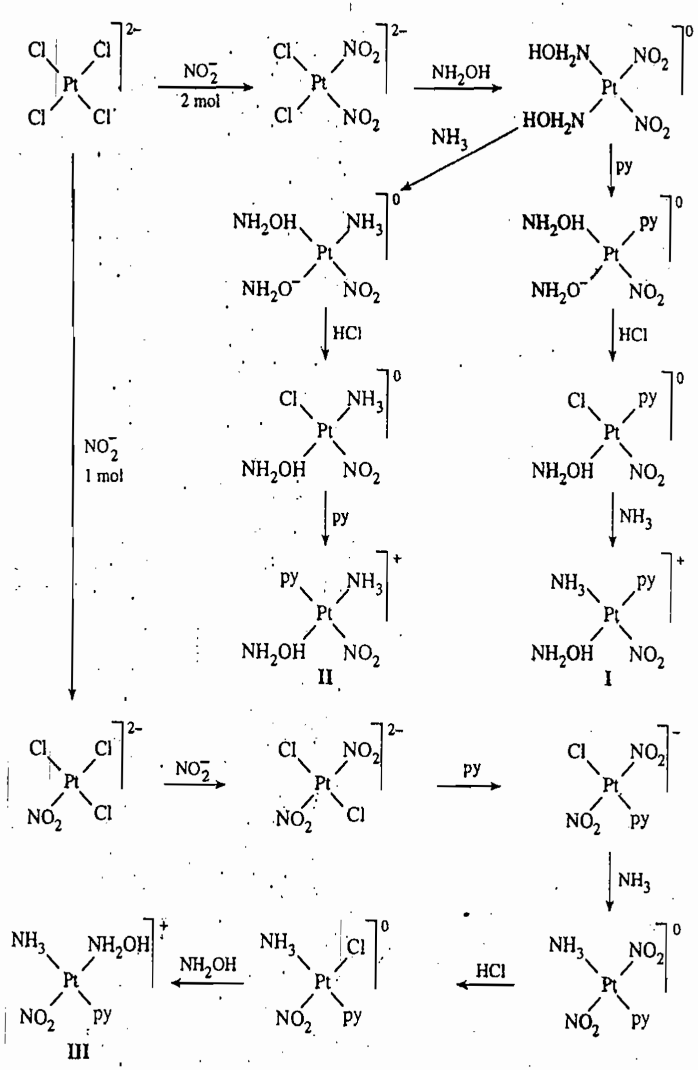


Q. **27.21** *Starting from* K_2PtCl_4 *and other ligands outline the synthesis of cis- and trans-* $[PtCl_2(NH_3)(C_2H_4)]$.

Hints : (i) C_2H_4 followed by NH_3 : *trans* isomer

(ii) NH_3 followed by C_2H_4 : *cis* isomer.

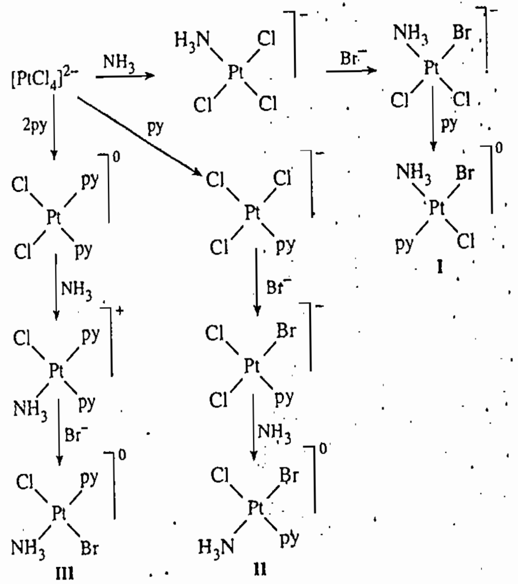
(ii) *Preparation of the three isomers of* $[Pt(NH_3)(NO_2)(NH_2OH)py]^+$



However, the "trans effect" merely gives an empirical guideline on the expected geometry of the product in a substitution process if we know the stoichiometry of the reaction. It does not foretell the nature of the product, i.e., which ligand is going to be replaced. Thus, both trans effect and order of bond strength have to be kept in mind in the following synthetic routes to three isomers of $[Pt(NH_3)(py)BrCl]$:

trans-effect : $Br > Cl > py > NH_3$

bond-strength : $Pt - NH_3 > Pt - py > Pt - Br > Pt - Cl$.



An inspection of the trans-effect series shows that simple σ-donor ligands like NH$_3$ and H$^-$ may have widely different trans-effect; similarly separated in position are the phosphines and pyridine, both of which can act as reasonable π-electron acceptors. The role of these ligands in enhancing substitution of their trans-ligands has been a subject of much discussion for a long time. It is now well established that this effect is a kinetic influence involving higher rate of substitution at the trans-position than at the cis-position. A higher rate of substitution implies a lower activation energy barrier. This may be possible in either of two ways : (i) the ground state may be raised in energy (destabilized) or (ii) the transition state may be stabilized. In fact, there is now enough evidence to conclude that both the ground state effect and activated state effect operate simultaneously with many trans-directing groups,

The ground state effect (σ-effect)

Grinberg first attempted to explain trans effect (1935) through his polarization theory. In essence, this theory explains ground state destabilization by weakening of the bond to ligands at trans-positions of pure σ-donors such as hydride and alkyl. These ligands are strongly polarizing and pull electron density towards themselves, thereby depriving the bonds to others, particularly the trans ligands. Such polarization is not expected in a symmetrical complex like PtX$_4$. When one X is replaced by another ligand L which is more polarizable than X, the primary charge on the metal ion induces a dipole on L; this may, in turn, induce a net polarization on the metal in a manner that will repel negative charge on a ligand X trans to L (Fig. 27.77). The following correlations between expectations from the theory and observations are noteworthy :

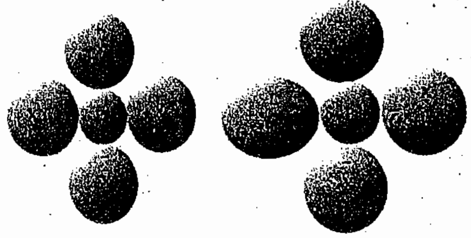


Fig. 27.77
Polarization theory of Grinberg.

The δ- charge developed on the central platinum repels the inherent negative charge on the ligand X trans to L.

(i) The more polarizable a ligand, the more will be its trans-directing power. This is consistent with the observed trends

$$H^- > I^- > Br^- > Cl^-; \quad NH_3 \geqslant H_2O.$$

(ii) The trans-effect will be significant only when the metal ion itself undergoes easy polarizations. In fact, trans-effect is not significant when the metal is less polarizable, as with Pd(II) or Pt(IV).

However, the theory cannot explain the strong trans-effect of π-bonding ligands like C$_2$H$_4$, CN$^-$, CO etc.

The transition state effect (π-effect)

This theory (developed independently by Chatt and Orgel) rationalizes trans-effect by assuming stabilization of a trigonal bipyramid transition state in the presence of strong trans-directing groups. π-acceptor ligands with empty acceptor orbitals can form π-bond with filled metal $d\pi$-orbitals when the M $\longrightarrow$ L electron drift reduces electron density on the metal and stabilizes the intermediate. In this intermediate, the leaving ligand, the entering ligand and the trans-directing ligand - all occupy the three equatorial positions in the trigonal bipyramid structure (Fig. 27.78). It is to be noted that the trans-ligand is uniquely positioned in the equatorial plane to accept the π-electron density from the metal. Hybrid dp orbitals ($5d + 6p$) on platinum(II) have been shown to undergo more extensive π-overlap.

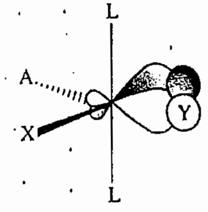
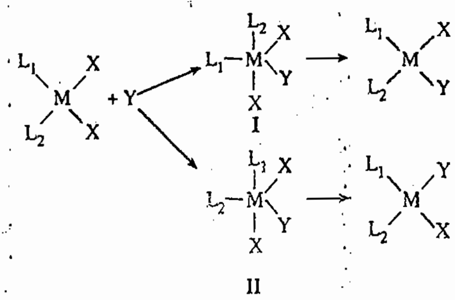


Fig. 27,78
π-bonding in the postulated tbp intermediate in square planar substitution.

As explained earlier, the 5-coordinate intermediate always contains the attacking ligand (Y), the leaving ligand (X) and the ligand originally trans to the leaving group (A) in the trigonal plane. The axial positions are occupied by two groups that were originally cis to the leaving group.

From the relative number of $d\pi$-orbitals available to a ligand at axial and equatorial positions in a trigonal bipyramid, it can be shown that M – L π-back bonding is most effective when a π-acceptor ligand occupies an equatorial position rather than an axial position. For a square-planar complex ML$_1$L$_2$X$_2$, substitution of a ligand X by Y may take place in either of the two ways :



- Rate of substitution of a ligand X depends upon the relative stability of the 5-coordinate intermediates - one having L_1 at the equatorial position(I), another having L_2 at the equatorial position(II). Obviously, if L_1 is a stronger π-acceptor, it will enter into a stronger interaction with the metal $d\pi$-electrons at the equatorial position and the intermediate I will be more stabilized. Hence L_1 will show stronger trans-effect than L_2. This explains why ligands with strong π-acidity e.g., CN^-, CO, olefins etc. are strong trans-directing ligands. Obviously, ligands which are strong π-donors (H_2O, OH^- etc.) show weak trans-directing power.

Very strong σ-donors may also stabilize the tbp intermediate by occupying an equatorial position. The metal s-orbital may be supposed to be equally available to the ligands at axial and equatorial positions. But the availability of the metal p-orbitals to the ligands in the axial and equatorial position are different : for the two axial ligands, one half of a metal p-orbital is available to each; but for the three equatorial ligands there are two p-orbitals (say p_x and p_y), making two-third of a p-orbital available to each ligand. Hence a strong σ-donor ligand like H^-, CH_3^-, etc., will also stabilize the tbp intermediate from an equatorial position and exert strong trans- directing effect.

We have earlier mentioned that both ground state and transition state effects are simultaneously involved in trans-effect. In fact, in $[Pt(C_2H_4)Cl_3]^-$, the Pt-Cl bond trans to C_2H_4 is longer (234.0 pm) than the other two Pt—Cl bonds (230.3 pm), a consequence of the relatively strong Pt—C_2H_4 σ-bond. This is supported by higher Pt—Cl stretching frequency for the trans chlorine.

As mentioned earlier, the *trans-influence* of a ligand is related to the effect of this ligand on the metal-ligand bond to a ligand *trans* to itself. Naturally, this involves ground state properties like bond lengths and stretching frequencies and is related to the weakening of the *trans* metal-ligand bond in the ground-state.

The occurrence of *trans-* effect is not so extensive in square planar complexes of other metals or even Pt(IV), presumably because of the low polarizability of these metals. The trans-effect order in Pt(IV) complexes appears to be $I^- > Br^- > Cl^- > OH^- > NH_3, NO_2^-$. Besides being less polarizable than Pt(II), Pt(IV) is also a much weaker pi-donor than Pt(II). Consistent with this, the Pt^{IV}—X bond length in *trans* L—Pt^{IV}—X systems does not change noticeably with the nature of L. Nearly similar arguments apply to complexes of Pd(II).

Q. 27.22 *The five-coordinate intermediate in square-planar substitution might also have a square pyramid geometry with higher LFSE. What factors favour the tbp geometry?*

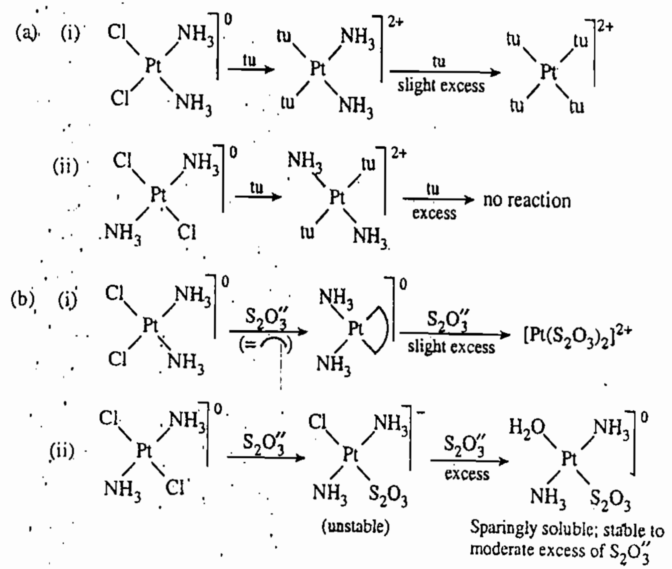
Hints : (i) The tbp configuration involves smaller repulsion between ligands.

(ii) The loss in CFSE is compensated by greater π-bonding in tbp structure. In the trigonal plane, two π-bonds can be formed simultaneously with any two of the equatorial ligands.

Q. 27.23 *In the series Ni(II), Pd(II) and Pt(II), only Pt(II) shows significant trans-effect. Comment.*

Hint : The separation between $5d$ and $6p$ orbitals is sufficiently small to give rise to dp hybrid orbitals suitable for π-bonding with the ligands in the trigonal bipyramid intermediate.

Q. 27.24 *Explain the following observations :*



Hints : (a) In (i) stronger trans-effect of thiourea greatly labilizes both NH_3.

(b) In (i) both NH_3 are trans to S_2O_3'' and are labilized due to the stronger trans effect of S_2O_3''. In (ii) Cl^- is labilized giving the aquo complex which is sparingly soluble.

Note : The reactions of tu are useful in differentiating between *cis-* and *trans-* isomers of a Pt(II) complex.

The vast majority of square planar complexes undergo substitution reactions with retention of stereochemistry i.e., *trans* complexes give *trans* products and *cis* complexes give *cis* products. This is in accordance with the mode of formation of the 5-coordinate intermediate explained earlier. Exceptions to this general trend may be observed in cases where

(a) the tbp intermediate undergoes some sort of pseudorotation (e.g., see Berry pseudorotation) to interchange axial and equatorial ligands;

(b) the energy barrier for intramolecular rearrangement between square planar and tetrahedral forms is low;

(c) the substitution involves a dissociative path.

Examples of the last kind are not very common.

Influence of the entering group : nucleophilicity parameter

We have earlier introduced the concept of nucleophilicity — a ligand property influencing the rate of attack at a metal centre.

Referring to square-planar substitution at Pt(II) we shall try to develop the idea of a nucleophilicity parameter.

It has been stated earlier that most substitution reactions of platinum(II) follow a combined first and second-order rate law. Thus, in reactions of the type

$$trans\text{-}[PtCl_2L_2] + Y \longrightarrow trans\text{-}[PtClYL_2]^+ + Cl^-$$

$$\text{Rate} = (k_1 + k_2\,[Y])\,[\text{complex}].$$

If the same reaction is carried out with a standard base, say methanol, the second-order rate constant k_2 is represented by k_2^0. For any base Y, it is now possible to set up a *nucleophilicity parameter* n_{Pt} (Y) according to the following relation :

$$n_{Pt}(Y) = \log [(k_2(Y)/k_2^0)]$$

$$\text{or, } \log k_2(Y) = n_{Pt}(Y) + \log k_2^0 \text{ ......(I)}$$

A few typical n_{Pt} values are given below :

nucleophile :	CH_3OH	Cl^-	NH_3	I^-	CN^-	Ph_3P
n_{Pt} :	0	3.04	3.06	5.42	7.0	8.8

For a large number of platinum complexes, it has been found that the nucleophilicity order of the entering ligand Y remains practically independent of the other ligands L and the reaction rate increases with the nature of Y as

$$ROH < OR^- < Cl^- \approx py \approx NO_2^- < Br^- < I^- < SCN^- < CN^- < PR_3$$

However, for different complexes of Pt(II), equation I is better expressed as

$$\log k_2(Y) = S n_{Pt}^0(Y) + C.$$

The parameter n_{Pt}^0 represents n_{Pt} corrected to zero ionic strength and C is the intercept on the log k_2 (Y) axis. S is called the *nucleophilic discrimination factor*; it is a measure of the sensitivity of the rate constant on n_{Pt}, , that is nucleophilicity of the attacking group and the center being attacked. A large value of S reveals that log k_2 (Y) is highly influenced by the nucleophilicity of Y and vice versa. C is sometimes called the intrinsic reactivity.

A look at the energy profile of the substitution reaction appears useful at this stage. In Fig. 27.79 (a), the relative energies of M – X + Y versus M – Y + X tell us that the bond M—Y is stronger than the bond M—X. The activation energy corresponds to E_a. The broken line shows the energy profile when a different Y ligand is involved and we note that E_a', the new energy of activation is only slightly lower than E_a. This corresponds to a small value of S.

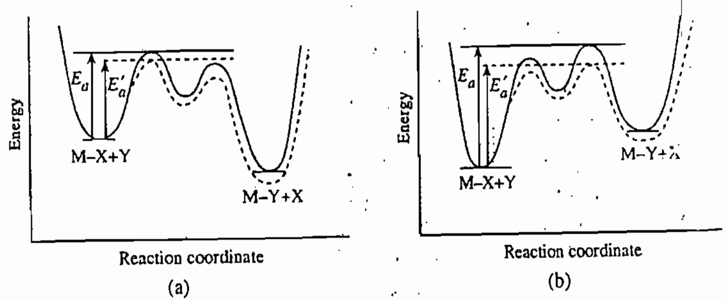


Fig. 27.79

Plot of energy profile for substitution reaction of Pt(II) of type $L_3Pt – X + Y \longrightarrow L_3Pt – Y + X$: (a) M – Y bond stronger than Pt – X bond (b) Pt – X bond stronger than Pt – Y bond.

In contrast, Fig. 27-79 (b) represents a substitution process in which the final product M – Y has a weaker bond than M – X. Again, the curved line shows that for a variation of Y, the energy of activation changes by a larger magnitude than in Fig. 27-79 (a). This indicates that the energy of the activated complex is largely influenced by the incoming group Y, a situation that corresponds to a large value of S. Though the reaction in this case is endothermic ($\Delta H^0 > 0$), it may proceed spontaneously when the overall ΔG is negative.

The role of solvent

It has been established that solvents also coordinate to the metal ions to form solvento-intermediates which subsequently react with the nucleophiles. This is consistent with the two term rate expression mentioned before. Moreover, it has been possible to trap the aquo-intermediate in substitutions of the type

$$[Pt(dien)I]^+ \xrightarrow[k_1]{H_2O} [Pt(dien)H_2O]^{2+} \xrightarrow{Y^-} [Pt(dien)Y]^+ \quad \text{(dien = diethylenetriamine)}$$

by adding a base which deprotonates the intermediate :

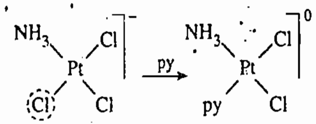
$$[Pt(dien)H_2O]^{2+} \overset{B}{\rightleftharpoons} [Pt(dien)OH]^+ + BH^+$$

The process of deprotonation does not involve any M—OH$_2$ bond cleavage and is much more rapid than the substitution. The hydroxo species being essentially inert to substitution, base-addition practically inhibits the replacement of I by Y. This has been confirmed experimentally under various conditions.

Dissociative mechanisms are also known to operate for a few square-planar complexes. *cis*- $[PtMe_2(SMe_2)_2]$, for example, reacts with a range of bidentate ligand by a dominantly dissociative pathway. A T-shaped three-coordinate intermediate is probably formed which may undergo intramolecular rearrangements resulting in nonstereospecific reactions.

cis-effect

Studies have also been made for a possible "*cis*-effect" in square-planar substitution, that is, labilization of a group *cis* to a particular group. Though such an effect does exist for a few platinum(II) complexes, it is not as strong as the *trans*-effect and is also very small in comparison. Thus, for the two substitution reactions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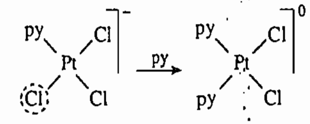
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reaction II is about 40% faster than reaction I. We may ascribe this to a greater *cis*-effect of pyridine over ammonia in labilizing the groups *cis*- to themselves (shown with dotted circle). Similar replacement of Cl^- *cis* to NH_3 is about 20% faster in comparison to replacement of a Cl^- *cis* to NO_2^-. Thus we may frame an order of *cis*-effect as

$$py > NH_3 > NO_2^-$$

Kinetic studies on the replacement of H_2O by Cl^- in several square planar platinum(II) complexes show the relative order as well as magnitude of *cis*- and *trans*-effect as follows :

cis-effect : $C_2H_4\ (0.05) < Br^-\ (0.3) < Cl^-\ (0.4) < NH_3\ (1) \approx H_2O\ (1) < \text{dmso}\ (5)$

trans-effect : $H_2O\ (1) < NH_3\ (200) < Cl^-\ (330) < Br^-\ (3000) < \text{dmso}\ (2 \times 10^6)$
$<< C_2H_2\ (10^{11})$.

It is evident that the *cis*-effect is much weaker than the *trans*-effect.

[However, the *cis*-effect is considerably stronger in substitution reactions of many octahedral complexes of cobalt(III).]

27.4.4 Substitution reactions of octahedral complexes

Substitution at an octahedral metal site in an aqueous medium is mainly concerned with (i) replacement of coordinated water by other ligands (deaquation), including exchange with water molecules in the medium and (ii) substitution of other ligands by water (*hydrolysis*). The exchange of water between the coordination sphere of a metal and the solvent water has been extensively studied using isotopically labelled water :

$$[M(H_2O)_6]^{n+} + H_2O^* \rightleftharpoons [M(H_2O)_5(H_2O^*)]^{n+} + H_2O$$

Except for a few cations like Cr(III) and Rh(III), such exchanges are very fast, as evident from the approximate first-order rate constants (s^{-1}) at room temperature; some non-transition metal ions are also included for comparison.

	Li^+	Na^+	Be^{2+}	Mg^{+2}	V^{2+}	Ni^{2+}	Co^{2+}	Fe^{2+}
$k \simeq$	10^8	10^9	10^2	10^5	10^2	10^4	10^5	10^6
	Mn^{2+}	Zn^{2+}	Cr^{2+}	Cu^{2+}	Cr^{3+}	Al^{3+}	Fe^{3+}	Ti^{3+}
$k \simeq$	10^7	10^7	10^8	10^9*	10^{-6}	10^6	10^2	10^5

*(Cu^{2+} has two water exchange rates, $10^9 s^{-1}$ for the axial water and $10^7 s^{-1}$ for equatorial water).

We observe that for the nontransition elements, rate of exchange increases as (i) the size of cation increases and (ii) the charge of cation decreases. Since the strength of the M—OH_2 bond should also decrease parallelly, it may be concluded that breaking of the M—OH_2 bond is most important in the transition state. It thus appears that the exchange mechanism is primarily dissociative.

For the elements in the first transition series, no such generalization is directly possible from the rate constants; but keeping in mind the extremely general nature of the correlation between M—OH_2 bond strength and the charge or size of M^{n+} ion, we may conclude that electronic configuration of the metal ion must also play an important part in dictating the mechanism. Extra-kinetic parameters like $\Delta S^\ddagger$ and $\Delta V^\ddagger$ of these exchange processes are also noteworthy :

	V^{II}	Mn^{II}	Fe^{II}	Co^{II}	Ti^{III}	V^{III}	Cr^{III}	Fe^{III}
$\Delta S^\ddagger$, J $K^{-1}mol^{-1}$	−0.4	+6.0	+21.0	+37.0	+1.0	−29.0	+12.0	+12.0
$\Delta V^\ddagger$, cm^3 mol^{-1}	−4.1	−5.4	+3.7	+6.1	−12.1	−8.9	−9.6	−5.4

A negative volume of activation corresponds to an associative process while a positive volume of activation indicates a dissociatively activated process. Hence the change in sign of $\Delta V^\ddagger$ from Mn^{II} to Fe^{II}, Co^{II} (and also Ni^{II} and Cu^{II}) signifies a changeover from associative to dissociative nature of the activated state.

The electron configuration of the transition metal ions may now be considered in more detail in the perspective of octahedral substitution. A water molecule (or any attacking nucleophile, say Y) must attack an octahedral metal site from directions which are least "protected" by the six ligands already bound to the metal. Remembering the geometry of the octahedral complex, we conclude that the attack must be along any direction of the t_{2g} orbitals, i.e., along one of the C_3 axes. When the t_{2g} orbitals are empty, they are in a position to accept an electron pair from the attacking nucleophile, offering an associative path. But as we move towards right along the transition series, the t_{2g} orbitals get gradually occupied and repulsion with the approaching water/ligand favours a dissociative pathway for the substitution.

In deaquation (anation) reactions of cobaltammines like

$$[Co(NH_3)_5H_2O]^{3+} + X^- \longrightarrow [Co(NH_3)_5X]^{2+} + H_2O$$

the rate constants do not vary widely when the incoming group X is varied along the series Cl^-, Br^-, NCS^-, N_3^-, $SO_4^=$ etc. With X = Cl^- or $SO_4^=$, $\Delta V^\ddagger$ of the reactions are also found to be positive. Experimental rate constants, combined with equilibrium studies, show that the reactions involve an I_d pathway consistent with the *Eigen-Wilkins mechanism* :

Step I : The complex species and the attacking ligand form an encounter-complex through an "outer-sphere" association. This may be formed through ion-pair formation (for oppositely charged species) or other forces like van der Waals' forces, hydrogen bonding etc.

Step II : The coordinated water molecule is now interchanged with the incoming ligand. This forms the rate determining step in which the activated complex involves mainly breaking of the M—OH_2 bond.

Complex formation by $[Ni(H_2O)_6]^{2+}$ also shows a similar trend but some complexes of Cr(III) appear to follow an associative process.

The reverse process of aquation of the Co(III) complex, that is,

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

also appears to follow a dissociative mechanism. The rate constant varies with the nature of the leaving group X, showing that the activation energy is mostly associated with the Co^{III}—X bond breaking. There is a linear free energy relation between the free energy of activation ($\Delta G^\ddagger$) and the free energy of the reaction ($\Delta G°$) showing that the former varies mainly with the Co^{III}—X bond strength.

Substitution reactions in aqueous solution appear to proceed always through the intermediate formation of an aquo-complex; e.g.,

$$[MX_5Y]^{n+} + H_2O \rightleftharpoons [MX_5(H_2O)]^{n+} + Y$$

The process takes place in acidic media (pH ≤ 4) and hence is often called *acid hydrolysis*. In basic media, a hydroxo-complex is formed through *base hydrolysis*.

$$[MX_5Y]^{n+} + H_2O \xrightleftharpoons{OH^-} [MX_5OH]^{(n-1)} + Y$$

Extensive studies have been made on aquation reactions of complex ions like $[Co(NH_3)_5X]^{2+}$. The general rate law has the form

$$\text{rate} = k_A\,[Co(NH_3)_5X^{2+}] + k_B[Co(NH_3)_5X^{2+}]\,[OH^-]$$

Where k_A is the rate constant for acid hydrolysis and k_B is the rate constant for base hydrolysis. In general, $k_B = (10^4 - 10^8)\,k_A$, that is the cobaltammines are much more reactive towards bases.

At low pH values (pH < 4), the second term in the rate law becomes negligible. A dissociative mechanism is suggested by different observations. For example, the aquation of $[Co(NH_3)_4Cl_2]^+$ is nearly 1000 times faster than that of $[Co(NH_3)_5Cl]^{2+}$; the increased charge in the latter complex resists M—Cl bond cleavage. Also, rate of aquation increases when NH_3 is replaced by a bulkier ligand and the steric crowding enhances bond cleavage.

At higher pH values, the rate expression becomes first-order in the complex and first order in OH^- ion. But the reaction is not actually S_N2; several experiments strongly suggest the following mechanism :

(i) Rapid, reversible deprotonation of a coordinated ammonia molecule

$$[Co(NH_3)_5X]^{2+} + OH^- \xrightleftharpoons{\text{fast}} [Co(NH_3)_4(NH_2)X]^+ + H_2O$$

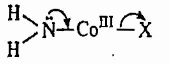
(ii) Slow, rate-determining loss of X^- from the amido complex, which is the *conjugate base* (*CB*) of the starting complex

$$[Co(NH_3)_4(NH_2)X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4(NH_2)]^{2+} + X^-$$

(iii) The five-coordinate amido complex now readily captures a water molecule

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

The mechanism is said to be S_N1CB (substitution, nucleophilic, unimolecular conjugate base) or DCB (dissociative conjugate base). The conjugate base presumably loses the X^- ion more easily owing to electron donation from NH_2 group and consequent weakeing of the Co^{III}—X bond



In all such substitution reactions, the usual balance of energies is always maintained to decide whether a given nucleophile Y will replace other ligands. The cyrstal field stabilization energy of the system, though only a small part of the total energy, may sometimes provide useful guidance to predict the path of a substitution. For reactions of a series of metal ions having the same charge and nearly equal size, the collision frequencies and entropy of activation may be reasonably supposed to remain unchanged; hence the variation in the enthalpies of activation may be expected to control the total energy of activation and hence the rate. It has been possible to calculate the change in crystal field stabilization energy on passing from the initial octahedral complex to a pentagonal bipyramid (C. N. 7; associative) or a trigonal bipyramid or square pyramid (CN 5; dissociative) intermediate. This difference in the stabilization energies, also called the *crystal field activation energy*, CFAE, for various d^n configurations are shown in Table 27.20. The other alternative five-coordinate intermediate, the trigonal bipyramid, does not possess higher CFSE than the square pyramid.

TABLE 27.20.

CFSE (in units of Δ_0) for various d^n configurations

(In octahedral (Oh), square pyramid (Sp) and pentagonal bipyramid (Pbp) coordinations)
(* = high spin)

Configuration	CFSE (Oh)	CFSE (Sp)	CFSE (Pbp)
d^0, d^{5*}, d^{10}	0	0	0
d^1, d^{6*}	0.4	0.46	0.53
d^2, d^{7*}	0.8	0.91	1.06
d^3, d^8	1.2	1.00	0.77
d^{4*}, d^9	0.6	0.91	0.49
d^4	1.6	1.46	1.30
d^5	2.0	1.91	1.83
d^6	2.4	2.00	1.55
d^7	1.8	1.91	1.27
d^9	0.6	0.91	0.49

Again referring to the substitution reactions of low-spin, d^6 Co(III), we find that change from the octahedral coordination to square-pyramid intermediate results in a loss of CFSE by 0.4 Δ_O; the tbp intermediate (not shown) has a CFSE of 1.25 Δ_O and involves still greater loss. The loss in CFSE on conversion to a pentagonal bipyramid intermediate is 0.854 Δ_O. The square pyramid thus involves minimum loss of CFSE, estimated at about 92 kJ mol^{-1} for $[Co(NH_3)_6]^{3+}$. This suggests that a dissociative route to the substitution will involve lower energy of activation in comparison to the associative path.

Examination of Table 27.20 further shows that d^3, d^6 (low spin) and d^8 ions will suffer highest loss in CFSE in forming a square pyramid intermediate. Except d^8 (Ni^{II}), these configurations give rise to "inert" complexes. Ni(II) forms labile complexes, but the rate constants are certainly lower than those for other +2 ions except V(II).

In contrast to the Co(III) complexes discussed, reactions of many Cr(III) complexes show characteristics of an associative type of mechanism (I_a), as in substitution reactions in aquo complexes like $[Cr(H_2O)_5X]^{2+}$, water exchange reaction of $[Cr(H_2O)_6]^{3+}$ in aqueous solution or solvent exchange of $[Cr(DMF)_6]^{3+}$ with solvent DMF. On the contrary, ligand exchange by $[Cr(NH_3)_5X]^{2+}$ and deaquation (anation) of $[Cr(NH_3)_5(H_2O)]^{3+}$ show rate behaviours consistent with an I_d mechanism. We may reasonably assume that three *d*-electrons in Cr(III) offer less repulsion to the electrons of the entering ligand than in Co(III) (six electrons). Besides, Cr(III) may be expected to use its lower lying empty e_g^* orbitals in bond formation. Since water is a weak σ-donor ligand, the energy of the e_g^* orbital will not be very high and the transition state for association via this orbital can be easily reached. With ammonia, a stronger σ-donor, the antibonding orbital is raised higher in energy, making the associative transition state less approachable. A dissociative path therefore appears more favourable in this case.

cis-trans isomerization

The dissociative mechanism discussed above helps us to understand *cis-trans* isomerization. Let us first consider the following sequence of reactions involving *cis-* and *trans-* $[Co(en)_2Cl_2]^+$.

(i) In the presence of Na_2CO_3 and ethylenediamine, aerial oxidation of $CoCl_2$ produces $[Co(en)_2CO_3]^+$.

(ii) $[Co(en)_2CO_3]^+ + HCl\ (aq) \longrightarrow$ mixture of *cis-* and *trans-* $[Co(en)_2Cl_2]Cl$.

(iii) slow evaporation of the HCl solution (mixture of *cis-* and *trans-*) deposits deep green *trans-* $[Co(en)_2Cl_2]Cl.HCl$.

(iv) the *trans-* compound is heated in air to remove the HCl of crystallization, the remaining compound dissolved in water and evaporated to a small volume. Purple crystals of *cis-* $[Co(en)_2Cl_2]Cl$ are deposited.

(v) repeated evaporation of the *cis-* compound with HCl transforms it almost completely to the *trans-* isomer.

It has been established that the reaction proceeds *via* the formation of the diaquo complex which subsequently isomerizes to a mixture of *cis-* and *trans-* isomers. The water molecules are then substituted by chloride ions during warming with HCl.

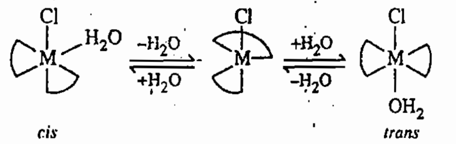
From strong acid medium, the *trans*-form deposits first since the *trans*-form is least soluble in this medium. In absence of acid, the *cis*-form is least soluble.

The nearly complete conversion to "all *cis-*" or "all *trans-*" variety is called *cis-trans* isomerization. In presence of HCl, the aquo-chloro complex is first formed :

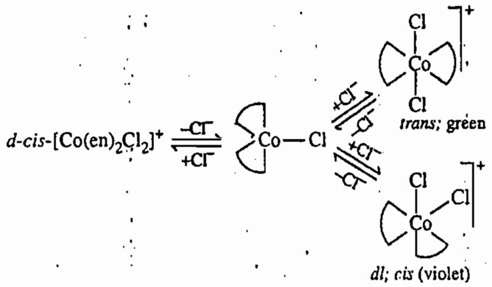
$$cis\text{-}\ [Co(en)_2Cl_2]^+ + H_2O \rightleftharpoons cis\text{-}\ [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$$

$$trans\text{-}\ [Co(en)_2Cl_2]^+ + H_2O \rightleftharpoons trans\text{-}\ [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$$

The aquochlorocomplex now isomerizes through the 5-coordinate intermediate :



Exchange reaction involving $^{36}Cl^-$ is considerably faster than the rate of *cis-trans* isomerization but has a rate equal to the rate at which *d*- $[Co(en)_2Cl_2]^+$ loses its optical activity. This is also consistent with a 5-coordinate intermediate :



Thus the 5-coordinate intermediate partly froms the *trans*- isomer and partly gives the racemic mixture. It has been estimated that 80% of the intermediate would give the *trans*-form and 20% would form the *cis*-isomer.

Racemization

In connection with optical isomerism we observed (Chapter 26) that resolution of many optically active complexes is rendered difficult owing to rapid interconversion of the isomers, i.e. *d*- or *l* complex producing the *dl*- complex. This is related to the lability of the complex species involved. Some inert complexes do not racemize readily, for example, solutions of *d*–$[Co(en)_3]^{3+}$ do not show any loss of optical activity at room temperature even after three months; racemization is very slow even at 100°C. We can trace the reason to the low-spin d^6 configuration of Co^{3+}.

For octahedral complexes which racemize at an observable rate, mainly two mechanisms are involved — an intermolecular process and an intramolecular process. In some cases both processes may occur simultaneously.

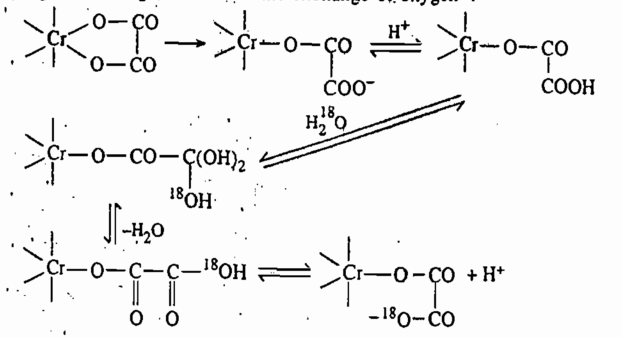
The rates of racemization of $[Ni(phen)_3]^{2+}$ fits an intermolecular process in which the primary step involves reversible dissociation of a ligand :

$$d\text{-}[Ni(phen)_3]^{2+} \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} dl\text{-}[Ni(phen)_2(H_2O)_2]^{2+} + \text{phen} \rightleftharpoons l\text{-}[Ni(phen)_3]^{2+}$$

The rate of racemization should then be equal to the rate of dissociation of the complex to form the bis-chelate. Also, one may expect that the trischelate would undergo ligand exchange with excess ligand at the same rate. Experimental data on the nickel complex meet these expectations. Kinetics of radioactive ligand exchange (^{14}C) agree with the dissociative nature of the primary step. In acid solution, the dissociated ligand is protonated at one end and hence cannot recombine with the bis-chelate. Hence the equilibrium is driven to right. In pure water, the rate of racemization does not change from that in acidic medium, while dissociation of the complex becomes practically negligible. This suggests that solvent molecules have no significant role in forming the transition state.

An intramolecular path of racemization is strongly suggested for a number of tris-chelate complexes, for example, $[M(C_2O_4)_3]^{3-}$, $[M(acac)_3]$ (M = Co^{III}, Cr^{III}), $[Co(edta)]^-$, $[Co(bigH^*)_3]^{3+}$ and $[Fe(phen)_3]^{2+}$. These complexes racemize faster than they exchange ligands. (* bigH = biguanide, Table 26.3).

Thus, an aqueous solution of $[Cr(ox)_3]^{3-}$ (ox = oxalate) does not contain any detectable amount of oxalate, showing negligible dissociation consistent with the d^3 configuration of Cr(III) (it is thus kinetically robust). No exchange is also observed with excess oxalate using radioactive ^{13}C in the ligand. Again, all twelve O-atoms of the complex undergo exchange with $H_2{}^{18}O$ at a rate slightly slower than the rate of racemization. These observations suggest that only one end of the oxalate ligands dissociate during racemization : this does not allow any ligand exchange, but allows the exchange of oxygen :



Since there is equal probability for either metal-oxygen bond to open, both the O-atoms of the oxalate which coordinate to the metal would ultimately exchange with ^{18}O in the solvent.

Another interesting alternative for such intramolecular path of racemization involves no opening of any end of the chelated ligands — racemization occurs through a twist in the structure. As early as 1943, P. Rây and N. Dutt proposed a twist mechanism for the racemization of $[Co(bigH)_3]^{3+}$ which is both kinetically and thermodynamically very stable. This is known as *Rây-Dutt twist* or tetragonal twist : instead of detachment of one end of a chelate ring, a distortion of the structure occurs by one chelate ring moving up and the other chelate ring moving down :

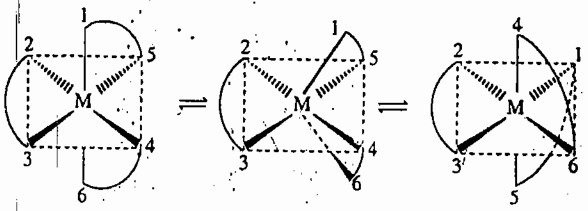


**Fig. 27.80
Rây-Dutt twist.**

Another twist mechanism involving a trigonal prism intermediate (*Bailar twist* or trigonal twist) is illustrated in Fig. 27.81. The chelate complex is looked down a C_3 axis when one gets an alternative representation of the octahedron (a trigonal antiprism); the solid triangle lies in the upper plane and dashed lines indicate a plane below the page. If the upper triangle of chelate atoms is twisted clockwise by 60°, one gets a trigonal prism. Further twisting by 60° results in inversion. Such trigonal twist is particularly suitable to explain the slow racemization of *cis*- $[Co(trien)Cl_2]$ where the tetradentate ligand trien (Ch. 26) does not allow a tetragonal twist. The transition state for the Bailar twist is more symmetrical and calculations show that this should be favoured with chelating ligands having smaller bite distance (distance between coordinating atoms).

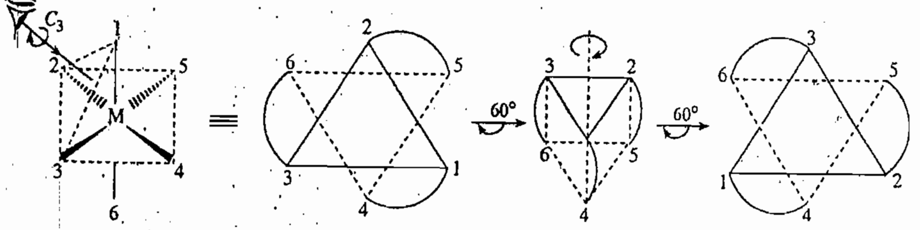
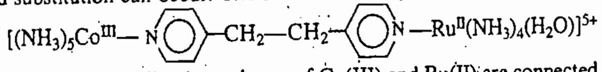


Fig. 27.81 : Bailar twist.

27.4.5 Oxidation-reduction (electron transfer) reactions

Two stoichiometric mechanisms of redox reactions were suggested by Henry Taube in the 1950s (awarded Nobel Prize 1983) :

(i) *An outer sphere process* which involves minimum electronic interactions by chemical bonding between the reactants. The inner coordination spheres of the reactants generally remain undisturbed and if the reagents are substitution-inert in the time scale of electron transfer, the electron-transfer process may be classified as an outer sphere process. Reduction of $[Fe(phen)_3]^{3+}$ by $[Fe(CN)_6]^{4-}$ is an example of this type. Here, both the complexes are nonlabile and during the extremely short time scale of redox reactions, no ligand substitution can occur. The intramolecular electron transfer in the binuclear complex  is also outer sphere though the coordination spheres of Co(III) and Ru(II) are connected by the bridging ligand.

$[(NH_3)_5Co^{III}—N(C_5H_4)—CH_2—CH_2—(C_5H_4)N—Ru^{II}(NH_3)_4(H_2O)]^{5+}$

(ii) *An inner sphere process* is one in which the coordination spheres of the reactants share a ligand to form a bridged intermediate. The reduction of $[CoCl(NH_3)_5]^{2+}$ by $[Cr(H_2O)_6]^{2+}$ occurs by this process where the products include both $[Co(H_2O)_6]^{2+}$ and $[CrCl(H_2O)_5]^{2+}$. Addition of $^{36}Cl^-$ to the solution fails to introduce any $^{36}Cl^-$ into the coordination sphere of Cr(III). This indicates that the transfer of Cl^- has occurred directly from the coordination sphere of one complex to that of the other.

Outer-sphere reactions

Many electron exchange reactions without any net chemical change belong to this category, for example, the following self exchange reaction between ordinary and isotopically labelled iron ($\overset{*}{Fe}$) which is moderately fast at room temperature (Table 27.21)

$$[Fe(H_2O)_6]^{2+} + [\overset{*}{Fe}(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [\overset{*}{Fe}(H_2O)_6]^{2+}$$

As the reaction proceeds, the radioactivity is spread over both the components. Since there is no net change in chemical composition of the mixture, we expect no heat change to be involved. However, some activation energy is required. The bond lengths in the complex of Fe(II) are slightly longer than the bond lengths in the Fe(III) counterpart. According to the *Franck-Condon principle*, electron movement is much faster than nuclear motion (because of the great difference in their mass); thus internuclear distances do not change during the instant of electron transfer. Therefore, it is assumed that on approaching the transition state, the bond lengths of the reactants will adjust to approach those of the products. Hence a part of the activation energy arises from the necessary adjustment of the bond lengths. Also, reorganization of the solvation sphere around each ion requires some energy. These, together with the electrostatic interaction energy between the two reactants, constitute the free energy of activation for the process.

The self-exchange reaction

$$[Fe(CN)_6]^{4-} + [\overset{*}{Fe}(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [\overset{*}{Fe}(CN)_6]^{4-}$$

is very fast (Table 27.21). Here the Fe—C bond in $[Fe(CN)_6]^{4-}$ is actually shorter (192 pm) than that in $[Fe(CN)_6]^{3-}$ (195 pm; reverse of the situation in hexaaquo complexes) owing to stronger π-bonding in the lower oxidation state. However, since the Fe—C bonds in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are not much different, the activation energy is small and the electron transfer is rapid.

[Sec. 27.4.5
Electron-transfer reactions]

Kinetics of many electron transfer processes with and without a net chemical reaction have been studied. Some second order rate constants have been collected in Table 27.21.

TABLE 27.21

Approximate second-order rate constants (25°C) for some outer-sphere electron transfer processes in aqueous media

Reactants	$k(dm^3mol^{-1}s^{-1})$
$[Fe(bipy)_3]^{2+}$, $[Fe(bipy)_3]^{3+}$	$>10^6$
$[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$	10^5
$[Mo(CN)_8]^{3-}$, $[Mo(CN)_8]^{4-}$	10^4
$[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$	3
$[Co(phen)_3]^{2+}$, $[Co(phen)_3]^{3+}$	1
$[Co(en)_3]^{2+}$, $[Co(en)_3]^{3+}$	10^{-4}
$[Co(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$	10^{-6}
$[Os(bipy)_3]^{2+}$, $[Mo(CN)_8]^{3-}$	2×10^9
$[Fe(CN)_6]^{4-}$, $[Fe(phen)_3]^{3+}$	10^8
$[Fe(CN)_6]^{4-}$, $[IrCl_6]^{2-}$	4×10^5

We observe that electron exchange reactions of ethylenediamine and ammine complexes of Co(II) and Co(III) are very slow. Here the Co(II) complexes have a high-spin configuration while the Co(III) complexes have a low-spin configuration. The ground-state metal-ligand distances are appreciably different, for example, Co—N distance is 196 pm and 211 pm in $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$ respectively. Reorganization of the bond lengths in the transition state now require greater activation energy, making the process slow.

Let us have a closer look at the electron configurations of the ions involved :

$$Co^{II}\left(t_{2g}^5 e_g^{*2}\right) + Co^{III}\left(t_{2g}^6\right) \longrightarrow Co^{III}\left(t_{2g}^5 e_g^{*1}\right) + Co^{II}\left(t_{2g}^6 e_g^{*1}\right).$$

Thus both Co^{II} and Co^{III} on the right will be in an excited state suggesting the involvement of an asymmetric activated complex. Instead, we may consider an excited state of one of the reactants to have a symmetric reaction. If the Co^{II} is in an excited state, the reaction would be,

$$Co^{II}\left(t_{2g}^6 e_g^{*1}\right) + Co^{III}\left(t_{2g}^6\right) \longrightarrow Co^{III}\left(t_{2g}^6\right) + Co^{II}\left(t_{2g}^6 e_g^{*1}\right).$$

If the Co^{III} is excited to $(t_{2g}^4 e_g^{*2})$, the process may be conceived as

$$Co^{II}\left(t_{2g}^5 e_g^{*2}\right) + Co^{III}\left(t_{2g}^4 e_g^{*2}\right) \longrightarrow Co^{III}\left(t_{2g}^4 e_g^{*2}\right) + Co^{II}\left(t_{2g}^5 e_g^{*2}\right).$$

The excitation energy will add to the energy of activation, making the process slow. In case of $[Co(H_2O)_6]^{3+}$, Δ_o is low and the energy for excitation to the high spin state is small. Hence the $[Co(H_2O)_6]^{2+}$– $[Co(H_2O)_6]^{3+}$ exchange reacton is fairly rapid ($k \simeq 5$ dm^3 mol^{-1} s^{-1}). On the other hand, for $[Co(phen)_3]^{2+}$, a high value of Δ_o makes excitation to the low-spin state relatively easier; the reaction rate is again moderately fast with the self-exchange rate constant $k \simeq 1$ $dm^3mol^{-1}s^{-1}$. The aromatic system in 1,10-phenanthroline may also promote the reaction through electron delocalization in the conjugated system.

Fairly satisfactory values for rate constants of outer-sphere reaction with a net chemical reaction may be obtained from the Marcus equation : if k_{11} and k_{22} are the rate constants for the electron exchange reactions in the two couples Ox_1-Red_1 and Ox_2-Red_2 respectively, then according to a simplified form of Marcus equation, the rate constant k_{12} for the cross reaction

$$Ox_1 + Red_2 \rightleftharpoons Ox_2 + Red_1$$

is given by

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}}$$

where K'_{12} is the equilibrium constant for the cross reaction. From the relation $\Delta G = -RT\ln K$, the equation indicates a linear relation between the free energies of activation and the overall free energy change :

$$2\Delta G^{\ddagger}_{12} = \Delta G^{\ddagger}_1 + \Delta G^{\ddagger}_2 + G^0$$

Nevertheless, k_{12} decreases instead of the expected increase with increasing driving force, ΔG^0 if ΔG^0 is high and exceeds certain limit.

Inner-sphere reactions

An inner-sphere redox reaction necessarily involves the formation of a bridged complex as an intermediate. The overall process may be considered to take place in three steps, as illustrated by the following reaction ($X^- $ = halide, NCS^-, N_3^-, SO_4^{2-} and PO_4^{3-}).

(i) *Formation of a precursor bridged complex :*

$$Co^{III}(NH_3)_5X + Cr^{II}(H_2O)_6 \longrightarrow (NH_3)_5Co^{III}\text{—}X\text{—}Cr^{II}(H_2O)_5 + H_2O$$

(ii) *Activation, electron transfer and formation of the successor complex : the redox process*

$$(NH_3)_5Co^{III}\text{—}X\text{—}Cr^{II}(H_2O)_5 \longrightarrow (NH_3)_5Co^{II}\text{—}X\text{—}Cr^{III}(H_2O)_5$$

(iii) *Separation of the successor complex*

$$(NH_3)_5Co^{II}\text{—}X\text{—}Cr^{III}(H_2O)_5 \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5X]^{n+}$$

Since Co(II) is fairly labile, the hexaaquo complex is more likely to be found in acidic aqueous media.

The transfer of the bridging group along with the electron provides an evidence for the bridge mechanism. The example with Cr(II) as the reducing agent is noteworthy : Cr^{2+} is labile to substitution but Cr(III) complexes are inert. The transfer of the X^- ligand must occur in the activated complex, which is also supported by the lack of exchange of $^{36}Cl^-$ into the coordination sphere. Sometimes solid bridged intermediates may even be isolated, e.g., in the oxidation of $[Co^{II}(CN)_5]^{3-}$ by $[Fe(CN)_6]^{3-}$, the intermediate $[(CN)_5Fe^{II}CNCo^{III}(CN)_5]^{6-}$ ion has been separated as the barium salt.

Though step (ii) above (redox process) is most commonly the rate determining step for the overall redox reaction, any one of the three steps mentioned above may be rate determining. Thus, oxidation of V^{II} *(aq)* by different Co(III) complexes shows more or less the same rate with various bridging ligands. Here the rate-determining step is the substitution of a molecule of water from the coordination sphere of V^{2+}.

The reactions considered above are sometimes called *one-equivalent processes* as they involve change in oxidation number by ±1. An example of a *two-equivalent* process is provided by the reaction

$$[Pt^{II}Cl_4]^{2-} + [{}^*Pt^{IV}Cl_6]^{2-} \longrightarrow [Pt^{IV}Cl_6]^{2-} + [{}^*Pt^{II}Cl_4]^{2-}$$

Here the Cl-bridged intermediate is formed by adding an extra Cl^- into the square planar platinum site.

Q. 27.25 *Why is reduction of Fe^{3+} by Sn^{2+} carried out in excess HCl?*

Hints : Cl^- is an efficient bridge for electron transfer; NO_3^-, SO_4^{2-}, ClO_4^- are not.

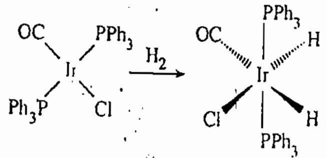
Q. 27.26 *Anhydrous $CrCl_3$ does not dissolve easily in H_2O. But addition of a piece of Zn makes the process faster- why?*

Oxidative addition reactions

These are characterized by an increase in oxidation state accompanied by an increase in oxidation number. This type of reaction is particularly observed when a metal is stable in a low oxidation state with a small coordination number but a high coordination number may be stable in a high oxidation state. Thus Pt^{II} (d^8) is stable in the 4-coordinate square-planar environment while Pt^{IV} (d^6) is most stable in the six-coordinate octahedral coordination : this gives rise to reaction of the type

$$Pt^{II}L_4 + Br_2 \rightleftharpoons [Pt^{IV}Br_2L_4]\ (trans)$$

Such reactions are finding importance in the study of catalysis, for example, in the activation of molecular hydrogen at room temperature and normal pressure through the reaction :



The reverse process of oxidative addition is called *reductive elimination.*

[Sec. 27.4.5 *Complementary reactions*]

Complementary and non-complementary reactions

Redox reactions in which the oxidant and reductant undergo the change in oxidation number by same units are sometimes called complementary reactions, as for example the reaction between Co(III) and Cr(II) mentioned before in which the oxidant and reductant react in 1 : 1 mole ratio. In *non-complementary reactions*, the oxidant and reductant change their oxidation numbers by different number of units, so that different numbers of moles of each are involved, for example :

$$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

$$5Fe^{2+} + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+}$$

$$6Fe^{2+} + Cr_2O_7^{=} \longrightarrow 6Fe^{3+} + 2Cr^{3+}$$

Such non-complementary reactions are expected to occur in stages, since encounter between three or more species with the requisite activation energy and proper orientation are highly improbable. These reactions often involve intermediate unstable oxidation states. Thus, the reduction of $Cr_2O_7^{=}$ or MnO_4^- by Sn^{2+} probably involves Sn(III) as an intermediate. Sn(II) cannot readily reduce $[Co(C_2O_4)_3]^{3-}$, but Sn(III) can. During the reduction of Hg^{2+} to Hg by Sn^{2+}, no reduction of $[Co(C_2O_4)_3]^{3-}$ occurs, suggesting that no Sn(III) is formed in the course of the reaction; it should then proceed by a direct two-electron transfer. Similarly, Mn^{2+} is not oxidized by $Cr_2O_7^{=}$, but during the oxidation of isopropanol by dichromate, any Mn^{2+} present is precipitated as MnO_2; Cr(V) or Cr(IV) is probably formed as an intermediate in this case. These intermediates are also probably formed in the oxidation of iodide by dichromate in dilute acid medium. The reaction is slow but is catalyzed by iron(II). Since iron(III) does not oxidize iodide rapidly in dilute acid, an intermediate oxidation state of chromium may be supposed to be involved in the catalyzed oxidation. With a large excess of iodide, two equivalents of iodide are oxidized per mole of Fe(II) added :

$$2Fe^{2+} + Cr_2O_7^{=} + 4I^- + 14H^+ \longrightarrow 2Fe^{3+} + 2I_2 + 2Cr^{3+} + 7H_2O$$

Formation of a chromium(V) intermediate is consistent with this observation

$$Fe^{2+} + Cr(VI) \longrightarrow Cr(V) + Fe^{3+}$$

$$Cr(V) + 2I^- \longrightarrow Cr(III) + I_2$$

The oxidation of Cr(III) to Cr(VI) by peroxodisulphate and catalyzed by Ag^+ is supposed to involve Ag(II) as an intermediate in the following sequence of steps :

$$Ag^I + S_2O_8^{=} \longrightarrow Ag^{II} + SO_4^{\dot{-}} + SO_4^{2-}$$

$$Cr^{III} + Ag^{II} \longrightarrow Cr^{IV} + Ag^I$$

$$Cr^{IV} + Ag^{II} \longrightarrow Cr^V + Ag^I$$

$$Cr^V + Ag^{II} \longrightarrow Cr^{VI} + Ag^I.$$

(Earlier, the reaction was supposed to involve Ag(III) as an intermediate. Now this is known to occur through a sulfate radical as shown. The $SO_4^{\dot{-}}$ oxidizes another Ag(I).)

Q. 27.27 Mn^{2+} strongly catalyzes the oxidation of AsO_3^{3-} by Ce(IV). Why?

27.4.6 Reactions involving activation of ligands

Studies on the reactions of ligands coordinated to a metal centre are likely to provide valuable information regarding reactions catalyzed by metals and help a lot in understanding the action of metalloenzymes. For example, the nitrogenases which contain iron, together with molybdenum or vanadium, can convert dinitrogen directly to ammonia. The enzyme carboxypeptidase containing zinc is specific in its capacity of cleaving peptides at the peptide carbonyl of the C-terminus. Similarly, studies on the cleavage of phosphates by metal ions throw much light on the mechanism of hydrolysis of ATP in biological systems.

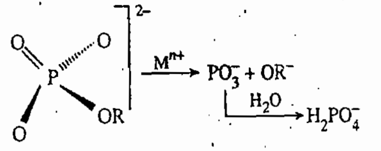
So far, we have come across three basic types of metal ligand interaction :

(i) Ligand to metal σ-bond (ii) Ligand to metal π-bond

(iii) Metal to ligand π-bond.

- The ultimate electron density on the ligand is determined by the net effect of these three interactions, as determined by their relative magnitudes.

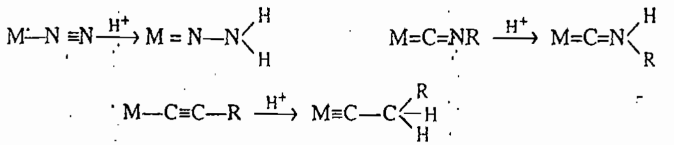
If the ultimate balance of electron density lies on the metal side, that is, the metal causes a net lowering of electron density on the ligand (interactions (i) and (ii) dominate), the bonds within the ligand will be somewhat weakened and the ligand will be more susceptible to attack by nucleophilic reagents. We should expect such behaviour from complexes of 'hard' metals, for example those of the first row transition metals, particularly in high oxidation states. Heterolytic cleavage of bonds within the ligand in such electron-poor complexes may be illustrated by the rapid cleavage of phosphates bound to Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} or Cu^{2+}. The metal ion withdraws sufficient electron-density from the phosphorus oxygen bond in the phosphate ligand, resulting in a higher rate for the cleavage of one P—O linkage.



The hard metal ions are also known to catalyze the hydrolysis of peptides, esters, amides etc. by making the carboxyl carbon atom more susceptible to attack by the nucleophile OH^-.

A 'soft' metal ion, usually from the second or third transition series and in a low oxidation state, may sufficiently "back-bond" to the ligand with an overall increase in electron density on the coordinated ligand, thereby increasing its nucleophilicity and making it more susceptible to attack by electrophiles. Such ligand activation by "electron-rich" sites is readily illustrated by ready protonation of dinitrogen, isonitriles and unsaturated hydrocarbons attached to a $[M(diphosphine)_2]$ core where M = Mo, W, Fe etc., and diphosphine = $R_2PCH_2CH_2PR_2$ (R = Et, Ph etc.).

Representing the metal core as M, the reactions may be summarily represented as



$$M{-}N{\equiv}N \xrightarrow{H^+} M{=}N{-}N\Big\langle{}^{H}_{H} \qquad M{=}C{=}NR \xrightarrow{H^+} M{=}C{=}N\Big\langle{}^{H}_{R}$$

$$M{-}C{\equiv}C{-}R \xrightarrow{H^+} M{\equiv}C{-}C\Big\langle{}^{R}_{H}{}_{H}$$

Dialkylation of coordinated dinitrogen has also been studied extensively.

SUMMARY

Effective Atomic Number (EAN) **:** It is calculated by counting the electrons belonging to a metal atom or ion and adding to this the electrons received through coordination (2 for each unidentate ligand). For many complex species, the EAN is equal to the atomic number of the inert gas next to the central metal and corresponds to filling of $(n-1)d$, ns and np orbitals of the metal by 18 electrons. The stability of the complex species is then assigned to the possession of 18 electrons in the valence shell of the metal — this is often called the 18-*electron rule* which is the counterpart of the 8-electron rule for lighter non-transition elements among transition elements.

Valence Bond Theory : According to this theory, a coordination entity is formed as a result of coordinate covalent bond formation by electron pairs from ligands through overlap of appropriate atomic orbitals (or their hybrids) of the bonded atoms. Where necessary, rearrangement of electrons may occur within the valence shell metal orbitals of similar energy to provide a set of empty orbitals to accomodate the ligand electrons. These empty orbitals may form suitable hybrids which will overlap with ligand orbitals containing lone pairs of electrons. The theory can explain the observed geometry and spin-only magnetic moment of many complexes but exceptions remain. Also the theory cannot explain (i) the variation of magnetic moment with temperature and (ii) the colours of complex compounds.

The **electroneutrality principle :** In a complex species the electrical charge tends to get distributed in such a manner that no atom in the complex gets a resultant charge much higher or lower than about 1*e*. A complex would be most stable when the electronegativity of ligand atoms results in a condition of essentially zero net electrical charge on the metal.

The **Crystal Field Theory (CFT)** considers the ligands as point negative charges while the metal electrons are associated with their usual atomic orbitals. The theory now considers only the electrostatic interaction between the metal and the ligands in two steps : (i) electrostatic attraction between the positive nucleus of the metal and the ligands (considered negative point charges). This results in an overall lowering in energy of the whole system. (ii) electrostatic repulsion force between the electrons in the valence shell of the metal and the point negative charges assumed on the ligands. This slightly raises the energy of the system. In step (ii), further consideration of the directional character of the *d*-orbitals leads to a situation in which the energies of a group of *d*-orbitals pointed at the ligands are raised while the energies of the remaining *d*-orbitals are lowered by a corresponding amount, keeping the total energy unchanged (conservation of barycenter). This is known as *crystal field splitting* and the energy lowering consequent to this is known as *crystal field stabilization energy* (CFSE). In an octahedral field, the d_{xy}, d_{yz} and d_{zx} group of orbitals (t_{2g}-group) are lowered in energy by $0.4\Delta_o$ (= $4Dq$) each while the $d_{x^2-y^2}$ and d_{z^2} orbitals are raised by $0.6\,\Delta_o$ (= $6Dq$) each where the magnitude of the splitting is Δ_o (= $10\,Dq$).

The nature of splitting is reversed in a tetrahedral field where the magnitude of splitting (Δ_t) is also less :

$$\Delta_t \approx \frac{4}{9}\Delta_o.$$

The magnitude of Δ depends upon several other factors like nature of the ligand, charge on the metal ion and nature of the *d*-orbitals involved (i.e., whether they are 3*d*, 4*d* or 5*d*).

The CFT can explain the observed colour and electronic spectra of complex compounds by invoking electron transfer between the split *d*-levels. It can also explain the magnetic moments of complexes to a large extent. However, the CFT fails to include metal-ligand orbital overlap and consequences thereof. Also it cannot explain the relative magnitude of splitting caused by different ligands, that is, their position in the spectrochemical series.

The **Molecular Orbital Theory** (MOT) is based on symmetry-based overlap of the metal orbitals with appropriate ligand group orbitals (LGO-s). The ultimate order of the resulting molecular orbital energy levels is influenced by both σ- and π- bonding. The MOT provides a better rationalization of the observed spectral and magnetic properties of complexes, besides being able to justify the relative positions of the ligands in the spectrochemical series.

Colour and Electronic Spectra : A complex compound may absorb electromagnetic radiation in the uv and visible region for a variety of reasons and consequently give rise to different type of spectra viz., (i) *d-d* or ligand feld spectra (ii) charge transfer spectra (iii) ligand spectra and (iv) counter-ion spectra. The *d-d* and charge-transfer transitions are most useful in the study of complex compounds.

The **Beer-Lambert** law relates the intensity of the incident radiation (I_0) of a particular wavelength with that of the radiation emerging (I) after travelling a thickness l of a solution of the complex having molar concentration c :

$$\log (I/I_0) = -\varepsilon c l.$$

ε is called the molar-absorption coeffecient. (I/I_0) is called the *transmittance* (*T*) and $\varepsilon c l$ is called the *absorbance* (*A*) of the solution.

Selection rules for *d-d* transitions : (i) *LaPorté rule* : In a centrosymmetric environment an allowed transition must involve orbitals having different symmetry properties with respect to inversion i.e.. allowed transitions are $g \longrightarrow u$ or $u \longrightarrow g$.

Since *d*-orbitals are *g*-type, a *d-d* transition is formally forbidden in a perfectly octahedral (centrosymmetric) complex. The rule may be relaxed due to deviation from symmetry (e.g., by asymmetric vibration) and mixing of orbitals (e.g., *d-p* mixing). Tetrahedral complexes (non-centrosymmetric) are not subject to LaPorté selection rule.

(ii) *Spin selection rule* : It states that a transition may occur only between two energy states which have the same spin multiplicity ($\Delta S = 0$). Thus transitions resulting in a change in the total number of unpaired electrons are spin-forbidden. The spin selection rule breaks down when spin-orbit coupling does not allow assignment of definite *S* values by L-S coupling.

The observed bands in the electronic spectra of complex species may be correlated with different spectroscopic states arising from the free-ion term in various ligand fields.

Magnetic Properties : The magnetic moment of a free atom or ion may be calculated from the resultant of spin and orbital angular momentum quantum numbers *L*, *S* and *J*.

$$\mu_{\text{eff}} = g\sqrt{J(J+1)} \quad \text{Bohr Magnetons (BM or } \mu_B\text{)}$$

where *g*, known as the Lande' splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

The Bohr magneton (μ_B) is an elementary unit of magnetism, classically conceived as the magnetic moment of an electron in the first Bohr orbit of hydrogen.

$$\mu_B = \frac{eh}{4\pi m} = 9.274 \times 10^{-24}\ \text{JT}^{-1} \text{ (Joule per Tesla)}$$

For most metal ions in the first transition series spin-orbit coupling may be practically ignored. The spin and orbital angular momenta of the electrons interact independently with an external magnetic field and the effective magnetic moment is given as

$$\mu_{eff} = \mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \quad \text{B.M.}$$

Ions with the following electron configurations are expected to make orbital contributions to the magnetic moment.

Octahedral :	High spin	d^1, d^2, d^6, d^7
	Low spin	d^4, d^5
Tetrahedral :		d^3, d^4, d^8, d^9

In these cases

$$\mu_{eff} = \mu_{\text{spin-only}}\left(1 - \alpha\frac{\lambda}{\Delta}\right)$$

where λ is the spin-orbit coupling constant, positive for *d*-shells less than half-filled and negative for *d*-shells more than half-filled. α is a constant depending on the ground state spectroscopic term for the ion and has a value equal to 2 for an *E* term and 4 for an A_1 term.

Reactions of Complex Compounds : Four general classes of reactions are important for a metal complex in a given geometry. These are

(i) *Substitution* : replacement of one coordinated ligand by another ligand.

(ii) *Isomerization* : cis-trans isomerization and racemization reactions.

(iii) *Electron transfer* : change of oxidation state of the metal.

(iv) *Activation of ligands* : attack at a ligand.

Inert and Labile complexes : A complex compound which readily undergoes substitution reactions, say within the time of mixing of the reagents, is said to be kinetically labile while complexes entering reactions with half-lives longer than one minute may be formally classified as inert.

Nucleophilicity : Relative nucleophilicity of a given ligand L with respect to a reference ligand L^0 is given by the ratio of their rates of attack on a chosen metal centre at a given oxidation state and stereochemistry.

Substitution reactions at tetrahedral complexes with a formal 18*e* count like $Ni(CO)_4$ follow a simple first order kinetics suggestive of a dissociative (*D*) mechanism. Complexes with fewer than 18*e* e.g., $[FeBr_4]^-$ usually show a second order kinetics suggesting an associative (*A*) mechanism.

Substitution reactions at square planar complexes are almost always found to follow an associative pathway.

The Trans Effect relates to higher rate of substitution observed at a position *trans* to certain ligands in square planar platinum(II) complexes,

EXERCISE

1. *Explain the electroneutrality principle.*
2. *What are the drawbacks of the valence bond theory when applied to describe the bonding in complex compounds?*
3. *What do you mean by "splitting of the d-orbitals"? How does the idea of splitting help us in explaining the properties of coordination compounds?*
4. *What do you understand by crystal field stabilization energy (CFSE)? Calculate the CFSE for d^0, d^3, d^4 and d^6 metal ions in octahedral and tetrahedral fields.*
5. *Show that for a given metal ion and a given set of ligands at the same internuclear distance the extent of crystal field splitting in a tetrahedral field is nearly 44% of the splitting in an octahedral field.*

6. *Give examples of complex compounds in which*

(i) Both $\Delta_o = 0$ and CFSE = 0

(ii) $\Delta_o \neq 0$ but CFSE = 0.

7. *Given Δ_o for H_2O is 13900 cm^{-1}, what would be the CFSE of $[Cr(H_2O)_6]^{2+}$ in high spin and low-spin configurations? (Mean pairing energy $P \doteq 23{,}500$ cm^{-1}).*

8. *ΔH (hydration) of the Fe^{2+} ion is 47.9 kJ/mol higher than would be expected if there were no CFSE. Find the magnitude of Δ_o for the high spin complex $[Fe(H_2O)_6]^{2+}$.*

[**Hint :** ΔH_{hyd} is higher because the complex is stabilized by this amount. In terms of the CFT, CFSE for d^6 (weak field) is $0.40\Delta_o$. Hence

$$0.40\ \Delta_o = 47.9 \text{ kJ mol}^{-1} \text{when } \Delta_o = 119.75 \text{ kJ mol}^{-1}.]$$

9. *Ni(II), Pd(II) and Pt(II) have the same number of d-electrons. But Pt(II) and Pd(II) form square planar complexes almost exclusively while only a few complexes of Ni(II) are square planar. Comment.*

10. *In terms of the CFT, explain why all six Cu—OH_2 distances in $[Cu(H_2O)_6]^{2+}$ are not equal.*

11. *Both $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ ions appear almost colourless in dilute aqueous solution, though one is low-spin and the other is high-spin. Explain.*

[**Hint** : The former absorbs in the uv region, the latter in the IR region. None absorbs in the visible region.]

12. *A metal ion M^{2+} forms complexes $[M(H_2O)_6]^{2+}$, $[MBr_6]^{4-}$ and $[M(en)_3]^{2+}$ which are variously coloured like blue, green and red. What is the expected colour of each complex from the CFT?*

[**Hint :** A complex absorbing in the visible region shows the complementary colour. Thus a green complex absorbs in the red region — lowest energy in the visible range. Since Br^- is the weakest among the given ligands, the bromo complex is expected to be green]

13. *Predict the colour of the $[Cr(H_2O)_6]^{3+}$ ion, given $\Delta_0 = 17{,}400$ cm^{-1}.*

[**Hint :** λ corresponding to the given Δ_o = 5750 Å. This suggests absorption in the yellow region, resulting in a violet colour.

However, the actual colour is green due to an additional absorption at 4050 Å. This shows the limitation of predicting colour from a consideration of Δ_o alone.]

14. *Show that for d^4 high spin metal ions, the relative energy of an octahedral over tetrahedral field is $-6Dq + 4Dq'$ where 10Dq and 10Dq′ are the crystal field splittings in octahedral and tetrahedral fields respectively.*

15. *An octahedral Ni(II) complex shows d-d absorption bands at 10,750, 17,500 and 28,200 cm^{-1}. Assign the bands from the Orgel diagram. Which transitions are responsible for the colour of the complex?*

Calculate 10Dq from the above data in kK unit.

16. *What is tetragonal distortion? which d^n configurations lead to (i) weak and (ii) strong Jahn-Teller distortion in octahedral complexes?*

Explain the nature of J-T distortion expected for a tetrahedral complex of a d^9 metal ion.

17. *A and B are two complexes of Ni(II), one of them being tetrahedral and the other octahedral. Each shows three abosrption bands but complex A has $\varepsilon \simeq 10$ and B has $\varepsilon \simeq 150$. Which one is probably the tetrahedral complex? Measurement of what physical property would exclude the possibility of either complex being square planar? Explain your answer.*

18. (a) *The thiocyanate ion SCN^- is an ambidentate ligand which can coordinate to a metal either through S or N. How will you determine the nature of such linkage?*

(b) *The nitrite ion forms both the complexes $[Co(NH_3)_5(ONO)]^{2+}$* (O-bonded) *and $[Co(NH_3)_5(NO_2)]^{2+}$* (N - bonded), *but the latter is more stable.—Explain.*

19. *Define magnetic susceptibility and magnetic moments of compounds. State the relationship between the two for a paramagnetic substance.*

20. *What are magnetically dilute substances? Explain : superexchange, antiferromagnetism, spin-only formula of magnetic moment, temperature-independent paramagnetism.*

21. *Explain whether the following complexes will have any orbital contribution to their μ_{eff} values :*

$$d^2\ (oh),\ d^4(Td),\ d^7\ (Td).$$

Comment on the observed magnetic moments (300 K)

K_3CoF_6 (5.5 B.M.); K_3CuF_6 (2.8 B.M.); K_2NiF_6 (0.0 B.M.).

22. (a) *A metal forms two complexes in the same oxidation state. In one complex, the magnetic moment is 4.9 B.M.; in another it is 0.0 B.M. Which of the following metals fit this description?*

Cr(III), Mn(II), Mn(III), Fe(II), Fe(III), Co(II).

[**Hint** (a) The metal has either four or no unpaired electron. This fits a d^6 ion.]

(b) *Which one of these metal ions will make complex compounds having magnetic moments 4.90 B.M. and 2.83 B.M.?*

23. *Effective magnetic moments (B.M.) for a few complex compounds are given below. Describe the structure and bonding of these compounds on the basis of these values.*

$K_2[NiF_6]$	0.0	$[Ni(PEt_3)_2Cl_2]$	0.0
$[Ni(NH_3)_2Cl_2]$	3.3	$[Ni(Ph_3AsO)_2Cl_2]$	3.95

24. *Explain*

(i) *The low-spin form of a d^5-transition metal complex is favoured at high pressure.*

(ii) *10Dq increases in the order*

$$[CrCl_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$$

(iii) *Diamagnetic $[NiCl_4]^{2-}$ would be highly unstable.*

(iv) *Co^{2+} (aq) forms a tetrahedral tetrachloro complex when treated with concentrated HCl, but Ni^{2+} (aq) does not do so.*

(v) *$[CuCl_4]^{2-}$ has a flattened tetrahedral structure while $[CoCl_4]^{2-}$ is a regular tetrahedron.*

(vi) *The electronic spectrum of $[CoF_6]^{3-}$ shows two bands having maxima around 11,500 and 14,500 cm^{-1}.*

(vii) *Tetrahedral Ni(II) complexes show magnetic moments of up to 4.1 B.M.*

(viii) *Both cis-$[Co(en)_2F_2]^+$ and trans-$[Co(en)_2Cl_2]^+$ are more intensely coloured than trans-$[Co(en)_2F_2]^+$.*

[**Hint :** The *trans*-species have a centre of symmetry. Cl^- to Co charge-transfer will intensify colour, but charge transfer from F^- is unlikely].

(ix) *The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ shows a broad shoulder with maximum around 20,300 cm^{-1}.*

(x) *A deep blue solution containing Co(II) in concentrated HCl gradually turns pale pink on addition of excess water.*

(xi) *At high temperatures, NiO is paramagnetic and the magnetic susceptibility decreases with increase of temperature. Below 374°C, the susceptibility decreases as the temperature is lowered and μ_{eff} falls.*

(xii) *Though a transition metal ion may attain various coordiantion number and stereochemistry, Co^{3+} is an exception, being found nearly always in an octahedral coordination.*

(xiii) *The fluoro complexes of Cu(III) and Au(III) are $[CuF_6]^{3-}$ (paramagnetic) and $[AuF_4]^-$ (diamagnetic).*

(xiv) *Ni(II), Cu(II), Pd(II), Pt(II), Rh(I), Ir(I) and Au(III) commmonly form square planar complexes.*

(xv) *A green aqueous solution of Ni(II) turns colourless on addition of cyanide.*

(xvi) *An aqueous solution of Co(III) sulfate is diamagnetic but becomes paramagnetic when a large excess of fluoride is added.*

(xvii) *The observed magnetic moments of Cr(II) and Mn(III) complexes tend to lie below the spin-only values, while those of Fe(II), Co(II) and Ni(II) tend to lie above.*

(xviii) *OH^- is lower than H_2O in the spectrochemical series.*

(xix) *The CrO_4^{2-} ion is a d^0 complex and is yet coloured.*

(xx) *CN^- forms tetracyano complexes with both Ni^{2+} and Pt^{2+}. But with NH_3, the same metal ions form $[Ni(NH_3)_6]^{2+}$ and $[Pt(NH_3)_4]^{2+}$ respectively.*

25. *How would you proceed to prepare cis- and trans-$[Pt(NH_3)(NO_2)Cl_2]^-$ from $[PtCl_4]^{2-}$ in two steps—using NH_3 and NO_2^- in either step?*

26. *$[Pt(NH_3)_2Cl_2]$ forms two isomers. One isomer gives $[Pt(NH_3)_2(tu)_2]^{2+}$ on treatment with thiourea (= tu); the other isomer gives $[Pt(tu)_4]^{2+}$ on similar treatment. Identify the isomers.*

[**Hint :** Trans-effect tu>Cl^->NH_3. In the cis isomer, NH_3 ligands are labilized by trans Cl^-. Subsequently, the Cl^- are labilized by tu. Hence the second complex is cis.

27. *In $[Cu(H_2O)_6]^{2+}$, two water molecules undergo exchange with the bulk solvent molecules much more rapidly than the other four—explain.*

28. *Arrange in the order of increasing lability.*

$[K(H_2O)_6]^+$, $[Ir(H_2O)_6]^{2+}$, $[Al(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, $[Y(H_2O)_6]^{3+}$

[Cr < Al < Fe < Y < Sr < K]

Half-lives (min) of a few exchange reactions involving isotopically labelled ligands are given below :

		Half-life (min)			*Half-life (min)*
$[Al(H_2O)_6]^{3+}$	$H_2\overset{*}{O}$	<1.5	$[Cr(CN)_6]^{3-}$	$\overset{*}{C}N^-$	40,000
$[Co(H_2O)_6]^{2+}$	$H_2\overset{*}{O}$	<1	$[Cr(CN)_6]^{4-}$	$\overset{*}{C}N^-$	<0.3
$[Co(NH_3)_5H_2O]^{3+}$	$H_2\overset{*}{O}$	2000	$[Fe(CN)_6]^{4-}$	$\overset{*}{C}N^-$	>5000
$[Cr(H_2O)_6]^{2+}$	$H_2\overset{*}{O}$	<1	$[Fe(CN)_6]^{3-}$	$\overset{*}{C}N^-$	<7000
$[Cr(H_2O)_6]^{3+}$	$H_2\overset{*}{O}$	2500	$[Mn(CN)_6]^{3-}$	$\overset{*}{C}N^-$	50
$[Fe(H_2O)_6]^{3+}$	$H_2\overset{*}{O}$	<2	$[Mn(CN)_6]^{4-}$	$\overset{*}{C}N^-$	<3
$[Co(CN)_6]^{3-}$	$\overset{*}{C}N^-$	<12,000	$[Ni(CN)_4]^{2-}$	$\overset{*}{C}N^-$	<0.3

(a) *Which electron configurations of the central **metal ion** are associated with inertness and lability of the complexes with respect to (i) **aquation** and (ii) cyanide exchange?*

(b) *Can any electronic feature of these ions be **correlated** with the inertness of their complexes?*

29. *The following Co(III) complexes show first order rate constants (25°C) for aquation which differ by a factor of 10^4. Suggest an explanation.*

$[Co(NH_3)_5Cl]^{2+}$	$k_1 \simeq 2 \times 10^{-6}\ s^{-1}$
trans-$[Co(NH_3)_4Cl_2]^+$	$k_1 \simeq 2 \times 10^{-2}\ s^{-1}$

30. *Substitution reactions of $[Cr(CO)_6]$ are very slow, consistent with a low-spin d^6 complex. But the isoelectronic complex $[V(CO)_5NO]$ is very reactive.—comment.*

[**Hint :** The nitrosyl ligand is a very good π-acceptor. It removes electron density from the t_{2g} metal orbital, thereby reducing the extent of backbonding to a **CO** group in trans position. This CO group dissociates much more readily than the other CO groups. Any associative path for substitution in $[Cr(CO)_6]$ would involve a 7-coordinate activated complex with **20** valence electrons on the chromium. Hence the process would be slow. In case of $V(CO)_5NO$, an electron pair may be transferred to the NO ligand, thereby avoiding the 20-*e* activated complex.]

31. *Electron transfer between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ is much faster than between $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$.*

[Discussion : Both are outer-sphere processes. While the iron complexes are both low-spin, the Co(II) complex is high-spin and the Co(III) complex is low-spin.

The Fe—C distances are nearly same in the ground states, 192-195 pm. The Co^{II}—N distance is 211 pm while the Co^{III}—N distance is 196 pm. Activation energy required to equalize distances in the transition state will be high.]

32. *What would be the d-orbital splitting pattern of the metal ion in $[NiCl_4]^{2-}$? State the effect on d-orbital splitting of Cl^- ions are completely replaced by CN^- ions? Discuss the magnetic properties of the above two complexes.*

CHAPTER TWENTYEIGHT

THE TRANSITION ELEMENTS (3*d*)

Sc—Cu

OBJECTIVES

- **28.1** Introduction to transition elements
  - Electron configuration [28.1.1]
  - General periodic trend [28.1.2]
  - Oxidation states [28.1.3]
  - Chemical properties [28.1.4]
- **28.2** Scandium
- **28.3** Titanium
- **28.4** Vanadium
- **28.5** Chromium
- **28.6** Manganese
- **28.7** Iron
- **28.8** Cobalt
- **28.9** Nickel
- **28.10** Copper

28

THE TRANSITION ELEMENTS

28.1 INTRODUCTION : THE *d*-BLOCK ELEMENTS

The *d*-block elements in the periodic table correspond to filling of the 3*d*, 4*d* and 5*d* atomic orbitals. The elements involving entry of electrons into 4*f* and 5*f* atomic orbitals are placed separately in the *f*-block. The major differences in properties of the *d*-block elements from the *s*- and *p*-block elements arise mainly from

(i) the poorer penetration of $(n-1)d$ orbitals compared to that of *ns* or *np* orbitals into the inner electron core;

(ii) the highly directional character of the *d*-orbitals; and

(iii) the pronounced effect of ionic charge as well as effective nuclear charge on the radial distribution of the *d*-orbitals.

In elements of Gr II (Ca, Sr, Ba), the *d*-orbitals remain essentially diffuse and have little chemical significance. Similarly, among the first members in each *d*-series (e.g., Sc in the 3*d* series), the $(n-1)d$- orbital is energetically very close to the *ns* orbital and the only common oxidation state of these elements is +3, the sum of $(n-1)d$ and *ns* electrons. As one proceeds along any *d*-series, the effect of increasing nuclear charge and poor screening provided by successive *d*-electrons gradually results in stronger binding of the *d*-electrons and towards the end of each series, the *d*-electrons become tightly bound to the core. Thus, the last elements in the *d*-block, Zn, Cd and Hg have no stable oxidation state involving ionization of these *d*-core. Thus, the title "transition element" to the *d*-block elements appears to coincide with a steady transition of the $(n-1)$ *d*-orbitals from diffuse excited orbitals through valence orbitals to core orbitals along each transition series.

Formally, the transition elements should contain an incomplete *d*-shell in the ground states of their atoms or in any of their principal oxidation states. However, the criterion of incomplete *d*-levels in their valence state are not satisfied in the first (d^1) and last members ($d^{10}s^2$) of any series. Hence these are often excluded from the category of transition elements, e.g., Sc and Zn in the first transition series.

As such, copper is treated as a transition element because Cu(II) has an incomplete 3*d* configuration, but zinc is excluded since its only stable oxidation state has the complete $3d^{10}$ configuration. Scandium ($3d^14s^2$) is included by definition, but only the +3 oxidation state is well-established for this element. Its chemistry resembles that of aluminium rather than those of other transition elements.

The transition elements are all hard metals with high melting and boiling points—a consequence of strong metallic bonding by the *d*- and *s*- electrons. They also form alloys with one another and with other elements.

We have already discussed one common distinctive feature of these transition elements, namely, their pronounced tendency to form coordination compounds. We have also discussed the magnetic properties and electronic spectra of such compounds which leads us to conclude that all transition metals should form at least some compounds with unpaired electrons which will be paramagnetic. Similarly, we expect these elements to produce a number of coloured compounds - either from *d*-*d* transition or due to charge-transfer bands in the visible region. Involvement of the *d*-electrons to different extent also suggests variable valence for the transition elements.

Before we undertake any discussion on the chemistry of these transition elements, it will be worthwhile to recapitulate the electron configurations of the atoms and ions of these elements.

28.1.1 Electron configurations of *d*-block elements

We have seen (Ch. 3) how the penetration of inner electron core influences the radial distribution functions of various orbitals. It may be recalled that the extent of penetration decreases as

$$s > p > d > f$$

In multi-electron atoms, the energy-levels of different individual orbitals change in a complicated manner depending upon the population of other levels, the qualitative nature of which is shown in Fig. 28.1.

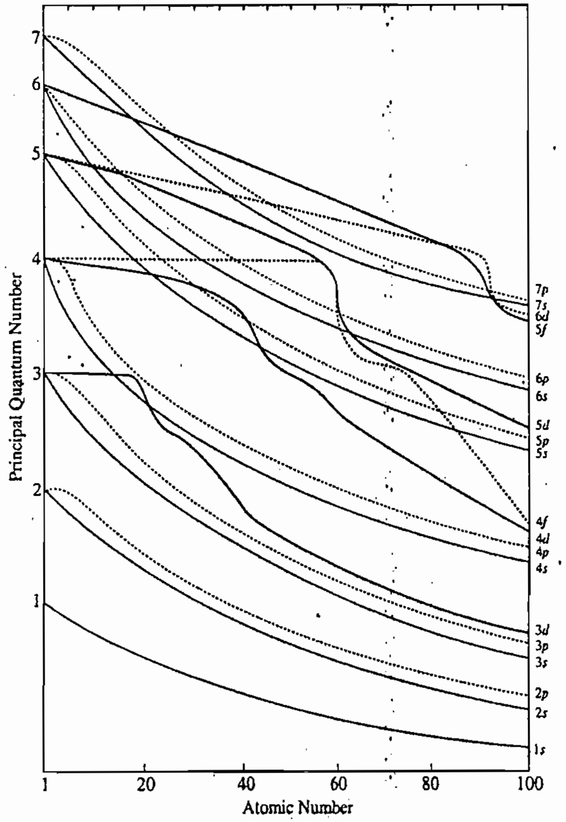


Fig. 28.1

Qualitative nature of the variation of energies of individual atomic orbitals with atomic number in neutral atoms.

In the hydrogen atom all the subshells in a principal shell (e.g., 3*s*, 3*p*, 3*d*) have the same energy. As we pass on to more complex atoms, the *ns* orbital experiences the highest increase in effective nuclear charge (since they are most penetrating) and drops in energy more than the *np* or *nd* atomic orbital. In the H atom, the 3*d* orbital is lower in energy than the 4*s* orbital (higher principal quantum number). As we proceed to more complicated atoms, greater penetration of the 4*s* orbital into the inner electron core results in a higher effective nuclear charge on a 4*s* electron than on a 3*d* electron. The radial distribution functions for the two orbitals are qualitatively shown in Fig. 28.2.

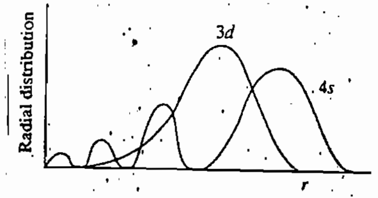


Fig. 28.2

Radial distributions of 3*d* and 4*s* atomic orbitals in H-atom (qualitative).

The last electrons in K and Ca thus enter the 4*s* orbital after argon core. But since the 4*s* and 3*d* orbitals are very close to each other in energy, the last electron in Sc marks the beginning of occupancy of the 3*d* orbital, having the ground state electron configuration $3d^1 4s^2$. The relative ordering of the energy levels in scandium is however changed, the binding energy of the 3*d* electron having risen sharply. The removal of this 3*d* electron now requires more energy than the removal of one of the 4*s* electrons. Hence the ground state configuration of the Sc^+ ion is $[Ar]3d^1 4s^1$ rather than $[Ar]3d^0 4s^2$.

In fact, as mentioned in the legend for Fig. 28.1, the variation of energy level for different orbitals shown refers to *individual* atomic orbitals and do not fully take into account interelectron repulsion factors for various overall configurations. For most of the *d*-block elements, such repulsions make the ground state configuration $(n-1)d^n ns^2$, that is the *ns* orbital remains fully occupied despite individual $(n-1)d$ orbitals being of lower energy. The ultimate configuration thus corresponds to a lower total energy for the whole configuration. In individual cases, formation of a half-filled (d^5) or filled (d^{10}) subshell by transfer of an *s* electron leads to extra stabilization by way of exchange energy (chapter 3); this is reflected in the electron configurations of $Cr(3d^5 4s^1)$ and $Cu(3d^{10} 4s^1)$ in the first transition series and in Pd in the second transition series. In other cases, the overall balance of orbital energy appear to favour the ground state configurations adopted.

The filling of the 3*d* orbital continues upto $Zn(3d^{10} 4s^2)$. After this, the next six elements have their last electron in the 4*p* level which is now lowest available in energy; these elements belong to the *p*-block.

Q. 28.1 *After the 4s orbital is filled, electrons enter the 3d level, rather than the 4p orbital which, like the 4s, has greater penetration into the core than the 3d orbital. Comment.*

Hint : After argon, the 4*s* orbital is filled in K and Ca while the nuclear charge increases by two units. Now, the 3*d* orbitals appreciably penetrate the electron density in the 4*s* orbitals and hence are not fully screened by the 4*s* electrons from the enhanced nuclear charge. Consequently their energy drops well below the 4*p* orbitals. As electrons start entering the 3*d* orbitals, the 3*d* electrons exert more screening on the 4*p*-orbitals than on the remaining 3*d* orbitals. Hence 3*d* remains the lowest available orbital.

After Krypton ($[Ar]\ 3d^{10} 4s^2 4p^6$), the 4*d* orbital stands again higher in energy compared to the 5*s* and 5*p*. The next two electrons thus enter the 5*s* orbital (Rb and Sr). Again, poor shielding of the 4*d* orbitals by the 5*s* electrons results in a steep drop in energy of the 4*d* orbitals which now become the lowest available orbital. The second transition series contains the elements $Y([Kr]4d^1 5s^2)$ to $Ag([Kr]4d^{10} 5s^1)$. This is followed by Cd and the six *p*-block elements ending at the next noble gas Xe ($Z = 54$).

A look at Fig. 28.1 around $Z = 50$ reveals the complicated nature in which the individual atomic orbitals change in energy with increasing nuclear charge. The 4*f* orbital runs nearly parallel to the atomic number-axis, showing that it gains little stability owing to poor penetration into the xenon core. However, as two electrons enter the 6*s* shell, into which the 4*f* penetrates appreciably, the enhanced nuclear charge sharply lowers the energy of the 4*f* orbital. The merger of the lines for 5*d* and 4*f* orbitals in this region of atomic number is significant. In fact in Ba ($Z = 56$), the 6*s*, 5*d* and 4*f* orbitals have nearly equal energy. In lanthanum ($Z = 57$), the last electron enters a 5*d* orbital, but cerium (Z = 58) has the configuration $4f^26s^2$. The filling of the 4*f* - orbital continues upto ytterbium (Z = 70). The filling of the 5*d* orbitals is resumed in Lutetium $\left([Xe]4f^{14}5d^16s^2\right)$. However, for chemical similarity the elements lanthanum to lutetium are conveniently classed as lanthanides. The third transition series then practically contains the elements hafnium, $[Xe]4f^{14}5d^26s^2$ to gold, $[Xe]4f^{14}5d^{10}6s^1$.

An almost similar sequence is repeated after the next noble gas radon (Z = 86) involving the 5*f*, 6*d* and 7*s* orbitals. The actinide series, characterized by filling of the 5*f* shell, contains all radioactive elements; among them the elements from neptunium onwards are all artificially prepared. After lawrencium, the 6*d*-series of transition elements are being progressively synthesized.

Complications arising from electron-electron repulsions are much relieved in the positive ions formed by the *d*-block elements, all of which have d^n configurations. As the energies of $(n-1)d$ orbitals fall well below that of the *ns* orbitals, the orbital energies provide a better guide for the total energy of any configuration. Similarly, all *f*-block elements form ions with f^n configurations. Certain useful generalizations regarding the energies of various orbitals may be arrived at as follows :

(i) Across each transition series, binding energies of *ns*, *np* and $(n-1)d$-electrons increase with increasing nuclear charge; exceptions occur only in case of *d*-electrons immediately following half-filled configurations. This is expected in view of strong repulsion between two *d*-electrons in the same orbitals which are highly directional in nature.

(ii) The electron binding energy increases most rapidly for $(n-1)d$-electrons, followed by *ns* and then by *np* electrons.

(iii) As the effective nuclear charge increases, $(n-1)d$-electrons become more stabilized in comparison to *ns* electrons. With increase in nuclear charge, ionization energy increases most in case of an element in the first transition series; the increase becomes less marked in the second and third transition series.

(iv) Since the *d*-orbitals are very susceptible to contraction with the charge on the atom or ion, towards the end of each transition series and with high charge, the $(n-1)$ *d*-orbitals may contract enough to become a part of the core. For the same reason, the effective overlap of *d*-orbitals with surrounding atoms is largely influenced by charge as well as atomic number.

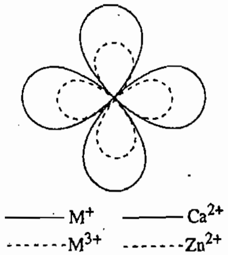


Fig. 28.3
Schematic representation of the contraction of 3*d* orbitals with charge and atomic number.

We shall apply these generalizations in our discussion on the general periodic trend and oxidation states of the transition elements.

28.1.2 General periodic trend

In our discussion on the general periodic trend among the *p*-block elements (Chapter 20), we found that the elements in any group form three distinct types — the first element, the middle elements and the last element. Among the *d*-block elements the vertical relation among the three elements in each group is not so prominent as in the *p*-block. We recall that poor shielding provided by the 4*f*-electrons causes lanthanide contraction among the elements from lanthanum to lutetium, which are interposed between the 4*d* and 5*d* series of transition elements. In fact, the expected increase in size between a second transition element ($4d^n$) and the third transition element ($5d^n$) in any vertical group is nearly cancelled by the effect of lanthanide contraction. As a result, the second and third members in any vertical group in the *d*-block have almost identical radii, as shown in Table 28.1.

TABLE 28.1
Atomic and ionic radii of a few transition elements

atomic radii, pm			ionic radii, pm
Ti : 132	V : 122	Cr : 117	Ti^{4+} : 68
Zr : 145	Nb : 134	Mo : 129	Zr^{4+} : 74
Hf : 144	Ta : 134	W : 130	Hf^{4+} : 75

Such similarity in size results in many similar characteristics among the second and third vertical members in a block, like ionization potential, solvation energies, redox behaviour, lattice energies etc. and the overall chemistry as well. Thus each group in the *d*-block is essentially divided into two parts (i) the first member ($3d^n$) with its individual chemistry and (ii) the second and third elements having nearly similar chemistry. The main difference between the first and the heavier members in a group in the *d*-block are those of size and the relative stabilities of different oxidation states. Quite expectedly, the heavier elements have a tendency to attain higher coordination number and to show greater stability in higher oxidation states. This is readily shown by the strongly oxidizing nature of chromium(VI) while molybdenum(VI) and tungsten(VI) are quite stable. In addition, all three members in a group show certain common general features; for example, they have the same range of oxidation states, with varying stability though. Among the earlier elements (up to d^5), all the *d* and *s*-electrons take part in valence, but once the d^5 configuration is crossed, the highest oxidation state is often less than the sum of *d* and *s* electrons. Except for Os(VIII) and Ru(VIII), this is generally true for iron, cobalt, nickel and copper groups. Where the group oxidation state is attained, the properties of the elements involving all valence electrons show certain similarities with the main group elements having the same number of valence electrons. Thus sulphates $\left(SO_4^{2-}\right)$ and chromates $\left(CrO_4^{2-}\right)$ are isostructural. But molybdenum and tungsten tend to attain higher coordination number with oxygen, as does tellurium.

Towards the right of the *d*-block, the similarity in chemistry between the two heavier elements in a group gradually disappears. This is because the simple size relationship is overruled : more intricate penetration effects which govern ionization energies and different crystal field stabilizations gained through the strongly directing *d*-orbitals and their varying extension in space seem to control the individual chemical behaviour in each metal. Thus in titanium and vanadium groups, the last two elements are quite similar in property; but the similarity gradually disappears as we proceed to the platinum metals, and in the copper group, silver and gold have more dissimilarities than similarities. In the zinc group, the trend is rather reversed : zinc and cadmium have many properties in common while mercury is distinctly different. The pattern is actually characteristic of the p-block elements where the last member in a group differs appreciably from the rest. Some physical properties and related data for the metals of the first transition series are given in Table 28.2.

TABLE 28.2

Some physical properties of the elements Sc—Cu

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configuration (ground state)	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$
Radius, pm (12-coordinate metallic)	164	147	135	129	137	126	125	125	128
ΔH atomization, kJ mol^{-1}	376	473	515	397	281	416	425	430	339
Ionization energy, kJ mol^{-1}; 1 st	631	656	650	653	717	762	758	736	745
2 nd	1235	1309	1414	1592	1509	1561	1644	1752	1958
3 rd	2393	2657	2832	2990	3260	2962	3243	3402	3556
$E°$, volt; M^{2+}–M	—	—	−1.18	−0.90	−1.18	−0.44	−0.28	−0.25	+0.34
M^{3+}–M^{2+}	—	—	−0.26	−0.41	+1.51	+0.77	+1.93	—	—
Density (g cm^{-3})	3.0	4.5	6.11	7.14	7.43	7.87	8.90	8.91	8.95
M.P. (°C)	1539	1667	1915	1900	1244	1535	1495	1455	1083
B.P. (°C)	2748	3285	3350	2690	2060	2750	3100	2920	2570

Metallic structure

The transition elements are all typical metals with high tensile strength, ductility, malleability, thermal and electrical conductivity and good metallic lustre. Except manganese, which has an atypical metal structure, the metals crystallize in cubic close-packed (ccp), hexagonal close packed (hcp) and body-centered cubic (bcc) structures (Table 28.3).

TABLE 28.3

Common structures of transition elements at ordinary temperatures

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
hcp	hcp	bcc	bcc	*	bcc	ccp	ccp	ccp
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp

* atypical metal structure containing atoms having 12, 13 or 16 nearest neighbours. At high temperatures, bcc and ccp structures are adopted.

Density

Consequent to their effective close-packed structures, the elements have high densities : except Sc and Ti, all the $3d$ transition metals have densities above 6 g cm^{-3} (Table 28.2). Elements in the second and third transition series have still higher densities - osmium (22.57 g cm^{-3}) and iridium (22.61 g cm^{-3}) topping the list among all elements.

Melting and Boiling points

The enthalpies of sublimation (also atomization, since the metals sublime as isolated atoms) and the melting and boiling points of the transition elements are also high. (Fig. 28.4 and 28.5; Table 28.2). Both of them rise in the first half of each transition series, and then fall in the second half. This observation suggests that interatomic interaction increases with the number of unpaired electrons and becomes maximum (with the exception of Mn and Tc) when each of the five d-orbitals is singly occupied. In an oversimplified band model, this corresponds to occupation of the band of bonding d-orbitals. Beyond the middle element, electrons progressively occupy the antibonding orbitals and weaken the bonding. The actual situation may be more complicated as shown by the complex magnetic behaviour of iron and other metals.

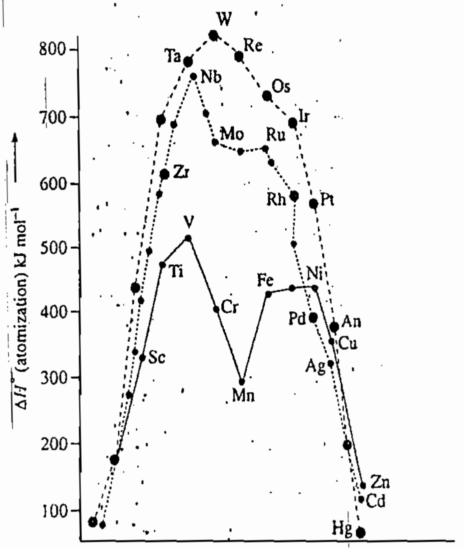


Fig. 28.4

Enthalpy of sublimation of transition metals.

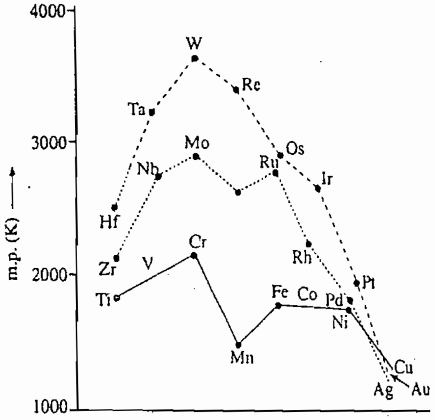


Fig. 28.5

Melting points of transition metals.

Size effects

As explained earlier, poor shielding by successive d-electrons results in a gradual decrease of atomic and ionic radii along each transition series. The last member in each series (Cu, Ag, Au), however shows a slightly upward trend. The atoms are smaller than elements in groups 1 and 2 in the same horizontal period since electrons are now added to the penultimate shell. The overall decrease in size along any transition series is often small between successive members giving rise to similarities in properties, for example in the chemistry of V^{3+} and Ti^{3+}. Iron, cobalt and nickel form a triad which have considerable similarity in the sizes of their +2 ions and hence in properties depending primarily on charge/size ratio, e.g., solubilities of salts and acidity of $[M(H_2O)_6]^{2+}$.

Alloy formation

Owing to similarity in atomic sizes and crystal types, one transition metal can readily replace another metal forming solid solutions and good alloys with improved qualities. Chromium, vanadium, molybdenum, tungsten and manganese are largely used in the production of numerous alloys including alloy steels and stainless steel.

Ionization energy

The first ionization energies of the transition elements (Fig. 28.6) are higher than the ionization energies of alkali and alkaline earth metals in the same row. In each series, the ionization energy shows an overall rising trend, but the variation is not smooth. Also, the total increase in ionization energy in any series is much less in comparison to that found among any period of the typical elements. The ionization energies vary in an irregular manner between the first and second transition series, but the elements for the third transition series have distinctly higher ionization energy owing to poor screening effect of the 4*f* electrons. In the first transition series, successive ionization energy values nearly double themselves at each step (Table 28.2).

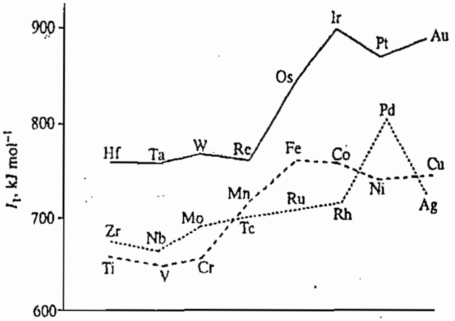


Fig. 28.6
Variation of first ionization energies among the transition elements.

The irregular pattern in the first ionization energy values in the first and second transition series arises mainly because of different stabilities associated with various electron configuration and the consequent variety in the ionization process. For example, relative energies of various configuration suggest the first ionization energy in vanadium to involve the process

$$V\ (3d^34s^2) \longrightarrow V^+\ (3d^4) \text{ and not } V^+\ (3d^34s^1).$$

Exchange energy appears to play an important role in stabilizing the electron configurations.

Thermodynamic stability of the transition metals in various oxidation states may sometimes be correlated directly with ionization energy values. Thus, for the elements Ni and Pt, the first four ionization energy values (MJ mol^{-1}) are as follows :

	$I_1 + I_2$	$I_3 + I_4$	**Total**	
Ni	2.49	8.80	11.29	MJ mol^{-1}
Pt	2.66	6.70	9.36	MJ mol^{-1}

The figures suggest that Ni(II) should be termodynamically more stable than Pt(II) while Pt(IV) will be thermodynamically more stable than Ni(IV). However, the actual thermodynamic stability of any oxidation state depends on several other factors like enthalpy of atomisation and hydration (solvation), crystal-field stabilization etc. We shall discuss oxidation states separately in the next section.

Interstitial compound formation

The transition metals can also take up small atoms like H, C and N in the vacant spaces in their lattice and form bonds with them. Very hard interstitial compounds are sometimes obtained in this manner. Steel and cast iron owe their hardness to formation of such interstitial carbides.

The magnetic behaviour of transition elements and their ions have been discussed in Chapter 27.

Catalytic properties

Many transition metal and their compounds have long been known for their catalytic action on a number of chemical reactions. Some of them are now finding extensive application in industry. A few examples are mentioned below :

$TiCl_3$: Ziegler-Natta catalyst in production of polythene.
V_2O_5 : Manufacture of H_2SO_4 : conversion of SO_2 to SO_3.
Fe : Haber-Bosch process for NH_3.

$FeCl_3$: CCl_4 from CS_2 and Cl_2.
Pd : Hydrogenation
$PdCl_2$: Wacker process : $C_2H_4 + H_2O + PdCl_2 \longrightarrow CH_3CHO + 2HCl + Pd$.
Pt : Conversion of $SO_2 \longrightarrow SO_3$ (now replaced by V_2O_5).
Pt is now being increasingly used to clean automobile exhausts.
Pt-Rh : Oxidation of NH_3 in manufacture of HNO_3.
Pt-PtO : Adam's catalyst, used in reduction.
Cu : Manufacture of $(CH_3)_2SiCl_2$ as a step to produce silicones.
Cu-V : Oxidation of cyclohexanol/cyclohexanone to give adipic acid (starting material for nylon).
Ni : Numerous reduction processes, hydrogenation of oils.

More examples will be found in individual contexts. It appears that the catalytic activity is often associated with the ability of transition metals to attain variable oxidation states and various coordination modes in forming an intermediate having low energy of activation. In many cases, the metals appear to offer suitable reaction sites at their surface.

The catalytic role of transition metals in traces has been established in several enzyme actions - the metal ions are said to be *cofactors* of these *metalloenzymes* (see later).

Colour

In the last chapter we have seen how the presence of incomplete *d*-level in transition metal ions may give rise to absorption of radiation in the visible range and hence different colours of the compounds. Colour may also develop due to charge transfer in metals with high positive oxidation state although such states may correspond to d^0 configuration of the metal, for example $CrO_4^=$ and MnO_4^- ions. Colours of some hydrated transition metal ions are given in Table 28.4.

TABLE 28.4

Colours of hydrated metal ions of the first transition series

Oxidation state of hydrated ions	**Colour**
Ti(III)	Purple
V(III)	Green
V(II), Cr(III)	Violet
Mn(III)	Violet
Fe(III)	Yellow
Mn(II)	Pink (pale)
Fe(II)	Green (pale)
Co(II)	Pink (pale)
Ni(II)	Green
Cu(II)	Blue

28.1.3 Oxidation states

In addition to the *s*-electrons, some or all the *d*-electrons always take part in the valence of transition elements. This gives rise to several possible oxidation states of the elements. The main positive oxidation states are shown in Table 28.5. The highest oxidation state shown by any transition metal is eight. The stability of a given oxidation state depends upon several factors like the nature of the element with which the transition metal is combined, solvent, nature of ligand etc. These are separately discussed below. The highest oxidation states are naturally found in combination with the most electronegative elements oxygen and fluorine.

TABLE 28.5

Main oxidation states* of transition elements

Element	Oxidation state (positive)	Element	Oxidation state (positive)
Sc	3	Y, La	3
Ti	(2) 3 4	Zr, Hf	(3) 4
V	2 3 4 5	Nb, Ta	(2 3 4) 5
Cr	2 3 (4)† (5)† 6	Mo	2 3 4 5 6
		W	2 (3) 4 5 6
Mn	2 (3) 4 (5)† (6)† 7	Tc	4 (5) 7
		Re	(1) (2) 3 4 5 (6) 7
Fe	2 3 (4) (5) (6)	Ru	2 3 4 (5) 6 (7) (8)
		Os	2 3 4 6 8
Co	2 3 (4) (5)	Rn	2 3 4 (5) (6)
		Ir	2 3 4 (5) (6)
Ni	2 (3) (4)	Pd	2 (3) 4 (6)
		Pt	2 (3) 4 (5) (6)
Cu	1 2 (3) 4	Ag	1 (2) (3) (4)
		Au	1 3 5

Besides those shown in the table, zero and other formally negative oxidation states are also known in certain complexes (see later). The following generalizations regarding the common oxidation states are useful :

(i) Scandium has the single common positive oxidation state III, corresponding to ionization of both the $3d$ and $4s$ electrons, which are similar in energy. After this, the most common oxidation state for the first transition series metals is +2, corresponding to ionization of the $4s$ electrons only. This shows that the $3d$ electrons are more stabilized after scandium. In line with this, oxidizing power increases in the series

$$\mathrm{Sc(III)} < \mathrm{Ti(IV)} < \mathrm{V(V)} < \mathrm{Cr(VI)} < \mathrm{Mn(VII)}.$$

Conversely, the oxidation state of +2 is strongly reducing for Ti, V, and Cr, but becomes fairly redox stable in the elements manganese onward.

---

[*] The most stable ones are shown in bold type. Unstable states are shown in parentheses.

[†] Indicates disproportionation.

(ii) In any period, the number of different oxidation states first increases, becomes maximum at the middle of the series and then again decreases. This is also consistent with the variation of binding of the d-electrons discussed earlier.

(iii) Within each group, higher oxidation states usually become more common with heavier elements (silver(I) is an exception). Thus iron shows the common oxidation states +2 and +3 while ruthenium and osmium readily form compounds in the +4, +6 and +8 oxidation states.

This is because the $4d$ and $5d$ orbitals become progressively more penetrating and the distinction between ns and $(n-1)d$ orbitals becomes smaller with increase in effective nuclear charge.

Q. 28.2 *Reactions of vanadium metal with fluorine, chlorine and bromine separately produce VF_5, VCl_4 and VBr_3 respectively. Comment.*

Hint : Vanadium (V) and vanadium (IV) are both oxidizing in nature. See under vanadium.

Energy considerations suggest that the compounds formed in oxidation states +2 and +3 are likely to show pronounced ionic character. With increasing charge on the metal ion, covalence should develop, as for example, in the following cases :

+2	+3	+4	+5
$TiCl_2$	$TiCl_3$	$TiCl_4$	
VCl_2	VCl_3	VCl_4	$VOCl_3$
solids, insoluble in benzene; weak acids.		liquids; soluble in benzene; strong acids.	

As shown above, there is also a corresponding increase in acidity with increase in oxidation state. The covalent halides are violently hydrolyzed by water and are also strong Lewis acids. The more ionic halides, weak Lewis acids, form aquo ions. The acidity of such ions again depend on the oxidation state, e.g., $[Fe(H_2O)_6]^{3+}$ is a stronger acid than $[Fe(H_2O)_6]^{2+}$.

The oxides also exhibit the same trend :

	Basic	Amphoteric		Acidic	
Oxidation states	II	III	IV	V	VI
	TiO	Ti_2O_3	TiO_2		
	VO	V_2O_3		V_2O_5	
	CrO	Cr_2O_3			CrO_3

Oxides of the metals from titanium to cobalt in their highest oxidation states form oxo-anion salts with alkalis : TiO_2 forms titanates (TiO_4^{4-}), V_2O_5 forms vanadates (VO_4^{3-}) and CrO_3 forms chromates (CrO_4^{2-}). On the other hand, the oxides of metals in their +2 oxidation state are only basic and dissolve in acids to form aquo ions.

The relative stability of different oxidation states of the transition metals may be obtained from the relevant electrode potential data. The use of such data in the form of Latimer diagram or Ebsworth diagram was illustrated for Mn, Fe, and Cu in section 9.3. Here we briefly repeat them in part :

TABLE 28.6

Standard reduction potential (aqueous) for a few transition metals in acid solution (Volt)

+7 +6 +5 +4 +3 +2 +1 +0

$$TiO^{2+} \xrightarrow{0{\cdot}1} \underbrace{Ti^{3+} \xrightarrow{-0{\cdot}37} Ti^{2+} \xrightarrow{-1{\cdot}63} Ti}_{-1{\cdot}21}$$

$$\underbrace{VO_2^+ \xrightarrow{1{\cdot}00} VO^{2+} \xrightarrow{0{\cdot}34} V^{3+}}_{0{\cdot}67} \xrightarrow{-0{\cdot}26} V^{2+} \xrightarrow{-1{\cdot}13} V$$

$$\underbrace{Cr_2O_7^{2-} \xrightarrow{0{\cdot}55} Cr^{V} \xrightarrow{1{\cdot}34} Cr^{IV} \xrightarrow{2{\cdot}10} Cr^{3+}}_{1{\cdot}38} \underbrace{\xrightarrow{-0{\cdot}42} Cr^{2+} \xrightarrow{-0{\cdot}90} Cr}_{-0{\cdot}74}$$

$$\underbrace{MnO_4^- \xrightarrow{0{\cdot}56} \overbrace{MnO_4^{2-} \xrightarrow{0{\cdot}27} MnO_4^{3-} \xrightarrow{4{\cdot}27} MnO_2}^{2{\cdot}27} \underbrace{\xrightarrow{0{\cdot}95} Mn^{3+} \xrightarrow{1{\cdot}5} Mn^{2+}}_{1{\cdot}23}}_{1{\cdot}51} \xrightarrow{-1{\cdot}18} Mn$$

$$\underbrace{Fe^{3+} \xrightarrow{0{\cdot}77} Fe^{2+} \xrightarrow{-0{\cdot}44} Fe}_{-0{\cdot}04}$$

$$CoO_2 \xrightarrow{1{\cdot}42} Co^{3+} \xrightarrow{1{\cdot}92} Co^{2+} \xrightarrow{-0{\cdot}28} Co$$

$$NiO_2 \xrightarrow{1{\cdot}59} Ni^{2+} \xrightarrow{-0{\cdot}26} Ni$$

$$\underbrace{Cu^{2+} \xrightarrow{0{\cdot}16} Cu^+ \xrightarrow{0{\cdot}52} Cu}_{0{\cdot}34}$$

Some of these values are plotted in Fig. 28.7; individual diagrams are given with respective metals.

[Sec. 28.1.3
*Redox
Potentials*]

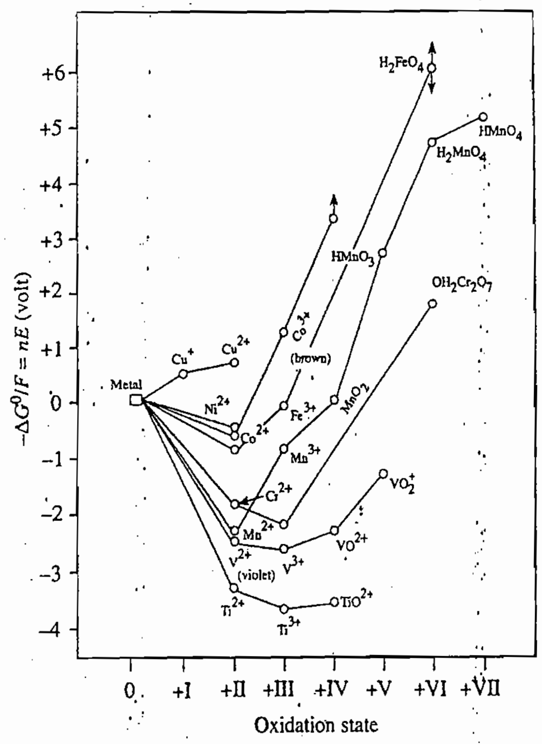


Fig. 28.7

Oxidation state diagram for some metals in the 1st transition series $(a_{H^+} = 1)$.

E^0 values corresponding to same pairs of oxidation states of different metals change in an apparently irregular manner along the series, e.g., E^0(V) for M^{2+} (aq) - M are :

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
−1·63	−1·13	−0·90	−1·18	−0·44	−0·28	−0·26	+0·34

We have seen (Ch. 9) how the electrode potential can be related to the enthalpies of sublimation, ionization and hydration of the species involved. On that basis, it can be said that irregular variation of ionization energies (in this case $I_1 + I_2$) and also the sublimation energies (e.g., 515 kJ mol^{-1} for V and 281 kJ mol^{-1} for Mn) would be mainly responsible for such observed variations in E^0.

It is possible to make a few comments on the redox potential data :

(i) The plots of nE^0 for all elements from Ti to Co show a sharp downward slope at the beginning, reaching minima at the +2 and +3 oxidation states. Hence higher and lower oxidation states are expected to revert to these oxidation states on reaction.

(ii) The +1 oxidation state is not common except copper. Cu is also susceptible to disproportionation. (The +1 state is however common for silver in the same group as copper. It appears that in copper, the difference in hydration energy between Cu^+ and Cu^{2+} becomes dominant over I_2 of copper; in silver, the reverse holds. This has been discussed later).

(iii) The potentials for higher oxidation states rise steadily after the minima at +2 or +3; the slope also increases from Ti to Co showing that the higher oxidation states become increasingly unfavoured. The metals become gradually more strongly oxidizing in these high oxidation states : permanganate is a stronger oxidizing agent than chromate while chromates are stronger oxidizing agents than vanadates. Permanganate (Mn^{VII}), ferrate (Fe^{VI}) and cobaltic (Co''') — all evolve oxygen from aqueous solutions; permanganate does so only slowly so that it can be used as a titrimetric reagent in aqueous medium.

(iv) The M^{2+} - M potentials suggest that all the metals except copper would liberate hydrogen from acids. Copper does not dissolve in nonoxidizing acids, but will dissolve if Cu(I) is stabilized through complex formation. In presence of thiourea, copper dissolves in 1 *N* HCl solution evolving hydrogen.

(v) Ti^{2+}, V^{2+}, Cr^{2+} are all expected to liberate hydrogen from acidic aqueous solutions. Reducing power decreases from left to right in the transition series. In volumetric analysis, Fe^{2+} is a common reducing agent; Cr^{2+}, V^{2+} and Ti^{3+} are stronger reducing agents. The Co^{3+} - Co^{2+} couple may also be forced to liberate hydrogen from aqueous solutions in presence of cyanides which strongly complex the Co(III).

The stabilization of unusual oxidation states through complexation is discussed below.

Stabilization of oxidation states

Stability is a relative term, meaningful only when referred to a given set of conditions or environment or both. Thus, compounds containing Cu(I) are thermally stable; but in aqueous solution, Cu^+ readily disproportionates into Cu^0 and Cu(II) (see section 9.3.3). In presence of cyanide ion, however, Cu(I) can be stabilized in aqueous solution.

Again, the stability mentioned above means that the species is thermodynamically more stable. Redox data informs us only about the thermodynamic feasibility of a process which may or may not actually take place at an appreciable rate. Thus the permanganate ion is expected to oxidize water in acid medium, but the reaction is so slow that it may be neglected in volumetric analysis. We shall briefly discuss the influence of acidity and nature of ligands on the thermodynamic stability of oxidation states.

Since acidity of a metal ion increases with the increase of oxidation state, high oxidation states are favoured by alkaline media. An aquo ion may be considered to form an equilibrium of the following type :

$$[M(H_2O)_6]^{n+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [M(OH)_6]^{(6-n)-}$$

Removal of an electron, (i.e., oxidation) is now easier from the hydroxo species which is negatively charged than from the aquo ion which is positively charged. This explains why many transition metal hydroxides are readily oxidized by atmospheric oxygen. Oxo species like chromate(VI), manganate(VI) and ferrate(VI) are all formed by oxidative fusion of the lower valent compounds in alkaline medium. Anodic oxidation in alkaline solution is also used in a number of cases, for example in the preparation of manganates, permanganates and ferrates.

The hydroxides of transition metals in higher oxidation state are often less soluble than the corresponding hydroxides in lower oxidation states. Thus, solubility product of $Mn(OH)_2 \simeq 10^{-13}$ and that of $Mn(OH)_3 \simeq 10^{-36}$. Hence in alkaline medium, Mn^{2+} is much more incompletely precipitated than Mn^{3+} and the potential for Mn(III) - Mn(II) couple is largely depressed, showing stabilization of Mn(III) :

$$Mn^{3+} + e \rightleftharpoons Mn^{2+}(aq) \quad ; \quad E^0 = +1{\cdot}51 \text{ V}$$

$$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^- \quad E = +0{\cdot}15 \text{ V}.$$

Complex formation by a ligand may have pronounced effect on the stability of a particular oxidation state relative to that in, say, water. Here again, problem arises to separate kinetic and equilibrium stabilities. Kinetic stabilization of a particular

oxidation state may be attained through for example, by (a) use of bulky ligands to prevent reactions by steric hindrance and (b) insolubility of the complex. As stated earlier, we shall try to frame some generalizations regarding the thermodynamic stability of an oxidation state.

It is easy to guess that low oxidation states will be stabilized with ligands having reducing power or in reducing solvents. The ligand field stabilization gained through the elctron configurations in different oxidation states and the ease of delocalization of charge with π-acceptor ligands also contribute significantly in the stabilization of different oxidation states. Several factors, many of which are intricately interconnected, are thus involved in the process and a single generalization is difficult to arrive at. We shall first consider a few common examples.

High oxidation states

High oxidation states are mostly stabilized in combination with the following types of ligands :

(i) Small, hard ligands with strong σ-donor properties like fluoride and oxide. While fluorine often brings out the maximum covalency of an element, the oxide ion is known to stabilize the highest oxidation states of V, Cr and Mn (VO_4^{3-}, CrO_4^{2-} and MnO_4^-). Iron, cobalt (in oxidation states above III) and nickel, copper (in oxidation states above II) are also stabilized in compounds containing oxygen or fluorine (see individual elements).

(ii) Anions containing a central atom in a high oxidation state are also known to stabilize high oxidation states of some transition metals. The following examples are noteworthy :

$$M_7^I[Ag^{III}(IO_6)_2], xH_2O \qquad M_9^I[Ag^{III}(TeO_6)_2], xH_2O$$

$$M_9^I[Cu^{III}(TeO_6)_2], xH_2O \qquad Na[Ni^{IV}(IO_6)], xH_2O$$

The stabilization by anions may be looked upon as an entropy effect. As a complex cation gets attached to an anion, the water molecules held around the cation are released in solution, increasing the total entropy of the system. Large anions with high charge are most efficient in this respect.

(iii) Certain organic ligands are also known to stabilize high oxidation states. Such ligands must be themselves stable towards oxidation by oxidizing agents used in the preparation or by the metal in its high oxidation state.

$[Ag^{II}(pic)_2]$ (pic^- = pyridine – 2-carboxylate); $[Ag^{II}(py)_4]^+$; $[Ag^{II}(dipy)_2]^{2+}$; $[Ag^{II}(o\text{-phen})_2]^{2+}$ are some common examples of this type.

The stabilization of a higher oxidation state in a redox couple is marked by a decrease in the reduction potential :

TABLE 28.7

Redox potentials for some transition metal complexes.

Couple	E^o (Volt)
$[Fe(H_2O)_6]^{3+} + e \rightleftharpoons [Fe(H_2O)_6]^{2+}$	0·77
$[FeF_6]^{3-} + e \rightleftharpoons [FeF_6]^{4-}$	0·40
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	0·36
$[Fe(oxinate)_3] + e \rightleftharpoons [Fe(oxinate)_3]^-$	−0·20

Couple	E^o (Volt)
$[Mn(H_2O)_6]^{3+} + e \rightleftharpoons [Mn(H_2O)_6]^{2+}$	1·50
$[Mn(CN)_6]^{3-} + e \rightleftharpoons [Mn(CN)_6]^{4-}$	0·22
$[Co(H_2O)_6]^{3+} + e \rightleftharpoons [Co(H_2O)_6]^{2+}$	1·84
$[Co(dipy)_3]^{3+} + e \rightleftharpoons [Co(dipy)_3]^{2+}$	0·31
$[Co(en)_3]^{3+} + e \rightleftharpoons [Co(en)_3]^{2+}$	0·18
$[Co(CN)_6]^{3-} + e \rightleftharpoons [Co(CN)_5(H_2O)]^{3-} + CN^-$	−0·8

The electron configurations and spin states of an ion play vital roles in the stabilization of oxidation states. The case of Co(III) stabilized by ligands like ethylenediamine may be taken as an illustration. If we recall the *d*-orbital splitting diagram and the discussion on CFSE made in chapter 27, we may arrive at the following computations for the CFSE for the two oxidation states (neglecting pairing energies which will be essentially constant for both ligands).

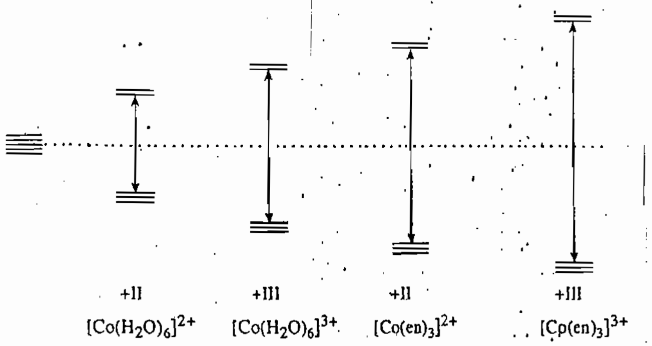


Fig. 28.8

Relative crystal field splitting for Co(II) and Co(III); not to scale.

$[Co(H_2O)_6]^{2+}$ and $[Co(en)_3]^{2+}$: $t_{2g}^5 e_g^2$; CFSE relative to spherical field = $-8Dq$

$[Co(H_2O)_6]^{3+}$ and $[Co(en)_3]^{3+}$: t_{2g}^6; CFSE relative to spherical field = $-24Dq$

But a glance at Fig. 28.8 reveals that the magnitude of 10*Dq* increases from +II state to +III state and also from H_2O to en. The ***additional gain*** in CFSE in the +3 state over the +2 state will be much higher in case of the ethylenediamine complex because the latter has a higher 10*Dq* value. The stabilization of the higher oxidation state may thus be ascribed to (i) greater stabilization in the low spin state and also (ii) greater σ-acceptor capacity of the metal in the higher oxidation state. However, this does not permit us to draw a generalized conclusion regarding the nature of ligands stabilizing high oxidation states. We shall presently find that soft polarizable ligands like dipyridyl, pyridine, cyanide, phosphines, arsines etc. may also stabilize low oxidation states in many cases (see below).

[Sec. 28.1.3 *Stabilization of oxidation states*]

Low oxidation states

Stabilization of low oxidation states of a metal implies that the valence shell electrons of the metal have been stabilized for some reason whatsoever. Thus (i) large saturated ligands like the iodide and sulphide which are good reducing agents (fluorides and oxides were poor reducing agents) are expected to stabilize low oxidation states; the difference in electrostatic energy between the higher and lower oxidation states in combination with these ligands are also expected to be small. (ii) Secondly, ligands with π-acceptor capacity provide a secondary mode for the "drainage" of electron density on the metal, thereby stabilizing the low oxidation states. Typical π-acid ligands in this category are CO, N_2, NO, PR_3, RNC, dipyridyl and *o*-phenanthroline.

The neutral CO molecule forms many complexes with metals in zero oxidation state, e.g., $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$. The $C \rightarrow M$ σ-bond in these complexes are reinforced by metal *dπ* to ligand π* back donation resulting in stable compounds in which the metal is still kept in a low oxidation state. In some cases, the metal may even attain a negative oxidation state as in $Na[Co(CO_4)]$ and $Na[Mn(CO)_5]$, the oxidation states of the central metal in each being −I.

Complexes of the isoelectronic dinitrogen molecule are expected to behave similarly. Such complexes are however less stable in comparison to the complexes of CO owing to lack of polarity of N_2 and greater stabilization of the HOMO and destabilization of the LUMO, making dinitrogen both a weak σ-donor and poor π-acceptor. Nevertheless, there are some complexes containing dinitrogen with other π-acid ligands having the metal in a low oxidation state e.g., $[Co(N_2)H(PPh_3)_3]$ and $[Fe(N_2)H_2(Ph_2EtP)_3]$. Bridging dinitrogen groups are also known, e.g., $[(NH_3)_5RuN{=}NRu(NH_3)_5]^{4+}$.

Nitrogen monoxide (nitric oxide, NO) contain one electron more than CO or N_2 in an antibonding **π* m.o.** which is readily lost to form NO^+. Most complexes of nitric oxide thus **contain NO^+** as the effective ligand, stabilizing low oxidation states as in the series of isoelectronic nitrosyl carbonyls : $[Mn(CO)(NO)_3]$, $[Fe(CO)_2(NO)_2]$ and $[Co(CO)_3NO]$ where the oxidation states of the metals are −III, −II and −I respectively.

Phosphine and arsine ligands form metal-ligand π-bonds by receiving electrons in the vacant *d*-orbitals on phosphorus or arsenic. Obviously nitrogen cannot provide this facility. In ammonia, the antibonding orbitals have σ-symmetry and hence are not suitable for π-bonding. But when the nitrogen atom acts as a donor from a delocalized π-electron system as in dipyridyl and *o*-phenanthroline, metal-ligand π-bonding may be established via the π* m.o. of the aromatic ring.

Stabilization of a lower oxidation state in comparison to water is marked by an increase in the standard reduction potential of the couple above the aqueous potential. A few reduction potential values for Fe(III) - Fe(II) are given in Table 28.8.

TABLE 28.8

Some standard reduction potential values for the Fe^{3+} - Fe^{2+} system

Couple	E^0 (Volt)
$[Fe(H_2O)_6]^{3+} + e \rightleftharpoons [Fe(H_2O)_6]^{2+}$	0·77
$[Fe(dipy)_3]^{3+} + e \rightleftharpoons [Fe(dipy)_3]^{2+}$	0·96
$[Fe(o\text{-phen})_3]^{3+} + e \rightleftharpoons [Fe(o\text{-phen})_3]^{2+}$	1·12

In this case, dipyridyl and *o*-phenanthroline form low-spin complexes with both Fe(III) and Fe(II). Now Fe^{2+} is a very good π-donor while Fe^{3+} is expected to be poorer in this respect. Hence π-bonding ligands stabilize Fe(II) more than Fe(III). On the whole, π-acceptor ligands would stabilize lower oxidation states.

However, the cyanide ion, a potential π-bonding ligand, stabilizes Fe(III) rather than Fe(II), as revealed by the potential.

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-} \quad E^0 = 0.36\ V$$

A thorough search has now established that the reverse influence exerted by CN^- (in comparison to, say, o-phenanthroline) on the E^0 of Fe(III) - Fe(II) system actually results from a large negative entropy of hydration of the $[Fe(CN)_6]^{4-}$ ion; the highly charged anion presumably results in a more ordered arrangement of water molecules in its vicinity. The Fe^{II}—C bond is actually slightly shorter (192 pm) than the Fe^{III}—C bond (195 pm) indicating stronger π-bonding in Fe^{II}—C (better back donation). In the hexaaquo ion, the Fe^{II}—OH_2 distance is longer than the Fe^{III}—OH_2 distance.

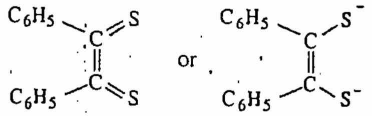
In the second and third transition series elements, lower ionization potential favours higher oxidation states but several other factors change in their own style making predictions difficult. In general, the larger atoms in these two series permit square planar coordination; 10*Dq* increases and at the same time covalence becomes dominant. Hence ligands which stabilize the lower oxidation state in a first transition series metal may not be as effective in later series. Thus for the Ru(III) - Ru(II) couple (c.f. Fe^{III} - Fe^{II}), chloride ions are most efficient to stabilize Ru(III), even more than pyridine and dipyridyl. In fact, the observed order is then found to be

$$py < NH_3 < H_2O < en < Cl^-.$$

Ambiguity in oxidation states

The assignment of oxidation states to the elements in a compound is a mere formalism which fails when we cannot decide upon the distribution of electrons between the individual atoms. This problem is particularly faced with polarizable π-bonding ligands. Thus $[Ti(dipy)_3]$ may be considered as a complex of (i) Ti(0) with neutral dipyridyl molecules or (ii) Ti(II) and dipyridyl anion i.e., Ti^{2+} and $dipy^-$ ion. Similarly, ferrocene (see later), $(C_5H_5)_2Fe$, may be considered as made up of (i) Fe(0) and two C_5H_5 radicals or (ii) Fe (II) and cyclopentadienide anions.

Ambiguities also arise in case of complexes formed by various other π-acid ligands e.g., the carbonyls and nitrosyls and also in the trigonal prismatic complexes of diphenylethylenedithiol,



The assignment of oxidation state of the central metal is determined by the mode of combination proposed for the ligand.

Other examples of oxidation state uncertainty have been given in appropriate cases.

28.1.4 Chemical properties of the elements

The transition elements are in general moderately reactive in nature - reactivity is extremely feeble for the noble metals like platinum and gold. However, some of the metals may be extremely reactive in excess of oxygen and in a finely divided form become pyrophoric (catching fire) in air. Rusting of iron, a slow combustion in presence of air and moisture, is a great concern all over the world. The metals also combine with sulphur and halogens on heating. The reaction with hydrogen, carbon, boron and nitrogen to form interstitial compounds has been mentioned earlier.

Except the few noble metals, the standard electrode potentials of most metals suggest that they will liberate hydrogen from aqueous acids. The real situation is often otherwise because the metals may have a high overpotential for hydrogen evolution or the metal surface may be passivated by a thin adherent oxide film. Passivity is most pronounced with iron and chromium by oxidizing acids. Titanium and vanadium dissolves in hydrochloric acid forming aquo or chloroaquo M^{3+} cations; the elements from chromium to nickel produce M^{2+} cations (also aquo or chloroaquo). Metals like titanium having a maximum oxidation state + IV or above which react with nitric acid produce hydrous oxides like $TiO_2.xH_2O$. Actually, high cation charge makes the $[Ti(H_2O)_6]^{4+}$ ion a strong acid which readily produces $Ti(OH)_4(H_2O)_2$ or $TiO_2, 4H_2O$.

While the lower valent halides of the elements are predominantly ionic, the higher valent halides are covalent. In constructing any Born-Haber type thermodynamic cycle, the lattice energy and bond energy terms should be used in appropriate cases. Coversion of a dihalide to hexahalide thus involves the steps

$$MX_2\ (ionic) + X_2 \longrightarrow MX_4\ (covalent)$$

$$MX_4\ (covalent) + X_2 \longrightarrow MX_6\ (covalent)$$

However, the simple stoichiometric formula may not always reveal the true oxidation state of the metal since metal clusters are often formed. Thus, the compound fitting the formula $MoCl_2$ is actually $[Mo_6Cl_8]Cl_4$—only one-third of the chlorine being present as Cl^- ion. Such cluster formation is common with elements of the second and third transition series.

The oxides MO are basic and often nonstoichiometric, particularly for Ti, V and Fe. The hexaaquo ions $[M(H_2O)_6]^{2+}$ are well-known for the elements—those having V(II), Cr(II) and Fe (II) are readily oxidized by air in acid medium.

The oxides M_2O_3 of the elements are also ionic, as are the fluorides MF_3. Covalence predominates in other halides. The elements from titanium to cobalt form stable $[M(H_2O)_6]^{3+}$ ions. $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ are readily oxidized by air while $[Co(H_2O)_6]^{3+}$ and $[Mn(H_2O)_6]^{3+}$ are readily reduced by water.

28.2 SCANDIUM

Sc : $[Ar]\,3d^1 4s^2$. **Atomic number : 21** **Atomic weight : 44.956**

M.P. : 1539°C **B.P. :** 2750°C **Density : 3·0 g cm^{-3}**

Scandium has only one common oxidation state +*III* with no *d*-electron. In fact, the element lacks the characteristics of transition elements and usually occurs with the lanthanides. The chemistry of scandium resembles that of aluminium very closely (Mendeleev rightly named it *eka-boron*).

Scandium occurs with the lanthanides and in uranium ores (0.02% Sc_2O_3) from which it may be obtained as a by-product. The rare mineral *Thortveitite* ($Sc_2Si_2O_7$; 35-40% Sc_2O_3) is found in Norway. This may be treated similar to bauxite to obtain insoluble ScO(OH) [soluble in aqueous alkali like AlO(OH)]. The hydrous oxide may be dehydrated to Sc_2O_3. The metal may be obtained by electrolysis of a molten mixture of $ScCl_3$, KCl and LiCl.

Scandium dissolves in both acids and alkalis and form ionic halides ScX_3 with halogens. Nitrogen combines at high temperature to form ScN which is hydrolyzed by water. ScF_3, the only insoluble halide, dissolves in NH_4F or alkali metal fluorides to give octahedral $[ScF_6]^{3-}$ ions. $ScCl_3$ is hydrolyzed by water. It is isostructural with $AlCl_3$. Reaction of $ScCl_3$ with excess scandium at high temperature gives lower halides : ScCl contains a layer structure of ClScScCl; Sc_7Cl_{10} and Sc_7Cl_{12} contain Sc_6 clusters.

There appears to be no important technical or industrial application of the element or its compounds.

28.3 TITANIUM

Ti : $[Ar]3d^24s^2$ **Atomic number : 22** **Atomic weight : 47.9**

M.P. : 1667°C **B.P. :** 3285°C **Density :** 4.5 g cm^{-3}

A number of good qualities like low density, high melting point, corrosion resistance etc. make titanium a very useful metal of today and tomorrow. Titanium compounds also find extensive industrial use : TiO_2 *is used in pigment;* $TiCl_3$ *in Ziegler-Natta catalysts for polymerization.*

28.3.1 Introduction

History **:** In 1791, Gregor attempted to isolate a new metal from titaniferous iron ore, ilmenite ($FeTiO_3$), but actually isolated the impure oxide. In 1794, Klaproth also prepared the same oxide from the mineral rutile. He named the element present in the oxide as titanium after the Titans (characters of Greek mythology).

The metal was isolated by Berzelius (1825) and in the pure form by M. Hunter in 1910 ($TiCl_4$ + Na).

Occurrence **:** Titanium constitutes nearly 0.63% of the earth's crust—it is the ninth most abundant among all elements and second among the transition elements

Ilmenite ($FeTiO_3$) and *Rutile* (TiO_2) are the principal ores of titanium. Rutile is mined principally in Australia; ilmenite occurs in Canada, USA, Australia, Malaysia and South India.

Ilmenite occurs in the Kerala and Tamil Nadu coasts as black, heavy sand along with monazite, zircon, garnet and other heavy minerals. The largest deposits are on the Kerala beaches on a 160 km stretch between Cape Comorin and Kayankulam. Small patches of the sand concentrates occur at Ratnagiri and further north on the Malabar coast (Purnagadh to Vengurla) and also on the east coast at Tuticorin, Visakapatnam and Ganjam (Orissa). The ilmenite is rich in TiO_2 (54 – 62%). The total reserve is estimated at over 152 million tonnes.

Titanium also occurs as titaniferous magnetite in large masses in Singhbhum and Mayurbhanj in the Bihar plateau. About 1000-2000 tonnes of rutile are also obtained annually in the magnetic separation of ilmenite from the raw beach sands.

In Orissa, the sands of the Wheeler islands, off the coast of Chandbali, (District Balasore) are also rich in ilmenite, magnetite, rutile and minor amounts of monazite.

28.3.2 The element

Extraction

Difficulties

Study of the Ellingham diagram (Fig. 15.3) suggests that TiO_2 should be reduced by carbon above 1500°C. However, extraction of the metal by carbon reduction presents a number of difficulties. Titanium is highly reactive at high temperature and readily forms carbides and nitrides. For example, if the oxide is reduced by carbon in air, a carbide-nitride is formed; in an electric arc furnace, on the other hand, reduction is incomplete, a brittle carbide being formed.

$$TiO_2 + 3C = TiC + 2CO.$$

Molten titanium also tends to react with every refractory material, making its handling very difficult.

The extraction of titanium is carried out as follows :

(i) Powdered ilmenite or rutile is heated with carbon and chlorine (900°C).

$$2FeTiO_3 + 6C + 7Cl_2 \longrightarrow 2TiCl_4 + 2FeCl_3 + 6CO.$$

$$TiO_2 + 2C + 2Cl_2 \longrightarrow TiCl_4 + 2CO.$$

(ii) $TiCl_4$ (b.p. 137°C) is separated from $FeCl_3$ (which sublimes at 285°C) by fractional distillation.

(iii) The $TiCl_4$ is reduced by molten magnesium in argon atmosphere at 1000° - 1150°C.

$$TiCl_4 + 2Mg = Ti + 2MgCl_2$$

Magnesium chloride and excess magnesium are removed by washing with water and dilute hydrochloric acid when spongy titanium is left.

(iv) The spongy titanium is melted under argon or in high vacuum in an electric arc furnace and cast into ingots.

In the original *Kroll process* (1932), reduction was achieved by calcium. At present, sodium is also used for the purpose - after washing out the NaCl, the metal is obtained in a granular form. This can be fabricated into metal parts by the "powder technique" followed by sintering in an inert atmosphere.

The magnesium and magnesium chloride in the reduction may also be separated by distillation.

Refining : Spongy titanium may be purified via the iodide. In the *van Arkel-de Boer method*, the metal is heated with iodine in an evacuated glass tube fitted with a tungsten filament at the center. The whole tube is heated to form volatile TiI_4 while the impurities are left. The TiI_4 (m.p. 150°C, b.p. 377°C under 1 atm) is now allowed to decompose in contact with the hot tungsten filament maintained at about 1300°C where Ti is deposited.

$$Ti + 2I_2 \longrightarrow TiI_4 \qquad TiI_4 \longrightarrow Ti + 2I_2$$

Titanium may also be extracted by reduction of TiO_2 with calcium. The oxide is separated from the ore as follows :

(i) Powdered ilmenite is digested with concentrated sulphuric acid. The "sulphate cake" so obtained is leached with water when a solution containing ferric sulphate and titanyl sulphate ($TiOSO_4$) is obtained.

(ii) Fe(III) is reduced by scrap iron and the solution concentrated by vacuum evaporation. On cooling, ferrous sulphate is mostly precipitated and filtered out.

(iii) The solution containing $TiOSO_4$ is boiled to hydrolyze when $TiO_2.xH_2O$ is precipitated. This is filtered, washed and calcined at 800-900°C.

(iv) The TiO_2 is reduced by calcium.

Properties

Titanium is a light silvery metal of high melting point, good tensile strength and thermal and electrical conductivity (sp. gravity 4.5; m.p. 1680 ± 10°C; Table 28.2). It forms a hexagonal close packed lattice (HCP) like most other transition metals. However, its strength and resistance to corrosion drops rapidly above 800°C.

The metal is rather unreactive at ordinary temperature but in the finely divided state it may catch fire in air (pyrophoric). On heating, it combines with dioxygen (TiO_2), dinitrogen (TiN) as well as several other nonmetals like B, C, Si and H_2. The nitrides, carbides (TiC) and borides (TiB, TiB_2) are interstitial compounds which are very hard, refractory (3000° - 4000°C), good conductors of electricity, and chemically inert. In these compounds, and also in TiH_2, the nonmentals occupy all the terahedral and octahedral holes in a close packed cubic lattice (CCP) of titanium, which differs little in energy from the usual HCP structure of the metal.

Titanium decomposes steam at 100°C but is not attacked by dilute mineral acids at ordinary temperature. Hot concentrated HCl dissolves it to give Ti(III), liberating H_2.

The metal dissolves in cold dilute HF. Hot concentrated nitric acid slowly forms "metatitanic acid", $H_2TiO_3.nH_2O$ or $TiO_2.nH_2O$.

Titanium is not attacked by hot aqueous alkali but fused alkali attacks it to give titanates.

Titanium forms a series of substitutional solid solution with vanadium and chromium which are close to it in properties and electron configurations. The tendency to form solid solutions decreases in the series V ≈ Cr > Mn > Fe > Co > Ni :

	Ti	V	Cr	Mn	Fe	Co	Ni
	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2
Solubility in Ti, mole percent :	—	100	100	28	20	13	10

However, the tendency to form intermetallic compounds increases from left to right in the series—molten titanium reacting energetically with iron to form Fe_3Ti and FeTi (also with Co, Ni, Cu, Zn).

Some reactions of titanium are shown in Fig. 28.9.

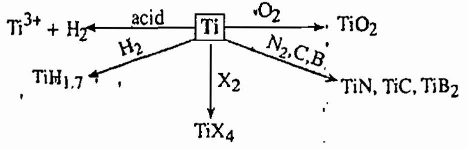


Fig. 28.9. **Some reactions of titanium.**

Uses

Titanium finds extensive use as an alloying material by virtue of its low density, high tensile strength and excellent corrosion resistance. The addition of even 0.1 percent of titanium to steel imparts superior mechanical strength, corrosion resistance and better weldability. As such, it is used in place of stainless steel in many fields of chemical and allied industries dealing with saline solutions, alkaline solutions, chlorine compounds, moist and other aggressive chemicals as well as in making rails, railway wheels and axles etc.

Titanium alloys with Mn, Cr-Fe-Mo, Al-Mn, Al-V, Al-Sn etc. also have the advantage of lightness and good mechanical strength and are mainly employed in the aeronautical and missile industries.

Ferrotitanium, prepared by smelting ilmenite or rutile with iron ore and coke in an electric furnance, is used as a scavenger in steel industry to remove dioxygen and dinitrogen from steel.

TiO_2 is extensively used as the white pigment 'titanium white' known for its excellent covering power. It is prepared along the same route as outlined in the extraction of the metal (see TiO_2).

28.3.3 Chemistry of titanium(IV)

Consistent with its valence shell electron configuration of $3d^24s^2$, the highest and most stable oxidation state of titanium is +IV; compounds in lower oxidation states (0, II, III) are readily oxidized to Ti(IV). High ionization energy required to form Ti^{4+} ion (8,800 kJ mol^{-1}) makes the compounds covalent; even TiF_4 sublimes readily.

The chemistry of Ti(IV) shows certain similarities with the elements of group IV (14), notably Sn (IV) :

(i) Both Ti^{IV} and Sn^{IV} have similar covalent radii (coordination no. 8), 136 pm and 145 pm respectively. The estimated ionic radii for Ti^{4+} and Sn^{4+} are also comparable, 68 pm and 71 pm respectively.

(ii) TiO_2 (rutile) and SnO_2 (cassiterite) are isomorphous and both become yellow when hot.

(iii) The chlorides $TiCl_4$ and $SnCl_4$ are both colourless liquids fuming strongly in moist air and getting readily hydrolyzed.

Both these compounds behave as Lewis acids and accept further donor ligands, e.g., they form $TiCl_6^{2-}$ and $SnCl_6^{2-}$.

(iv) $Ti(NO_3)_4$ and $Sn(NO_3)_4$ are isomorphous.

The oxidation state-free energy diagram of Ti is shown in Fig. 28.10.

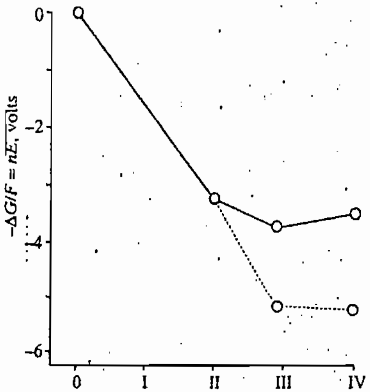


Fig. 28.10
Oxidation state-free energy diagram for titanium. Ti(IV) is most stable.

See Table 28.6 for values of *E*.

The potential values are not certain since Ti^{4+} (*aq*) and Ti^{2+} (*aq*) ions have doubtful existence. Solid line corresponds to TiO_2, broken line for $[Ti(OH)_3]^+$.

Among the principal compounds of Ti(IV), the dioxide TiO_2, tetrahalides TiX_4 (X = F—I), disulphide TiS_2, disulphate $Ti(SO_4)_2$ etc. are known. Also known are numerous titanates (actually mixed oxides), oxosalts (e.g., $TiOSO_4$) and derivatives of anionic complexes in C.N. 6 e.g., $[TiX_6]^{2-}$, $[TiO_4]^{4-}$, $[Ti(SO_4)_3]^{2-}$ etc.

Aqueous chemistry

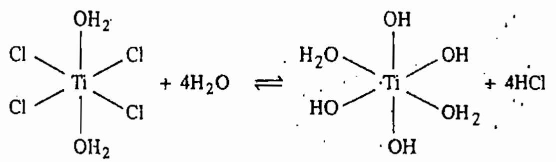
High charge/size ratio does not permit the existence of the ion $[Ti(H_2O)_6]^{4+}$ in solution where it is extensively hydrolyzed :

$$[Ti(H_2O)_4(OH)_2]^{2+} + H_2O \rightleftharpoons [Ti(H_2O)_3(OH)_3]^+ + H_3O^+$$

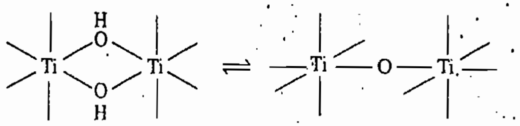
$$[Ti(H_2O)_3(OH)_3]^+ + H_2O \rightleftharpoons [Ti(H_2O)_2(OH)_4] + H_3O^+$$

There is no evidence for $Ti(OH)_4$; TiO_2, xH_2O has the composition $[Ti(H_2O)_2(OH)_4]$. In aqueous solutions containing Ti(IV), the species is often represented by TiO^{2+} for simplicity, particularly in strongly acid medium. The simple monomer $[TiO(H_2O)_5]^{2+}$ does not appear to be important in aqueous solution, in contrast to the chemistry of vanadium (IV) where the predominant species appears to be $[VO(H_2O)_5]^{2+}$. Oxo-species of Ti(IV) are usually polymeric with zigzag -Ti-O-Ti-O- chains.

Hydrolysis of Ti(IV) in aqueous solution may be illustrated by taking the case of $TiCl_4$. First there will be coordination saturation of $TiCl_4$ to $TiCl_4, 2H_2O$, with subsequent splitting off of four HCl molecules.



In the next steps, hydroxo and oxo-bridged polymeric species are formed :



The formation of hydroxyaquo- to hydroxo- to oxo- species appears to be favoured by high temperature, alkaline medium and prolonged standing. Further polymerization may result in polynuclear complexes growing to the size of colloid particles and the precipitation of gelatinous TiO_2, nH_2O.

Anions present in solution may replace the molecules of water and OH groups in the polynuclear species. Thus, interaction of the oxides or hydroxides with acids do not produce the neutral salts; instead oxysalts are produced of the type $TiOX_2$ where $X = Cl^-, Br^-, I^-, NO_3^-$ or $\frac{1}{2} SO_4^=$.

$$\text{“}Ti(OH)_4\text{”} + 2HCl = TiOCl_2 + 3H_2O$$

$$TiO_2 + H_2SO_4 = TiOSO_4 + H_2O.$$

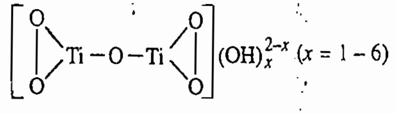
Crystalline hydrates like $TiOCl_2.2H_2O$ or, $TiOSO_4.2H_2O$ may be precipitated from acid solutions.

Crystalline $TiOSO_4.H_2O$ has infinite zigzag chains of -Ti-O-Ti-O- in which each Ti completes an octahedral coordination by SO_4^{2-} and H_2O. $TiO(acac)_2$ is also dimeric with two bridge O-atoms.

TiO^{2+} may exist in solution in strongly acidic medium, say 1*M* $HClO_4$. Crystalline salts of the tetragonal pyramidal $[TiOCl_4]^{2-}$ anion also contain the TiO^{2+} moiety. Short Ti = O bonds also characterize a number of [TiO(ring)] species where the ring is porphyrin and phthallocyanine.

Peroxo complexes

Aqueous solutions of Ti(IV) in mild acidic medium develop an intense orange colour with H_2O_2 which may be used to estimate titanium colorimetrically. The principal species at pH < 1 appear to be $[Ti\ (O\text{-}O)\ OH\ aq]^+$ together with other peroxo complexes. At higher pH (1 - 2), the following type of ions may be present (28-I), which then preciptate the yellow TiO_3, nH_2O (n = 1 or 2).



28-I

The orange colour is discharged by the addition of fluoride which forms a stronger complex. Other peroxo complexes of titanium will be mentioned later (see complexes).

Titanium(IV) oxide

TiO_2 has three crystalline forms — rutile, anatase and brookite, rutile being the more commonly occurring natural form. In all of these structures, titanium is coordinated to six oxygen atoms, octahedrally in rutile and in distorted octahedral environments in others.

TiO_2 is prepared industrially for use as a white pigment by

(i) vapour phase oxidation of $TiCl_4$ with oxygen at around 700°C :

$$TiCl_4 + O_2 \longrightarrow TiO_2 + 2Cl_2$$

The $TiCl_4$ is prepared by heating rutile with carbon and chlorine (vide extraction).

(ii) Ilmenite may be dissolved in H_2SO_4 to obtain $TiOSO_4$ (see extraction) which is then hydrolyzed by hot water. The precipitate is ignited at 900°C to get TiO_2.

Titanium dioxide is a high-melting white solid* with high negative enthalpy and Gibbs energy of formation :

M.P. (°C)	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})
1870	–944	–889

The formal representation of TiO_2 as consisting of Ti^{4+} and O^{2-} ions appears doubtful in view of the high ionization energy (8800 kJ mol^{-1}).

TiO_2 is amphoteric and dissolves in concentrated base or acid but gets easily hydrolyzed on dilution. The strongly roasted oxide is chemically very inert. It dissolves with difficulty in hot concentrated H_2SO_4 but more readily in fused alkali metal bisulphates.

Dissolution of TiO_2 in hot concentrated aqueous alkali produces *titanates* which are also formed by fusing TiO_2 with metal oxides. These are formally designated as metatitanates $\left(M_2^I\ TiO_3, M^{II}\ TiO_3\right)$ and orthotitanates $\left(M_4^I TiO_4, M_2^{II} TiO_4\right)$, though the discrete titanate anions are not known. In fact, these are mixed oxides with different structures - perovskite ($CaTiO_3$), ilmenite ($FeTiO_3$) and spinel (Mg_2TiO_4).

Barium "titanate" $BaTiO_3$ is one of several mixed oxide species (e.g., Ba_2TiO_4, $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$) obtained from BaO and TiO_2 (Fig. 28.11). These have important ferroelectric and piezzoelectric properties (section 17.3.6; p-99) and are used in micorphones and gramophone pickups. The large Ba^{2+} ions make a cubic close packed structure with oxygen atoms at six face centers (Fig. 28.12). The octahedral hole of the O-atoms is so large that the small Ti^{4+} ion fits only loosely in it (it can "rattle around"). When an electric field is applied, all the Ti^{4+} ions are drawn to one side of their respective

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* (Naturally occurring varieties may be coloured owing to the presence of impurities of other oxides).

holes, resulting in an enormous electric polarization of the crystal as a whole and thereby increasing its permittivity.

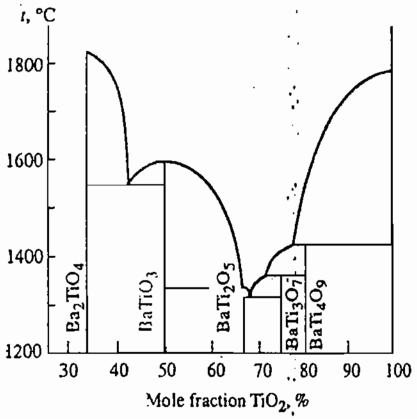


Fig. 28.11

Phase diagram of BaO-TiO$_2$ system.

1. Ba_2TiO_4 2. $BaTiO_3$ 3. $BaTi_2O_5$ 4. $BaTi_3O_7$ 5. $BaTi_4O_9$.

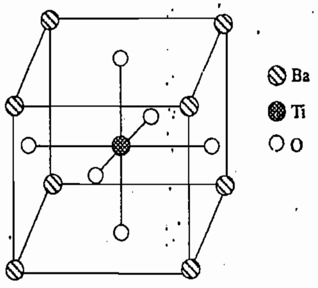


Fig. 28.12

The structural model of BaTiO$_3$.

This is the structure of *perovskite*, $CaTiO_3$.

No definite hydroxide like $Ti(OH)_4$ is known and the gelatinous precipitate produced by adding base to Ti(IV) solution (or acid to alkali titanates) are actually hydrous oxides of various composition, TiO_2, xH_2O. Fresh precipitates (α-form) have a relatively large number of –OH groups and are therefore more readily soluble in acids than aged ones (β - form) in which the –OH groups are replaced by – O – groups. The hydrous oxide also dissolves in alkali to form "titanates". One form of the precipitated hydrous oxide with a composition like $4TiO_2, 2.2\,H_2O$ or $H_2Ti_4O_9, 1.2\,H_2O$ in a layer structure has been used as an ion-exchanger.

Halides

All the four tetrahalides are known. TiF_4 may be obtained by reacting (i) the metal with fluorine at 200°C or (ii) anhydrous HF on $TiCl_4$. Other tetrahalides may be prepared by heating TiO_2 with carbon and halogen as mentioned for $TiCl_4$ during extraction.

Except $TiCl_4$ which is a liquid, all other tetrahalides are solids (Table 28.9).

TABLE 28.9

Physical properties of Ti(IV) halides

Halide	Colour	M.P. (°C)	B.P. (°C)
TiF_4	White solid	—	284
$TiCl_4$	Colourless liq	−23	136
$TiBr_4$	Yellow solid	39	230
TiI_4	Violet-black	150	377

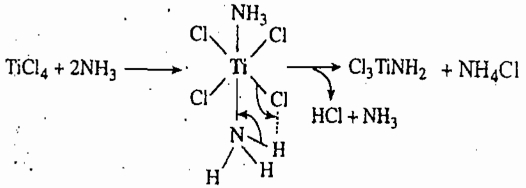
The fluoride is a volatile hygroscopic solid insoluble in nonpolar solvents. It's high boiling point suggests a fluorine bridged polymeric structure with six-coordinate titanium. It dissolves in aqueous HF to form TiF_6^{2-} which is stable to hydrolysis.

[Sec. 28.3.3 *Ti(IV) halide*]

The chloride, bromide and iodide dissolve in nonpolar solvents as monomers. The solids have molecular crystal lattices consisting of tetrahedral TiX_4 molecules with possible π-bonding as indicated by the short Ti-Cl distance (217 pm) in $TiCl_4$. Their m.o. electron-configuration (Fig. 27.28) corresponds to

$$[\sigma]^8\,[\pi]^{10}\,[\pi_{nb}]^6$$

The titanium tetrahalides produce copious fumes in moist air—their hydrolysis has been discussed before. They also act as potential Lewis acids to a number of Lewis bases forming adducts, usually six coordinate. Solvolysis may also occur in many cases :



As ammonia coordinates to titanium, the charge on the metal is partially neutralized while the hydrogen atoms linked to nitrogen have their partial positive charges enhanced. Subsequently the hydrogen atoms form bonds with adjacent chlorine atoms, eliminating a molecule of HCl. The HCl will actually combine with an available NH_3 molecule to form NH_4Cl. The Cl_3TiNH_2 may be attacked by another molecule of base and may again eliminate HCl and thus proceed to complete solvolysis. In each step, the chlorine atoms are replaced by less electronegative NH_2 groups and the fractional positive charge on titanium is lowered with consequent reduction in Lewis acidity. A stage may be reached when further ligands can coordinate only weakly and no more HCl will be eliminated. For example, in liquid ammonia, $TiCl_4$ gives $TiCl(NH_2)_3(NH_3)_2$; on warming to room temperature, the weakly bonded ammonia molecules split off, leaving $TiCl(NH_2)_3$.

Some solvolytic reactions of $TiCl_4$ are shown below (Fig. 28.13).

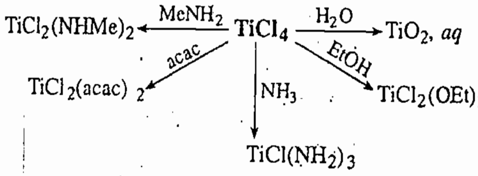


Fig. 28.13

Some solvolytic reactions of TiCl$_4$

The extent of solvolysis may be enhanced by using bases as catalysts. Thus, alkoxides are formed by alcohols in presence of ammonia.

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl$$

Such solvolytic products usually contain six-coordinate titanium in a polymeric structure and are insoluble in non interfering solvents. Solid $Ti(OEt)_4$ consists of a tetrameric unit containing approximately octahedral titanium (Fig. 28.14). In benzene, however, this and many other alkoxides are trimeric.

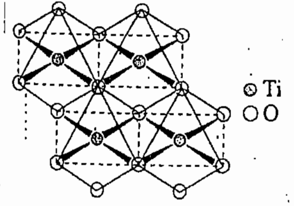


Fig. 28.14

Ti-O skeleton showing octahedral coordination around Ti in Ti(OEt)$_4$ crystals.

There are four TiO_6 octahedra, two sharing two edges and two sharing three edges.

The trimer in benzene has three TiO_6 octahedra, with one sharing two faces and two sharing three faces each.

Titanium alkoxides deposited on a surface are ultimately hydrolyzed to TiO_2 on exposure to the atmosphere — hence their widespread use in water-proofing fabrics and heat-resistant paints. Chelated with β-diketonates, these are also used to make "thixotropic" paints which do not drip.

Titanium (IV) halides also form a wide range of six-coordinate adducts of the type TiX_4L_2 with nitrogen, phosphorus, arsenic, oxygen and sulphur donor molecules (Fig. 28.15). These adducts are mostly *cis* when steric requirements permit since this allows maximum use of the t_{2g} *d*-orbitals of metal for dative π-bonding.

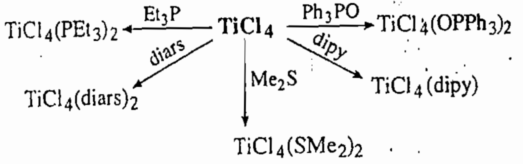


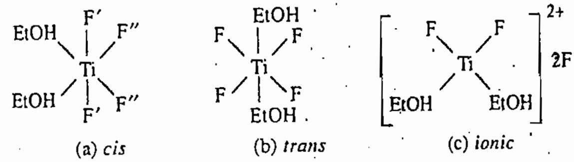
Fig. 28.15 A few adducts formed by $TiCl_4$.

Q. 28.3 TiF_4 reacts with anhydrous ethanol to give $TiF_4.2EtOH$.

(a) ^{19}F nmr spectrum of the adduct below 0°C shows two triplets of equal intensity. If the nuclear spin of ^{19}F is 1/2, which is the likely stereochemistry of the complex?

(b) Above 0°C, the spectrum collapses to a single peak. Comment.

Hint : Three reasonable structures for the adduct are shown in 28.II (a—c).



28-II

The two peaks in the nmr spectrum indicate two different environments for the fluorine atoms; equal intensity of the peaks mean that the fluorine atoms occur equally in these two environments, i.e., two F atoms in each.

The *trans*-structure (b) offers only one kind of fluorine atom and hence is excluded first.

In the extreme ionic structure (c), the two F^- ions would be expected to show merely a single peak. Since the observed peaks are both triplets, this structure is also excluded.

Structure (a) containing two environmentally different types of F atoms (marked F′ and F″) fits the observed spectrum best. Each pair, with a total nuclear spin $S = 1$, will split the resonance of the other pair into a triplet.

In fact, *cis*-structures of this and similar adducts are favoured when steric conditions permit as the ligands can then make the best use of the metal *d* orbitals for dative π-bonding.

(b) Intermolecular exchange processes through dissociation and recombination become more rapid above 0°C and the distinction between the two types of F atoms is destroyed.

Ti(IV) halides form anionic complexes by adding further halide ions. As already menioned, TiF_6^{2-} can be prepared in aqueous HF but the other halogenoanions are hydrolyzed in presence of water. Salts containing the yellow octahedral $TiCl_6^{2-}$ and black $TiBr_6^{2-}$ are best made in thionyl halides. They are coloured due to charge transfer.

The monomeric anionic complexes may condense further by linking of the octahedral units around them. In liquid SO_2, TiF_4 acts on TiF_6^{2-} to give anions like $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{2-}$ and $Ti_2F_9^-$ with structures shown in Fig. 28.16.

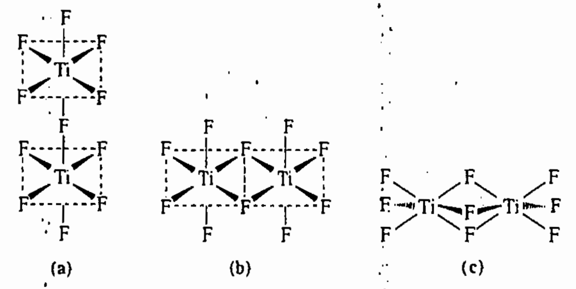


Fig. 28.16 : Sharing of TiF_6 octahedral units.

(a) $Ti_2F_{11}^{2-}$ (common vertex). (b) $Ti_2F_{10}^{2-}$ (common edge) and (c) $Ti_2F_9^-$ (common face) as suggested by fluorine nmr.

PCl_5 reacts with $TiCl_4$ to give a compound of formula $(PCl_4TiCl_5)_n$ which, however, does not contain $TiCl_5^-$ ions; instead, halogen-bridged $[Ti_2Cl_{10}]^{2-}$ anions are present to provide octahedral coordination around titanium (structure same as 28.16 (b) for $Ti_2F_{10}^{2-}$). Similarly, the tetraethylammonium salt of the anion $[Ti_2Cl_9]^-$ contains two $TiCl_6$ octahedra joined at a face by bridging chlorine atoms.

A few five-coordinate adducts of $TiCl_4$ are also known, e.g., $TiCl_4AsH_3$ (trigonal bipyramid, As at equatorial position) and $TiCl_5^-$ ion in $Et_4N^+\,TiCl_5^-$ (also trigonal bipyramid).

Miscellaneous compounds of Ti(IV)

Titanium disulphide, TiS_2 (Ti, + S, heat) has a layer structure (like CdI_2) containing Ti in octahedral interstices between closepacked layers of sulphur atoms. Aliphatic amines and other Lewis bases may be intercalated between these sulphur layers to form compounds with interesting electric properties like superconductivity.

Titanium(IV) sulphate, $Ti(SO_4)_2$ cannot be prepared in aqueous solutions (see aqueous chemistry). It may be formed by fusing TiO_2 with $K_2S_2O_7$ (heat $KHSO_4$) or by the reaction of $TiCl_4$ and SO_3 in liquid sulphuryl chloride (SO_2Cl_2)

$$TiO_2 + 2K_2S_2O_7 = Ti(SO_4)_2 + 2K_2SO_4$$

$$TiCl_4 + 6SO_3 = Ti(SO_4)_2 + 2S_2O_5Cl_2 \text{ (in } SO_2Cl_2)$$

Titanium(IV) nitrate, $Ti(NO_3)_4$ can be prepared by reacting $TiCl_4$ with N_2O_5 or TiI_4 with N_2O_4 in liquid N_2O_4 as solvent :

$$TiI_4 + 4N_2O_4 \rightleftharpoons Ti(NO_3)_4 + 4NO + 2I_2$$

$TiCl_4$ tends to give $TiO(NO_3)_2$ with N_2O_4.

The white sublimable solid is highly reactive. The titanium is eight coordinate in a dodecahedral environment of oxygen atoms from bidentate NO_3 groups (Fig. 28.17).

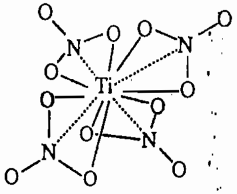


Fig. 28.17

Structure of Ti(η^2-NO$_3$)$_4$.

The N-atoms occur at the corners of a flattened tetrahedron (shown by dotted lines). Eight O-atoms form a dodecahedron around the Ti.

Ti(ClO$_4$)$_4$, a volatile solid obtained by reacting TiCl$_4$ with anhydrous HClO$_4$ or Cl$_2$O$_6$ has a similar 8-coordinate structure involving η^2-ClO$_4$ groups.

Complex compounds of Ti(IV)

Several complex compounds of Ti(IV) have been mentioned in connection with its aqueous chemistry and the adducts formed by Ti(IV) halides. While most of the complexes are octahedral, there are a few examples in other coordination numbers, too. Some representative complex compounds of Ti(IV) are shown in Table 28.10.

TABLE 28.10

Complex compounds of Ti(IV)

Co-ordination number	Stereochemistry	Examples
4	Tetrahedral	TiCl$_4$
5	Trigonal bipyramid	[TiCl$_5$]$^-$, [TiOCl$_2$(NMe$_3$)$_2$], [TiCl$_4$.NMe$_3$]
	Square pyramid	[TiOCl$_4$]$^{2-}$, TiO(porphyrin)
6	Octahedral	[TiF$_6$]$^{2-}$, [Ti(acac)Cl$_2$]
		[TiCl$_4$(OPCl$_3$)]$_2$
7	Pentagonal bipyramid	[TiCl(S$_2$CNMe$_2$)$_3$]
	Capped trigonal prism.	[TiF$_5$(O$_2$)]$^{3-}$
8	Dodecahedral	[Ti(ClO$_4$)$_4$], [Ti(NO$_3$)$_4$]
	Distorted dodecahedral.	[TiCl$_4$(diars)$_2$]

As we have already observed, titanium attains octahedral coordination in many oxygen containing compounds through bridging oxygen atoms, as in TiOSO$_4$.H$_2$O and TiO(acac)$_2$. The adducts formed by Ti(IV) halides with other donor ligands (Fig. 28.18) are usually coloured yellow, red or black owing to charge-transfer absorptions extending to the visible region. Many of them are crystalline solids soluble in nonpolar solvents, e.g., TiCl$_4$(OMe$_2$)$_2$. The octahedral structuring of the phosphorus oxochloride adducts TiCl$_4$(OPCl$_3$) and TiCl$_4$(OPCl$_3$)$_2$ have been confirmed by X-ray studies. TiCl$_4$(OPCl$_3$) is dimeric with halogen bridges (Fig. 28.18) while TiCl$_4$(OPCl$_3$)$_2$ is *cis*-octahedral.

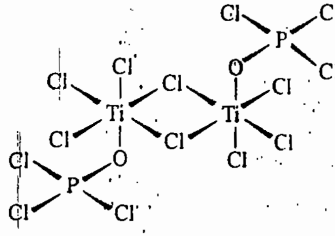


Fig. 28.18

Halogen-bridged octahedral environment of Ti in dimeric [TiCl$_4$(OPCl$_3$)]$_2$.

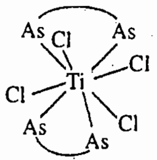


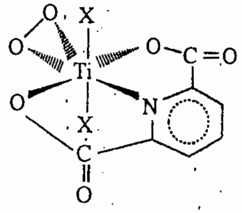
Fig. 28.19

Structure of TiCl$_4$(diars)$_2$ (distorted dodecahedral).

As an example of five-coordination, we have already mentioned TiCl$_5$ (tbp), stabilized by large cations like NEt$_4^+$. Another example of this coordination number (also tbp) is TiCl$_4$.Me$_3$N which is monomeric in benzene.

X-ray studies have also confirmed the eight-coordinate structure (Fig. 28.19) of TiCl$_4$(diars)$_2$, TiCl$_4$(diars) is octahedral (diars = *o*-phenylenebisdimethylarsine). Dodecahedral structures in this coordination number are known in Ti(NO$_3$)$_4$ and Ti(ClO$_4$)$_4$.

In addition to the orange peroxo species mentioned earlier which exists in solutions, a few crystalline peroxo complexes are also known. Reaction of TiO$_2$ with 40% HF and 30% H$_2$O$_2$ gives salts M_3^I [Ti(O$_2$)F$_5$] at pH = 6 and M_2^I[Ti(O$_2$)$_2$F$_2$] at pH = 9. In both the complexes, the peroxo group acts as a bidentate ligand (O—O = 146 pm); the first complex is thus an example of coordination number 7.



28-III

The peroxo-2,6-pyridinedicarboxylate complex (28-III) is also an example of seven-coordinate Ti(IV) with O—O distance 146 pm characteristic of η^2-peroxo ligand.

A few other complexes of Ti(IV) will be discussed in connection with organometallic compounds, e.g., the complexes with cyclopentadiene.

28.3.4 Chemistry of Ti(III)

The +III oxidation state of titanium has been studied extensively in solid compounds as well as in solution. Unlike Ti(IV), Ti(III) compounds are paramagnetic ($3d^1$; $\mu_{eff} \simeq 1.7$ B.M.) and coloured due to *d-d* absorption even in absence of charge-transfer.

Derivatives of Ti(III) are readily obtained by reducing Ti(IV) compounds, e.g.,

$$2TiO_2 + H_2 \xrightarrow{1200°C} Ti_2O_3 + H_2O$$

$$2TiCl_4 + H_2 \xrightarrow{650°C} 2TiCl_3 + 2HCl$$

Oxide

Ti$_2$O$_3$, violet, has a structural type similar to that of α-Al$_2$O$_3$. It is practically insoluble in water. Addition of alkali to solutions containing Ti(III) results in the formation of a dark violet precipitate Ti$_2$O$_3$, nH$_2$O which does not dissolve in excess alkali, showing its basic nature.

Halides

TiF_3 is prepared by heating titanium (700°C) in a stream of hydrogen and hydrogen fluoride (or heating TiH_2 in HF). It is a blue crystalline solid insoluble in water and stable in air at room temperature. It disproportionates above 950°C

$$4TiF_3 \longrightarrow 3TiF_4 + Ti$$

$TiCl_3$ and $TiBr_3$ are prepared by reduction of the tetrahalides with hydrogen, while TiI_3 is prepared by heating (700°C) stoichiometric quantities of titanium and iodine in a sealed tube.

$TiCl_3$ obtained by reducing $TiCl_4$ with H_2 is obtained in the common α-form (violet). A brown β-form is obtained by reducing $TiCl_4$ in inert solvents by aluminium triethyl (100°C). It reverts to the α-form around 250-300°C.

All the three trihalides are insoluble in nonpolar solvents and consist of halogen-bridged polymers with six-coordinate titanium. α-$TiCl_3$ has a layer lattice containing $TiCl_6$ groups; the β-form contains single chains of $TiCl_6$ octahedra each sharing two faces, and is therefore fibrous. This form acts as the heterogeneous catalyst in the Ziegler-Natta process for stereoregular polymerization of alkenes.

The halides disproportionate above 400°C in vacuum :

$$2TiCl_3(s) \longrightarrow TiCl_4(g) + TiCl_2(s); \quad \Delta H^\circ = 142 \text{ kJ mol}^{-1};\ \Delta S^\circ = 171 \text{ JK}^{-1}.$$

The involatile dihalide will disproportionate further above 700°C.

$$2TiCl_2(s) \longrightarrow Ti(s) + TiCl_4(g); \Delta H^\circ = 274 \text{ kJ mol}^{-1}, \Delta S^\circ = 155 \text{ JK}^{-1}$$

Both the reactions are endothermic but favoured at high temperature by a positive entropy term.

Unlike TiF_3, all three trihalides are readily oxidized in moist air :

$$4TiCl_3 + O_2 + 2H_2O = 4TiOCl_2 + 4HCl$$

TiO_2, xH_2O is ultimately formed.

The titanium(III) halides are all Lewis acids, though to a less extent than the corresponding tetrahalides. TiF_3 readily adds F^- to produce green TiF_6^{3-}. The other trihalides also dissolve in aqueous hydrogen halides forming haloaquo complexes. $TiCl_3$ forms green and violet hydrates : the violet hydrate may be represented as $[Ti(H_2O)_6]^{3+}Cl_3^-$ while the green form is $[Ti(H_2O)_5Cl]^{2+}Cl_2^-$.

Various adducts of TiX_3 (X = Cl, Br, I) are known :

$TiX_3.3L$ (L = py, CH_3CN, THF, acetone) : pseudo octahedral.

$TiX_3.2L$ (L = Me_3N, α-picoline). *trans*-TBP

$TiX_3.3LL$ (LL = en, propylenediamine) : octahedral

$TiX_3.1.5LL$ (LL = dipy, phen) : structure unknown.

Aqueous chemistry

Reduction of solutions containing Ti(IV) electrolytically or by zinc-HCl readily produces the hexaaquo ion $[Ti(H_2O)_6]^{3+}$. The violet solution gets readily oxidized by air and must be kept under nitrogen.

[Sec. 28.3.4
Titanium(III)]

The violet aquaion is strongly acidic, liberating CO_2 from sodium carbonate

$$[Ti(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Ti(OH)(H_2O)_5]^{2+} + H_3O^+ \ (pK = 1.4)$$

$$2H_3O^+ + CO_3^{2-} \longrightarrow CO_2 + 3H_2O.$$

In concentrated solution of hydrochloric acid, substitution of water molecules by chloride ions takes places, $[Ti(H_2O)_5Cl]^{2+}$ and $[Ti(H_2O)_4Cl_2]^+$ being the predominant species.

Aqueous solutions of Ti(III) are good reducing agents :

$$TiO^{2+} + H^+ + e \rightleftharpoons Ti^{3+} + H_2O \quad E_0 = 0.2V$$

Slightly stronger than stannous chloride, it is a kinetically fast reducing agent. It reduces ClO_4^- to Cl^- and nitrocompounds to amines :

$$RNO_2 + 4Ti^{3+} + 12H_2O \longrightarrow RNH_2 + 4TiO^{2+} + 10H_2O + 4H^+$$

The reducing power increases markedly in alkaline medium : $Ti_2O_3.aq$ is rapidly oxidized in air.

Titanium(III) sulfate, $Ti_2(SO_4)_3$ may be obtained by (i) reduction of Ti(IV) in sulphuric acid by zinc or electrolytically or (ii) by evaporating a solution of titanium in dilute sulphuric acid when violet crystals of $Ti_2(SO_4)_3.6H_2O$ separate. This may be used as a standard reducing agent in volumetric analysis. It forms alums $MTi(SO_4)_2, 12H_2O$ (M = Rb, Cs) containing octahedral $[Ti(H_2O)_6]^{3+}$ ions in the crystal.

Complexes

We have already come across a few complexes of Ti(III). Since most complexes of Ti(III) with neutral donor molecules get hydrolyzed in aqueous medium, they are better prepared in anhydrous condition. Thus $[Ti(NH_3)_6]^{3+}$, which is hydrolyzed in water to $[Ti(H_2O)_6]^{3+}$ and eventually $Ti_2O_3.aq.$, can be prepared in liquid ammonia. However, urea forms a stable complex $[Ti(urea)_6]I_3$ in aqueous solution where it is stable against hydrolysis and oxidation. The crystal contains Ti(III) coordinated octahedrally by oxygen atoms from the six urea molecules.

It has been mentioned earlier that hydrated $TiCl_3$ does not necessarily contain the $[Ti(H_2O)_6]^{3+}$ ion. The same remark applies to $TiBr_3.6H_2O$ (Ti + hot HBr). In both cases, the description fits $[TiX_2(H_2O)_4]^+X.2H_2O$ with *trans*-octahedral structure. Crystalline salts like $Cs_2[TiCl_5(H_2O)].3H_2O$ have also been prepared.

Pyridinium salts of the anionic complexes $TiCl_6^{3-}$ and $TiBr_6^{3-}$ can be isolated by reaction between $TiX_3.3MeCN$ and the pyridinium halide in chloroform. The hexahalo ions also occur in chloride ion melts and at high temperature may exist in equilibrium with the tetrahedral anions :

$$TiCl_6^{3-} \rightleftharpoons TiCl_4^- + 2Cl^-$$

9-coordinate Ti(III) occurs in the volatile $Ti(BH_4)_3$ where each BH_4 group is linked to the metal by three bridging hydrogens; the overall structure is a shallow pyramid.

3-coordinate planar Ti(III) is present in $[Ti\{N(SiMe_3)_2\}_3]$.

The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ has been discussed earlier. The transition from $t_{2g} \longrightarrow e_g$ is observed in many other octahedral complexes and the broad band may be similarly explained from Jahn-Teller distortion of the excited state. The stronger of the two bands is taken as the value of $10Dq$ which varies among common ligands in accordance with the spectrochemical series :

$$Br^- < Cl^- < urea < NCS^- < F^- < H_2O.$$

The room-temperature magnetic moments of Ti(III) complexes lie mostly around the spin-only value of 1.73 B.M. for one unpaired electron. Though the t_{2g}^1 configuration is fit for some orbital contribution to the magnetic moment (section 27.3), the effective magnetic moment is levelled to the spin-only value at room temperature by combined effects of distortion and covalence of the metal ligand bond.

28.3.5 Lower oxidation states of titanium

Titanium(II) is very unstable and there is no aqueous chemistry because of oxidation by water. However, ice-cold solutions of TiO in dilute HCl has been reported to contain Ti(II) ions for some time.

TiO may be made by heating (1600°C) TiO_2 with Ti. It has the sodium chloride structure but is usually non-stoichiometric with one-sixth vacant sites for both ions. It is a metallic conductor (Fig. 28.20).

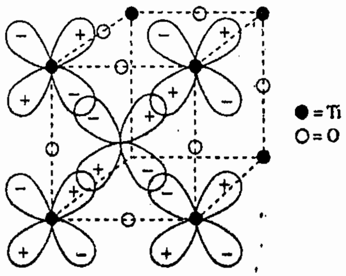


Fig. 28.20

Overlap of t_{2g} orbitals of Ti on one face of TiO lattice (NaCl).

The resulting band is only partly filled and gives rise to metallic conduction.

Black solid TiX_2 (X = Cl, Br, I) may be prepared by reducing the tetrahalides with titanium or by thermal disproportionation of the trihalides. They vigorously evolve hydrogen from water. $RbTiCl_3$ and Rb_2TiCl_4 may be prepared by heating together requisite quantities of RbCl and $TiCl_2$ in an inert atmosphere. The halides act as weak Lewis acids and form blue-black adducts like $TiCl_2.2DMF$ or $TiCl_2.2MeCN$. These adducts are also unstable in water, liberating H_2. The dihalides are polymeric with extensive metal-metal bonding. This is also suggested to exist in the adducts which show room-temperature magnetic moments in the range 1.0 - 1.2 B.M. against the spin-only value of 2.83 B.M. calculated for two unpaired electrons.

Titanium(II) is thought to be involved in a model nitrogen-fixation cycle :

$$Ti(OR)_4 + 2Na^+C_{10}H_8^- \longrightarrow Ti(OR)_2 + 2RONa + 2C_{10}H_8 \text{ (naphthalene)}$$

$$Ti(OR)_2 + N_2 \longrightarrow [Ti(OR)_2N_2]_n$$

$$[Ti(OR)_2N_2]_n + 4Na^+C_{10}H_8^- \longrightarrow ? \longrightarrow 2NH_3 + Ti(OR)_4 + 4RONa$$

The titanium(II) alkoxide plays the crucial role of binding dinitrogen from air at ordinary temperature and pressure, similar to that observed in biological nitrogen fixation.

Oxidation states 0 and less for titanium have been formally reported in dipyridyl complexes and several organometallic compounds. $TiCl_4$ has been reduced by lithium in tetrahydrofuran (THF) in presence of an excess of dipyridyl to give compounds like $Ti(dipy)_3$, $Li[Ti(dipy)_3].3.5$ THF and $Li_2[Ti(dipy)_3].5THF$. The oxidation states of titanium in these compounds are formally assigned as 0, –I and –II respectively. However, such assignment of oxidation states is a mere formality and often disputed. Delocalization of charge into the antibonding π^* orbtials of the ligand may occur to an appreciable extent to justify the complexes involving $dipy^-$ as the effective ligand. Thus, the formally Ti(0) complex $Ti(dipy)_3$ is best formulated as $[Ti^{3+}(dipy^-)_3]$.

Other examples of Ti(0) are π-complexes like $CpTi(CO)_4^-$, $Ti(CO)_2(PF_3)(dmpe)_2$ and Ti(σ, σ, N, N -*i*-Prdab)$_3$. (Cp = cyclopentadienyl; dmpe = 1,2-bis-(dimethylphosphino)-ethane; dab = 1,4-diaza-1,3-butadienes). Organometallics containing titanium (–III) and (–IV) have also been reported.

28.3.6 Organometallic compounds

Interest in organometallic compounds of titanium developed since 1960-s following the discovery of Ziegler-Natta catalysts (Chapter 20). A large number of both σ-and π-bonded organometallics are now known. Only a few will be mentioned.

The σ-bonded molecular alkyls of Ti^{IV} and Ti^{III} are thermally unstable and get readily oxidized in air. $TiMe_4$ may be prepared by slowly adding lithium methyl (in ether) to a suspension of $TiCl_4.2Et_2O$ (in ether) at –80°C.

$$TiCl_4.2Et_2O + 4CH_3Li \xrightarrow[-80°C]{ether} Ti(CH_3)_4 + 4LiCl + 2Et_2O$$

The yellow solid decomposes above about –40°C.

It appears that the high reactivity of σ-bonded transition metal alkyls is associated with their rapidity of reaction in which the low-lying vacant *d*-orbital may be involved. The reason is thus kinetic rather than thermodynamic since the Ti-Me bond is known to be stronger than the Pb—Me bond. Stability of such compounds is greatly enhanced when electron-withdrawing groups (e.g., CF_3 or C_6H_5) or π-acceptor groups are present. Thus, the adduct $(CH_3)_4Ti(dipy)$ is thermally stable to 30°C; $C_6H_5Ti(O\text{-}i\text{-}Pr)_3$ is stable to 10°C. However, these compounds are sensitive to air and water. CH_3TiCl_3, stable at 25°C, probably involves some dative π-overlap of the C—H bonds with the low-lying *d*-orbitals on Ti. This is supported by the presence of symmetrically flattened CH_3 groups in the gaseous molecule.

No stable carbonyls of titanium are known, presumably owing to inadequate back-bonding. $Ti(CO)_6$ has been characterized spectroscopically in a noble gas matrix at 10K. A few carbonyl complexes are known with other π-bonding ligands, e.g., $[(\pi\text{-}C_5H_5)_2Ti(CO)_2]$ and $[(\pi\text{-}C_6H_6)Ti(CO)_4]Br$.

Titanium forms a number of stable π-cyclopentadienyl compounds. $Ti(C_5H_5)_4$ is prepared by the reaction of C_5H_5Na with $TiCl_4$:

$$TiCl_4 + 4C_5H_5Na \xrightarrow{THF} Ti(C_5H_5)_4 + 4NaCl$$

X-ray diffraction analysis of the green-black solid shows that the compound contains two σ-bonded monohapto $(\eta^1\text{-})C_5H_5$ groups bonded through only one carbon atom and two π-bonded pentahapto $(\eta^5\text{-})C_5H_5$ groups bonded through all five C-atoms; the compound is thus $[Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2]$. ^1H and ^{13}C nmr spectra at 20°C show that all protons and all carbon atoms in the compound are equivalent, suggesting fluxional character (see Fig. 28.21).

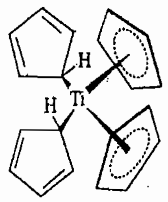


Fig. 28.21

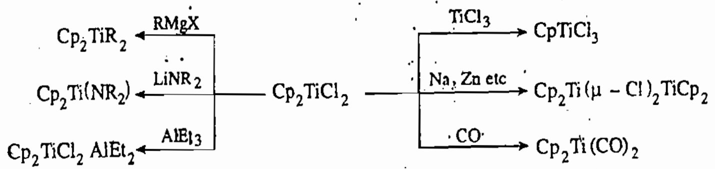
Molecular structure of [Ti(η^1-C_5H_5)$_2$(η^5-C_5H_5)$_2$].

Two fluxional processes occur within the nmr time scale :

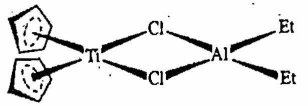
(i) the η^1- and η^5 - rings interchange between themselves.

(ii) the point of attachment of each monohapto ring moves continuously over all five carbon atoms in the ring ("ring whizzing").

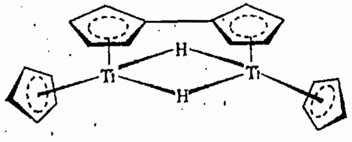
Reaction of NaC_5H_5 and $TiCl_4$ also produces [(η^5 - C_5H_5)$TiCl_3$] and [(η^5 - C_5H_5)$_2$ $TiCl_2$]. Both are orange crystalline diamagnetic compounds stable in dry air which can be sublimed in vacuum without decomposition. These are used as the starting material for a large number of other η^5-cyclopentadienyl (= Cp) derivatives e.g.,



All the compounds contain η^5-cyclopentadienyl groups in approximately tetrahedral orientation around the metal. The blue crystalline compound $Cp_2TiCl_2AlEt_2$ has the structure 28-IV and is also known to polymerize ethylene.



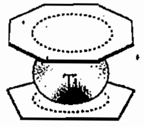
28-IV



28-V

Reduction of Cp_2TiCl_2 (or reaction of $TiCl_2$ with NaCp produces a compound with formula $TiCp_2$ — formal analogue of ferrocene ("titanocence"). The dark green compound is pyrophoric and diamagnetic in nature. It has the dimeric structure 28-V. (^{13}C nmr): The compound is thus μ-(η^5, η^5-fulvalene)-di-(μ-hydrido)-bis(η^5-cyclo-pentadienyltitanium). The monomer may be obtained as an intermediate only.

The formation of the dimer exemplifies the tendency of early *d*-metals to activate the C-H bond leading to its cleavage with transfer of the H-atoms to the Ti-atom. The pentamethyl cyclopentadienyl group, $C_5(CH_3)_5$ (= $\overset{*}{Cp}$) has no H-atoms on the ring and hence ring to metal H-transfer cannot occur. It also forms stronger metal ligand bonds since the ring is richer in electron. The complexes of $\overset{*}{Cp}$ are further stabilized by the greater bulk of methyl groups which shields the metal from further attack. Thus, it is possible to prepare the monomer (η^5-$\overset{*}{Cp}$)$_2$Ti.



28-VI

[Ti(η^8 – C_8H_8)(η^5 – C_5H_5)] (Fig. 28-VI) is an example where the $C_8H_8^{2-}$ ion (derived from cyclooctatetraene) acts as a planar aromatic system (10 π electrons) with nearly equal C—C distances ranging between 138-141 pm.

28.3.7 Detection and estimation

Titanium is detected by the orange colour developed by H_2O_2 on Ti(IV) (see text). The colour is discharged by fluorides owing to the formation of the more stable fluoro complex TiF_6^{2-}. Iron salts may interfere in the test, but may be masked by H_3PO_4.

Titanium may also be estimated colorimetrically by the intensity of the orange peroxo complex.

Titanium precipitates in group IIIA in the systematic group separation of cations. The precipitate may be fused with $KHSO_4$ and extracted with water. Metatitanic acid separates on boiling the extract; this may be dissolved in H_2SO_4 and tested with H_2O_2.

Titanium may be estimated volumetrically by reducing Ti(IV) to Ti(III) with zinc amalgam or cadmium reductor in an atmosphere of CO_2; the Ti(III) is next titrated by a standard solution of Fe(III) alum using potassium thiocyanate as indicator (faint red colour at the end point).

Gravimetrically, titanium may be precipitated as hydrated TiO_2 or the yellow cupferron complex $Ti(cup)_4$ (dilute acid solution). The precipitates may be ignited to TiO_2 and weighed.

28.4 VANADIUM

V : [Ar] $3d^24s^2$	**Atomic number** : 23	**Atomic weight** : 50.94
M.P. : 1720°C	**B.P.** : 3000°C	**Density** : 5.8 g cm^{-3}.

An element that was "born" twice and named after the Goddess of Beauty in recognition of the brilliant colours of its compounds.

28.4.1 Introduction

History : The presence of a new element in some Mexican lead ore was first declared by A. del Rio in 1801 who named it erythronium (Greek erythros = red). The matter subsided when the mineral was wrongly thought to be basic lead chromate. In 1830, Sefström found the same new element in a Swedish iron ore - the element gave compounds with variety of brilliant colours. So he named it vanadium after the Scandinavian Goddess of beauty, Vanadis. In 1831, Wöhler showed that vanadium and erythronium were the same element. Berzelius prepared a number of its compounds; the metal was, however, first isolated by Roscoe (1867) by the reduction of VCl_2.

Occurrence : Vanadium is the fifth most abundant transition metal (nineteenth among the elements), comprising about 0.0136% of the earth's crustal rocks. The metal occurs scattered in a number of other minerals as vanadates, e.g.,

Vanadinite : $PbCl_2$, $3Pb_3(PO_4)_2$ (N-Rhodesia); and

Carnotite : $2K(UO_2)(VO_4)$, $3H_2O$. A complex sulfide mineral is ***patronite***, (VS_4).

Vanadium also occurs in some crude oils (specially at Venezuela).

In India, large deposits (> 2.5 million tonnes) of vanadiferous ores, mainly titanium bearing iron oxide with V_2O_5 content ~ 0.8 - 3% occur in Orissa (Mayurbhanj) and Bihar (Deblabera in Singhbhum). Ashes of some lignites also contain some vanadium.

Certain invertebrates and plants have high concentration of vanadium in their body.

28.4.2 The element

Extraction

Vanadium is obtained mainly as a bye-product in the production of uranium from carnotite. The principal steps are as follows :

(i) Crushed and concentrated ore is roasted in air and leached with sodium carbonate solution. Sodium uranyl carbonate and sodium vanadate passes into the filtrate.

(ii) Sodium diuranate is precipitated by adding sodium hydroxide solution. Alternatively, the uranium (as carbonate complex) is selectively absorbed on an anion exchange resin.

(iii) The filtrate containing sodium vanadate is treated with ammonia (and ammonium chloride) to precipitate orange ammonium vanadate :

$$NaVO_3 + NH_4Cl = NH_4VO_3 + NaCl$$

Alternatively, the sodium vanadate solution may be acidified with dilute H_2SO_4 (pH 2-3) to precipitate a red polyvanadate.

(iv) The ammonium vanadate (or the "red cake") is ignited to vanadium pentoxide (black due to impurities).

$$2NH_4VO_3 = V_2O_5 + 2NH_3 + H_2O.$$

(v) The oxide is mostly (90%) used directly to make ferrovanadium steel. Vanadium may be obtained from V_2O_5 by reduction with hot calcium in an inert atmosphere :

$$V_2O_5 + 5Ca = 2V + 5CaO.$$

Some $CaCl_2$ is added to flux the CaO formed.

Refining

(vi) The metal may be purified by conversion to VCl_4 followed by reduction with magnesium. From this, very pure vanadium may be obtained by the pyrolysis of VI_3 (van Arkel process).

Ferro-vanadium

(vii) Most of the commercial grade vanadium pentoxide is converted to ferrovanadium - an alloy containing about 50% iron. This is obtained by reducing V_2O_5 in presence of molten steel turnings with silicon or ferrosilicon in an electric furnace lined with magnesia.

$$2V_2O_5 + 5Si = 4V + 5SiO_2$$

Lime is added to form slag with the silica : $CaO + SiO_2 = CaSiO_3$.

Carbon reduction is avoided since it leads to the unmanageable formation of carbides.

Vanadium containing residues from other minerals and crude oils may be roasted with NaCl or Na_2CO_3 (800°C) to form water soluble sodium vanadate. This is leached with water and the solution acidified with H_2SO_4 (pH 2-3) when the red polyvanadate is precipitated. This is converted to V_2O_5 or ferrovanadium or vanadium metal as described above.

Properties

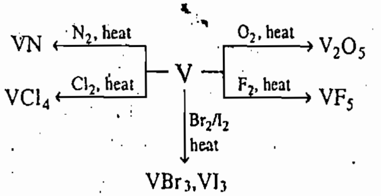
Vanadium is a shining silvery white metal (bcc structure) with high melting and boiling points and low density (Table 28.2).

The pure metal is soft, malleable and ductile but impurities make it hard and brittle.

melting point

The melting point and density of vanadium are higher than those of titanium showing greater involvement of the additional *d*-electron in metallic bonding. This participation of 3*d* electrons in metallic bonding appears highest in vanadium after which the rapidly increasing effective nuclear charge gradually sinks them into the core. As such vanadium has the highest melting point in the first transition series and a stable +5 oxidation state (involving *s* + *d* electrons) which is not strongly oxidizing.

The pure massive metal is stable in air at ordinary temperature but it burns in air/oxygen. The heated metal also reacts with nitrogen, carbon, silicon etc. non-metals to form nitride (VN), carbide and silicide respectively. Only fluorine and oxygen form compounds in +V state :



V-atoms and N_2 molecules may be condensed together at 20-25K to form $[V(N_2)_6]$.

Vanadium dissolves in HF and other oxidizing acids like nitric acid or aqua regia. Water and alkali solutions have no action on it.

Uses

alloys

Vanadium is largely used in making alloy-steels for making springs and high speed tools. Even in small percentage (0.1 - 0.3) the vanadium metal combines with the carbon present in steel to form finely dispersed carbides (V_4C_3) - the resulting fine-grain steel has increased mechanical strength even at high temperature. Chrome-vanadium steel (0.15% V and 1% Cr) is particularly suitable for making shafts, axles and motor car frames. Useful alloys are also formed with other metals like copper, nickel, aluminium etc. Vanadium or its alloys are being tried as a substitute for lead in storage cells.

other uses

Vanadium is a good scavenger in metallurgical operations as it removes the last traces of oxygen. Vanadium and its oxide are widely used as a catalyst in organic and inorganic chemical industries, e.g., oxidation of napthalene to phthalic acid and toluene to benzaldehyde; hydrogenation of alkenes and aromatic hydrocarbons; Cu-V alloy in the oxidation of cyclohexanol-cyclohexanone mixture to adipic acid (as a part of manufacture of nylon-66) and oxidation of sulphur dioxide to sulphur trioxide (manufacture of H_2SO_4).

General chemical features

The oxidation state-free energy diagram for vanadium is shown in Fig. 28.22.

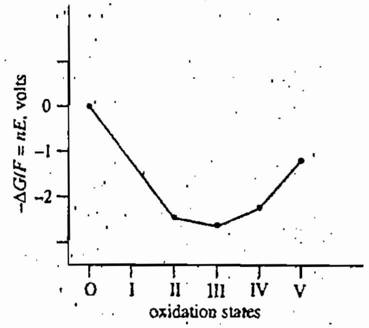


Fig. 28.22
Ebsworth diagram for vanadium.

Values of *nE* (volt) :

V(II) : −2.26; V(III) : −2.52;
V(IV) : −2.18 V(V) : −1.18.

Vanadium has a total of five valence electrons ($3d^3 4s^2$) and shows all oxidation states from –I, to +V, the states from +II ⟶ +V being most important. Vanadium(V) is mildly oxidizing and is associated mostly with oxospecies and fluoride. Its aqueous chemistry is characterized by polymeric species commonly known as isopolyvanadates. Vanadium (IV) is the most stable state under normal conditions and is represented by the halides and the vanadyl ion VO^{2+}. Vanadium (III) is a milder reducing agent than titanium (III) and is stable in aqueous solution; it is only slowly oxidized in air.

In contrast, vanadium (II) is strongly reducing in nature and gets rapidly oxidized in air and water. The solid tends to disproportionate to vanadium (III) and vanadium (0).

Compounds containing vanadium in IV, III and II oxidation states are normally coloured and paramagnetic.

$$\underset{\text{blue}}{VO^{2+}} \longrightarrow \underset{\text{green}}{V^{3+}} \longrightarrow \underset{\text{violet}}{V^{2+}}$$

28.4.3 Compounds of vanadium(V), d^0

Oxide

Vanadium pentoxide V_2O_5 is prepared by heating ammonium vanadate (see extraction). It is also formed when vanadium metal (or its lower oxides) is heated in excess oxygen. The pure oxide is an orange crystalline solid (mp 670°C) but the technical variety is brown.

The oxide loses oxygen reversibly on heating — a property likely to be mostly responsible for its catalytic activity in numerous oxidation processes.

V_2O_5 is slightly (0.007 g/L at 25°C) soluble in water, giving a pale yellow acidic solution. The oxide is mostly acidic in nature, dissolving in alkalis to form vanadates (see below) It also dissolves in acids giving salts of the dioxovanadium(V) ion (the *vanadyl* ion, VO_2^+). The oxidizing nature is shown by the liberation of chlorine when V_2O_5 is boiled with hydrochloric acid. The estimated potential for VO_2^+—VO^{2+} is about 1.0 V :

$$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O \quad E^0 = 1.01\,V$$

Some reactions of V_2O_5 are shown in Fig. 28.23.

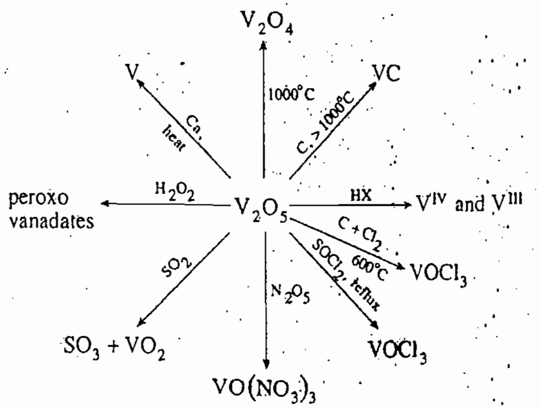


Fig. 28.23
Some reactions of V_2O_5.

V_2O_5 has a high negative free energy of formation, ΔG_f^0 (298K) = –1427 kJ mol^{-1}. Its structure consists of distorted trigonal bipyramids of VO_5 units sharing edges to form zigzag double chains.

The vanadates

V_2O_5 dissolves in strong bases to form "vanadates" which have different compositions at different pH. In strongly basic solution (pH > 12.6), the colourless monomeric tetrahedral ion VO_4^{3-} (orthovanadate) is the main species. As the pH is gradually lowered, the units start to condense — first a dinuclear species (pH 12-9), and then tri and tetra nuclear species (pH 9-7) are formed. These are also colourless.

$$VO_4^{3-} + H^+ \rightleftharpoons VO_3(OH)^{2-}$$

$$2[VO_3(OH)]^{2-} + H^+ \rightleftharpoons [V_2O_6(OH)]^{3-} + H_2O$$

$$3[VO_3(OH)]^{2-} + 3H^+ \rightleftharpoons V_3O_9^{3-} + 3H_2O$$

As the pH is further lowered, red to red-brown polynuclear species ($n \approx 5$-∞) are formed until, at pH ≈ 6, $V_2O_5.xH_2O$ is precipitated.

In more acidic solution (pH ≈ 6-2), the precipitate dissolves, the colour of the solution varying from brown to yellow where the main species is the orange decavanadate ion :

$$10V_3O_9^{3-} + 12H^+ \rightleftharpoons 3V_{10}O_{28}^{6-} + 6H_2O$$

$$V_{10}O_{28}^{6-} + H^+ \rightleftharpoons HV_{10}O_{28}^{5-}$$

$$HV_{10}O_{28}^{5-} + H^+ \rightleftharpoons H_2V_{10}O_{28}^{4-}$$

Below pH 2.2, the monomeric dioxovanadium(V) ion (*vanadyl ion*) VO_2^+, is formed :

$$H_2V_{10}O_{28}^{4-} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O.$$

The decavanadate ion has been isolated as crystalline salts like $Ca_3V_{10}O_{28}.18H_2O$. Raman and nmr (^{17}O and ^{51}V) spectra have established that the same ions are also present in solution. The unit has ten VO_6 octahedra fused together.

Salts of the polymeric $(VO_3^-)_n$ ion are known as metavanadates. The salts MVO_3 are isomorphous for M = NH_4, K, Rb and Cs having infinite chains of corner shared tetrahedral VO_4 units. The hydrate $KVO_3.H_2O$ has chains of edge linked VO_5 units. Four VO_4 tetrahedra linked into a ring by sharing oxygen atoms is present in the cyclic $HV_4O_{12}^{3-}$ ion.

The tendency of the oxoanions to polymerise is a general trend observed in this region of the periodic table (Mendeleef form) - as we have observed earlier with borates, phosphates and silicates. Among the *d*-block elements also, such tendency is observed among vanadium, chromium and notably molybdenum and tungsten (see iso and heteropolyacids, chapter 29).

Halides and oxohalides

VF_5 is the only pentahalide of vanadium(V). It may be prepared by heating the metal in fluorine at 300°C or by disproportionation of VF_4

$$VF_4 \xrightarrow[N_2]{600°C} VF_5 + VF_3$$

VF_5 is a volatile solid/liquid (m.p. 19.5°C) which hydrolyzes readily in moist air. It is a violent oxidizing and fluorinating agent. Ligands like NH_3, py etc. usually give adducts containing vanadium(IV) fluoride, for example $VF_4.NH_3$, $VF_4.py$ and $VF_4.en_3$. KF reacts with VF_5 at room temperature to form KVF_6. Salts of VF_6^- ion are also formed by reacting VCl_3 and any alkali metal halide with BrF_3.

In the vapour phase, VF_5 is monomeric with the trigonal bipyramid structure. The solid consists of chains of VF_5 octahedra with two bridging fluorines in cis positions to each other.

Oxohalides VOX_3 (X = F, Cl, Br), VO_2F and VO_2Cl are known.

VOF_3 may be prepared by reacting VF_5 with air or by oxidizing VF_3 with O_2. It may also be obtained by fluorination of $VOCl_3$ (e.g., by HF). It is a highly reactive yellow solid (m.p. 300°C).

$VOCl_3$ and $VOBr_3$ may be prepared by the action of Cl_2 or Br_2 on V_2O_5, or better, a mixture of V_2O_5 + C at 300°C. $VOCl_3$ is a yellow liquid (bp 127°C) and $VOBr_3$ is a deep red solid which decomposes at 180°C.

Thermal stabilities of the oxohalides decrease from VOF_3 to $VOBr_3$ (VOI_3 is yet to be prepared) with increasing reducing power of the halide ion, $VOBr_3$ liberating bromine at room temperature. All the oxohalides are readily hydrolyzed in moist air forming copious brown fumes of V_2O_5. The reactions of VOF_3 with ligands have not been studied well but $VOCl_3$ and $VOBr_3$ may enter both addition and substitution (solvolytic) reactions together with expected reduction reactions (more so for $VOBr_3$).

Addition : $VOCl_3 + Cl^- \longrightarrow VOCl_4^-$

$VOCl_3 + \text{dipy} \longrightarrow VOCl_3(\text{dipy})$

Substitution : $VOCl_3 + NH_3 \longrightarrow VO(NH_2)_3$

$VOCl_3 + EtOH \longrightarrow VOCl_2(OEt),\ VOCl(OEt)_2$

Reduction : $VOCl_3 + Me_3N \longrightarrow VOCl_2(NMe_3)_2$

$VOCl_3 + Et_2S \longrightarrow VOCl_2(SEt_2)_2$

$VOBr_3 + Br^- \xrightarrow{CH_3CN} VOBr_3^-/VOBr_4^-$ (depends upon the cation)

However, $VOCl_3$ does not react with metals, even with sodium. It also dissolves many nonmetals and hence bears the potentiality of a nonaqueous solvent.

The $VOCl_3$ molecule is monomeric and tetrahedral in the vapour phase (electron diffraction). $VOCl_2(NMe_3)_2$ is nearly tbp with axial Me_3N groups.

Complex compounds

Complex compounds of vanadium(V) are also very few. The white, diamagnetic hexafluorocomplexes MVF_6 (M = alkali metal) are readily formed e.g., by direct reaction between KF and VF_5 at room temperature, but the compounds are extremely moisture sensitive. Various peroxocomplexes of vanadium(V) are formed by the addition of hydrogen peroxide to aqueous solutions of vanadium(V) under varying conditions of acidity. In acid solution, the red-brown peroxo analogue of vanadyl cation, $[V(O\text{-}O)]^{3+}$ is formed; in alkaline solution, yellow complexes are formed of the type $[V(O\text{-}O)_2O_2]^{3-}$. In strongly alkaline medium and using highly concentrated (~ 100 volume) H_2O_2 solution, further substitution takes place, giving blue $[V(O_2)_4]^{3-}$ and $[V(O_2)_3]^-$ ions. These peroxo complexes are also formed by reacting V_2O_5 with strong H_2O_2 solution. In presence of KCl or NH_4Cl, salts of the ion $[V(O_2)_3Cl]^{2-}$ have been isolated. The complex $[VO(O_2)_2(C_2O_4)]^{3-}$ ion has a distorted pentagonal bipyramid structure (Fig. 28.24).

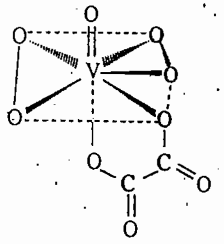


Fig. 28.24

Structure of $[VO(O_2)_2C_2O_4]^{3-}$ in the potassium salt.

For each peroxo group one V—O distance is 186 pm and the other V—O distance is 192 pm, the shorter V—O bonds being *trans* to the oxalate.

28.4.4 Compounds of vanadium(IV)

Oxide

Dark blue VO_2 is readily formed by mild reduction of V_2O_5 e.g., by fusion with oxalic acid. VO_2 again forms V_2O_5 on heating in air. The oxide is amphoteric, though more basic than acidic.

VO_2 dissolves in acids to give the blue vanadyl(IV) ion, VO^{2+} which forms a variety of salts. Reaction of VO_2 with alkali forms a number of vanadate(IV) anions like VO_3^{2-}, VO_4^{4-} and polyanions like $V_4O_9^{2-}$ and $V_{18}O_{42}^{12-}$. All these species give rise to an extensive aqueous chemistry of vanadium(IV).

The oxide VO_2 has a distorted rutile structure (TiO_2). The high temperature form of this is a metallic conductor but ordinarily it is an insulator owing to weak metal-metal interaction.

Aqueous chemistry of vanadium(IV)

The V^{4+} ion has a high charge density and as such the $[V(H_2O)_6]^{4+}$ ion is too acidic to exist in aqueous solution; instead, the aqueous chemistry of vanadium(IV) is dominated by the oxovanadium(IV) cation, $[VO(H_2O)_5]^{2+}$ or simply the VO^{2+} (vanadyl) ion, formed by dissolving VO_2 in acids.

$$VO_2 + 2H^+ + 4H_2O = [VO(H_2O)_5]^{2+}$$

Cationic species of V^{4+} are virtually unknown, $[V(en)_3]F_4$ being a rare exception.

The VO^{2+} grouping is very stable since the V—O bond is close to a double bond (See Fig. 28.25) resulting from π-overlap of a filled 2*p* orbital on oxygen to an empty 3*d* orbital on vanadium.

Fig. 28.25

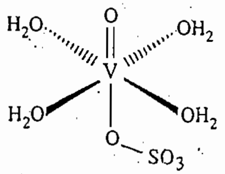
The structure of $VOSO_4$, $5H_2O$

V = O : 159 pm

V — OH_2 : 198-205 pm

V — OSO_3 : 222 pm

The V=O group has a I.R. stretching frequency around 950-1000 cm^{-1}; the V—O single bonds respond at about 480 cm^{-1}.



The VO^{2+} ion is neither strongly oxidizing nor reducing :

$$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O \qquad E° = +0.34\ V$$

$$[V(OH)_4]^+ + 2H^+ + e \rightleftharpoons VO^{2+} + 3H_2O \quad E° = 1.0\ V$$

Acidified solutions containing VO^{2+} are not oxidised by atmospheric oxygen.

Estimation of vanadium

The oxovanadium(IV) is quantitatively oxidized to vanadium(V) by acidified permanganate solution (70°C). This forms the basis of estimation of vanadium. All the vanadium in a sample is first oxidized to +V state by acid—$KMnO_4$ and then reduced to V(IV) by SO_2 or sulphite. The excess SO_2 is removed by boiling (V^{IV} does not change) and the V^{IV} is titrated by standard $KMnO_4$ solution (acid).

The $[VO(H_2O)_5]^{2+}$ ion is weakly acidic :

$$[VO(H_2O)_5]^{2+} \rightleftharpoons [VO(OH)(H_2O)_4]^+ + H^+ (aq); \qquad pK \approx 6.0$$

Addition of sodium carbonate precipitates the yellow-brown basic oxide $VO(OH)_2\ aq$, while strong alkalis form brown solutions of vanadate(IV). Crystalline compounds of the type $M^I_2V_4O_9.7H_2O$ and having other large anionic aggregates like $Na_{12}V_{18}O_{42}.24H_2O$ may be isolated from such solutions.

The VO^{2+} ion forms numerous oxovanadium(IV) complexes which may be anionic, cationic as well as neutral. These may be prepared easily by reduction of V_2O_5, e.g.,

$$V_2O_5 + 10HCl \longrightarrow 2[VOCl_4]^{2-} + 4H^+ + Cl_2 + 3H_2O$$

Similarly, V_2O_5 may be dissolved in hot oxalic acid solution to form $[VO(C_2O_4)_2]^{2-}$ ion. The complexes are usually 5-coordinate square pyramidal with the oxygen of the VO unit occupying an apex. The V-atom is often slightly above the base. The position opposite to the apex remains vacant in 5-coordinate complexes or takes an additional ligand to attain coordination number 6. A 5-coordinate trigonal bipyramidal structure has also been established in $VOCl_2(NMe_3)_2$ (28.26).

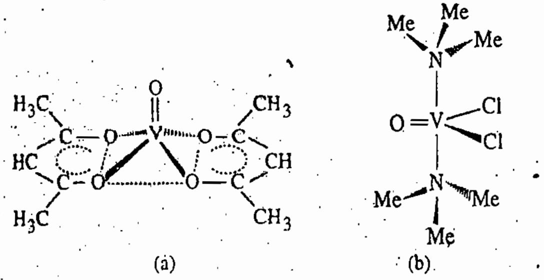


Fig. 28.26 5-coordination in (a) square pyramidal $[VO(acac)_2]$ and (b) trigonal bipyramid $[VOCl_2(NMe_3)_2]$.

The 5-coordinate complexes may become 6-coordinate by picking up an extra ligand, e.g., $[VO(acac)_2.py]$. Certain polymeric compounds with V—O—V bonding also contain six coordinate vanadium as in vanadyl acetate, $VO(CH_3COO)_2$, a greyish green compound sparingly soluble in water. The compound also contains bridging acetate groups.

> **Q. 28.4** *Solutions of $[VO(acac)_2]$ in benzene or CS_2 show V—O stretching frequency (ν) around 1006 cm^{-1} (close to the value for solid : 996 cm^{-1}). When pyridine or ethylenediamine are added, ν decreases by about 50 cm^{-1}. Comment.*
>
> **Hint :** Benzene or CS_2 are nonpolar and noncoordinating solvents. Coordination by pyridine or ethylenediamine increases charge density on V, thereby reducing O⟶V π-donation.

The V = O bond can be ruptured by thionyl chloride :

$$(pyH)_2[VOCl_4] + SOCl_2 \longrightarrow (pyH)_2[VCl_6] + SO_2$$

Treatment of VO^{2+} complexes with B_2S_3 produces complexes of VS^{2+}.

Halides

The tetrahalides VX_4 (X = F, Cl, Br) may be prepared by direct reaction. VF_4 tends to disproportionate into VF_5 and VF_3 and can be separated by sublimation.

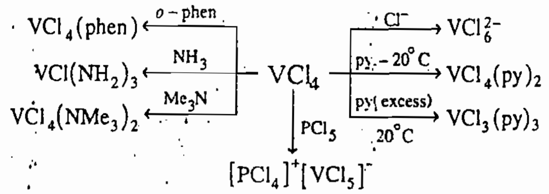
$$2VF_4 \longrightarrow VF_3 + VF_5$$

VCl_4 and VBr_4 also tend to dissociate into VX_3 and X_2 (X = Cl, Br). VCl_4 slowly at room temperature and VBr_4 appreciably above −23°C. VBr_4 is actually obtained by thermal decomposition of VBr_3 at 325°C and condensing the vapours at −78°C.

Physical properties of the tetrahalides are as follows :

VF_4	VCl_4	VBr_4
lime-green solid	dark red-brown liq.	magenta
sublimes > 150°	m.p. −26°, b.p. 148°C	dec > −23°C

All the tetrahalides are hydrolyzed by moist air. VF_4 and VCl_4 act as Lewis acids —VF_4 forms 1 : 1 adducts with SeF_4, NH_3 and pyridine. VCl_4 forms a large number of adducts and substitution products which may be neutral or anionic :



VCl_4 is more easily reduced to V(III) than $TiCl_4$ — when reduction occurs, the product is commonly five-coordinate rather than the common six-coordinate ones.

o-phenylenebis(dimethylarsine), diars, forms $[VCl_4(diars)_2]$ — the eight-coordinate adduct is isomorphous with its titanium analogue.

Complexes

The majority of complex compounds of vanadium(IV) belong to the oxovanadium complexes mentioned before. Most of them conform to the spin-only magnetic moment expected for one unpaired electron. However, the electronic spectra of the complexes are not simple to the same extent though they formally belong to the d^1 case. Deviation of the complexes from regular octahedral stereochemistry seems to be the main reason for such complicacy. On a simple crystal field model, transition from the $^2B_2$ ground term to ^2E, $^2B_1$ and $^2A_1$ terms may be associated with the commonly observed bands in the regions 11,000—15,000 cm^{-1}, 14,500—20,000 cm^{-1} and 21,000—31,000 cm^{-1}. But quantitative agreement with observed spectra is not satisfactory on the CFT. Somewhat better fit is obtained from molecular orbital treatment of $[VO(H_2O)_5]^{2+}$ taking axial pi-bonding into account.

There are also many complexes of vanadium(IV) outside the oxovanadium range, the adducts formed by the halides being the most ready examples. Another example in this category is the tris-catecholate complex $[V(cat)_3]^{2-}$.

28.4.5 Compounds of vanadium(III), d^2

Oxide

"V_2O_3" is a black refractory substance formed when V_2O_5 is reduced with hydrogen or CO. The compound easily loses oxygen from the lattice — compositions as low as $VO_{1.35}$ are known. The corundum structure is retained in all such compositions.

The trioxide is basic — it dissolves in acids to give $[V(H_2O)_6]^{3+}$ ions. Addition of alkali to such solutions precipitates the hydrous oxide $V_2O_3.aq.$ which is readily oxidized in air.

Aqueous chemistry

Solutions containing $[V(H_2O)_6]^{3+}$ ions may be obtained by (i) dissolving the black trioxide in nonoxidizing acids; (ii) reduction (electrolytic or chemical) of V^V or V^{IV}; (iii) dissolving the halides VX_3 in water :

$$VCl_3 + 6H_2O \longrightarrow [V(H_2O)_6]^{3+} + 3Cl^- \,(aq)$$

$[V(H_2O)_6]^{3+}$ is susceptible to aerial oxidation in accordance with the potential

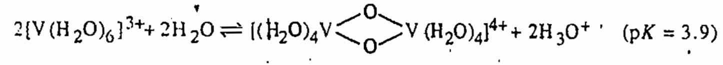
$$VO^{2+} + 2H^+ + e \longrightarrow V^{3+}\,(aq) + H_2O \quad E^\circ = 0.34\ V$$

The ion hydrolyzes partially to VO^+ and $[V(OH)]^{2+}$ and shows acidic properties

$$[V(H_2O)_6]^{3+} + H_2O \rightleftharpoons [V(OH)(H_2O)_5]^{2+} + H_3O^+ \;(pK_1 = 2.9).$$

The ion $[V(H_2O)_6]^{3+}$ occurs in solid alums M_2SO_4, $V_2(SO_4)_3$, $24H_2O$. The ammonium alum can be obtained as blue violet air-stable crystals by reducing NH_4VO_3 electrolytically in H_2SO_4 solution followed by crystallization.

$[V(H_2O)_6]^{3+}$ also undergoes olation reaction to form binuclear species :



$$2[V(H_2O)_6]^{3+} + 2H_2O \rightleftharpoons [(H_2O)_4V\begin{smallmatrix}O\\ \\O\end{smallmatrix}V(H_2O)_4]^{4+} + 2H_3O^+ \quad (pK = 3.9)$$

This is characterized by a strong charge-transfer band around 22,930 cm^{-1}. A linear $[V—O—V]^{4+}$ unit is formed as a brown intermediate when solutions of V^{2+} and VO^{2+} are mixed; the ultimate product is of course V^{3+}.

The V^{3+} ion forms a variety of complexes with oxygen, nitrogen or halogen donor ligands, the most common ones being octahedral. As expected for a d^2 ion (t_{2g}^2), such complexes are labile as the vacant t_{2g} orbital offers a low-energy path for attack. The hydrated halides $VCl_3.6H_2O$ and $VBr_3.6H_2O$ (crystallized from acidic solution) have the structure *trans*- $[VX_2(H_2O)_4]X.2H_2O$. Other cationic complexes include $[V(urea)_6]^{3+}$ and in alcohols, $[VX_2(EtOH)_4]^{3+}$. Typical anionic complexes are exemplified by $[V(NCS)_6]^{3-}$ and $[V(C_2O_4)_3]^{3-}$. The complex $[V(CN)_6]^{3-}$ can be made in alcohol but it precipitates $V(CN)_3$ on adding water. When an excess of potassium cyanide solution is added to an aqueous solution of V^{III} in dilute HCl, the solution turns deep blue; on standing at room temperature in absence of air, the colour of the solution changes to wine-red. From this red solution, addition of methanol precipitates red crystals of $K_4[V(CN)_7].2H_2O$.

The $[V(CN)_7]^{4-}$ ion is an example of the relatively rare coordination number seven having a pentagonal bipyramid structure (Fig. 28.27). From the deep blue solution formed initially, a deep blue complex may be isolated at low temperatures which may contain vanadium in two different oxidation states, one being V^{II}.

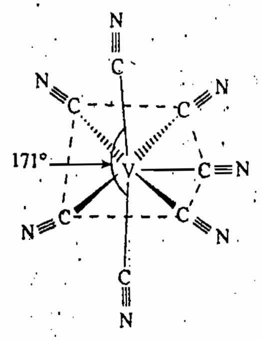


Fig. 28.27

Structure of $[V(CN)_7]^{4-}$ ion.

The equatorial bond angles are on the average 72°. The axial C—V—C angle is slightly bent at 171°.

Halides

All four trihalides are stable solids at room temperature. VF_3 and VCl_3 are obtained from disproportionation of the tetrahalides while VBr_3 and VI_3 may be prepared by direct combination. Yellow-green VF_3 has a notably high melting point (800°C); VCl_3 (violet), VBr_3 (grey-brown to black) and VI_3 (black) decompose on heating :

$$2VCl_3 \longrightarrow VCl_2 + VCl_4 \;(400°C); \quad 2VI_3 \longrightarrow 2VI_2 + I_2 \;(300°C)$$

VF_3 is not very soluble in water; but others are hygroscopic and are hydrolyzed and oxidized in moist air.

Except VF_3, the trihalides dissolve in coordinating solvents forming complexes. Some reactions of VCl_3 are shown in Fig. 28.28.

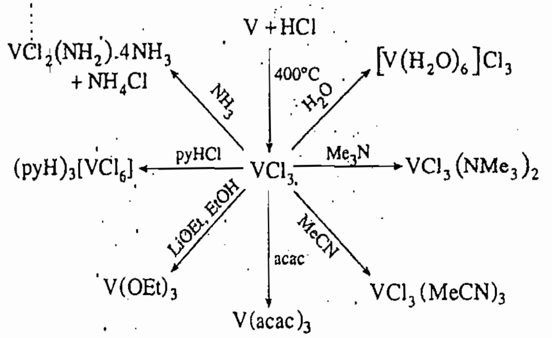


Fig. 28.28
Reactions of VCl_3.

The magnetic moments of the trihalides are slightly less than 2.83 B.M., the spin-only value expected for 2 unpaired electrons.

Vanadium(III) forms a dimeric triacetate similar to that of Cr(II). (Fig. 28.34).

28.4.6 Compounds of vanadium(II) (d^3)

Oxide

Vanadium(II) oxide "VO" tends to be non-stoichiometric ($VO_{0.9}$ – $VO_{1.3}$). It is formed by reacting V_2O_5 with vanadium and has a rock-salt structure. The oxide is basic and dissolves in acid to form the violet $[V(H_2O)_6]^{2+}$ ion. The ion is strongly reducing in nature, turning green in air due to oxidation to $[V(H_2O)_6]^{3+}$. In absence of oxygen or other oxidizing agents, water itself is slowly reduced to liberate hydrogen.

Aqua ions

Reduction of ammonium vanadate by zinc and acid ultimatley gives vanadium(II) through other intermediate oxidation states. Thus, addition of zinc dust to an HCl solution of NH_4VO_3 (yellow) successively produces blue $[VO(H_2O)_5]^{2+}$; green $[VCl_2(H_2O)_4]^+$ and other vanadium(III) species and finally $[V(H_2O)_6]^{2+}$. Using sulphuric acid, addition of ethanol to the final solution followed by evaporation in vacuum over phosphorus pentoxide gives violet crystals of VSO_4, $6H_2O$. Double sulphates $\overset{I}{M_2}SO_4$, VSO_4, $6H_2O$ ($M = \overset{+}{NH_4}$, K^+, Rb^+, Cs^+) known as *Tutton salts* are somewhat more stable to oxidation than the simple sulphate. The crystals and their solutions give absorption spectra characteristic of $[V(H_2O)_6]^{2+}$ ions. The magnetic moments are also close to the spin-only value.

Substitution reactions of $V(H_2O)_6^{2+}$ are slow — the kinetic inertness is consistent with its $d^3(t_{2g}^3)$ configuration (sec. 27.4). The ion forms weak complexes with F^- and SCN^- but complexing with Cl^-, Br^-, I^- or SO_4^{2-} is not well established.

Halides

All four dihalides VX_2 are known. VF_3 may be reduced to VF_2 by H_2/HF at 1200°C. The fluoride forms blue crystals with the rutile structure. VCl_2, VBr_2 and VI_2 are obtained by disproportionation of the trihalides. The dihalides dissolve in water giving the hexaaqua ion (violet). Hydrated crystals VX_2, $6H_2O$ (X = Cl, Br, I) may be obtained by electrolytic reduction of vanadium(IV) in presence of respective HX. These crystals also contain the hexaaqua ion; this is also present in RbCl, VCl_2, $6H_2O$. VCl_2 dissolves in hot pyridine to form $VCl_2(py)_4$. Reduction of VCl_3 by zinc in THF gives the dinuclear cation $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, formerly reported as $VCl_2(THF)_2$.

Complexes

$[V(dipy)_3]^{2+}$ may be prepared by adding an alcoholic solution of the ligand to aqueous VSO_4, $7H_2O$; the ion may be precipitated using I^- or ClO_4^- as counterion. The orange cyrstalline complex $K_4[V(CN)_6]$, $7H_2O$ contains octahedral $[V(CN)_6]^{4-}$ ions. $K_4[V(CN)_6]$ is also formed by reducing $[K_4\{V(CN)_7]$ with potassium in liquid NH_3; but further reduction occurs to $K_5[V^I(CN)_6]$.

28.4.7 Lower oxidation states (I, 0, –I, –III)

These oxidation numbers are known only in complexes with strong π-acceptor ligands like CO, NO and dipyridyl. The main geometry is octahedral, though a few examples of 7-coordination are also known.

Vanadium(I) is present in the nitrosyl cyanide complex $K_3[V(CN)_5NO].2H_2O$. The N—O stretching frequency around 1530 cm^{-1} suggests that NO is present as NO^+, thus counting for the formal +I oxidation state for vanadium. $K_5[V(CN)_6]$ and $[V(dipy)_3]^+$ are examples of other vanadium(I) species.

Vanadium(0) is present in the carbonyl $V(CO)_6$ and carbonylnitrosyl $V(CO)_5(NO)$. $V(CO)_6$ is prepared according to the sequence

$$VCl_3 + Na \xrightarrow[CO,\ 25\ MPa\ pr]{100°C/diglyme} [Na\ (diglyme)_2]^+\ [(VCO)_6]^- \xrightarrow{H_3PO_4} V(CO)_6.$$

Vanadium carbonyl

The blue-green air-sensitive sublimable crystals decompose above 60°C. It is monomeric both in the solid and in benzene solution with a room-temperature paramagnetic moment of 1.8 B.M. corresponding to one unpaired electron. The valence shell of vanadium thus contains 17 electrons, one electron short of the 18*e* formalism. Interestingly, $V(CO)_6$ does not dimerize and form M-M bond like other odd-electron transition metal carbonyls. The $[V(CO)_6]^-$ ion conforms to an 18*e* count; $V(CO)_6$ disproportionates with many oxygen and nitrogen donor ligands (L) into $[V(CO)_6]^-$ and $[VL_6]^{2+}$ ions. Substitution reactions typical of monomeric carbonyls are also shown by $V(CO)_6$; thus phosphines (R_3P) react with $V(CO)_6$ producing red-brown paramagnetic *trans*-$[V(PR_3)_2(CO)_4]$. When NO is passed through a solution of $V(CO)_6$ in cyclohexane at 0°C, violet-red unstable $[V(CO)_5NO]$ is formed.

V(0), V(–I)

Vanadium also forms complexes with dipyridyl and *o*-phenanthroline in oxidation states 0 and –1 : $V(dipy)_3$ and $V(o\text{-}phen)_3$ have magnetic moments corresponding to only one unpaired electron; on the other hand, the complexes $Li[V(dipy)_3].4THF$ and $Li[V(phen)_3]$. 3.5 THF are diamagnetic, supporting the presence of V(–I). As expected, the compounds are highly susceptible to aerial oxidation.

V(–III)

The lowest formal oxidation state of vanadium is –III reported in $[V(CO)_5]^{3-}$ which is obtained by further reduction of $[Na(diglyme)_2][V(CO)_6]$ with sodium metal in liquid ammonia. The Rb- and Cs- salts of the ion are thermally stable, the K-salt is highly shock-sensitive.

28.4.8 Organometallic compounds of vanadium

Vanadium forms sandwich type complexes with cyclopentadiene and benzene. $V^{II}(\eta^5\text{-}C_5H_5)_2$, vanadocene, is a paramagnetic violet black solid, mp 167°C. $V(C_6H_6)_2$, bis(benzene)vanadium is also thermally stable (m.p. 277°C) though both these compounds are readily oxidized in air.

Vanadocene undergoes oxidative additions with many compounds to give cyclopentadienyls of V(III) and V(IV). Cp_2VCl_2 possesses potential antitumour activity.

When $VCl_3.3THF$ is treated with a large excess of lithium phenyl in ether, the purple complex $Li_4[VPh_6]$. 3.5 Et_2O is obtained. The compound is decomposed by air and moisture and corresponds to V(II) from its magnetic moment ~ 3.8 B.M.

28.4.9 Detection and estimation

A solution of vanadate(V) produces a red colouration with H_2O_2 (*avoiding excess*) in presence of 15-20% H_2SO_4. The colour is not removed by shaking the solution with ether nor is it discharged by phosphates or fluorides (distinction from titanium). The colour is most likely due to $[V(OO)]_2(SO_4)_3$ (see complex compounds of V(V)).

H_2S reduces a vanadate solution (acid) to blue V(IV) with the separation of sulfur. Ammonium sulfide solution produces a red colour due to the formation of thiovanadates. Brown V_2S_5 is incompletely precipitated on acidifying the solution, leaving a blue filtrate. The precipitate is soluble in aqueous alkalis.

Vanadium may be estimated gravimetrically by precipitation with cupferron followed by ignition to V_2O_5. Vanadates are reduced to blue vanadyl salts by Mohr's salt; the exces Mohr solution may be back-titrated by standard $K_2Cr_2O_7$.

28.5 CHROMIUM

Cr : $[Ar]3d^54s^1$ **Atomic number : 24** **Atomic weight : 51.996**

M.P. : 1900°C **B.P. :** 2700°C **Density :** 7.14 g cm^{-3}

A beautiful red mineral from the urals was carried to Europe by an academician-traveller P.S. Pallas in the 1770-s. A sample of this fell in the hands of a french chemist.

28.5.1 Introduction

History : in 1797 - 98, L.N. Vauquelin (France) first isolated and introduced a new element from a siberian mineral (now established as crocoite, $PbCrO_4$). This was named chromium owing to the rich colours found in its compounds (Greek *chroma* = colour).

Abundance and occurrence : Chromium is moderately abundant in the earth's crust (0.04% by weight). It occurs mainly as chromite ($FeCr_2O_4$), found in South Africa, Russian countries and the Philippines. Crocoite ($PbCrO_4$) and chrome ochre (Cr_2O_3) are other minerals of the metal. In the gemstone ruby, Cr^{III} ions substitute some Al^{III} ions in α-Al_2O_3; emerald also contains some Cr^{III} in beryl.

Indian scenario

In India, chromite occurs in Orissa, Ladakh, Maharashtra, Bihar, Tamilnadu and Karnataka. High grade deposits are found in the Keonjhar, Cuttack and Dhenkanal districts in Orissa. In Ladakh, chromite occurs sporadically as veins amidst dunites in the volcanic rocks of Drus, at a height of ~12000 ft. (Brown Hill). Reasonably good deposits are found in the Hassan district in Karnataka (48-50% Cr_2O_3) and Singhbhum district of Bihar. Low grade ores are sporadically distributed in other areas like Maharashtra (Ratnagiri and Bhandara districts) and Salem (Chalk Hills) in Tamilnadu. The ore at Tamilnadu has a peculiar chemical composition that requires special treatment. Hence the ore is not economical in comparison to other deposits.

28.5.2 The element

Extraction

Chromium is extracted from chromite via Cr_2O_3. The main steps are as follows :

(i) *Aerial oxidation of chromite*

Powdered chromite is heated (1000°-1300°C) with sodium carbonate and quicklime in a reverberatory furnace with free access of air. Lime keeps the mass porous.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Chromium is oxidized to sodium chromate. The iron is converted to Fe_2O_3.

(ii) *Formation of sodium dichromate*

The sodium chromate is leached out with water and converted to sodium dichromate by adding conc. H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

The sodium sulphate separates first from the concentrated solution. On evaporation to a specific gravity ~1.7, deliquescent red crystals of $Na_2Cr_2O_7.2H_2O$ deposit on cooling.

(iii) *Reduction of Cr(VI) to Cr(III)*

The sodium dichromate is reduced to Cr_2O_3 by heating with carbon (wood-charcoal or saw-dust may also be used).

$$Na_2Cr_2O_7 + 2C = Cr_2O_3 + Na_2CO_3 + CO.$$

(iv) *Reduction to metallic chromium by aluminothermy*

Chromium(III) oxide is reduced to metallic chromium by aluminium powder (*Thermite process*) : a mixture of powdered Cr_2O_3 and Al-powder is ignited in a refractory crucible; the heat produced in the reaction melts the chromium metal which forms a layer under fused alumina. The metal is nearly 99.5% pure (iron and silicon are main impurities).

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr \qquad \Delta G° = -523\ kJ$$

$$2Cr_2O_3 + 3Si \longrightarrow 4Cr + 3SiO_2$$

Pure Chromium may be obtained by reducing chromium(III) chloride with metallic calcium in a $CaCl_2$ or $BaCl_2$ melt.

Chromium for the steel industry is produced as *ferrochrome*, an alloy with iron containing up to 60 per cent Cr. For this, chromite is reduced directly by carbon in an electric arc furnace :

$$FeCr_2O_4 + 4C = Fe + 2Cr + 4CO.$$

Low-carbon ferrochrome is now produced by reduction with ferrosilicon. The ferrochrome obtained is directly added to steel to prepare hard and "stainless" steel (13-14% Cr, 1% Ni).

Chromium plating is done by dissolving Cr_2O_3 in sulphuric acid and electroplating the articles using antimonial lead anode and a high current density.

Properties

Chromium is a hard but malleable, greyish (blue tinge) white shiny metal with a typical body centered cubic lattice. The main physical properties are given in Table 28.2. The metal does not tarnish in air and hence its use in chromium plating.

The m.p., b.p. and enthalpy of vaporization of chromium are less than those of vanadium. This suggests that the 3*d* electrons are beginning to become a part of the inner electron core with less participation in metallic bonding.

Chromium dissolves slowly in dilute HCl and H_2SO_4, evolving hydrogen.

$$Cr + 2HCl = CrCl_2 + H_2$$

The chromium(II) chloride in solution is readily oxidized by air to chromium(III), turning green (see redox potential).

$$4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O.$$

Concentrated sulphuric acid attacks chromium forming chromium(III) sulphate :

$$2Cr + 6H_2SO_4 = Cr_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Nitric acid, whether dilute or concentrated, and aqua regia render the metal passive, presumably due to the formation of an impervious oxide layer. This may be removed by touching the metal with zinc in dilute sulphuric acid.

When heated, particularly in the powdered state, chromium burns in oxygen :

$$2Cr + \frac{3}{2}O_2 = Cr_2O_3 \qquad \Delta G^0_{298} = -1059\ kJ$$

The heated metal also reacts with steam ($CrCl_3 + H_2$), HCl gas ($CrCl_2 + H_2$) and halogens (CrX_3).

Uses

Chromium is largely used in making stainless steel and other alloys. Chromium makes steel tough and corrosion resistant, hence the use of *chromium steel* (1.5-2% Cr) in cutting tools, armour plates, ball bearings etc. *Stainless steel* contains about 12-14% Cr and 1% Ni. Steels with higher chromium content (17-18%) and 7% or more of nickel have superior corrosion resistance. ***Chromium vanadium steel*** (1% Cr + 0.15%V) and *chromium-tungsten steel* (3-8% Cr, 14-20% W) are used in making springs, shafts, axles and high speed tools. *Nichrome* (60% Ni, 14% Cr + 25% Fe + 0.2-1% C) is widely used as resistance coils in electrical heating; it has high m.p., high electrical resistance and is not readily oxidized.

Chromium is also used in chromium plating which does not tarnish by sulphur compounds in the atmosphere.

General Chemical Features

The oxidation state-free energy diagram (Fig. 28.29) for chromium suggests that Cr(III) is the most stable state, while, Cr(II) will be reducing and Cr(VI) oxidizing in nature. Cr(II) readily disproportionates. Other low oxidation states are found in complexes and organometallic compounds.

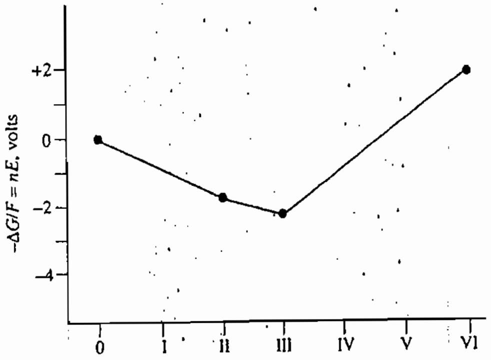


Fig. 28.29

The oxidation state-free energy diagram for chromium.

$Cr^{2+} + 2e = Cr \quad E° = -0{\cdot}91V$

$Cr^{3+} + 2e = Cr \quad E° = -0{\cdot}74V$

$Cr_2O_7^{2-} + 14H^+ + 6e$

$= 2Cr^{3+} + 7H_2O$

$E° = 1.33V$

28.5.3 Chemistry of chromium(VI), $3d^0$

Compounds of chromium(VI) are limited — the principal species being CrO_3; unstable CrF_6; the oxohalides $CrOX_4$ (X = F, Cl), CrO_2X_2 and CrO_3X^- (X = F, Cl, Br, I); the oxoions $Cr_nO_{3n+1}^{2-}$ (n = 1, 2, 3, 4) and the peroxo compounds.

Oxide

Chromium(VI) oxide, CrO_3 (chromium trioxide) is formed by adding concentrated H_2SO_4 to a concentrated aqueous solution of potassium dichromate :

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3 + H_2O$$

Dark red shining crystals separate on cooling the solution which may be filtered through *asbestos*, washed with concentrated HNO_3 and dried in air.

Chromium burns in air to produce Cr_2O_3 having a more negative energy of formation :

$$2Cr\ (c) + \frac{3}{2} O_2\ (g) = Cr_2O_3\ (c) \qquad \Delta G^0_{298} = -1059 \text{ kJ}$$

$$Cr\ (c) + \frac{3}{2} O_2\ (g) = CrO_3\ (c) \qquad \Delta G^0_{298} = -506 \text{ kJ}$$

CrO_3 melts at 197° and begins to decompose :

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

The oxide is acidic and highly soluble in water — the strongly acidic red solution contains H_2CrO_4 as the main species below pH 1 but at higher pH $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions predominate. The CrO_4^{2-} ion becomes the principal species above pH 6 (see aqueous chemistry).

CrO_3 is a very powerful oxidizing agent — the concentrated solution oxidizes paper, sugar, oxalic acid etc. Alcohol inflames in it. Glacial acetic acid is not oxidized by it and a solution of CrO_3 in it may be used as an oxidizing agent. SO_2, H_2S, Fe(II), Sn(II) etc. reduce CrO_3 to Cr(III).

The solid oxide consists of infinite chains —O—CrO_2—O— in which tetrahedral CrO_4 units share corners.

Halides

Chromium(VI) halides]

CrF_6 is the only known binary halide of Cr(VI). It is formed as a yellow solid by direct fluorination of chromium at 400°C and 200-300 atm pressure or reacting CrO_3 with F_2 at 170°C and 25 atm pressure. The solid decomposes into CrF_5 and F_2 above −100°C at low pressures.

$CrOF_4$ is obtained by fluorination of CrO_3 as a red solid (m.p. 55°C) with a fluorine-bridged polymeric structure. The gaseous molecule is square pyramidal. Salts $[NO]^+[CrOF_5]^-$ and $Cs^+[CrOF_5]^-$ are known.

CrO_2Cl_2, chromyl chloride (red liquid, bp 117°C) is the most important oxohalide of chromium(VI). It is formed when an ionic chloride is heated with potassium dichromate and concentrated H_2SO_4 :

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O.$$

Note :

Chromyl chloride test

(i) Under identical conditions, bromides and iodides evolve free halogens and hence this reaction may be used as a specific test for chlorides - the brown fumes evolved is collected in a drop of dilute sodium hydroxide solution :

$$4NaOH + CrO_2Cl_2 = Na_2CrO_4 + 2NaCl + 2H_2O$$

The drop is acidified with acetic acid and treated with lead acetate solution - a yellow precipitate of lead chromate indicates the presence of chloride in the sample.

(ii) Fluorides must be removed, otherwise CrO_2F_2 may be formed which behaves similar to CrO_2Cl_2.

(iii) CrO_2Cl_2 is formed only by those chlorides which form HCl with conc. H_2SO_4. Chlorides of mercury and silver, which are insoluble or only slightly ionized, do not give this test.

Chromyl chloride is also formed by adding conc. H_2SO_4 to a cold solution of CrO_3 in conc. HCl or by reacting HCl gas on CrO_3.

$$CrO_3 + 2HCl = CrO_2Cl_2 + H_2O.$$

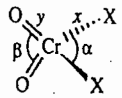
CrO_2Cl_2 is violently hydrolyzed by water :

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl.$$

It is soluble in most nonpolar solvents like CCl_4 and CS_2. The solution in CS_2 is used to oxidize toluene to benzaldehyde (*Etard's reaction*).

Chromyl chloride is a violent oxidizing agent and inflames phosphorus, sulphur, alcohol etc. It combines with N_2O_5 to give brown volatile chromyl nitrate, another violent oxidizing agent; benzene inflames in contact with it.

$$CrO_2Cl_2 + 2N_2O_5 = CrO_2(NO_3)_2 + 2NO_2Cl.$$



X = F : α = 112°, β = 108°; x = 172 pm, y = 157.5 pm

X = Cl : α = 113°, β = 108°; x = 213 pm, y = 158.1 pm

Fig. 28.30

Structure of CrO_2X_2 molecules.

The molecules are roughly tetrahedral and monomeric in vapour and in solution in nonpolar solvents.

No straightforward explanation appears for the larger XCrX bond angles(α) in comparison to O=Cr=O angles(β) (difference from SO_2X_2).

The stability of chromyl halides (CrO_2X_2) decreases in the order $F^- > Cl^- > Br^-$.

CrO_2F_2 forms violet red crystals (mp 316°) which sublime at 30°C and is obtained by the action of (i) F_2 on CrO_2Cl_2 (150°C) or (ii) anhydrous HF on CrO_3. It is also hydrolyzed by water. Though monomeric in the liquid, it forms F-bridged polymer in the solid having 6-coordinate chromium. In the monomer, $\angle OCrO = 108°$ and $\angle FCrF = 112°$.

CrO_2Br_2 is unstable at room temperature but may be prepared by adding excess liquid HBr on CrO_2Cl_2 at −60° to −80°C.

CrO_2I_2 exists only in low temperature matrices.

Potassium chlorochromate, $CrO_2(OK)Cl$, known as *Peligot's salt*, is formed by adding chromyl chloride to a saturated aqueous solution of KCl :

$$CrO_2Cl_2 + H_2O + KCl = CrO_2(OK)Cl + 2HCl.$$

The corresponding chlorochromic acid is not known. The salt is also formed by heating potassium dichromate in hot 6*M* HCl and crystallizing.

$$K_2Cr_2O_7 + 2HCl \longrightarrow 2CrO_2(OK)Cl + H_2O$$

Alkali splits the chlorochromate ion into chromate and chloride ions :

$$CrO_3Cl^- + 2OH^- = CrO_4^{=} + Cl^- + H_2O$$

The halochromate(VI) species are stable because the oxidation of halide ions by dichromate is kinetically very slow. Other halochromates CrO_3X^- are also known with X = F, Br and I. The pyridinium salt of CrO_3F^- has been used as an oxidant in organic chemistry.

Aqueous solution chemistry

Chromate dichromate equilibria

The principal Cr(VI) species in aqueous solution are the chromate ion, CrO_4^{2-} (yellow) and the dichromate ion, $Cr_2O_7^{2-}$ (orange). The CrO_4^{2-} ion predominates in alkaline solutions (pH > 6) while $HCrO_4^-$ and $Cr_2O_7^{2-}$ exist in equilibrium between pH 2 and 6. H_2CrO_4 appears to be the main species in strong acid medium (pH < 1). The main equilibria in HNO_3 or $HClO_4$ medium are

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K \simeq 4$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K \simeq 158$$

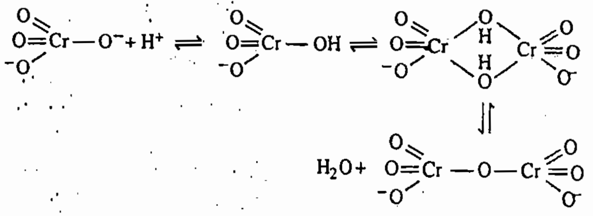
$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K \simeq 1-3\times10^{-6}.$$

The principal species in acid medium is thus $Cr_2O_7^{2-}$. In alkaline medium, the CrO_4^{2-} ion becomes the main species :

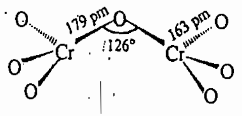
$$Cr_2O_7^{2-} + OH^- \rightleftharpoons CrO_4^{2-} + HCrO_4^-$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O$$

The chromate-dichromate equilibrium is established very rapidly. Thus, addition of cations forming insoluble chromates, e.g., Ag^+, Pb^{2+} or Ba^{2+} to solutions of potassium dichromate causes essentially quantitative precipitation of these metals as chromates, (the dichromates are more soluble). The conversion of CrO_4^{2-} ions to $Cr_2O_7^{2-}$ ions proceeds via bridging OH groups.



The chromate ion is tetrahedral and the dichromate ion has two tetrahedral CrO_4 units linked by sharing an O-atom (Fig. 28-VII). The bond angles and distances shown relate to $Cr_2O_7^{2-}$ ion in $Rb_2Cr_2O_7$.



28-VII

Q. 28.5 *In aqueous solutions, the VO_4^{3-} ion forms a large series of polyvanadates (sec 28.2.2); but the CrO_4^{2-} ion, also d^0, condenses mainly upto the $Cr_2O_7^{2-}$ ion. Comment.*
Hint : A higher effective nuclear charge and smaller size ensure stronger Cr = O pi-bond in the CrO_4^{2-} ion.

Note : Condensed anionic species $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ may be crystallized as alkali metal salts from strongly acid medium. These ions also contain tetrahedral CrO_4 units joined by sharing corner O-atoms.

Cr(VI) may be formed in solution by oxidation of Cr(III) with, for example, sodium peroxide (alkaline medium) or persulphate (acid medium, Ag^+ catalyst). The dichromate ion is a strong oxidizing agent in acid medium; the chromate ion is much milder an oxidizing agent :

$$Cr_2O_7^{=} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E° = 1.33V$$

$$CrO_4^{=} + 4H_2O + 3e \rightleftharpoons Cr(OH)_3\,(s) + 5OH^- \qquad E° = -0.13V$$

In neutral medium, $Cr(OH)_3$ is precipitated.

$$Cr_2O_7^{2-} + 3(NH_4)_2S + H_2O = 2Cr(OH)_3 + 3S + 6NH_3 + 2OH^-$$

In alkaline medium the anionic complex $[Cr(OH)_6]^{3-}$ is formed.

$$2CrO_4^{=} + 3(NH_4)_2S + 2OH^- + 2H_2O = 2[Cr(OH)_6]^{3-} + 3S + 6NH_3$$

Potassium dichromate is widely used as a primary standard oxidizing agent owing to its non-hygroscopic nature.

Chromates and dichromates

Sodium dichromate, $Na_2Cr_2O_7$, is prepared by heating powdered chromite with sodium carbonate and quicklime (see extraction of chromium). The red crystalline $Na_2Cr_2O_7$, $2H_2O$ may be made anhydrous by heating above 83°C. The deliquescent crystals melt at 320° and decompose above 400°C.

Sodium dichromate is much more soluble in water than potassium dichromate. It is used as an oxidant in many chemical processes and as the source of other chromates which are largely used as corrosion inhibitors and fungicides. Sodium dichromate is also used in making pigments for use in paints, inks, ceramics etc. But it is not used as a primary standard in volumetric analysis because it is hygroscopic.

Potassium dichromate is readily prepared by adding potassium chloride to a concentrated solution of sodium dichromate.

$$2KCl + Na_2Cr_2O_7 = K_2Cr_2O_7 + 2NaCl$$

Sodium chloride separates first and is filtered out. The filtrate, on cooling, separates deep orange-red crystals of potassium dichromate. This may be recrystallized to get 99.9% $K_2Cr_2O_7$ of analytical requirement.

Crystals of $K_2Cr_2O_7$ (m.p. 396°C) are not deliquescent.

Sodium chromate, Na_2CrO_4 is formed by adding sodium carbonate to sodium dichromate solution.

$$Na_2Cr_2O_7 + Na_2CO_3 = 2Na_2CrO_4 + CO_2$$

The lemon yellow crystalline solid is much less soluble than sodium dichromate.

Potassium chromate, K_2CrO_4 is obtained by adding K_2CO_3 (or KOH) to $K_2Cr_2O_7$. It is not deliquescent.

Ammonium dichromate, $(NH_4)_2Cr_2O_7$ may be prepared by neutralizing a solution of CrO_3 with ammonia. It decomposes on heating leaving a green residue of Cr_2O_3.

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$$

Chromates of alkali metals and ammonium are all soluble in water and highly poisonous. Chromates of Pb^{2+}, Ba^{2+}, Ag^+, Hg_2^{2+}, and Bi^{3+} are insoluble and may be prepared by double decomposition. Lead chromate is used as a pigment (*chrome yellow*). It is insoluble in ammonium acetate, acetic acid or ammonia but dissolves in dilute NaOH or HNO_3 (sparingly in the latter). Basic lead chromate (*chrome red*), $PbO.PbCrO_4$ is obtained by digesting lead chromate with a little cold dilute sodium hydroxide solution. It may be mixed with further lead chromate to give the orange pigment *chrome orange*.

Barium chromate is insoluble in dilute acetic acid but soluble in dilute mineral acids. Barium or chromium may be estimated by precipitation of $BaCrO_4$, dissolving the precipitate in dilute H_2SO_4 and titrating the Cr(VI) liberated in solution.

In this above titration, the precipitate of $BaCrO_4$ has to be repeatedly washed to make it free from any chromate. This is tested by adding a drop of the filtrate to dil. acetic acid and silver nitrate solution. A brick-red precipitate of Ag_2CrO_4 indicates the presence of chromate in the filtrate.

Detection of trace amount of CrO_4^{2-} in $Cr_2O_7^{2-}$ (Feigl's test) : To $NiSO_4$ (*aq*) is added excess of dimethylglyoxime in alcohol solution. The rose-red precipitate is filtered out. To the filtrate is added the test solution. If CrO_4^{2-} is present the rose-red precipitate reappears.

In neutral medium Ni^{2+}-DMG is incompletely precipitated due to reversibility of the reaction :

$$2DMGH + Ni^{2+} \rightleftharpoons Ni(DMG)_2 + 2H^+$$

CrO_4^{2-} removes H^+ ion, itself being changed to $Cr_2O_7^{2-}$, leading the reaction to the right. So the rose-red precipitate of Ni^{2+} - DMG reappears.

Q. 28.6 *The equilibrium constant for the reaction*

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

is 4.2×10^{14} (25°C).

A solution which is 1M in chromium has 20% of the metal as dichromate and the rest as chromate. What is the pH of the solution?

[**Hint** : $[CrO_4^{2-}] = 0.8\ M$, $[Cr_2O_7^{2-}] = 0.1\ M$. Substitution in the expression of K gives $[H^+] = 1.7 \times 10^{-8}$].

Peroxo complexes of chromium(VI, V and IV)

Addition of H_2O_2 to an acidified solution of potassium dichromate produces a deep blue-violet colour which soon disappears with the evolution of oxygen. If the solution is shaken with ether, the colour concentrates in the ether layer where it is more stable. Addition of pyridine to this ether solution gives the explosive solid adduct "pyridine perchromate", $[(py)CrO(O_2)_2]$ (Fig. 28.31). This dissolves as a monomer is benzene and is diamagnetic.

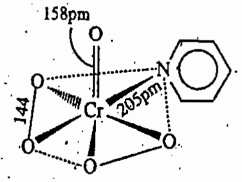
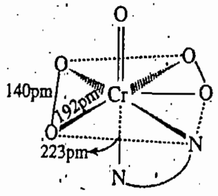


Fig. 28.31

Structure of $[(py)CrO(O_2)_2]$.

The four O-atoms and the N-atom forms a pentagonal base (broken line) with the chromium atom at the center of a pentagonal pyramid with the oxide oxygen at an apical position.



28-VIII(a)

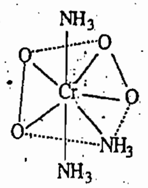
The dipyridyl adduct of CrO_5 has a pentagonal bipyramid structure [28-VIII(a)].

In faintly acidic or neutral medium, H_2O_2 acts on potassium, ammonium or thallium dichromate solutions to give violet explosive salts like $KHCrO_6$ (diamagnetic). The anion is supposed to be $[Cr^{VI}O(O_2)_2OH]^-$.

Chromium(V)

Alkaline solutions of potassium chromate react with 30% H_2O_2 to produce a red-brown paramagnetic species which has been characterized as K_3CrO_8. This actually contains chromium(V) as $[Cr(O_2)_4]^{3-}$ in a dodecahedral structure. The Cr-O distances to the two O-atoms in the same peroxo group are not equal — one Cr-O distance is of 194 pm while the other is of 185 pm; the O-O distance is 141 pm. The salt is isomorphous with K_3MO_8 (M = Nb, Ta).

Chromium(IV)



28-VIII(b)

When the red $[Cr(O_2)_4]^{3-}$ complex ion is warmed (50°C) with aqueous ammonia and cooled to 0°C, a dark red-brown complex of Cr(IV), $[Cr(O_2)_2(NH_3)_3]$ crystallizes out. This also has the pentagonal bipyramid structure 28-VIII(b). The compound may also be obtained by adding H_2O_2 to an ammoniacal solution of $(NH_4)_2CrO_4$.

$CrO_4.3KCN$ may be an analogue of this Cr(IV) species.

Other Cr(IV) complexes like the olive-green $[Cr(en)(H_2O)(O_2)_2]. H_2O$ may be obtained by the action of H_2O_2 on aqueous solutions of CrO_3 containing ethylenediamine and other amines.

28.5.4 Compounds of chromium(V), d^1

This oxidation state offers few compounds but the list is on the increase. The peroxo complex of chromium(V) mentioned above, CrF_5, $CrOF_3$, some oxohalide ions (e.g., $CrOF_4^-$) and oxoanions (e.g., CrO_4^{3-}) are the main compounds.

CrF_5 is formed as a red solid (m.p. 30°C) in the reaction between the elements at 400°C in a flow system or by fluorination of CrO_3 at 200°C. It is rapidly hydrolyzed by water and is a strong oxidizing agent. The compound is polymeric with F-bridges (*cis*).

$CrOF_3$ may be obtained by fluorination of CrO_3 with ClF_3 or BrF_3; the pure solid is prepared by the reaction

$$XeF_2 + 2CrO_2F_2 \longrightarrow 2CrOF_3 + Xe + O_2$$

The purple crystals decompose on heating into CrF_3 and O_2. In water, $CrOF_3$ disproportionates into Cr(III) and Cr(VI). It adds fluoride ions to form stable crystalline salts of $CrOF_4^-$ ion. This ion is also square pyramidal with rather short Cr-O distance (152 pm). The magnetic moment of 1.7 B.M. corresponds to the spin-only value for one unpaired electron. $KCrOF_4$ and $AgCrOF_4$ may be obtained as purple powders by the action of BrF_3 on $K_2Cr_2O_7$ or $Ag_2Cr_2O_7$.

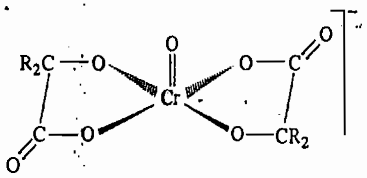
$CrOCl_3$ is a dark red volatile solid which may be prepared by the reaction of (i) CrO_3 with thionyl chloride ($SOCl_2$) or (ii) BCl_3 with CrO_2Cl_2. Its crystal structure is not known. It resembles $CrOF_3$ in other properties, including formation of stable salts containing $CrOCl_4^-$ ions. Garnet red crystals $M_2[CrOCl_5]$, (M = K, Rb, Cs, NH_4) may be obtained by adding MCl to $CrOCl_3$.

Alkali metal chromates(V) (*hypochromates*) are formed as dark blue solids by fusing chromate(VI) with alkali. The discrete tetrahedral CrO_4^{3-} ion (distorted) is present in Li_3CrO_4, Na_3CrO_4 as also in the alkaline earth metal salts. The latter may be prepared by thermal decomposition of the chromates with basic oxides or carbonates in nitrogen atmosphere :

$$4BaCrO_4 + 2BaCO_3 = 2Ba_3(CrO_4)_2 + 2CO_2 + O_2$$

Compounds with the stoichiometry $M^I_3CrO_8$ do not contain Cr(V); they are built up of tetrahedral $Cr^{VI}O_4$ and octahedral $Cr^{III}O_6$ units.

The tetraperoxochromates(V) mentioned earlier are the most important complexes of Cr(V). A number of stable complexes of the type $[Cr^VOL_2]^-$ are known, where L = $^-OCR_2COO^-$, formed by the loss of two protons from α-hydroxybutyric acid and similar compounds. The four oxygen atoms from the acid anion occupy basal positions of a square pyramid around the chromium with axial Cr = O bond (Fig. 28-IX). The solid compounds are stable in air and also in solution in presence of excess ligand.



28-IX

Similar square pyramid Cr(V) complexes have also been prepared with Schiff bases.

Cr(V) intermediates have been detected by esr studies during the reduction of Cr(VI) by organic reducing agents like oxalic acid, citric acid, isopropanol etc. Blue Cr(V) species are also formed on dissolving chromates(VI) in 65% oleum.

28.5.5 Compounds of chromium(IV), d^2

Compounds of chromium(IV) are also few - the oxide CrO_2 and the fluoride CrF_4 being the principal binary compounds. $CrOF_2$, complex CrF_6^{2-} ion and mixed oxides containing Cr(IV) are also known.

CrF_4 is prepared by direct reaction at 350°C. The green solid sublimes at 100°C. It disproportionates in water to Cr(III) and Cr(VI). $CrCl_4$ and $CrBr_4$ are formed only in the gas phase when the trihalides are heated in excess halogen.

CrO_2 is a brown-black solid with rutile structure which may be prepared by heating $Cr(OH)_3$ in oxygen at 350°C or by controlled reduction of CrO_3. The oxide is ferromagnetic and shows metallic conductance - probably arising from delocalization of electrons into energy bands formed by overlap of chromium 3*d* and oxygen *p* orbitals. It is widely used in magnetic tapes for better resolution and high frequency response.

K_2CrF_6 has been prepared by the action of F_2 on a mixture of $CrCl_3$ and KCl. It shows the same X-ray diffraction pattern as K_2MnF_6.

Stable mixed oxides containing Cr(IV) may be prepared by high temperature fusion (~ 1000°C)

$$NaCrO_2 + 2Na_2O = Na_4CrO_4 + Na$$

$$SrCrO_4 + Cr_2O_3 + 5Sr(OH)_2 = 3Sr_2CrO_4 + 5H_2O.$$

The sodium salt is deep-green while the strontium and barium salts are blue-black in colour having discrete CrO_4^{4-} ions. Magnetic moments ~2.8 B.M. correspond to the spin-only value for two unpaired electrons.

The sulphide Cr_5S_8 is formulated as $Cr_4^{III}Cr^{IV}S_8$.

The peroxocomplex of Cr(IV) has been mentioned before. Other stable complexes with dmpe [1,2-bis (dimethylphosphino) ethane] and other ligands have been reported. Other compounds containing Cr(IV) are the green $Cr(NEt_2)_4$, prepared from $CrCl_3$ and $LiNEt_2$ and the blue alkoxides $Cr(OR)_4$, obtained by alcoholysis of the tetrakis(diethylamide). The alkoxides are monomeric and tetrahedral, with magnetic moments around 2.8 B.M.

28.5.6 Compounds of chromium(III), d^3

This is the most stable and common oxidation state of chromium. Cr(III) forms the most stable trivalent cation in water solution, also forming series of stable, substitution inert complexes (having a half-filled t_{2g} set of orbitals).

Oxide

Cr_2O_3 results when chromium burns in air and dichromates are reduced (C, S etc.) or ammonium dichromate is heated. The green oxide has a corundum structure and isomorphous replacement of Al^{III} by Cr^{III} in corundum forms the mineral ruby (see ruby laser, Ch. 27). When ignited strongly, the oxide does not react with acids or bases easily. Mixed oxides of the spinel type are formed on fusion with basic oxides. Cr_2O_3 is widely used as a green pigment.

Halides

All three trihalides are known :

	CrF_3	$CrCl_3$	$CrBr_3$	CrI_3
colour :	green	red-violet	dark green	drak green
m.p.(°C) :	1404	1150	1130	—

These may be prepared by direct combination at various temperatures. CrF_3 is better prepared by heating $CrCl_3$ with HF at 500°C.

$CrCl_3$ may be made by heating Cr_2O_3 with carbon and chlorine ;

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

It dissociates if heated alone :

$$2CrCl_3 = 2CrCl_2 + Cl_2$$

Dissolution of $CrCl_3$

But it can be sublimed at a red heat in a current of chlorine. The crystalline compound dissolves extremely slowly in water but dissolution is rapid in presence of a reducng agent like $CrCl_2$, $SnCl_2$ etc. It is likely that the Cr^{2+} ions attach to the Cr^{3+} ions in the lattice via chlorine bridge :

$$Cr^{3+} \text{ (crystal)} - Cl - Cr^{2+} \text{ (solution)}.$$

Electron-transfer now takes place to form Cr(II) in the lattice. The Cr^{2+} ion so formed in the solid does not fit the lattice and is lost easily, repeating the process of dissolution.

A green solution of $CrCl_3$ is obtained when CrO_3 is boiled with concentrated HCl :

$$2CrO_3 + 12HCl = 2CrCl_3 + 3Cl_2 + 6H_2O$$

The crystalline hydrate $CrCl_3.6H_2O$ may exist as three hydrate isomers :

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$	$[Cr(H_2O)_4Cl_2]Cl.2H_2O$
violet	*light green*	*dark green (trans)*

Anhydrous $CrCl_3$ has a layer structure with octahedrally coordinated Cr in a cubic close-packed array of Cl-atoms. Metal atoms occupy octahedral holes between alternate planes of Cl - atoms; the alternate layers of Cl-atoms are held only by weak van der Waal's forces. Hence the lattice is easily cleaved parallel to such layers.

$CrCl_3$ forms a large number of adducts with donor molecules e.g., $CrCl_3.3py$ and $CrCl_3.3THF$. Trimethylamine forms a 5-coordinate adduct with *trans*-tbp structure : $CrCl_3(NMe_3)_2$.Two series of complex halides are formed with alkali metal chlorides — M_3CrCl_6 and $M_3Cr_2Cl_9$. These are paramagnetic showing the presence of three unpaired electrons per Cr. There is no spin-pairing between the two chromium centers (magnetically dilute). The Cr-Cr distance in $Cr_2Cl_9^{3-}$ (310 pm) is larger in comparison to the W—W distance in $W_2Cl_9^{3-}$ (240 pm). In the latter, W ≡ W cluster formation leads to diamagnetism.

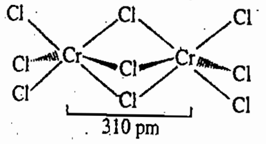


Fig. 28:32

The skeleton of $Cr_2Cl_9^{3-}$ ion.

Three bridging Cl share a face of the twin-octahedra.

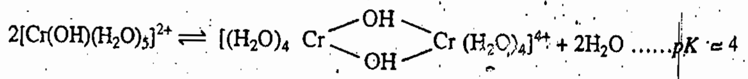
Aqueous chemistry

The violet hexaaqua ion $[Cr(H_2O)_6]^{3+}$ exists in solution as well as in crystalline salts like chrome alum ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$) and the sulphate $Cr_2(SO_4)_3.18H_2O$. But the green $Cr_2(SO_4)_3.6H_2O$ contains sulphate ions coordinated to the metal.

The hexaaqua ion is largely acidic :

$$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+} + H_3O^+ \quad , \quad pK_1 \approx 1.6$$

The hydroxo ion readily condenses to a dimeric hydroxo-bridged species :



$$2[Cr(OH)(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_4\,Cr\overset{OH}{\underset{OH}{<>}}Cr\,(H_2O)_4]^{4+} + 2H_2O \;\ldots\ldots\; pK \approx 4$$

With increase in pH, greyish-blue hydrated chromium(III) oxide ("chromic hydroxide") is precipitated. This redissolves in acids, but solubility decreases on aging.

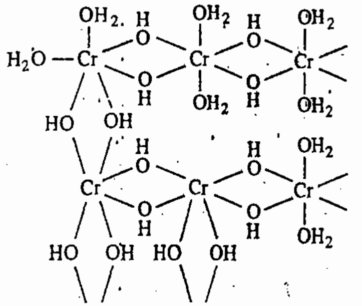


Fig. 28.33

Structural motif of Cr_2O_3, nH_2O ("chromic hydroxide").

It is a polynuclear polymer with a layer structure in which OH^- and H_2O act as ligands with further OH groups as bridges. On standing, the Cr—OH—Cr bonds change to Cr—O—Cr ones and the substance becomes unreactive.

Due to the acidic nature of the aqua ion, salts of weak acids like S^{2-} and CO_3^{2-} are not formed from aqueous solutions :

$$2Cr^{3+}aq + 3CO_3^{2-} + 3H_2O = 2Cr(OH)_3 + 3CO_2$$

[Cr_2S_3 can be made by direct reaction between chromium and sulphur or anhydrous $CrCl_3$ with H_2S. It is a stable black solid inert to non-oxidizing acids.]

Addition of alkali to solutions containing $Cr(H_2O)_6^{3+}$ precipitate $Cr(OH)_3.aq$ which dissolves in excess alkali to form species like $[Cr(OH)_6]^{3-}$. The hydroxide dissolves slowly in aqueous ammonia, eventually forming soluble ammine complexes $[Cr(NH_3)_6]^{3+}$ to $[Cr(NH_3)_2(H_2O)_4]^{3+}$. There are also a wide variety of mixed complexes e.g., $[Cr(NH_3)_5X]^{2+}$, and $[Cr(NH_3)_2(H_2O)_3X]^{2+}$ where X is an acid radical like halide, SCN^- etc. Complete replacement of coordinated water or ammonia molecules gives complexes of the type $[CrF_6]^{3-}$, $[Cr(C_2O_4)_3]^{3-}$ etc.

Chromic nitrate, $Cr(NO_3)_3.9H_2O$ separates as purple monoclinic prisms from a solution of $Cr(OH)_3$ in excess dilute HNO_3. The solution turns green on heating, but again changes to violet on cooling.

Anhydrous $Cr(NO_3)_3$ may be obtained as a green precipitate by adding chromium carbonyl to N_2O_5 in CCl_4 solution :

$$Cr(CO)_6 + 3N_2O_5 = Cr(NO_3)_3 + 6CO + 3NO_2$$

Chromic sulphate, $Cr_2(SO_4)_3.18H_2O$ forms violet octahedral crystals from a solution of $Cr(OH)_3$ in conc. H_2SO_4. The hexahydrate $Cr_2(SO_4)_3.6H_2O$ (green) may be obtained by gently heating the violet crystals to 90°. The red anhydrous sulphate may be prepared by heating $Cr_2(SO_4)_3.18H_2O$ in a stream of CO_2 at 280 - 400°C.

The anhydrous sulphate is insoluble in water while the green and violet hydrates are soluble. A freshly prepared solution of the green hexahydrate does not give any precipitate with barium chloride solution. On standing, the green solution gradually turns violet from which all the sulphate ions may be precipitated. The violet crystals may then be formulated as $[Cr(H_2O)_6]_2(SO_4)_3.6H_2O$.

The change of colour from green to violet is consistent with the higher position of water as a ligand in the spectrochemical series in comparison to sulphate.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ may be obtained as deep purple octahedral crystals from a mixed solution of the violet chromium(III) sulphate and potassium sulphate. It is generally prepared by reducing potassium dichromate in acidic solution with sulphur dioxide (until the colour changes to green).

Chrome alum is used as a mordant in dyeing and in "tanning" of leather.

The chromium(III) solution hydrolyzes on the surface of the fabric, depositing colloidal hydroxides and other polynuclear hydroxobridged complexes which fix the dye. On leather, the polynuclear complexes bridge neighbouring protein chains by coordinating to the carboxyl groups of the proteins and prevent putrefaction.

Complex compounds

Several halo, aqua and mixed aqua ammine complexes of chromium(III) have already been mentioned. With very few exceptions, these are all octahedral. Owing to the inherent kinetic inertness of the $[Cr(H_2O)_6]^{3+}$ ion, simple addition of a ligand does not always ensure substitution of all of the coordinated water molecules. Cr(III) complexes are therefore usually prepared by indirect methods :

(a) The ammine (and amine) complexes are conveniently prepared by aerial oxidation of $[Cr(H_2O)_6]^{2+}$ in presence of ammonia (or the ligand).

(b) Salts of $[CrX_6]^{3-}$ anions (X = halide, CN, SCN etc.) are prepared by fusing CrX_3 with alkali metal salt. The ammine and amine complexes may also be prepared by such anhydrous procedure reacting CrX_3 with NH_3 or the amines.

(c) Reduction of Cr(VI) compounds, commonly CrO_3 or $K_2Cr_2O_7$ in presence of the ligands. $K_3[Cr(C_2O_4)_3]$ is readily prepared by this method.

Preparation of potassium trisoxalatochromate(III). Dissolve 3g of potassium oxalate and 7 g of oxalic acid in 100 ml water. Add 2.5 g of $K_2Cr_2O_7$ to the solution in small portions and continue stirring. After the reaction is over, evaporate the solution to a small volume and allow the blue crystals to separate.

$$K_2Cr_2O_7 + 7H_2C_2O_4 = K_2C_2O_4 + Cr_2(C_2O_4)_3 + 6CO_2 + 7H_2O$$

$$Cr_2(C_2O_4)_3 + 3K_2C_2O_4 = 2K_3[Cr(C_2O_4)_3]$$

Potassium hexacyanochromate(III), $K_3[Cr(CN)_6]$ is obtained by aerial oxidation of chromium(II) acetate in presence of KCN. It may also be prepared by reacting chromium(III) acetate ($Cr(OH)_3$ + acetic acid). The bright yellow monoclinic crystals are isomorphous with $K_3[Fe(CN)_6]$.

Reinecke's salt. $NH_4[Cr(NH_3)_2(NCS)_4].H_2O$ is prepared by heating ammonium dichromate with ammonium thiocyanate around 150°C. Unchanged ammonium dichromate is washed with ice-water and the complex is quickly extracted with warm (60°C) water. Reinecke's salt crystallizes on cooling the filtrate in ice.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

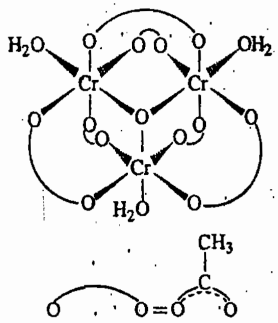
$$Cr_2O_3 + 8NH_4SCN \rightarrow 2NH_4[Cr(NH_3)_2(NCS)_4] + 3H_2O + 2NH_3$$

The large monovalent anion of Reinecke's salt is a good precipitant for large cations e.g., those arising from primary and secondary amines, proteins and amino acids.

The strong tendency of chromium(III) aqua species to undergo polymerization has been metnioned. Similar dinuclear hydroxo-bridged ammine complexes and ethylene diamine complexes are known in which the temperature-dependent paramagnetic moment is lower than the value expected for octahedral Cr(III), suggesting partial pairing of spin via the OH bridges. The red μ-hydroxobispentaammine complex may be converted to a blue μ-oxo complex by the action of alkali :

$$\underset{red}{[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]^{5+}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{blue}{[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}}$$

Magnetic moment of the blue oxo-bridged complex at room temperature is ~1.3 B.M. only, indicating greater spin-pairing between the two chromium(III) centers via $d\pi - p\pi$ bonds in the linear oxo-bridge (the hydroxobridge was bent).

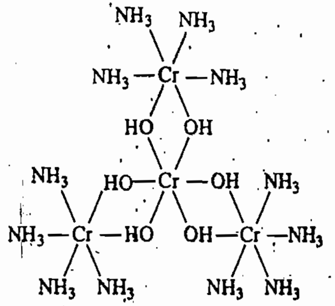


28-X

A trinuclear complex is exemplified by the basic acetate. $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ (28-X). The oxygen atom is at the center of an equilateral triangle of ocatahedrally coordinated chromium atoms; each pair of chromium atoms has two bridging acetate groups, the sixth coordination being completed by a terminal H_2O molecule. Many other basic carboxylates have similar structure.

In these complexes also, the room temperature magnetic moment around 2 B.M. only suggests partial coupling of spin through $d\pi$-$p\pi$ overlap with the bridge oxygen atom.

Distorted octahedral CrF_6 units are present in anhydrous $KCrF_4$. Three CrF_6 units share fluorine corners to form a ring which are linked by axial fluorines (perpendicular to the ring) into an infinite array.



28-XI

The ion $[Cr\{Cr(OH)_2(NH_3)_4\}_3]^{6+}$ contains a central CrO_6 octahedron hydroxo-bridged to three $Cr(NH_3)_4$ units.

Among the few nonoctahedral complexes of Cr(III), we have mentioned the trigonal bipyramid adduct $CrCl_3.2Me_3N$ with axial amine groups. The unusual three-coordination occurs in $Cr(NR_2)_3$ where R = isopropyl or $SiMe_3$. Steric factors and multiple bonding are involved to explain the geometry which is most likely planar.

The gross features of the electronic spectrum of Cr(III) have been discussed in the last chapter (Fig. 27.52). The magnetic moments of the mononuclear complexes are also close to that expected for three unpaired electrons, but slightly below the spin-only value of 3.88 B.M.

28.5.7 Chemistry of chromium(II), d^4

Chromium(II) offers a fair number of compounds including the dihalides, aquaion and several complexes. The oxide CrO, a black powder formed by exposing chromium amalgam to air, is not well-characterized or CrS can be made by direct reaction. All chromium(II) compounds are readily oxidized to Cr(III) species.

Halides

All four dihalides CrX_2 are known which may be prepared by reducing CrX_3 with H_2(300 – 500°C) or by reacting the metal and gaseous HX or I_2 at 700 - 1000°C. The solids are deliquescent.

	CrF_2	$CrCl_2$	$CrBr_2$	CrI_2
colour :	green	white	white	red-brown
m.p.°C :	894	820	842	868

CrI_2 is also formed by simply heating CrI_3 alone — the net balance of lattice energy and ionization energy drives the reaction (see Ch. 24, section 24.3.1).

The hydrated halides may be prepared by dissolving chromium in aqueous HX or by reducing Cr(VI)/Cr(III) with nascent hydrogen. $CrCl_2$ is produced by reduction of potassium dichromate with zinc and hydrochloric acid *in absence of air* :

$$K_2Cr_2O_7 + 8HCl + 6H = 2KCl + 2CrCl_3 + 7H_2O$$

$$CrCl_3 + H = CrCl_2 + HCl.$$

The orange solution of $K_2Cr_2O_7$ first turns green (Cr^{3+}) and then blue. $CrCl_2, 4H_2O$ and other hydrates are known.

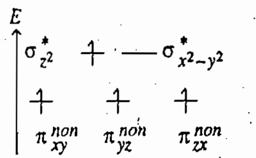
A solution of chromous chloride absorbs oxygen. It absorbs ammonia to form various ammoniates, e.g., $CrCl_2.6NH_3$(blue); $CrCl_2.5NH_3$(violet); $CrCl_2.3NH_3$ (blue) etc. Chromium(II) halides also form adducts with other donor molecules like pyridine and triphenylphosphine oxide of the type $CrX_2.2L$ which are tetragonal polymeric in nature. Complex halides $M^I_2CrCl_4$ and M^ICrCl_3 are also formed in melts.

All chromium(II) halides are strongly reducing in nature—they can even reduce water, in the absence of an oxidant, to liberate H_2

$$2CrCl_2 + 2H_2O = 2Cr(OH)Cl_2 + H_2$$

$$2CrCl_2 + 2HCl = 2CrCl_3 + H_2$$

All the dihalides have distorted octahedral structure consistent with expected Jahn-Teller distortion for a d^4 (high spin : $\overset{3}{t_{2g}}\overset{1}{e_g}$) configuration. CrF_2 has a distorted rutile structure with four F^- ions at 200 pm and two F^- ions at 243 pm from the metal. In case of $CrCl_2$, corresponding Cr-Cl distances are 239 and 290 pm respectively.



The electron distribution among the molecular orbitals will be $[\sigma]^{12}[\pi_d^{non}]^3[\sigma_d^*]^1$.

Removal of the antibonding electron from the highest occupied $\sigma^*_{z^2}$ results in a stable configuration $[\sigma]^{12}[\pi_d^{non}]^3$.

This is consistent with the strongly reducing nature of Cr(II).

A mixed Cr(II)-Cr(III) **fluoride, *Cr_2F_5***, is known with alternating chains of Cr(II) and Cr(III) forming CrF_6 octahedra linked by apices. While the $Cr^{III}F_6$ unit has a regular octahedral environment, the $Cr^{II}F_6$ unit has four short and two long Cr—F bonds.

Aqueous solution chemistry

The blue $[Cr(H_2O)_6]^{2+}$ ion, formed by reduction of Cr(III) with nascent hydrogen, is readily oxidized in air to the green $[Cr(H_2O)_6]^{3+}$ ion

$$Cr^{3+}aq + e \rightleftharpoons Cr^{2+}aq \qquad E^\circ = -0.41\ V$$

Neutral solutions are somewhat more stable; in absence of any oxidizing agent, hydrogen is evolved (see $CrCl_2$).

The $[Cr(H_2O)_6]^{2+}$ ion may also be obtained in several hydrated salts, also blue in colour, e.g., $CrSO_4, 7H_2O$; $Cr(ClO_4)_2, 6H_2O$; $CrCl_2, 4H_2O$; $CrBr_2, 6H_2O$ and the double salt $M^I_2SO_4, CrSO_4, 6H_2O$.

Addition of dilute sodium hydroxide solution to aqueous Cr^{2+} precipitates the brownish yellow $Cr(OH)_2$. This yields Cr_2O_3 on heating :

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$$

The hydroxide reacts only with acids, forming blue aqua complexes

$$Cr(OH)_2 + 2H_3O^+ + 2H_2O = [Cr(H_2O)_6]^{2+}$$

The chromium(II) acetate dihydrate $Cr(CH_3COO)_2.2H_2O$, in contrast to the above mentioned blue hydrates, is red in colour and is comparatively more stable. It is formed as a red precipitate when a saturated solution of sodium acetate is added to a solution containing Cr(II) under nitrogen or hydrogen. The precipitate is oxidized in air, though less readily than other Cr(II) salts.

The compound is actually diamagnetic with a dimeric structure : $Cr_2(CH_3COO)_4.2H_2O$, having a Cr—Cr quadruple bonding interaction (Fig. 28.34). The Cr—Cr distance of 235 pm is quite short (in comparison to 258 pm in the metal), suggesting involvement of all four unpaired electrons on each Cr(II) in metal-metal bonding.

If we assume that the Z-axis passes through the Cr-atoms, the s, p_x, p_y, p_z and $d_{x^2-y^2}$ orbitals of each chromium may be involved in bonding the ligands (H_2O and acetate); we are now left with d_{z^2}, d_{xy}, d_{yz} and d_{zx} orbitals on each chromium. The d_{z^2} orbitals can overlap to form a Cr-Cr σ bond; the d_{yz} and d_{zx} orbitals give rise to two π - bonds and the d_{xy} orbitals form a δ-bond. Such quadruple bonding characterizes many heavy metal compounds.

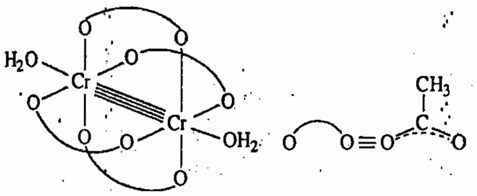


Fig. 28.34

Structural motif of chromium(II) acetate with Cr-Cr quadruple bond.

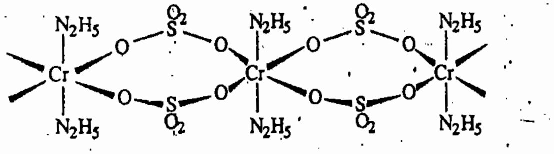
Each chromium is octahedrally coordinated by four O-atoms of two bridging acetate groups, one H_2O and the other chromium.

Numerous other compounds of the general formula $Cr_2(RCOO)_4L_2$ have similar structure and bonding, the Cr—Cr distances varying from 228 to 254 pm. In $Cr_2(CH_3COO)_4$, the Cr—Cr distance is 196 pm, suggesting stronger quadruple bonding. However, there appears to be no direct relation between the reactivity of the compound and the strength (indicated by the length) of the Cr—Cr bond. The glycine complex $[Cr_2(gly)_4X_2]X_2$, (X = Cl, Br; gly = $NH_2CH_2COO^-$) is permanently stable in air, though the Cr—Cr distance is quite large, ~251 pm.

Chromous sulphate, $CrSO_4$, $7H_2O$ may be prepared by dissolving chromium in dilute H_2SO_4 (air excluded) and cooling. The blue crystals are isomorphous with $FeSO_4, 7H_2O$. It forms double salts with alkali sulphates, e.g., $K_2SO_4.CrSO_4.6H_2O$.

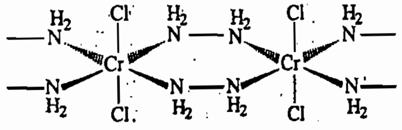
Complex compounds

Chromium(II) forms a large number of octahedral complexes which may be either high-spin or low-spin. High-spin complexes have room-temperature magnetic moments around 4.9 B.M. corresponding to four unpaired electrons. Many of these complexes are susceptible to aerial oxidation, specially under moist condition. The most air-stable compound appears to be the hydrazinium salt $(N_2H_5)_2[Cr(SO_4)_2]$, consisting of sulphate-bridged chain of chromium atoms (28 - XII).



28-XII

Another air-stable high-spin chromium(II) complex is formed by hydrazine as a bridge ligand. When aqueous $CrCl_2$ is added to an excess of hydrazine solution, a pale violet precipitate having the composition $CrCl_2(N_2H_4)_2$ is obtained. The complex has a polymeric hydrazine bridged structure (28 - XIII) with $\mu_{eff} = 4.9$ B.M.



28-XIII

Low-spin octahedral complexes of Cr(II) are formed with strong-field ligands, ready examples being $[Cr(CN)_6]^{4-}$, $[Cr(dipy)_3]^{2+}$, $[Cr(phen)_3]^{2+}$, $[Cr(diars)X_2](X = Cl, Br, I)$. The hexacyano complex has $\mu_{eff} = 3.2$ B.M.

The dipyridyl complex undergoes disproportionation in alkaline solution producing Cr(I) which turns the solution deep blue.

$$2[Cr(dipy)_3]^{2+} \longrightarrow [Cr(dipy)_3]^{+} + [Cr(dipy)_3]^{3+}$$

$Cr(acac)_2$ is square planar which is in fact an extreme limit of tetragonal J–T distortion.

28.5.8 Lower oxidation states

Oxidation states of chromium lower than II are very uncommon and occur only in few complexes and organometallic compounds, including the carbonyls.

Chromium(I) is known to be present in the deep blue complex $[Cr(dipy)_3]^{+}\ ClO_4^{-}$, produced from the corresponding Cr(II) complex by reduction or disproportionation (see before). $K_3[Cr(CN)_4]$ and the deep blue $[Cr(CO)_5I]$ are other examples of this oxidation state. The last compound is prepared by oxidation of Cr(0) in $[Cr(CO)_5I]^{-}$ with Fe^{3+}:

$$\begin{array}{c} Cr(CO)_6 + Et_4NI \xrightarrow{THF} Et_4N[Cr(CO)_5I] + CO \\ \Big\downarrow Fe^{3+} \\ Cr(CO)_5I \end{array}$$

Chromium(0) occurs in $K_6[Cr(CN)_6]$, $[Cr(dipy)_3]$, $[Cr(CO)_5I]^{-}$ and of course in the hexacarbonyl $Cr(CO)_6$ and dibenzene chromium $Cr(C_6H_6)_2$ (see organometallic compounds).

Chromium (–I and –II) are present in the carbonyls $Na_2[Cr_2(CO)_{10}]$ and $Na_2[Cr(CO)_5]$ respectively. Both may be obtained by reduction of $Cr(CO)_6$ by sodium in liquid ammonia or by sodium borohydride in THF.

28.5.9 Organometallic compounds

Chromium hexacarbonyl, $Cr(CO)_6$ conforms to the 18-electron rule. It is an air-stable white crystalline diamagnetic solid which decomposes at 130°C but may be sublimed in vacuo. It may be prepared by either of the following paths :

(i) $CrCl_3 + CO \xrightarrow[115°C/70\ atm]{LiAlH_4\ in\ ether} Cr(CO)_6\ (+LiCl + AlCl_3)$

(ii) $CrCl_3 + CO \xrightarrow[(ii)\ H^+]{(i)\ C_6H_5MgBr\ in\ ether} Cr(CO)_6$

Reduction of $Cr(CO)_6$ forms other lower oxidation states of chromium as noted above. The carbon monoxide is also displaced by other ligands like PF_3, PPh_3, and unsaturated organic compounds, e.g.,

$$Cr(CO)_6 + C_6H_6 \longrightarrow [(C_6H_6)Cr(CO)_3] + 3CO$$

$Cr(CO)_6$ is octahedral with Cr – C distance 191 pm.

Organometallic compounds of chromium were prepared as early as 1919 when Hein reacted PhMgBr with $CrCl_3$ producing some "polyphenyl" compounds formulated Ph_xCr and Ph_xCrI, $x = 2, 3, 4$ or 5. Zeiss reinvestigated these compounds in 1954 and showed that they actually contained atoms of chromium sandwiched between aromatic rings such as benzene and biphenyl. At about the same time, it was deduced by Fischer that dibenzenechromium, $Cr(C_6H_6)_2$, by analogy with the known structure of the sandwich compound ferrocene, might be quite stable (18-*e* species). Subsequently $Cr(C_6H_6)_2$ was synthesized as follows :

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \longrightarrow 3[Cr(C_6H_6)_2]^{+}[AlCl_4]^{-}$$

Reduction of the cation with aqueous sodium dithionite gives $Cr(C_6H_6)_2$.

$$2[Cr(C_6H_6)_2]^{+} + S_2O_4^{2-} + 4OH^{-} \longrightarrow 2Cr(C_6H_6)_2 + 2SO_3^{2-} + 2H_2O$$

Recently the compound has been prepared by direct reaction between benzene and chromium atoms produced by rapid condensation of the vapour at 77K.

Dibenzenechromium (Fig. 28.35) is a brown crystalline diamagnetic solid (mp 284°C), much more sensitive to air than ferrocene (see iron). Surprisingly, it gets easily oxidized to the 17-e species $[Cr(C_6H_6)_2]^{+}$. It also does not undergo electrophilic substitution reactions. Carbon monoxide displaces one benzene ring giving $[Cr(C_6H_6)(CO)_3]$ which is much more stable than dibenzene chromium. The arene ring in this compound responds to nucleophilic attack. Some ligands completely replace both benzene rings from dibenzenechromium, for example,

$$Cr(C_6H_6)_2 + 6PF_3 \longrightarrow Cr(PF_3)_6 + 2C_6H_6$$

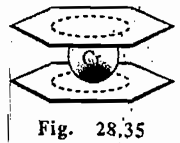


Fig. 28.35 Dibenzenechromium.

It contains a chromium atom sandwiched between the π-cloud of two benzene rings. Since the rings are uncharged, the compound contains Cr(0) and is an 18-*e* system (Cr : 6*e*; $2C_6H_6$: 12*e*).

28.5.10 Detection and estimation

Chromium is readily detected by the borax bead test (green) and the yellow melt of chromates formed on fusion with alkali and an oxidizing agent. Chromates produce a deep blue colour with H_2O_2 in acid solution; the CrO_5 formed may be extracted with ether.

Chromium(III) may be quantitatively oxidized to Cr(VI) by boiling with sodium peroxide or ammonium persulfate (Ag^{+} as catalyst). The Cr(VI) may be reduced by Mohr solution and the excess back-titrated. The Cr(VI) may also be titrated by iodometry. Chromium is determined gravimetrically after precipitation with ammonia followed by ignition to Cr_2O_3.

28.6 MANGANESE

Mn : [Ar] $3d^5 4s^2$ Atomic number : 25 Atomic weight : 54.938

M.P. : 1244°C B.P. : 2060°C Density : 7.43 g cm^{-3}.

A black mineral powder has been known from ancient times and used in making glass free from yellow or green tint — it was called "glass soap" or "Lapis manganensis" (Greek manganese means purify) and later on "pyrolusite." (pyro = fire, luo = I wash).

28.6.1 Introduction

History **:** Pyrolusite, known since ancient time, used to be mined near the town of Magnesia in Asia Minor and hence was also called black magnesia. (White magnesia or MgO was also extracted from the same place). In 1770, the Austrian scientist I. Kaim seems to be the first to have obtained a small amount of metallic manganese by heating this black magnesia with coal and K_2CO_3. But he did not complete his work which remained unknown to contemporary scientists.

The swedish chemist Bergmann recognized the presence of a new element in the black magnesia but he also failed to isolate it. Ultimately, the element was isolated by another Swedish chemist J. Gahn in 1774 and studied by C. Scheele. At first the metal was named in Latin "manganesium" (from the old name of pyrolusite); when magnesium was obtained in 1808, the Latin name of manganese was changed to "manganum" to avoid confusion.

Occurrence **:** Manganese is the third most abundant transition element (after iron and titanium) and twelfth among all elements (~ 1000 ppm in earth's crust). It occurs in a variety of minerals, formed mainly by weathering of primary silicate deposits :

Pyrolusite, MnO_2. (Russia, India, South Africa, Ghana, Brazil, Chile). *Hausmannite*, Mn_3O_4; *Braunite*, Mn_2O_3; *Rhodocrosite* or *Manganese spar*, $MnCO_3$.

Colloidal particles of the oxides of manganese, iron and other metals carried into the sea form compact manganese nodules which contain ~15-30% of Mn on dry basis with Cu(~10%), Ni(1.5%) and Co(0.25%). More than 10^{12} tonnes of such nodules have already accumulated in the ocean bed, receiving an annual addition of about 10^7 tonnes. This large deposit may gain commercial significance in the future. At present, the lower limit set for commercal interest is 35% manganese content. Ores containing 35-45% manganese are considered only third grade, those with 45-48% Mn are considered second grade and ores with more than 48% Mn are considered first grade.

India is one of the major producers of pyrolusite. The main part of Indian output of good quality ore comes from Balaghat and Chhindwara districts in *Madhya Pradesh* and the Keonjhar-Bonai belt of *Orissa*, followed by the Koraput-Kalahandi area in the same state (total reserve of all grades ~ 22 million tonnes). Some good deposits also occur in Nagpur and Bhandara districts in *Maharastra* (total reserve ~ 4.5 million tonnes). The deposits in the Ratnagiri district in the same state are not of high quality. Manganese ores of all grades occur in *Goa* (~4.7 million tonnes, mainly in the southern parts); *Gujarat* (Panch Mahal and Baroda districts); *Bihar* (Gua, Chaibasa and Jamda area) and *Andhra Pradesh* (Srikakulam and Vishakapatnam). The deposits from Andhra have high phosphorus content, a disadvantage for use in steel industry. *Rajasthan* offers important deposits in Banswara and Udaipur districts (>254,000 tonnes; 45-50% Mn). Sandur in *Tamil Nadu* also possesses low-phosphorus pyrolusite.

Manganese is present in traces in plants and in the animal body and plays an important role in biological processes.

28.6.2 The Element

Extraction

Manganese is produced by electrolysis of aqueous solution of manganese(II) sulphate. This, in turn, is prepared from pyrolusite by heating with concentrated H_2SO_4 at temperature above 150°C and heating the residue to dull redness (<800°C) to decompose the ferric sulphate formed by the iron oxide impurities.

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

Alternatively, pyrolusite may be heated (below 800°C) with dehydrated green vitriol ($MnSO_4$ decomposes above 800°C).

$$2MnO_2 + 2FeSO_4 = 2MnSO_4 + Fe_2O_3 + \frac{1}{2} O_2$$

In both procedures, $MnSO_4$ is leached out from the residue leaving behind iron oxide and other siliceous impurities.

The manganese(II) sulphate may be further purified by crystallization before subjecting to electrolysis.

Formerly, manganese metal was prepared by aluminothermic reduction of its oxide. The reaction with MnO_2 being violent, it was first converted to Mn_3O_4 by strong heating in air. This was then mixed with aluminium powder and ignited in a fireclay crucible.

$$3MnO_2 = Mn_3O_4 + O_2; \ 3Mn_3O_4 + 8Al = 4Al_2O_3 + 9Mn$$

Reduction of MnO_2 may also be carried out with silcon (silicothermy) :

$$MnO_2 + Si = Mn + SiO_2$$

Carbon reduction of MnO_2 yields manganese contaminated with much carbide (mainly Mn_3C) and hence is considered unsuitable.

Ferromanganese **:** Since the principal use of manganese is as an additive to steel, about ninetyfive percent of the mined ore is directly converted to ferromanganese, an alloy of iron and manganese containing about 90% Mn. This is obtained by carbon reduction of a mixture containing calculated amount of MnO_2 and Fe_2O_3 in a blast furnace or in an electric arc furnace. Removal of silica is aided by addition of limestone or dolomite which acts as a flux, forming $CaSiO_3(MgSiO_3)$ as slag.

From low grade ores, alloys are prepared with lower manganese content, for example, *silicomanganese* (~70% Mn, 20% Si and 10% Fe) or *spiegeleisen* (5-20% Mn and remaining Fe). These alloys are also used as additives to steel.

Properties

Elemental manganese exists in four allotropic modifications. The form stable at room temperature (α - form) has a bcc structure which is atypical with four distinct types of Mn atoms. The properties given below refer to this form.

Manganese is a greyish white paramagnetic metal, hard and brittle. Its melting point is much lower than that of chromium (Table 28.2). This is consistent with our discussion on the general trend : the *d*-electrons gradually form a part of the inner core beginning with manganese. However, the melting point is also lower than that of iron (Cr 1900°C; Mn 1244°C; Fe 1535°C) and we recall that manganese assumes an atypical crystal structure. The enthalpies of atomisation also show a parallel trend which may be associated with the stable d^5 configuration as well as efficiency of packing in the solid.

Manganese is not easily oxidized by air when very pure, but traces of impurity (mainly carbon) render it more reactive. The finely divided metal is pyrophoric and burns in air. The product of oxidation is mostly Mn_3O_4 but above 1200°C, nitrogen also reacts to form the nitride Mn_3N_2.

Unless very pure, manganese decomposes cold water, liberating H_2

$$Mn + 2H_2O = Mn(OH)_2 + H_2$$

The pure metal is slowly attacked by steam.

The metal is fairly electropositive

$$Mn^{2+}(aq) + 2e \rightleftharpoons Mn; \quad E^\circ = -1.185V$$

It liberates hydrogen from all dilute acids, including dilute HNO_3. Hot concentrated H_2SO_4 and HNO_3 are reduced to SO_2 and NO respectively.

Manganese also combines with carbon, sulphur and halogens, specially on heating in the powdered state, producing Mn_3C, MnS and MnX_2 respectively (fluorine giving both MnF_2 and MnF_3)

Uses

The main use of manganese is as an additive to steel. It combines with the sulphur present in steel, preventing the formation of FeS which would render steel brittle; the MnS passes into the slag. At the same time, it combines with oxygen to form MnO which is also removed in the slag as $MnSiO_3$. This reduces the formation of bubbles in the finished steel, rendering it harder and shock resistant. A typical good composition is achieved in *Hadfield steel* which contains ~13% Mn and 1.25% C. This is used in works requiring high shock resistance, as in drilling, dredging and crushing machines. Various other specifications of alloy steels are also known e.g. with 17-19% Cr, 8-10% Mn, 0.75-1% Cu, 0.1% C and 0.2-0.5% Si, which compare well with stainless steel in resisting atmospheric corrosion and chemical attack. Several non-ferrous alloys are also important; for example, *manganin* (Cu 83-84, Mn 12-13, Ni 4) is largely used in electrical instruments since its electical resistivity remains practically unchanged with temperature. *Manganese bronze* (Cu 55-65, Zn 30-45, Fe 0.5-2 Mn 0.2-4, Al 0.2-4) is used in making propeller blades as it is stable towards sea-water. *Heusler's alloy* (Cu 55, Al-15, Mn 30) is ferromagnetic.

Manganese and its compounds also find use as catalysts, pharmaceuticals and fertilisers. MnO_2 is extremely useful in glass industry as decolorizer and in electrical dry cells as depolarizer.

General chemical features

The reduction potential oxidation state diagram for manganese has been discussed in Chapter 9 (Fig. 9.6). The marked stability of the +II state is consistent with the half-filled d^5 configuration. The Mn^{2+} ion is known to exist in solids, in solution and in the form of complexes. In alkaline medium, it is readily oxidized to MnO_2. From the diagram we also note the very strong oxidizing nature of the +VII state and the marked tendency of Mn(III) and Mn(VI) to disproportionate. Low oxidation states of manganese may be found, as in the case of others, among carbonyls, nitrosyls etc complexes and other organometallic compounds.

28.6.3 Chemistry of Mn(VII), $3d^\circ$

Manganese(VII) is familiar to us in the form of potassium permanganate, $KMnO_4$, a strong oxidizing agent. Besides the corresponding permanganic acid, an oxide (Mn_2O_7) and oxohalides mark the chemistry of Mn(VII).

Oxide and oxohalides

Manganese(VII) oxide, Mn_2O_7 ($\Delta G_f^0 = -544$ kJ mol^{-1}; $\Delta H_f^0 = -743$ kJ mol^{-1}) is obtained by carefully reacting dry $KMnO_4$ with concentrated H_2SO_4 :

$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O.$$

The green oil (m.p. 5.9°C) is highly explosive and detonates around 95°C, but loses oxygen slowly on standing :

$$2Mn_2O_7 = 4MnO_2 + 3O_2$$

As expected, the oxide is vigorously oxidizing in nature : alcohol and ether ignite when brought into contact. It is strongly acidic in nature, giving with water permanganic acid $HMnO_4$.

$$Mn_2O_7 + H_2O = 2HMnO_4$$

Both in the gas phase and in the solid, the oxide contains linked MnO_4 tetrahedra (Fig. 28.36)

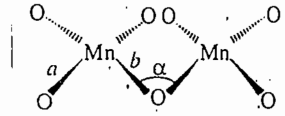


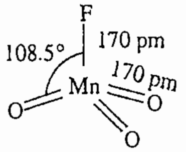
Fig. 28.36
Structure of Mn_2O_7.
$a = 159$ pm, $b = 177$ pm, $\alpha = 121°$

Mn_2O_7 reacts with chlorosulphonic acid to produce oxochlorides containing manganese VII, VI and V :

$$\underset{}{Mn_2O_7 + SO_2.OH.Cl} \longrightarrow \underset{black}{MnO_3Cl} + \underset{brown}{MnO_2Cl_2} + \underset{green}{MnOCl_3}$$

The oxohalides are unstable volatile liquids which tend to explode but may be handled in CCl_4 solution.

MnO_3F may be prepared by treating $KMnO_4$ with fluorosulphonic acid HSO_3F. It is a dark green liquid, m.p. −78°C and b.p. (extrapolated) 60°C. The molecule has a distorted tetrahedral structure (28-XIV).



28-XIV

It reacts vigorously with water :

$$MnO_3F + H_2O = HMnO_4 + HF$$

Aqueous solution chemistry

The only stable representative of Mn(VII) is the permanganate ion, MnO_4^-, known as the free acid as well as various salts of which potassium permanganate is most common.

The permanganate ion is a very strong oxidizing agent in acid medium and moderately strong in neutral and alkaline medium :

acidic :	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	$E^\circ = 1.51$ V
faintly acidic :	$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	
neutral and basic :	$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$	$E^\circ = 0.60$ V
strongly alkaline :	$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	$E^\circ = 0.56$ V

In acid solution, most oxidations by permanganate are quantitative :

$$2MnO_4^- + 10Fe^{2+} + 16H^+ = 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

The last reaction is carried out at about 60°C; the reaction is at first slow, but soon gets catalyzed by the Mn^{2+} ions produced.

Theoretically, permanganate should oxidize water at $[H^+] = 1$. However, the above reactions, and several other oxidations by permanganate can be used in quantitative analysis because of the fact that permanganate oxidizes water negligibly slowly. However, aqueous solutions containing MnO_4^- cannot be stored for a long time since it gets slowly reduced to MnO_2, specially in presence of light and acid. Traces of organic matter from grease etc. are sufficient to initiate the reduction of MnO_4^-; the MnO_2 produced catalyzes the decomposition further (*autocatalytic decomposition*) :

$$4MnO_4^- + 4H^+ = 4MnO_2 + 2H_2O + 3O_2$$

Analytical use

The conventional source of MnO_4^- ion is $KMnO_4$. Sodium permanganate cannot be used as it is hygroscopic. $KMnO_4$, however, cannot be used as a primary standard since it is difficult to obtain it absolutely free from MnO_2. Also, solutions of $KMnO_4$ are always contaminated with traces of MnO_2 as explained above. Hence the recommended practice is to keep a solution of $KMnO_4$ overnight (preferably after boiling to complete oxidation of all impurities) and filter it before standardization. Glass wool or sintered glass crucible is used for this purpose since cellulose fibres from filter paper will again reduce it to MnO_2. Standardization can be done against standard oxalic acid/sodium oxalate solution or Mohr salt solution. Hydrochloric acid medium cannot be used since chloride ions are susceptible to oxidation by permanganate ($E°_{Cl_2,Cl^-} = 1.36V$).

However, iron(II) may be estimated by titration against permanganate in HCl medium in presence of a preventive solution (Zimmermann Reinhardt or Z.R. solution) containing manganese(II) sulphate and phosphoric acid. The excess concentration of Mn^{2+} ion reduces the formal potential of the $MnO_4^- - Mn^{2+}$ couple (or of the Mn(III) – Mn(II) couple which is actually involved) and prevents oxidation of chloride. This decrease in the potential will also reduce the jump of potential across the endpoint (Chapter 9) and hence phosphoric acid is used to lower the potential of the Fe^{3+}/Fe^{2+} couple also.

Solutions of permanganate are widely used in the volumetric estimation of Fe(II), Ti(III), VO^{2+} etc. as well as of hydrogen peroxide, oxalates, formates and nitrites.

In neutral medium, permanganate may be used to oxidize Mn(II) according to the reaction

$$2MnO_4^- + 3Mn^{++} + 2H_2O = 5MnO_2 + 4H^+$$

The reaction is quantitative only in presence of zinc sulphate or suspended zinc oxide in *hot solution* and forms the basis of *Volhard's method* of estimation of Mn(II)). In absence of Zn(II), some of the Mn(II) may escape oxidation presumably due to the formation of insoluble $Mn^{II}[MnO_3]$. The zinc probably binds to the MnO_2 forming $ZnMn_2O_5$, when the Mn(II) gets completely oxidized.

Neutral or faintly acidic solutions of permaganate oxidize thiosulphate to sulphate :

$$8KMnO_4 + 3Na_2S_2O_3 + H_2O = 8MnO_2 + 3Na_2SO_4 + 3K_2SO_4 + 2KOH$$

[**Sec. 28.6.3** *Potassium permanganate*]

Hydrogen peroxide reduces neutral $KMnO_4$ to MnO_2 (in acid solution to Mn^{2+})

$$2KMnO_4 + 3H_2O_2 = 2KOH + 2MnO_2 + 2H_2O + 3O_2$$

In alkaline medium, permanganate oxidizes iodide to iodate :

$$2KMnO_4 + KI + H_2O = KIO_3 + 2MnO_2 + 2KOH$$

Formates are quantitatively oxidized by permanganate in hot sodium carbonate solution :

$$3HCOOK + 2KMnO_4 = 2MnO_2 + 2K_2CO_3 + KHCO_3 + H_2O$$

Potassium permanganate, $KMnO_4$, is prepared from pyrolusite (MnO_2) as follows :

(i) Finely ground pyrolusite is fused with caustic potash with free access of air to form potassium manganate :

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$

(ii) The fused mass is leached with water and the alkaline solution is oxidized electrolytically (at about 90°C) in an iron vessel using iron electrodes and a high current density. Oxidation occurs at the anode :

$$MnO_4^{=} = MnO_4^- + e$$

The high current density minimises the reduction of $KMnO_4$ at the cathode.

$KMnO_4$ crystallizes on cooling the solution. Further concentration of the mother liquor in vacuum evaporators produces more $KMnO_4$.

(iii) The potassium manganate may also be oxidized by passing chlorine through the alkaline solution.

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

On fractional crystallization, the less soluble $KMnO_4$ separates first.

(iv) Potassium manganate may also be converted to permanganate through disproportionation by CO_2 :

$$3K_2MnO_4 + 2H_2O + 4CO_2 = 2KMnO_4 + MnO_2 + 4KHCO_3$$

But the method is uneconomical since one-third of the manganese is reconverted to MnO_2.

$KMnO_4$ forms dark purple crystals (rhombic prisms) with a green iridescence. The crystals are fairly soluble in water (~63 gL^{-1} at 20°), forming deep purple solutions. As we have noted earlier, the colour arises from charge-transfer transition. $KMnO_4$ also exhibits temperature independent paramagnetism.

$KMnO_4$ crystals decompose on heating to liberate O_2.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

(The manganate decomposes further at a red heat : $2K_2MnO_4 = 2K_2MnO_3 + O_2$)

Potassium permanganate is a widely used oxidant in the laboratory as well as in industry. It can be dissolved in benzene by cryptands and crown ethers and the solution used as a potential oxidizing agent for organic compounds. It is also used as a disinfectant and in water purification; $KMnO_4$ is preferred over ozone for this latter purpose since it leaves no smell and the MnO_2 formed helps coagulation of other suspended matter.

The MnO_4^- ion is tetrahedral — $KMnO_4$ is isomorphous with $KClO_4$. The distribution of valence electrons among the molecular orbitals is

$$[\sigma]^8 [\pi]^{10} [\pi^{non}]^6$$

In the valence bond description, this corresponds to d^3s hybridization of the valence orbitals of manganese.

Sodium permanganate, $NaMnO_4.3H_2O$ is prepared in the same manner as used for $KMnO_4$. The crystals are deliquescent and as such unsuitable for use in volumetric analysis. It is used as an industrial oxidant and in water purification.

Sodium permanganate is more soluble in water than potassium permanganate (and hence difficult to crystallize). The solubility of the alkali metal permanganates follow the order

$$LiMnO_4 > NaMnO_4 > KMnO_4 > RbMnO_4 > CsMnO_4.$$

The relatively large MnO_4^- ion packs better with larger alkali metal ions.

Calcium permanganate, $Ca(MnO_4)_2$, $5H_2O$ is also highly soluble in water and used in water purification.

Permanganic acid, $HMnO_4$ may be obtained in deep purple aqueous solution by double decomposition reactions :

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2HMnO_4$$
$$2KMnO_4 + H_2SiF_6 = K_2SiF_6 + 2HMnO_4$$

The solution may be concentrated in vacuum and at low temperature, the solid dihydrate $HMnO_4$, $2H_2O$ may be separated. The solid decomposes above 3°, often explosively. It is a violent oxidant, causing ignition of hydrocarbons on contact.

28.6.4 Chemistry of Mn(VI), d^1

The only stable representative of Mn(VI) is the manganate ion, MnO_4^{2-}, which is formed as a green mass on fusing pyrolusite with alkali in excess air, or better, in presence of an oxidizing agent like KNO_3 :

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$
$$MnO_2 + 2KOH + KNO_3 = K_2MnO_4 + KNO_2 + H_2O$$

The green mass may be extracted with water containing little alkali and the solution on evaporation in vacuum yields dark green crystals of potassium manganate K_2MnO_4. The sodium salt, prepared in the same manner, crystallizes as Na_2MnO_4, $10H_2O$.

The green manganate ion is also formed in solution by adding concentrated alkali to a solution containng MnO_4^-

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$$

Barium manganate may be precipitated as a green salt from a solution of manganate ion. This is sometmes used as a green pigment.

The green solution containing $MnO_4^=$ ion is stable only in presence of alkali; it readily disproportionates to permanganate and MnO_2 :

$$3MnO_4^{2-} + 4H^+ = 2MnO_4^- + MnO_2 + 2H_2O \quad K \approx 10^{58}$$
$$3K_2MnO_4 + 2H_2O + 4CO_2 = 2KMnO_4 + MnO_2 + 4KHCO_3$$

Free manganic acid H_2MnO_4 is therefore unknown. Sodium manganate is used in water purification. The manganate ion is tetrahedral and paramagnetic with one unpaired electron. The electron distribution among the m.o.s.

$$[\sigma]^8 [\pi]^{10} [\pi^{non}]^6 [\pi^*]^1$$

is consistent with ready conversion of MnO_4^{2-} to MnO_4^- by losing the single antibonding electron. K_2MnO_4 is isomorphous with K_2SO_4 while Na_2MnO_4, $10H_2O$ is isomor-phous with Na_2SO_4, $10H_2O$.

28.6.5 Chemistry of manganese(V), d^2

Examples of Mn(V) are also rare — besides the oxochloride $MnOCl_3$, the blue oxo anion MnO_4^{3-} and Mn^V esters are only of transient existence as reduction intermediates of MnO_4^-.

$MnOCl_3$ is prepared by reducing $KMnO_4$ with sucrose in chlorosulphonic acid medium. The compound decomposes above 0°C to $MnCl_3$ and undergoes ready hydrolysis.

The MnO_4^{3-} ion appears to be an intermediate in the reduction of permanganate by sodium sulphite, the ultimate product being MnO_2. The blue MnO_4^{3-} ion is supposed to be formed in the reduction of MnO_4^{2-} by alkaline formate or when MnO_2 is fused with Na_2CO_3 and $NaNO_3$. The blue compound $Ba_5(MnO_4)_3Cl$ has an apatite like structure in which Mn(V) is supposed to replace P(V) in normal apatite structure. The +V state for manganese (d^2) is supported by magnetic studies. The Mn—O distance in the tetrahedral MnO_4^{3-} ion is 170 pm. Na_3MnO_4, $10H_2O$ is isomorphous with Na_3VO_4.

Q. 28.7 *Addition of KCN to a solution of permanganate in concentrated aqueous KOH forms a blue precipitate supposed to contain Mn(V). How would you test this chemically?*

Hint : Acidification will lead to disproportionation to MnO_2 and MnO_4^-. Filter and estimate each.

28.6.6 Chemistry of manganese(IV), d^3

Examples of stable compounds of manganese(IV) are the dioxide MnO_2, the halide MnF_4 and the complexes MnX_6^{2-} where X = F, Cl, CN and IO_3.

Oxide

Manganese dioxide, MnO_2 common in the earth's crust as pyrolusite, is the main source of manganese compounds. The oxide in hydrous form is also a common precipitate from manganese compounds in an oxidizing medium or in the reduction of permanganate in insufficiently acidic media.

MnO_2 is a slightly brownish black solid mostly insoluble in water and inert to cold acids. It oxidizes concentrated hydrochloric acid and decomposes concentrated sulphuric acid and nitric acid on strong heating.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$
$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

Green $Mn_2(SO_4)_3$ is formed around 140°C with concentrated H_2SO_4 :

$$4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2$$

The oxide is amphoteric in nature — it forms oxomanganate(IV) with fused alkali ("*manganite*") which have varied compositions

$$MnO_2 + CaO = CaMnO_3$$

Though it does not directly give Mn(IV) salts with acids, black $Mn(SO_4)_2$ is formed by oxidizing $MnSO_4$ in concentrated H_2SO_4 by hot $KMnO_4$ (50-60°C) or electrolytically. The salt is readily hydrolyzed by water to precipitate MnO_2.

MnO_2 is a strong oxidant :

$$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O \quad E° = 1.23 \text{ V}$$

However, it is further oxidized to Mn(VI) or Mn(VII) by stronger oxidizing agents :

$$3MnO_2 + KClO_3 + 6KOH = 3K_2MnO_4 + KCl + 3H_2O$$

$$2MnO_2 + 3PbO_2 + 6HNO_3 = 2HMnO_4 + 3Pb(NO_3)_2 + 2H_2O$$

MnO_2 is used as a ready oxidant in industry. It is used in the glass industry to decolourize glass and in the manufacture of matches. It is also widely used as a depolarizer in dry cells.

The common dry cells consist of a zinc metal casing acting as cathode and a central carbon rod as anode with a paste of carbon dust, ammonium chloride and manganese dioxide. The main reactions involved are

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$Zn^{2+} + 2NH_4Cl + 2OH^- \longrightarrow [ZnCl_2(NH_3)_2] + 2H_2O$$

$$2MnO_2 + 2H_2O + 2e \longrightarrow 2[MnO(OH)] + 2OH^-$$

Valuation of pyrolusite : MnO_2 quantitatively oxidizes Fe(II) to Fe(III) and oxalic acid to carbon dioxide in hot dilute sulphuric acid medium :

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + H_2O$$

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$$

These reactions may be used to evaluate the percent manganese dioxide in pyrolusite. In another method, the pyrolusite is boiled with concentrated HCl and the liberated chlorine is passed into a solution of KI. The iodine set free is titrated against thiosulphate.

MnO_2 has a rutile type structure at high temperature but tends to be nonstoichiometric at ordinary temperature when it becomes polymorphic.

Halide

MnF_4, the only halide of Mn(IV) may be prepared by direct reaction. The blue hygroscopic compound decomposes slowly at room temperature into MnF_3 and F_2. It shows $\mu_{eff} \approx 3.84$ B.M. at room temperature and obeys the Curie-Weiss law.

Salts of the yellow MnF_6^{2-} ion may be obtained by reduction of permanganate with H_2O_2 or diethyl ether in aqueous HF. These are readily hydrolyzed by water.

A reaction in which fluorine is generated by chemical reaction (i.e. non-electrolytically) involves heating of K_2MnF_6 with SbF_5 :

$$K_2[MnF_6] + 2SbF_5 \longrightarrow 2K[SbF_6] + MnF_2 + F_2$$

K_2MnCl_6 slowly liberates chlorine at room temperature in dry air. $K_2[Mn(CN)_6]$ has been prepared by oxidation of $K_3[Mn(CN)_6]$ with NOCl in dimethyl formamide.*

28.6.7 Chemistry of manganese(III), d^4

Manganese (III) is known in several binary compounds, aqua ions and complex compounds.

Oxide

Mn_2O_3 occurs in nature as *braunite* and is produced by heating Mn(II) salts or MnO or MnO_2 in air between 470-600°C. Aerial oxidation of $Mn(OH)_2$ also results in the brown hydrated Mn_2O_3, *aq*; this gives MnO(OH) on drying at 100°C. The mineral *manganite* also has the composition MnO(OH); magnetic data suggest the presence of both Mn(II) and Mn(IV). A similar mixed oxidation state occurs in the black Mn_3O_4 produced by heating Mn_2O_3 above 940°C; this has a spinel structure, $Mn^{II}Mn_2^{III}O_4$ (Chapter 27). Many mixed oxide systems containing Mn(III) are also known, e.g., $LiMnO_2$, Na_5MnO_4 and $K_6Mn_2O_6$.

Halide

MnF_3 is obtained as a red-purple solid by fluorination of Mn(II) halides at 250°C.

$$2MnCl_2 + 3F_2 = 2MnF_3 + 2Cl_2$$

The compound is instantly hydrolyzed by moisture. The solid shows $\mu_{eff} \approx 5.0$ B.M. at room temperature and has a distorted octahedral structure corresponding to high spin d^4 ($t_{2g}^3 e_g^1$) configuration. The crystal structure consisting of corner shared MnF_6 octahedra shows three pairs of Mn–F distances : 179, 191 and 209 pm.

$MnCl_3$ (black) can be prepared by chlorination of MnO(OH) in CCl_4 below –40°C. It is also obtained by the action of ethanolic HCl on Mn(III) acetate or MnO_2 at –63°C followed by precipitation with CCl_4. It decomposes above –40°C but its solution in diethyl ether is somewhat stable at –10°C. It forms several complexes which are thermally more stable, though extremely sensitive to moisture, e.g., $MnCl_3(PR_3)_3$, $(R_4N)_2MnCl_5$, $MnCl_2(acac)$ and $MnCl_3(dioxan)_2$. The $[MnCl_6]^{3-}$ ion may be isolated as tris-(1,2-propanediamine)cobalt(III) salt.

Several fluorocomplexes are obtained by reduction of permanganate in HF. K_3MnF_6 has been prepared in melts while $K_2[MnF_5(H_2O)]$ has been prepared from aqueous HF. Similarly, addition of CsF to a solution of MnO(OH) in HF gives trans-$Cs[MnF_4(H_2O)_2]$. $(NH_4)_2MnF_5$ contains chains of MnF_6 octahedra linked by trans-bridging F^- ions.

Aqueous solution chemistry

The red **aqua ion $Mn(H_2O)_6^{3+}$** can be prepared by oxidation of $Mn^{2+}(aq)$ ions electrolytically (or with peroxodisulphate) and isolated as the alum Cs_2SO_4, $[Mn(H_2O)_6]_2(SO_4)_3$, $12H_2O$. The ion is strongly acidic, undergoing ready hydrolysis :

$$[Mn(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Mn(OH)(H_2O)_5]^{2+} + H_3O^+ \quad (pK_1 \approx 0.9)$$

The Mn(III)–Mn(II) couple is also strongly oxidizing in nature, $E° = 1.56$V in 3*M* $LiClO_4$. Water is slowly oxidized by it :

$$2Mn^{3+}(aq) + H_2O = 2Mn^{2+}(aq) + 2H^+(aq) + \frac{1}{2}O_2$$

Disproportionation also takes place simultaneously :

$$2Mn^{3+}(aq) + 2H_2O = Mn^{2+}(aq) + MnO_2 + 4H^+(aq)$$

$Mn_2(SO_4)_3$ may be prepared by heating precipitated MnO_2 with concentrated H_2SO_4 (~ 140°C)

$$4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2$$

The solid product is drained on a porous plate and washed with nitric acid. The nitric acid is removed by drying at 130°C. The dark green crystals dissolve in water to a purple solution which gets readily hydrolyzed.

$Mn_2(SO_4)_3$, H_2SO_4, $4H_2O$ forms red crystals from solutions of Mn_2O_3 in cold moderately concentrated H_2SO_4.

$MnPO_4.H_2O$ is obtained as a green precipitate when Mn(II) is oxidized by $KMnO_4$ in presence of acetic and phosphoric acids at 100°C. It forms violet solutions in concentrated sulphuric and phosphoric acids.

$K_3[Mn(C_2O_4)_3] . 3H_2O$, potassium trioxalatomanganate(III) is isomorphous with the corresponding Fe(II) compound. It is obtained by reducing alkaline $KMnO_4$ solution with oxalic acid in cold. The deep red-violet crystals are highly soluble in water. The compound decomposes above ~60°C.

$Mn(CH_3COO)_3$ is prepared by heating $Mn(NO_3)_2 . 2H_2O$ with acetic anhydride when the liberated nitric acid oxidizes the Mn(II) to Mn(III). The dihydrate may be isolated from a solution obtained by oxidizing manganese(II) acetate in acetic acid with permanganate or persulphate. The compound is actually an oxo-centered species like the chromium-analogue (Fig 28-X), $[Mn_3O(CH_3COO)_6]^+$.

Complex compounds

The halo, oxalato and acetato complexes have already been mentioned. Mn(III) is also stabilized in aqueous solution by other anions like SO_4^{2-} and $EDTA^{4-}$. However, most of these complexes are readily hydrolyzed. The Mn(III) state is also stabilized by other potential complexing agents like CN^-, acetylacetone etc. Nearly all of them (except the cyano complex) are octahedral high spin with μ_{eff} close to 4.9 B.M.

$K_3Mn(CN)_6$ is obtained by adding an excess of aqueous KCN to manganese(III) acetate followed by precipitation with ethanol. The $[Mn(CN)_6]^{3-}$ ion is also formed by oxidizing Mn(II) in presence of excess cyanide or by aerial oxidation of $K_4Mn(CN)_6$ (bubbling air through Mn(II) *aq* and CN^-).

$$MnSO_4 + 6KCN = K_4[Mn(CN)_6] + K_2SO_4$$

$$4K_4[Mn(CN)_6] + 2H_2O + O_2 = 4K_3[Mn(CN)_6] + 4KOH$$

The solution yields deep red monoclinic crystals which are isomorphous with $K_3Fe(CN)_6$ and stable in air. Unlike most other complexes of Mn(III), this complex is *low-spin*.

Tris(acetylacetonato)manganese(III), $Mn(acac)_3$, is obtained by the oxidation of Mn(II) solutions in presence of excess acetylacetone. Earlier reports claimed that the complex shows no distortion from regular octahedral geometry. Now it has been established that the complex actually has two forms : (a) one form has four Mn—O distances at 200 pm. and two Mn—O distances at 195 pm. (tetragonal compression) (b) the other form shows tetragonal elongation : two Mn–O at 212 pm and four Mn–O = 193 pm. (tetragonal elongation).

$[Mn(urea)_6]^{3+}$ shows six equal Mn–O distances at ~ 199 pm which is due to dynamic Jahn-Teller effect.

The red or red-brown colours of high-spin complexes of Mn(III), e.g., $Mn(H_2O)_6^{3+}$ and $[Mn(ox)_3]^{3-}$, may be attributed to a broad band appearing in the visible electronic spectrum around 20,000 cm^{-1}. This corresponds to the transition between ^5E_g to $^5T_{2g}$ terms arising from the ^5D ground state.

28.6.8 Chemistry of manganese(II), d^5

Oxide, hydroxide and sulfides

This is the most common oxidation state of manganese which is well represented by a large number of binary compounds and complexes.

MnO is prepared by heating MnO_2 in hydrogen or roasting $MnCO_3$ in H_2 or N_2 atmosphere. It is also obtained by heating manganese(II) oxalate or by the action of steam on $MnCl_2$ at 600°C.

$$MnC_2O_4 = MnO + CO + CO_2$$

The greyish-green oxide (m.p. 1780°C) has the rock salt structure but its composition is variable. It shows antiferromagnetic behaviour through superexchange mechanism (Section 27.3). It is readily oxidized in air even at ordinary temperature (to Mn_2O_3 or Mn_3O_4):

MnO is insoluble in water — its basic character is shown by ready dissolution in acids forming Mn(II) salts.

$$MnO + 2H_3O^+ + 3H_2O = [Mn(H_2O)_6]^{2+}$$

The oxide ordinarily does not react with alkali (see below).

$Mn(OH)_2$ is a true hydroxide (not a hydrated oxide) which is thrown as a white precipitate on adding alkali to Mn^{2+} solutions. It is isomorphous with $Mg(OH)_2$.

$Mn(OH)_2$ rapidly darkens in presence of air owing to oxidation..

It is very feebly amphoteric :

$$Mn(OH)_2 + OH^- \longrightarrow Mn(OH)_3^-$$

It reacts with alkali only after quite strong and prolonged heating

$$Mn(OH)_2 + 4OH^- = [Mn(OH)_6]^{4-}$$

Hydroxomanganates(II) like $K_4[Mn(OH)_6]$, $Ba_2[Mn(OH)_6]$ (red) and certain others have been isolated in the free state. They all completely dissociate in aqueous solution — the reason why the hydroxide (or oxide or Mn itself) does not react with alkali under ordinary condition.

$Mn(OH)_2$ is only incompletely precipitated by ammonia from $Mn^{2+}(aq)$ in solution and may not be precipitated at all in presence of sufficient concentration of NH_4^+ ion. The solubility product (25°C) is 2.2×10^{-13} only.

The amount of *dissolved oxygen in water* may be estimated by precipitating $Mn(OH)_2$ in the aqueous medium when the dissolved oxygen oxidizes it rapidly to $Mn(OH)_3$. The precipitate is dissolved in HCl and titrated iodometrically.

Other chalcogenides MnS, MnSe and MnTe are also very stable when dry but the hydrated forms are slowly oxidized to MnO_2 in air. All of them have the NaCl structure and show antiferromagnetic behaviour through superexchange mechanism. MnS appears as a pale pink precipitate (flesh-coloured) by H_2S in ammoniacal medium (NH_4HS) which is soluble in dilute HCl (difference from CoS, NiS) and in acetic acid (difference from ZnS). On exposure to air, MnS turns brown owing to oxidation. On long storage (air excluded) or on boiling with excess of ammonium sulphide the pale pink precipitate changes to green crystalline anhydrous MnS found native in manganese blende, *alabandite*.

MnS_2, having the same crystal structure as FeS_2, contains Mn(II) and S_2^{2-} ions. It is formed by heating a solution of $MnCl_2$ and alkali polysulphide in a sealed tube. It occurs native as *hauerite*.

Halides

All four halides MnX_2 (X = F, Cl, Br, I) are stable compounds isomorphous with the magnesium halides. They may be conveniently prepared by reacting $MnCO_3$ with the appropriate halogen hydracid.

$MnCl_2$ is prepared on a large scale by heating pyrolusite with concentrated hydrochloric acid :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

The resulting solution contains much iron from the iron oxide present in pyrolusite. About one-tenth of the solution is evaporated to drive off HCl and Cl_2 and treated wth sodium carbonate. The precipitated ferric hydroxide and manganous carbonate are added to the remainder of the solution and boiled, when all iron(III) is precipitated :

$$2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2$$

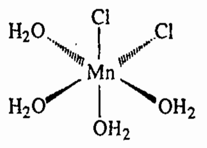
This is filtered out and the filtrate is evaporated (below 58°C) when pink monoclinic crystals of $MnCl_2$, $4H_2O$ are obtained.

$MnCl_2$ is also formed when pyrolusite is heated with solid ammonium chloride. The product is extracted with hot water and crystallized.

$$3MnO_2 + 6NH_4Cl = 3MnCl_2 + N_2 + 4NH_3 + 6H_2O$$

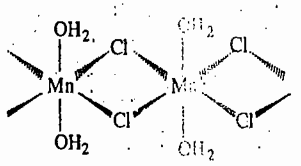
The ammonia may be converted to NH_4Cl and recycled. The method, unlike the previous one, does not pollute the atmosphere by chlorine.

$MnCl_2$ also forms two other hydrates — $MnCl_2 . 2H_2O$ and $MnCl_2 . 6H_2O$. and ammines with 1, 2 or 6 molecules of ammonia. The anhydrous chloride forms crystals of $MnCl_2.3C_2H_5OH$ from its green alcoholic solution. Other adducts like $MnCl_2.2py$ (isomorphous with $CoCl_2.2py$) and double salts with alkali metals are known : KCl, $MnCl_2$, $2H_2O$; 2KCl, $MnCl_2$, H_2O.



$MnCl_2.4H_2O$

28-XV



$MnCl_2.2H_2O$

28-XVI

In $MnCl_2.2H_2O$ and $MnCl_2.4H_2O$, the Mn(II) attains octahedral environment by water molecules and Cl^- ions (28- XV and XVI). $MnCl_2 . 4H_2O$ has *cis*-$MnCl_2(H_2O)_4$ units; $MnCl_2.2H_2O$ has polymeric chains with *trans* - $Mn(H_2O)_2Cl_4$ octahedra sharing edges.

Complex halides of Mn(II) are readily prepared in nonaqueous media. Those of the type M^IMnX_3 contain Mn(II) coordinated octahedrally by the X^- ions. Tetrahedral MnX_4^{2-} ions are present in complexes of the type $M_2^IMnX_4$.

Aqueous solution chemistry

The $[Mn(H_2O)_6]^{2+}$ cation is only faintly acidic and hence Mn(II) forms a large number of salts including the carbonate. The $Mn(H_2O)_6^{2+}$ ion is present in many hydrated salts like $MnSO_4.7H_2O$ and $Mn(ClO_4)_2$. $6H_2O$. Addition of alkali to solutions containing $Mn^{2+}(aq)$ precipitates $Mn(OH)_2$ (mentioned earlier). Addition of sodium carbonate to Mn(II) in solution usually precipitates basic manganese(II) carbonate but manganous carbonate $MnCO_3$ is formed as a white (or pale buff) precipitate on adding sodium bicarbonate solution to a solution of Mn^{2+} in presence of carbon dioxide.

$MnCO_3$ is isomorphous with calcite and is found native as manganese spar (*rhodocrosite*). It is insoluble in water but dissolves slightly as the bicarbonate when carbon dioxide is present. The solution deposits brown $Mn(OH)_3$ on exposure to air.

$MnCO_3$ decomposes on heating below 100°C (MnO + CO_2); higher oxides are formed above 300°C.

The $Mn(H_2O)_6^{2+}$ ion can be easily oxidized to permanganate by periodate, persulphate, bismuthate and red lead in nitric acid medium.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

$$2Mn^{++} + 5BiO_3^- + 14H^+ \longrightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

$MnSO_4$. $4H_2O$ is prepared by digesting pyrolusite wth concentrated H_2SO_4. The mass is dried and heated to dull redness to decompose iron(III) sulphate :

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

The residue is leached with water. Rose-pink efflorescent monoclinic crystals $MnSO_4$. $4H_2O$ crystallize on evaporation. It may also be prepared by strongly heating pyrolusite with ferrous sulphate

$$2MnO_2 + 2FeSO_4 = 2MnSO_4 + Fe_2O_3 + \tfrac{1}{2}O_2$$

Other hydrates are also known over restricted ranges of temperature. $MnSO_4.7H_2O$, stable below 9°C, is isomorphous with $FeSO_4.7H_2O$.$MnSO_4.5H_2O$ (9°—27°C) is isomorphous with $CuSO_4.5H_2O$. A rhombic form of $MnSO_4.4H_2O$ exists between 26°—27°C.

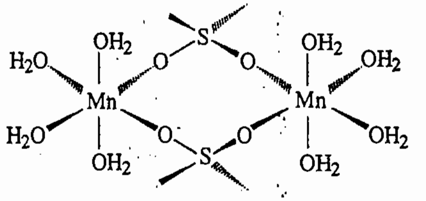


Fig. 28.38

Structure of $MnSO_4.4H_2O$.

Manganous sulphate melts at 700°C. The double salt $(NH_4)_2SO_4 \cdot MnSO_4 \cdot 6H_2O$ is isomorphous with the corresponding Fe(II) salt.

$Mn(NO_3)_2 \cdot 6H_2O$ forms pink deliquescent crystals from a solution obtained by boiling MnO_2 with dilute HNO_3 in presence of sugar or oxalic acid. It is also formed by dissolving $MnCO_3$ in dlute HNO_3. Tetra, tri and monohydrates of Mn(II)-nitrate are also known. The hexahydrate changes to the monohydrate when heated with concentrated nitric acid. When the monohydrate is further heated with conc. HNO_3 containing N_2O_5, the anhydrous salt is obtained. The hexahydrate decomposes on heating.

$$Mn(NO_3)_2 \cdot 6H_2O = MnO_2 + 2NO_2 + 6H_2O$$

Several double salts with rare earth metals are known.

$Mn_3(PO_4)_2 \cdot 7H_2O$ (white) is precipitated from a neutral solution containing $Mn^{2+}(aq)$ with Na_2HPO_4 solution. $Mn(NH_4)PO_4 \cdot H_2O$ precipitates in presence of ammonium chloride and ammonia.

$$MnSO_4 + NH_4OH + Na_2HPO_4 = Mn(NH_4)PO_4 + Na_2SO_4 + H_2O$$

The shining reddish-white crystals are converted to pyrophosphate on heating :

$$2Mn(NH_4)PO_4 = Mn_2P_2O_7 + 2NH_3 + H_2O$$

$Mn(CH_3COO)_2$ may be prepared by heating $Mn(NO_3)_2$ with acetic anhydride. $Mn(ClO_4)_2$ is stable to 150°C, above which the perchlorate oxidizes the Mn(II) to MnO_2.

Complexes

Manganese(II) forms an extensive range of complex compounds in different stereo chemistry. The d^5 configuration offers no CFSE in high-spin octahedral or tetrahedral complexes both of which are adopted in a large number of complexes. Both stereochemistries are present together in $[Mn(DMSO)_6]^{2+}[MnCl_4]^{2-}$. Stable high-spin octahedral complexes are formed by NH_3, edta, oxalate, ethylenediamine, SCN^- (though hexahalo complexes are not formed). The equilibrium constants for the formation of these ions from the aqua-ion are very low, which may again be attributed to the absence of any gain in CFSE. All the high-spin complexes are very stable and resistant to attack except by the very strong oxidizing or reducing agents. The very pale colours associated with these compounds are due to very weak Laporte forbidden and spinforbidden transitions (Ch. 27). In tetrahedral complexes, transition probabilities are about 100 times stronger as they are only spin-forbidden; they exhibit a pale yellow-green colour. This may also be accompanied by an intense yellow-green fluorescence.

Square-planar Mn(II) is present in $[Mn(H_2O)_4]SO_4 \cdot H_2O$ which is isostructural with $CuSO_4 \cdot 5H_2O$. $Mn(acac)_2 \cdot 2H_2O$ has a distorted octahedral structure in which the bidentate acetylacetonate groups form a square plane around manganese. The dehydrated product, $Mn(acac)_2$, is thus expected to have a square planar environment.

Tetrahderal MnX_4^{2-} species (X = halogen) may be prepared as the salt of large cations, but these are unstable in water or other donor solvents where they change to octahedral ones.

MnI_2(terpy) where terpy = 2,2′,2″-terpyridyl, is an example of 5-coordinate manganese(II) complex. Dodecahedral eight-coordination is represented by $[Ph_4As]_2[Mn(NO_3)_4]$.

Low-spin complexes of Mn(II) are represented by the cyanides and related complexes, for example $[Mn(CN)_6]^{4-}$, $[Mn(CN)_5NO]^{3-}$ and $[Mn(CNR)_6]^{2+}$. These complexes are comparatively more reactive than the high-spin ones, getting readily oxidized, as in

$$[Mn(CN)_6]^{4-} \xrightarrow{air} [Mn(CN)_6]^{3-}$$

[**Sec.28.6.10** *Manganese-organometallics*]

It has been suggested that the CFSE, which is sufficient to provide spin-pairing, is only marginally greater than the loss in exchange energy accompanying such spin-pairing. In the higher oxidation state, the CFSE is considerably increased, favouring the equilibrium towards right.

28.6.9 Lower oxidation states

Manganese(I) occurs in the $[Mn(CN)_6]^{5-}$ ion. $Na_5[Mn(CN)_6]$ may be prepared by dissolving powdered manganese metal in air-free sodium cyanide solution. Reduction of $[Mn(CN)_6]^{4-}$ by Al/NaOH also gives the anion. The +I oxidation state is also present in $[Mn(CNR)_6]^+$, obtained in the reaction of MnI_2 with RNC. The carbonyl derivatives $Mn(CO)_5Cl$ and $CH_3Mn(CO)_5$ may also be included in this category (see below).

Manganese(0) is represented in the dimeric carbonyl $Mn_2(CO)_{10}$ — the simple monomer $Mn(CO)_5$ (7 + 10 = 17 electron species) is not formed. The dimer contains a metal-metal bond. The yellow crystalline carbonyl is slowly oxidized by air. It can be reduced by sodium amalgam in tetrahydrofuran to obtain $NaMn(CO)_5$, sodium pentacarbonylmanganate (−I). This can be used to prepare other compounds like.

$$NaMn(CO)_5 + RX \longrightarrow NaX + RMn(CO)_5$$

$$NaMn(CO)_5 + X_2 \longrightarrow Mn(CO)_5X + NaX$$

Thermal decomposition of $Mn(CO)_5X$ compounds at 100°C gives the halogen-bridged species $(CO)_4MnX_2Mn(CO)_4$.

Mn(−I) is also present in $[Mn(CO)_4PR_3]^-$ and the $Mn(phthalocyanine)^-$ anions. The anion $[Mn(phthalocyanine)]^{2-}$ is an example of Mn(−II). Mn(−III) is present in the nitrosylcarbonyl $Mn(NO)_3CO$.

28.6.10 Organometallic compounds

Simple σ-bonded alkyls and aryls of manganese are not stable in air. $Mn(CH_3)_2$ is obtained as a polymeric powder which catches fire in air. Alkyls containing π-acceptor groups are comparatively more stable, e.g. $CH_3Mn(CO)_5$ is stable to both air and water.

The cyclopentadienyl-manganese compound $Mn(C_5H_5)_2$ differs from other metallocenes in its ionic composition $Mn^{2+}(C_5H_5^-)_2$ rather than the covalent sandwich compounds of other transition metals. While other π-bonded cyclopentadienyls do not react with water, $Mn(C_5H_5)_2$ reacts with water to give MnO and cyclopentadiene. π-cyclopentadienyl complexes are also formed by manganese when other π-bonding ligands are present, for example $(\pi\text{-}C_5H_5)Mn(CO)_3$ (*cymantrene*) and $(\pi\text{-}C_6H_6)Mn(\pi\text{-}C_5H_5)$.

28.6.11 Detection and estimation

(i) Manganese compounds produce an amethyst coloured borax bead in oxidizing flame (Mn^{III} - borate) and colourless bead in the reducing flame (Mn^{II}-borate).

(ii) Manganese compounds are readily detected by the green coloured melt produced on alkaline fusion with oxidizing agents. The green solution of manganate(VI) turns pink through disproportionation on acidification.

(iii) Manganese compounds are also detected by the purple colour of $HMnO_4$ produced on oxidation with red lead or sodium bismuthate in dilute nitric acid medium.

(iv) Manganese may be estimated by the Volhard's method described before. It is most conveniently determined volumetrically by oxidation to purple MnO_4^- by ammonium persulphate ($AgNO_3$ as catalyst) or potassium periodate (dilute H_2SO_4).

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O = 2HMnO_4 + 10NH_4HSO_4 + 2H_2SO_4$$

$$2MnSO_4 + 5KIO_4 + 3H_2O = 2HMnO_4 + 5KIO_3 + 2H_2SO_4$$

These reactions may be utilized to determine the percent of manganese in steel.

(v) Gravimetrically, manganese may be estimated as $Mn(NH_4)PO_4 \cdot H_2O$; the precipitate may be dried at 100-150°C and weighed as such or ignited to $Mn_2P_2O_7$.

28.7 IRON

Fe : [Ar] $3d^64s^2$ **Atomic number** : 26 **Atomic weight** : 55.847

M.P. : 1535°C **B.P.** : 2750°C **Density** : 7.87 g cm^{-3}

Some ancient peoples treasured iron more than gold. Only the wealthiest noblity could afford wearing iron decorations which were often set in gold. In ancient Rome even wedding rings were made of iron.

28.7.1 Introduction

History : Iron joined the race of human civilization much later than copper, gold and silver and that too, in the role of a rare metal. Probably the first samples of iron used by our forefathers around 4000 B.C. were of meteoritic origin and hence very rare and expensive. The knowledge of extracting iron from its ore developed in different countries at long intervals of time. In Egypt and Mesopotamia, the process was discovered about 2000 B.C.; in the Trans-caucasus, Asia Minor and ancient Greece at the end of the second millenium (millenium = 1000 year) B.C. India developed a sophisticated method of preparing high grade iron in the middle of the second millenium B.C. while China did so in the middle of the first millenium B.C. Early methods of heating iron ores with coal on windy sites yielded only low grade spongy metal which had to be shaped by prolonged hammering. The technique of making good quality iron was developed using furnaces open at the top and lined with a refractory material inside. Excavations of ancient towns in Syria indicate that iron of a rather good quality was produced in this way. It is believed that the *Hittites* in Asia Minor and Syria enjoyed a monopoly expertise in iron smelting in the third millenium B.C. The knowledge dispersed with the fall of their empire around 1200 B.C.

In modern times, iron smelting furnaces became widespread by the end of the 15th century. Improvisations to manufacture steel were reached in the nineteenth century. The name "iron" comes from old English while the symbol Fe comes from Latin *ferrum*, iron.

Occurrence : Iron is the second most abundant metal (after Al) and fourth most abundant element (after O, Si and Al) in the earth's crust, occurring to an extent of more than 5% i.e., 50,000 ppm. Native iron is scarce, except in meteorites and a deposit in Greenland. The core of the earth is believed to contain iron (and nickel) at high temperature and pressure. About 0.5% of lunar soil consists of metallic iron; which means a huge quantity (~ 10^{12} tonnes) of total iron over the entire moon's surface (up to an average depth of 10 m).

Iron occurs mostly as oxide : *red haematite* Fe_2O_3; *brown haematite* $2Fe_2O_3.3H_2O$ also called *limonite*); and *magnetite* Fe_3O_4. Other minerals include spathic iron ore or *siderite*, $FeCO_3$; and iron pyrites ("fool's gold"), FeS_2. The last one cannot be economically processed to obtain iron and hence is not considered an ore of iron. Iron ores are found in many countries—more than 1000 million tonnes are produced per year all over the world of which the country-wise contributions are approximately : China 22%, Russian countries 18%, Brazil 16%, Australia 12%, USA and India 6% each. The production of crude steel in 1996 over the world stood around 700 million tonnes.

[Sec. 28.7.2 *Iron—element*]

Indian deposits

India has rich deposits of high grade iron ore, chiefly haematite, which contains 60 per cent iron on an average. The total reserve of better grade iron ore is estimated to exceed 21,000 million tonnes, wth Bihar, M.P. and Orissa topping the list. In *Bihar* alone, the estimated reserve of iron-ore in Singhbhum and adjoining area of Bonai and Keonjhar, occurring at the surface and capable of open-cast mining, is computed at over 8000 million tonnes (60-69% iron content). In *Madhya Pradesh*, the hillocks in the Dalhi-Rajhara range (Durg district) and Bailadila range (Bastar district) contain high grade ore (65% iron) at an estimated reserve of about 4000 million tonnes. In *Orissa*, the most important deposits occur at Sundargarh, Mayurbhanj, Cuttack, Sambalpur and Koraput districts and in Keonjhar area, the total estimated reserve being more than 2500 million tonnes. *Goa* has an estimated iron ore deposit of nearly 400 million tonnes, richest in north Goa. In *Karnataka*, high-grade ore deposits occur at Bababudan (Chikmagalur district); Sandur and Hospet (Bellary) and on the western coast near Mangalaore. The total reserve may be around 200 million tonnes. Ores with slightly lower iron content (35-40%) occur in Tamil Nadu, Andhra and some other places. In *West Bengal*, some local concentrations of haematite are found in the Bankura, Jalpaiguri and Darjeeling districts but these are of lower grade. High quality ores have been reported from the Buxa-Dooars area but this has not yet been explored owing to transport problems.

28.7.2 The element

Extraction

Iron is extracted through carbon reduction in the blast furnace. The ore is sometimes washed and calcined to increase the iron content and partly remove earthy matter.

A charge of ore, coke and limestone (usually in the ratio 8 : 4 : 1 parst by weight) enters the top of the furnace while a blast of preheated air at about 900°C is blown through holes near the bottom. The burning of coke produces immense heat and the temperature approaches ~2000°C near the base and falls gradually towards the top where it is around 400°C. As we have noted earlier (see Ellingham diagram), burning of carbon above 700°C produces carbon monoxide which rises upward and reduces the iron oxide. Some reduction is also done by carbon. The limestone decomposes around 900°C to give CaO which combines with silica to form slag ($CaSiO_3$). Some representative reactions are :

Reduction :	$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$	400°C
	$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$	400°C
	$Fe_3O_4 + CO \longrightarrow 2FeO + CO_2$	
	$FeO + CO \longrightarrow Fe + CO_2$	800°-1000°C
	$FeO + C \longrightarrow Fe + CO$	
Slag formation :	$CaCO_3 \longrightarrow CaO + CO_2$	900°C
	$CaO + SiO_2 \longrightarrow CaSiO_3$	1800°C

Carbon formed by decomposition of CO at lower temperature (500-600°C) reduces FeO and also MnO and SiO_2 at high temperatures (1800°C) :

$$MnO + C \longrightarrow Mn + CO; \quad SiO_2 + 2C \longrightarrow Si + 2CO.$$

The manganese and silicon as well as some carbon dissolve in the finished iron. Any phosphatic ore present is also reduced to phosphorus which also dissolves in the iron :

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

Some sulphur is also derived from coke and sulphate ores :

$$FeS + CaO = FeO + CaS$$

The molten slag and crude iron collects at the base of the blast furnace where they form separate layers. The slag floats on the molten iron, preventing it from oxidation. These are drawn through separate holes and the molten iron is allowed to solidify in sand mould into ingots of "pig iron" or cast iron. Typical impurities present in cast iron are (per cent)

C	Si	P	S	Mn
2-4.5	0.7-3	0.05-2	0.05-1	0.2-2

These impurities make cast iron brittle.

The *slag* is usually a mixture of calcium and aluminium silicates which are put to various uses after analysis. They find use in the making of cement, as road paving material and insulation blocks.

Direct reduction of iron ore, including lower grade ones, is possible in *electric arc furnaces*. A very high temperature is attained by electric arcs established between carbon electrodes placed directly in the ore (plus some coke). Direct reduction occurs as

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

The evolved CO is put to other uses, thereby partly compensating the high cost of electrical energy. The method is suitable where electricity is cheaper in comparison to coal.

Wrought Iron

When most of the impurities present in pig iron are removed, the "pure" commercial iron is known as wrought iron. It contains 0.1-0.25% of carbon and less than 0.25% of other impurities like S, P, Mn and Si.

Wrought iron is usually prepared from cast iron by the *puddling* process. The cast iron is melted on the hearth of a reverberatory furnace lined with heamatite, some scrap iron is added and the whole melt is stirred (puddled) with a long pole. The impurities (C, Si, S, P etc) are oxidized by the iron oxide in scrap iron and also in the haematite lining. The carbon monoxide rises through the molten metal and burns on its surface. Other impurities form a slag with the lining. As the impurites are eliminated, the molten mass becomes thick (m.p. rises). The pasty mass is gathered into large lumps which are steam-hammered to squeeze the slag. The pure iron is then rolled into sheets or transferred into bars.

Wrought iron is comparatively soft and malleable. It is used in making cores of electromagnet, chains, wires etc. It does not harden when heated to redness and quenched (suddenly cooled). It is also more resistant to corrosion and oxidation. The iron pillar near Qutab Minar in Delhi is made of very pure wrought iron.

Wrought iron containing phosphorus is brittle at ordinary temperature; this is termed *cold-short*. When sulphur is present, the wrought iron becomes brittle at red heat when it is termed *red-short*.

Steel

Steel is essentially a refined alloy (of iron) with respect to the elements which accompany the crude iron from blast furnace, especially C, S and P. It is often alloyed with other metals to impart desired properties. Steel making thus consists essentially of refining of cast iron followed by addition of alloying elements.

All steel production processes consist of the same general principle :

(i) removal of carbon, sulphur and phosphorus from molten "pig iron" by oxidation (usually by O_2). Carbon and sulphur are oxidized to CO_2 and SO_2 which then escape as gases. Manganese, silicon and phosphorus also form oxides which combine with lime added to form slag :

$$MnO + SiO_2 \longrightarrow MnSiO_3; \; P_4O_{10} + 6CaO \longrightarrow 2Ca_3(PO_4)_2; \; SiO_2 + CaO \longrightarrow CaSiO_3.$$

Some sulphur is also eliminated through slag formation :

$$S + CaO \longrightarrow CaO + S.$$

(ii) separation of slag followed by addtion of requisite quantities of deoxidizer and other alloying elements. Reducing agents like petroleum coke together with ferro-silicon and ferromanganese are used as the deoxidizer—they reduce any FeO left.

A typical composition of the impurities in mild steel may be compared with that of pig iron (in %) :

	C	Si	S	P	Mn
Pig-iron	3-5	1-2	0.05-0.1	0.05-1.5	0.5-1.0
Mild steel	0.15	0.03	0.05	0.05	0.5

The nature of steel depends critically on the percentage of carbon content (along with other components) :

mild steel : 0.15-0.3; medium steel : 0.3-0.6; high-carbon steel : 0.6-0.8; tool steel : 0.8-1.4.

The techniques of steel production have undergone vast changes in the last fifty years. At present, there are three main steel-making processes : (i) Basic oxygen, (ii) Open hearth and (iii) Electric arc. The basic oxygen process is a development of the old Bessemer process.

(i) *The basic oxygen process*

The process uses pure oxygen (99%) as the oxidizer which is blown onto the surface of molten pig iron at great speed through water-cooled pipes. The charge of hot molten pig iron and lime is taken in a converter lined with dolomite and magnesium oxide. The oxygen penetrates into the molten charge creating large turbulence and oxidizes the impurities. The exothermic reaction keeps the contents molten though the melting point rises as impurites are gradually eliminated. The slag is separated by tilting the converter and a rapid analytical check is performed to bring the metal to its desired composition and necessary additions of C, Mn and other alloying metals are made.

In the *Kaldo process*, the converter is rotated to ensure thorough mixing.

Notes :

(i) The basic oxygen process is much faster than the open hearth process or the older Bessemer process.

(ii) The use of air in the Bessemer process (blown through the bottom) introduces nitrogen into the molten metal. In concentrations above 0.01%, N_2 makes steel brittle. Also. formation of surface nitride renders welding of the metal difficult.

(iii) If the oxygen was blown through the bottom of the converter (as air was blown in the Bessemer process), the bottom would get excessively heated and would melt.

(ii) *The open hearth process*

In this process, conversion to steel is carried out on the hearth of a furnace heated by burning gas or oil in air or oxygen. The hearth is lined with dolomite and magnesite on which the charge of cast iron and scrap iron together with 5-6% lime is melted. Oxygen is injected into the furnace through water-cooled pipes to oxidize the impurities.

The process requires much longer time than the Basic Oxygen Process (10 hrs. vs. 40 mins) and is getting gradually replaced by the latter and by the electrothermal process.

(iii) *The electric arc process*

High grade steels are often prepared in electric arc furnaces which may be either direct arc or indirect arc type. *Direct arc electric furnaces* are usually fitted with three electrodes which penetrate into the furnace crucible and strike short circuited arcs between their lower extremeties and the molten charge. The crucibles are made of sheet steel and lined internally with dolomite or magnesia. In *indirect arc furnaces*, the arc is struck between two large carbon electrodes. Radiation from the arc heats the charge. Arc furnaces are also used in direct reduction of oxide minerals. In steel making, the charge usually consists of solid scrap iron, pig iron, coke and anthracites (if enough cast iron is not present). On the other hand, if decarburization etc. is necessary, pure oxygen is used.

Melting and alloying is also conveniently carried out in *induction furnaces* which contain a vertical basin around which an induction coil is wound. The charge in these furnaces forms the short-circuited secondary winding of a transformer - it converts into heat the electrical energy which would be withdrawn in a normal transformer.

Arc furnaces are available according to capacity required. They provide a reasonably clean atmosphere.

The iron-carbon system has been discussed under properties of the element.

Chemically pure iron may be prepared by reducing ferric oxide with hydrogen at 1000°C. It is also obtained by thermal decomposition of iron pentacarbonyl :

$$Fe(CO)_5 = Fe + 5CO.$$

Properties

Some physical properties of iron have been mentioned in Table 28.2.

Pure iron is a silvery white lustrous metal, malleable and ductile. It does not harden on quenching. It is the most magnetic substance among all elements.

Iron has four allotropic forms :

$$\begin{array}{llllllll} \alpha\text{-Fe} & \xrightarrow{768°C} & \beta\text{-Fe} & \xrightarrow{910°C} & \gamma\text{-Fe} & \xrightarrow{1394°C} & \delta\text{-Fe} \\ \text{bcc} & & \text{bcc} & & \text{fcc} & & \text{bcc} \\ \text{ferromagnetic} & & \text{paramagnetic} & & \text{paramagnetic} & & \text{paramagnetic} \end{array}$$

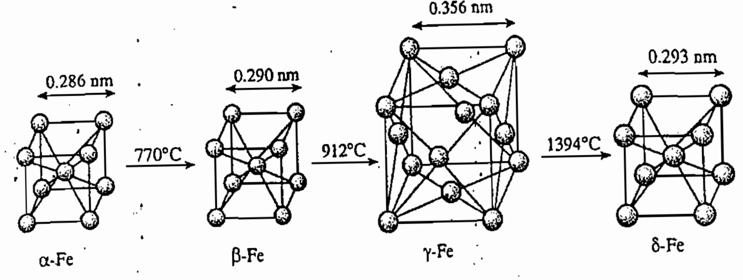


Fig. 28.38

The polymorphic transformation of iron.

Chemically, iron is a moderately active metal. The finely divided metal is pyrophoric in air at room temperature. The massive metal forms Fe_2O_3 and Fe_3O_4 in dry air above 150°C. In damp air, hydrous oxide (rust) is formed even at ordinary temperature. Steam reacts above 500°C liberating H_2 and forming Fe_3O_4 and FeO. When heated, especially in a finely divided state, iron reacts with almost all nonmetals to form solid solutions (C, Si, N, B, P, H); metal-like compounds (Fe_3C, Fe_3Si, Fe_3P, Fe_4N, Fe_2N); or binary compounds which may range from ionic to covalent in character (FeF_3, $FeCl_3$, FeS). The hard crystalline carbide Fe_3C(*cementite*) is mainly responsible for the variation in properties of steel with carbon content (see use).

In absence of oxygen, iron reacts with dilute mineral acids to give iron(II) solutions

$$Fe^{2+}(aq) + 2e = Fe; \quad E° = -0.44V$$

In presence of air (or warm dilute HNO_3), some of the iron is oxidized to Fe(III).

Dilute alkali solutions and air-free water hardly attacks iron but hot concentrated or fused alkali metal hydroxides may attack it. Potassium ferrate(VI), K_2FeO_4 is formed slowly by heating iron filings with potassium hydroxide with exposure to air. It is formed rapidly when iron is heated with nitre :

$$Fe + 2KNO_3 = K_2FeO_4 + N_2 + O_2$$

Anodic oxidation of cast iron in warm NaOH(or KOH) also produces the $FeO_4^{=}$ ion.

Concentrated HNO_3 and H_2SO_4 make iron "*passive*" (Schonpein, 1836). Such passivated iron does not dissolve in dilute nitric acid nor does it reduce Ag(I) or Cu(II) in solution-it thus lacks the usual "activity" of the metal. Passivity is also known for chromium and aluminium.

Passivity may be effected by other methods also, for example immersing the metal in chromic acid, chromates or solutions of other strong oxidizing agents or by anodic oxidation. Passivity may be eliminated by scratching the surface of the metal, hammering etc. or by action of dilute solutions of non-oxidizing acids e.g. HCl.

There has been many suggestions about the origin of passivity. The oxide film theory, first forwarded by Michael Faraday (1836), and confirmed by Evans (1927), ascribes passivity to the formation of a thin protective oxide film on the metal surface by the action of oxidizing agents. The oxide film is very thin and adhering, and does not affect the surface shine of metals. The metal inside the oxide coat may be corroded by iodine and the thin film isolated from the metal. It is also likely that a unimolecular layer of oxygen ions is strongly absorbed on the metal surface (without displacing the metal from their lattice as in an oxide) and the metal atoms lose their surface electrons and hence lack the tendency to enter instantaneous chemical reaction.

However, the reactivity of iron, rather than its passivity, has been the greatest concern about its use as a major structural material. This is separately discussed under the head "corrosion".

Uses

Iron is principally used as a structural material. Mild steel is most widely used. Machine parts, tools and utensils are made of various kinds of alloy steels (see below).

Iron is also used as a catalyst in the Haber-Bosch process for manufacture of ammonia, in small scale production of hydrogen and as a reducing agent.

Alloy steels : Mechanical and other properties of steel are greatly modified by alloying with different transition metals and silicon. Some of these alloy steels are :

Silicon steel	3.5% Si and very little carbon; used in making electromagnets and transformers.
Stainless steel	12-15% Cr; resists corrosion and action of acids. Stainless steel utensils and other articles are made from it.
Manganese steel	12-13% Mn; extremely hard and resistant to wear. Making of grinding machinery, safe, rock drill.
Cobalt steel	up to 35% cobalt; highly magnetic. Making permanent magnets.
Nickel steel	2-4% Ni; high tensile strength—making cablos, propeller shafts, gears etc.
Invar	up to 36% Ni : low coefficient of thermal expansion—used in scientific instruments.
Chrome-nickel steel	1-4% Ni; 0.5-2% Cr. High tensile strength, greater corrosion resistance—motor car and bicycle parts.
Platinite	46% Ni; coefficient of thermal expansion same as that of glass. Used in glassmetal seals, electric bulbs etc.
Chrome-vanadium steel	1-10% Cr, 0.14-0.55% V. High tensile strength, resistant to stress and torsion. Making of automobile axles and springs.
Tungsten steel	10-20% W, 3-8% Cr. Very hard, corrosion-resistant and retains temper at high temperature. Used in making high-speed cutting tools.
Molybdenum steel	6-7% Mo; this also retains temper at high temperature and is used in making high-speed cutting tools.
Misch-metal	70% Ce and traces of other rare earth metals. Used to produce spark in gas and cigarette lighters.

The iron-carbon (and also iron-silicon) phase equilibria (Fig. 28.39) play a vital role in the technical metallurgy of iron. The varying properties of steel with its carbon-content are mainly associated with the formation and distribution of the hard carbide Fe_3C, called *cementite.* When steel containing about 1% carbon is cooled slowly from 720°, a soft malleable product is obtained (*pearlite*) which has layers of α-iron interleaved with cementite. If the same mixture is cooled rapidly, the layers cannot get separated, producing the hard and brittle form called *martensite.* The ultimate constituents in an iron-carbon alloy are the soft and malleable α-iron and the hard and brittle cementite.

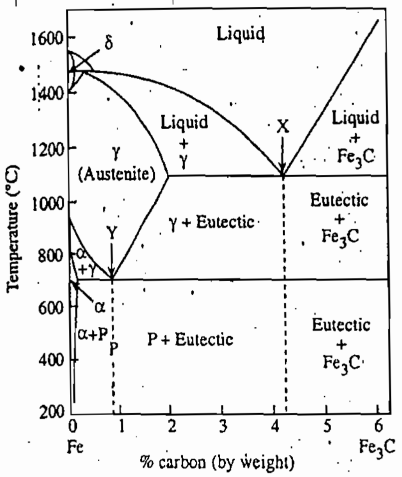


Fig. 28.39

Part of iron-carbon phase diagram.

Austenite is a solid solution of carbon in γ-iron.

Steel containing 0.87% C consists of pearlite(P) alone. Less than 0.87% C gives *hyopeutectoid steels* containing a mixture of α-iron and pearlite. *Hypereutectoid steels* containing carbon between 0.87% and 1.80% consist mainly of cemetite and pearlite. Steels with 1.8 to 4.3 per cent carbon are *hypoeutectic alloys* which ultimately consist of a mixture of pearlite and cementite.

Corrosion

Corrosion involves chemical reaction of metals with the environment leading to permanent loss of the metal (that is, the metal is unrecoverable). Rusting, the commonest type of corrosion of iron, may be said to be the most important reaction of iron from an economic point of view. Thousands of crores of rupees are spent annually all over the world (the figure for India alone exceeds Rs. 2000 crores) to protect steel objects against corrosion and to replace corroded articles. Corrosion is, in one sense, the reverse process of extracton of a metal from its ore — the metal passing from its elemental state to several combined forms to be distributed in nature. There are four main types of corrosion : (i) Atmospheric corrosion (ii) Immersed corrosion (iii) Underground corrosion and (iv) Chemical corrosion.

(i) **Atmospheric corrosion** : As the term implies, atmospheric corrosion involves corrosion of metal surfaces exposed to the atmosphere; though the principal attacking agent is oxygen, other gases like CO_2 and SO_2 as well as dust particles and water vapour also contribute significantly to atmospheric corrosion.

Rusting of iron is the most important type of atmospheric corrosion. It is well known that a freshly cleaned surface of iron soon gets covered with a brown layer of hydrated iron(III) oxide, commonly known as rust. Both oxygen and water are necessary for rust formation; but other factors influence the rate of rusting considerably. These include impurities or stress on the iron surface, availability of dissolved oxygen and electrolytes in contact with the iron surface.

The corrosion of iron by rusting may be summarized as formation and breakdown of an oxide film (hydrated) on the heterogeneous iron-air interface through electrochemical action by the intermediary of water :

(i) The oxygen is reduced at the cathodic region :

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- (aq)$$

(ii) Iron is oxidized in the anodic region :

$$Fe \longrightarrow Fe^{2+} (aq) + 2e$$

This forms iron(II) hydroxide with the hydroxyl ion

$$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$$

The electrons are taken up by hydrogen ions, present in appreciable concentration when the water/air is polluted by SO_2, NO_2 etc. :

$$2H^+(aq) + 2e \longrightarrow H_2(g)$$

(ii) The $Fe(OH)_2$ is now oxidized by dissolved oxygen to hydrated Fe_2O_3 or rust :

$$2Fe(OH)_2(s) + O_2 \longrightarrow Fe_2O_3.xH_2O + (H_2O)$$

The process is schemtically shown in Fig. 28.40. When a drop of water covers an iron surface, cathodic regions will develop near the edges. One apparent reason for this is the excess of oxygen dissolved from the air in this region. In the anodic region near the center of the drop where there is less oxygen, the Fe(II) ions have enough time to move away from the surface before they form $Fe(OH)_2$. This is ultimately converted to rust by oxygen, but this is not formed right on the surface. As a result, the iron surface never gets coated with the rust and the process of corrosion continues below the rusted surface. Air containing SO_2, CO_2 etc. gases and suspended particles containing, say, ammonium sulphate in towns and sodium chloride in sea shores, adds electrolyte to the system and enhances corrosion.

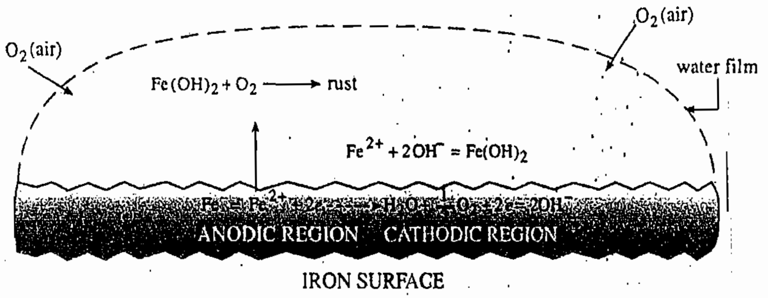


Fig. 28.40

Rusting of iron (schematic).

The moisture content of air is an important factor determining the extent of atmospheric corrosion. The optimum humidity is about 70 percent relative humidity below which atmospheric corrosion is negligible. This is often called the critical humidity. Iron shows a primary critical humidity around 50-60 per cent (relative humidity) when the primary oxide film formed on the metal surface gets ruptured and attack begins on the metal surface. Fine layers of rust now begin to deposit on the iron surface. As the humidity exceeds about 80 per cent (secondary critical humidity), the rate of corrosion becomes rapid with the formation of common red rust.

Certain types of atmospheric corrosion proceed even at low relative humidity, the nature of the primary film on the metal surface being different. Thus copper and silver tarnishes in air containing traces of hydrogen sulphide; copper deposits basic copper sulphate in air containing SO_2. The "fogging" of polished nickel surfaces is ascribed to the formation of a thin film of sulphuric acid on the surface.

We have just seen that the process of corrosion proceeds in a continuous manner since the product of corrosions (here the oxide layer) fails to protect the metal surface. When oxygen has ready access to the site of corrosion so that the Fe^{2+} ions are oxidized before they can leave the surface, the metal will get a protective coating of Fe(III) oxide. This is why iron does not rust in an atmosphere of oxygen at high pressure (>25 atm.).

(ii) **Immersed corrosion :** This includes corrosion in water pipes, heating systems, boilers, river-jetties and similar structures. The situation is complicated by the involvement of metal-gas-liquid interfaces where several factors contribute to the corrosion—e.g., pH of the solution, presence of electrolytes and dissolved oxygen, the rate at which oxygen can diffuse through the liquid phase, the possibility of formation of any local galvanic cell, the overpotential of the metal and so on. The nature of the corrosion product also partly determines the rate of such corrosion. The corrosion product of immersed iron and steel consists of about 30-35% iron(II) hydroxide because oxidation is incomplete due to lack of oxygen. In highly concentrated solutions of sodium etc. chlorides, low solubility of oxygen actually retards the rate of corrosion. The overall mechanism of corrosion is again electrochemical, similar to that in atmospheric corrosion. Consequently corrosion is enhanced when iron is in contact with a less electropositive metal; the iron acts as the anode and corrodes rapidly. When copper water pipes are joined to galvanized iron tanks, the iron corrodes rapidly.

(iii) **Underground corrosion :** This type of corrosion is mainly associated with underground pipelines and structures and is similar to immersed corrosion but the nature of the soil, stresses in the structure or the pipeline, contact with less basic metals etc. are also involved in such corrosion.

Underground pipes may corrode severely by the nearby presence of rails of electric trains and trams. When the intermediate ground is wet, a part of the current may leave the rails and travel some distance along the pipe. The point where the current leaves the pipe to return to the rails develops severe corrosion.

(iv) **Chemical corrosion :** Such corrosion occurs specifically by the action of chemicals like acids, acid vapours, bases, salts and their hydrolysis products etc. which are ambient in and around any chemical industry.

Differential aeration plays a great role in enhancing corrosion of iron. If a situation prevails to restrict the access of atmospheric oxygen to some part of an iron object than the remainder, the least aerated zone will become anodic to the rest and develop corrosion by the same electrolytic mechanism outlined in atmospheric corrosion.

A minute crack on an iron surface will have more oxygen near the outer surface and the interior portion (being anodic) will corrode in a cumulative manner. Underground pipelines may undergo such corrosion — the portion immersed in dry soil will have an easier access to oxygen than the part immersed in moist soil. Similarly, a leaking oil pipe will have restricted supply of oxygen near the leak owing to the oil-film on its surface and undergo rapid corrosion.

Several methods are used to prevent corrosion :

(i) Paints are largely used to minimise corrosion. Red lead or zinc chromate primers are often used for better protection against corrosion. Engine parts and other machinery and tools are protected from corrosion by oil or grease. Another effective treatment is to treat the iron surface with phosphoric acid or acid solutions of $Mn(H_2PO_4)_2$ or $Zn(H_2PO_4)_2$.

(ii) Removal of mechanical strains in the body of a metal by annealing or heat treatment or even by simple polishing helps fight corrosion. Alloying with a suitable metal is also very helpful in preventing corrosion — stainless steel is an alloy of iron with chromium. An impervious oxide film on the surface of the metal is supposed to prevent corrosion. Corrosion of magnesium-base alloys by spray of sea-water is resisted by selenium treatment : the articles are dipped in a bath of selenious acid (or sodium selenite + acid) when a thin layer of magnesium selnide coated with elemental selenium is formed on the surface.

(iii) Application of a sacrificial metal is also adopted largely to prevent corrosion. Galvanizing, the process of protecting iron with a thin layer of zinc is very popular, though galvanized iron cannot be used for canning food-stuffs (zinc is poisonous). The more costly tin-plating is used in this latter case. However, a galvanized article lasts longer since any scratch on its surface forms a local cell with the more basic metal zinc as anode and the less basic iron as cathode. Hence it is the zinc(anode)-coating which corrodes faster. A tin-plated vessel, under similar conditions, develops a local galvanic cell with the less basic tin as cathode — the iron corrodes faster as it forms the anode.

Cathodic protection is extensively used in underground pipelines (made of steel) using sacrificial anodes made of zinc or manganese alloys placed at regular intervals along the pipe line. These form a galvanic cell with the steel pipe which becomes the cathode. The anode undergoes the corrosion and is replaced from time to time.

General chemical features

The oxidation-state-free energy diagram for iron is shown in Fig. 28.41. It appears that the +II state is most stable while the +III state is only slightly oxidizing. The states lie closer in energy in comparison to II and III oxidation states of other transition metals. Higher oxidation states of iron are not common. In fact, from iron onwards, the transition elements cease to use all the valence shell electrons in bonding. The group oxidation state VIII is not found, the highest oxidation state being VI. This again, is found not in combination with fluorine but with oxygen.

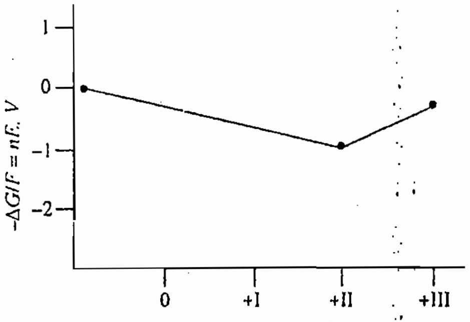


Fig. 28.41 **Oxidation state-free energy diagram for iron.**

$E°$ for states higher than + III are not known with certainty.

28.7.3 Higher oxidation states (Fe^{VI}, $3d^2$; Fe^{V}, $3d^3$; Fe^{IV} $3d^4$)

A red-purple solution containing Fe(VI) as FeO_4^{2-} ions is obtained by oxidation of hydrated iron(III) oxide by hypochlorite in concentrated alkali

$$2Fe(OH)_3 + 3ClO^- + 4OH^- \longrightarrow 2FeO_4^{2-} + 3Cl^- + 5H_2O$$

The FeO_4^{2-} (ferrate) ion is stable only in a strongly alkaline medium. In neutral or acid solution, it rapidly decomposes to Fe(III) :

$$2FeO_4^{2-} + 10H_3O^+ \longrightarrow 2Fe^{3+} + 15H_2O + \tfrac{3}{2}O_2 \quad E^0 \simeq 2.0 \text{ V at } [H_3O^+] = 1$$

Ferrates are stronger oxidizing agents than permanganates; ammonia is oxidized to nitrogen at room temperature, chromium(III) to chromate.

The discrete tetrahedral FeO_4^{2-} ion has been characterized in Na_2FeO_4 and K_2FeO_4. K_2FeO_4 is isomorphous with K_2SO_4, $KMnO_4$ and K_2CrO_4. As expected for a magnetically dilute d^2 ion, ferrates show room - temperature magnetic moments around 2.8-3.1 B.M.

Iron(V) is reported in potassium ferrate(V), K_3FeO_4; this may be prepared by thermal decomposition of potassium ferrate(VI), K_2FeO_4, at 700°C.

Iron(IV) is present in ferrate(IV) which is known in three different formula types : FeO_3^{2-}, FeO_4^{4-} and FeO_5^{6-}. FeO_3^{2-} is present in perovskite $MFeO_3$, (M = Ca, Sr) under an atmosphere of oxygen at high pressure. It disproportionates into Fe(V) and Fe(III).

Strontium and barium salts of FeO_4^{4-} ion are known. These may be prepared by heating iron(III) hydroxide with the alkaline earth oxide (or hydroxide) in oxygen around 700-800°C.

$$Fe(OH)_3 + 4Sr(OH)_2 + \tfrac{1}{2}O_2 \longrightarrow 2Sr_2FeO_4 + 7H_2O$$

The sodium salt, prepared in the same manner, disproportionates immediately :

$$3Na_4FeO_4 + 8H_2O \longrightarrow Na_2FeO_4 + 2Fe(OH)_3 + 10NaOH$$

However, evidences for the discrete FeO_4^{4-} ion are lacking and these compounds are better regarded as mixed oxides.

There are some examples of complexes containing Fe(IV), e.g., $[Fe(diars)_2X_2]^{2+}$ (X = Cl, Br), obtained by oxidation of the corresponding Fe(III) complex with concentrated nitric acid, and isolated as salts of large anions like $FeCl_4^-$ or ReO_4^-. Magnetic moments of these compounds indicate a low-spin t_{2g}^4 configuration. Mössbauer studies also indicate a tetragonal (D_{4h}) structure with a low-spin ground state. $[Fe(dipy)_3]^{4+}$ is octahedral with two unpaired electrons.

28.7.4 Compounds of iron(III), d^5

This may be called the main oxidation state of iron represented by simple compounds like oxides, halides (except iodide) and other salts, together with large number of complex compounds.

Oxides and hydroxides

Red-brown iron(III) oxide occurs naturally as haematite. This is actually α-Fe_2O_3 which may be obtained by heating the hydrated oxide (iron(III) solution + alkali) at 200°C. The oxide ions form a hexagonal close-packed arrangement with the octahedral interstices occupied by Fe(III). This is used in red pigments and as a polishing agent (*rouge*).

Fe_2O_3 is insoluble in water but dissolves in acids to form salts of iron(III). However, the ignited oxide is only sparingly soluble. It is a basic oxide, but forms sodium ferrite when fused with sodium carbonate :

$$Fe_2O_3 + Na_2CO_3 = 2NaFeO_2 + CO_2$$

γ-Fe_2O_3 is obtained by careful oxidation of Fe_3O_4 or heating γ-FeO(OH) (lepidocrocite). It has a cubic closepacked environment of oxide ions in which Fe(III) ions are distributed in both octahedral and tetrahedral interstices and is ferromagnetic. There is another rare variety, β-Fe_2O_3.

Fe_3O_4 is a mixed oxide of iron(II) and iron(III), occurring naturally as magnetite. It may be prepared by reacting air or steam with red hot iron or by oxidation of iron(II) with alkaline KNO_3 in presence of phosphite. This is converted to Fe_2O_3 by prolonged heating in air/O_2. The oxide, has an inverse spinel structure and is strongly ferromagnetic. Its electrical conductivity is about 10^6 times that of Fe_2O_3 and may be associated with rapid oscillation of the valence electrons among the iron sites in the lattice.

Ferric hydroxide, $Fe(OH)_3$ is of doubtful existence — one claim for its preparation is cobalt-catalysed oxidation of $FeSO_4$ with H_2O_2 in acid solutions. The brown precipitates obtained by alkali from iron(III) solutions are actually hydrous oxides $FeO(OH)$ having different chain structures involving FeO_6 octahedra. They are designated by α, β, γ etc. types. The hydrous oxides are soluble in acids and also in strong bases. $Ba_3[Fe(OH)_6]_2$ can be crystallized by boiling Fe(III) aqueous solutions with $Ba(OH)_2$ following by cooling.

The hydrous oxide is used in the purification of coal gas.

Halides

FeF_3, $FeCl_3$ and $FeBr_3$ are known in the solid state. FeI_3 cannot be prepared since iron (III) oxidizes iodide — the iodine-iron reaction produces FeI_2.

FeF_3 is formed as a white (very pale green) solid by the reaction of fluorine with iron or iron(III) oxide with HF; it is sparingly soluble in water. It consists of FeF_6 octahedral units in a lattice of the ReO_3 type which sublimes at 1000°C and is chemically rather inactive. It forms complex salts with alkali or ammonium fluorides, mainly of the type $M_2[FeF_5]$, $M_3[FeF_6]$ and $M[FeF_4]$. The affinity of Fe(III) for F^- is high :

$$Fe^{3+} + F^- \rightleftharpoons FeF^{2+} \qquad K_1 \simeq 10^5$$

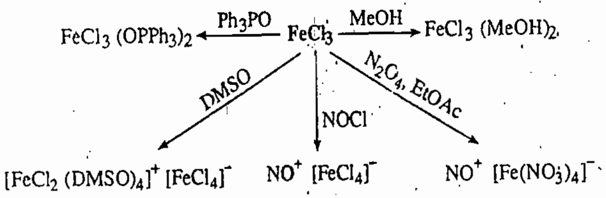
$$FeF^{2+} + F^- \rightleftharpoons FeF_2^+ \qquad K_2 \simeq 10^5$$

$$FeF_2^+ + F^- \rightleftharpoons FeF_3 \qquad K_3 \simeq 10^3$$

$FeCl_3$ and **$FeBr_3$** may be formed anhydrous by direct reaction. Aqueous solutions are made by dissolving the hydrated oxide in HCl/HBr. The compounds are coloured due to charge-transfer transitions : the anhydrous halides are brown-black. Crystals of $FeCl_3$ possess a green iridescence and consists of a layer structure in which Fe(III) is octahedrally surrounded by chlorines. The crystals melt at 308°C and rapidly vaporize on further heating (b.p. 315°C). Vapour density at 400°C corresponds to the dimeric formula Fe_2Cl_6 with tetrahedral coordination around iron. Heating in vacuum above 500°C leads to decomposition into $FeCl_2$ and Cl_2.

Iron(III) chloride fumes in moist air undergoing rapid hydrolysis. It dissolves in water to produce an acidic solution due to hydrolysis; a yellow-brown "hexahydrate" can be crystallized from this solution which is actually *trans* - $[FeCl_2(H_2O)_4]Cl.\,2H_2O$.

$FeCl_3$ is also soluble in alcohol, ether and benzene. In many cases, adducts are formed, for example $FeCl_3(THF)_3$ but there may also be ionic species as shown below (DMSO and N_2O_4). Redox and substitution reactions are also known.



Ferric bromide is difficult to obtain pure as it decomposes into $FeBr_2$ and Br_2 slightly above 200°C, while its formation from iron and bromine takes place at 200°C. An aqueous solution of $FeBr_3$ also evolves bromine on boiling.

[Sec. 28.7.4 *Iron(III)—complexes*]

Several complex halides of iron(III) are also known which are mainly of the type $M_3^IFeX_6$, $M_2^IFeX_5(H_2O)$ and M^IFeX_4. The pale yellow $FeCl_6^{3-}$ ion can be isolated from solution using large cations like $Co(NH_3)_6^{3+}$. The $FeCl_4^-$ ion, also yellow, can be extracted from hydrochloric acid into ether (solvent extraction). The ion is roughly tetrahedral.

Aqueous solution chemistry

The pale violet hexa-aqua-ion, $[Fe(H_2O)_6]^{3+}$ is known in solution as well as in crystals like those of ferric alum. The ion undergoes further hydrolysis producing acids :

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+ \qquad pK_1 = 3.05$$

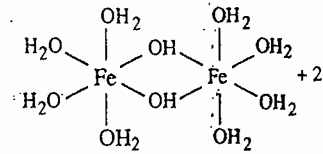
$$[Fe(H_2O)_5OH]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H_3O^+ \qquad pK_2 = 3.26$$

The hydroxo species are brown due to charge transfer absorption in uv having a tail into the visible region.

Above pH ≈ 2, the reactions proceed further to right, eventually precipitating the "hydroxide", which may be $Fe(H_2O)_3(OH)_3$ or $FeO(OH)$. *aq*. Addition of sodium carbonate or magnesium metal to an acidic solution of iron(III) chloride removes the H_3O^+ ion (with liberation of CO_2 or H_2 as the case may be) and ultimately the hydrous oxide is precipitated.

The hexa-aqua ion also forms hydroxo-bridged dinuclear species (*ol* bridges : the process is called *olation*) :

$2[Fe(H_2O)_6]^{3+} + 2H_2O \rightleftharpoons$



$+ 2H_3O^+ \quad (pK = 2.91)$

Further loss of proton followed by condensation may proceed, until large aggregates give rise to colloidal gels. Oxo-bridges (*oxolation*) are also involved in the condensation process.

The hexa-aqua ion may substitute its coordinated water molecules by other coordinating anions. Thus, addition of concentrated hydrochloric acid forms various chlorocomplexes from $[Fe(H_2O)_5Cl]^{2+}$ to $FeCl_4^-$. Several stable complex compounds of iron (III) can be prepared from the hexaaqua ion. These are discussed separately.

Complex compounds

Iron forms numerous complex compounds in this oxidation state of which the halo complexes have been mentioned earlier.

Fe(II) shows reluctance to form complexes with unidentate nitrogen donors like ammonia and amines. Addition of aqueous ammonia to aqueous Fe(III) precipitates the hydrous oxide and no simple ammine complex exists in water. $[Fe(NH_3)_6]X_3$ may be formed in anhydrous liquid ammonia but this is readily hydrolyzed by water. Chelating ligands like 2, 2′– dipyridyl and *o*-phenanthroline form water-stable low-spin complexes $[Fe(dipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ which are remarkably inert towards ligand substitution reactions. The complexes may be isolated in crystalline forms using large anions. The EDTA (H_4Y) forms a seven-coordinate complex $[FeY(H_2O)]^-$; the rubidium salt of the ion has a nearly pentagonal bipyramid environment of the donor atoms around Fe(III).

Iron(III) forms the three-coordinate **$Fe[N(SiMe_3)_2]_3$** with planar $FeNSi_2$ units involving extended π-bonding. $[Fe(N_3)_5]^{2-}$ **has a trigonal** bipyramid arrangement of donor N-atoms.

Iron(III) also produces many complexes **with oxygen donor** ligands like phosphate and oxalate ions, glycerol, sugars and β-diketones. **Very stable** anionic complexes are formed by oxo-anions. As we have seen in the estimation of **iron, aqueous** solutions of Fe(III) chloride, coloured yellow due to charge-transfer absorptions, **are rendered** colourless by the addition of phosphoric acid. In equimolar mixtures **containing $FeCl_3$** and H_3PO_4, the main cationic species appears to be $[Fe(HPO_4).aq]^+$ but the ions $[Fe(PO_4)_3]^{6-}$ and $[Fe(HPO_4)_3]^{3-}$ are present in solutions of iron(III) phosphate in phosphoric **acid**. The green tris-oxalatoferrate(III), $[Fe(C_2O_4)_3]^{3-}$ (preparation in section 26.2.3) **can be resolved** into the optical isomers which racemize in less than an hour at room **temperature. Stable** neutral complexes are formed by chelating ligands, for example, the red $Fe(acac)_3$ **which may be** prepared readily by adding the ligand to aqueous iron(III) chloride in the presence **of a base** like **sodium** acetate. The high-spin **complex** has a regular octahedral environment **of the oxygen** atoms around iron and is a non-electrolyte in water. A dodecahedral **complex (C.N.8)** of iron(III) is exemplified by the nitrate complex $[Fe(NO_3)_4]^-$.

The "basic" acetate of iron(III) has the same general formula as with other + III metal ions, $[Fe_3O(O_2CCH_3)_6(H_2O)_3]^+$ and contains O-centered trinuclear Fe(III) units with bridging acetate groups (see chromium (III), Fig. 28-X).

Iron(III) forms hexacyanoferrate(III) (the ferricyanide), $[Fe(CN)_6]^{3-}$, most commonly prepared as the potassium salt. Addition of alkali cyanide to a solution of iron(III) precipitates the hydrated oxide :

$$Fe^{3+} + 3CN^- + 3H_2O = Fe(OH)_3 + 3HCN$$

$K_3Fe(CN)_6$ is conveniently prepared by **oxidizing** $K_4Fe(CN)_6$ in solution by chlorine :

$$2K_4[Fe(CN)_6] + Cl_2 = 2K_3[Fe(CN)_6] + 2KCl$$

It may be separated from KCl by repeated **crystallization**. The dark red monoclinic crystals, isomorphous with $K_3[Cr(CN)_6]$ and $K_3[Mn(CN)_6]$, form yellow powder on crushing and a yellow aqueous solution. The solution is **a fairly strong** oxidizing agent :

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-} \quad E° = 0.36V$$

Some of its oxidizing reactions are

$$2[Fe(CN)_6]^{3-} + H_2O_2 + 2OH^- = 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$$

$$4[Fe(CN)_6]^{3-} + N_2H_4 + 4OH^- = 4[Fe(CN)_6]^{4-} + 4H_2O + N_2$$

$$3[Fe(CN)_6]^{3-} + Cr(OH)_3 + 5OH^- = 3[Fe(CN)_6]^{4-} + CrO_4^{=} + 4H_2O \text{ (hot)}$$

$$2[Fe(CN)_6]^{3-} + 2I^- = 2[Fe(CN)_6]^{4-} + I_2$$

$H_3[Fe(CN)_6]$ is formed in brown needles by **adding fuming** HCl to a cold saturated solution of $K_3Fe(CN)_6$.

A solution of $K_3Fe(CN)_6$ produces a **deep blue precipitate** with aqueous Fe(II) (*Turnbull's blue*) - the ultimate product is same as **Prussian blue** (see later) and is a mixed valence compound $Fe_4^{III}[Fe^{II}(CN)_6]_3.xH_2O$, the intense **colour** arising from charge transfer. The transfer of iron(III) from the coordination site **is associated** with greater CFSE and structural stabilization (see Prussian blue; also linkage **isomerism**).

The $Fe(CN)_6^{3-}$ ion is low-spin (μ_{eff} = 2.25 B.M. at room temperature) and relatively labile to substitution. The CN^- ion may be replaced by water and other ligands to give products like $[Fe(CN)_5H_2O]^{2-}$. Owing to this greater lability, the $[Fe(CN)_6]^{3-}$ ion is quite poisonous, a contrast to the iron(II) counterpart, the $[Fe(CN)_6]^{4-}$ ion.

The intense blood-red colour developed on adding potassium or ammonium thiocyanate solution to solutions of Fe(III).*aq* is due to the ion $[Fe(SCN)(H_2O)_5]^{2+}$. The $[Fe(SCN)_6]^{3-}$ ion is formed when hydrous iron(III) oxide is dissolved in aqueous thiocyanic acid in presence of an alkali metal cation. The intensity of the red colour may be used to detect and estimate iron colorimetrically. Fluorides and mercuric chloride discharge the red colour due to the formation of fluoro complex and weakly ionised mercury(II) thiocyanate respectively.

$$2[Fe(SCN)(H_2O)_5]^{2+} + HgCl_2 \rightleftharpoons 2[Fe(H_2O)_6]^{3+} + Hg(SCN)_2 + 2Cl^-$$

Sodium salt of dialkyldithiocarbamate react with iron(III) chloride in aqueous solution to give the complexes $Fe(S_2CNR_2)_3$ mentioned earlier for their magnetic properties (Ch. 27 : high-spin low-spin equilibria). Action of HX (X = halogen) on these complexes produce the black halocomplexes $FeX(S_2CNR_2)_2$ which are examples of square pyramid (5-coordinate) complexes of iron(III) (Fig. 28.42). Their magnetic moments (3.9-4.0 B.M.) correspond to three unpaired electrons.

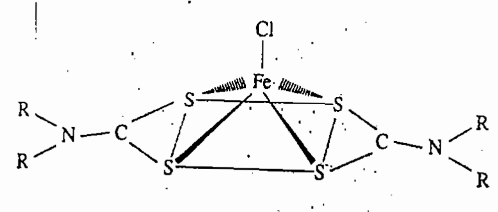


Fig. 28.42

Skeleton of chlorobis-(N,N-dialkyl-dithiocarbamato)-iron(III).

The iron atom is 63 pm above the basal plane of S-atoms.

Like manganese(II), complexes of iron(III) are also mostly high spin; only those with the very strong ligands are low spin e.g., $[Fe(CN)_6]^{3-}$, $[Fe(dipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$. Magnetic moments of the high-spin complexes are found close to the spin-only value (5.9 B.M.) for five unpaired electrons. We also do not expect any orbital contribution since the ground state (derived from free ion ^5S state) has no orbital angular momentum and there is no likelihood of any contribution from higher excited states. In contrast, the low-spin t_{2g}^5 configuration allows notable orbital contribution — around 2.3 B.M. at room temperature which falls to about 1.9 B.M. at liquid nitrogen temperature (77 K).

As a consequence of the higher charge on the metal in iron(III) compared to the isoelectronic manganese(II), both d^5, complexes of iron(III) are more susceptible to charge-transfer transitions. Thus the weak spin-forbidden *d-d* bands in the electronic spectrum of iron(III) complexes are often rendered obscure by charge-transfer bands in the near-uv region with prominent tails in the visible.

28.7.5 Compounds of iron(II), $3d^6$

Iron(II) is in general reducing in nature, though a large number of both simple and complex compounds are quite stable in this state. Hydrated salts of Fe(II) with all common anions are known — these are mostly pale green in colour and often isomorphous with similar compounds formed by other +II transition metal ions. The halides, nitrate, perchlorate and sulphate are soluble in water; the hydroxide, carbonate, phosphate and oxalate are only sparingly soluble. Iron(II) carbonate occurs naturally as siderite or spathic iron ore.

Oxide and hydroxide

Iron(II) oxide, FeO ("ferrous oxide") may be prepared by heating ferrous oxalate in absence of air :

$$FeC_2O_4 = FeO + CO + CO_2$$

This is also obtained by reducing iron(III) oxide with hydrogen at 400°C. The oxide (a pyrophoric black powder) is stable only at high temperature; it disproportionates into Fe_3O_4 and Fe when cooled slowly :

$$4FeO = Fe + Fe_3O_4$$

FeO is reduced to iron by hydrogen at 700°C. It has a sodium chloride structure with a tendency to be non-stoichiometric.

Iron(II) hydroxide, $Fe(OH)_2$ is formed as a white precipitate by adding sodium hydroxide solution to aqueous iron(II) in complete absence of air :

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4$$

It readily turns green and then brown on exposure to air when it gets oxidized :

$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3$$

Halides

All four halides of iron(II) are known.

Iron(II) fluoride, FeF_2 is formed as a white powder when iron powder (or $FeCl_2$) is heated in HF. Complexes with alkali metal and ammonium fluoride are formed, for example $K[FeF_3]$, $2H_2O$ (pink); $NH_4[FeF_3]$, $2H_2O$ (green); $K_2[FeF_4]$ (green).

Iron(II) chloride, $FeCl_2$ may be prepared anhydrous by heating iron in dry HCl gas or by reducing iron(III) chloride with hydrogen (heat). Aqueous solutions of iron(II) chloride may be obtained by dissolving iron in dilute hydrochloric acid. The pale green monoclinic crystals $FeCl_2$, $4H_2O$ that separate from such solutions above 12.3°C have discrete $[FeCl_2(H_2O)_4]$ units while $FeCl_2$, $6H_2O$, which crystallizes below 12.3°C, has *trans* - $[FeCl_2(H_2O)_4]$ units. The anhydrous chloride may be obtained from these hydrates by heating in dry HCl gas.

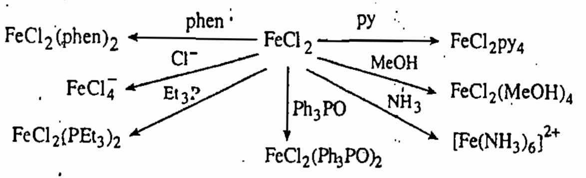
The anhydrous chloride does not melt until red heat and volatilizes at about 1000°C with vapours containing Fe_2Cl_4 and $FeCl_2$. Normal vapour density is observed between 1300-1500°C. The anhydrous chloride also dissolves in alcohol and ether.

$FeCl_2$ is oxidized on heating in air. Hydrogen is evolved on heating in steam :

$$12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3 \text{ (volatilizes)}$$

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$$

Iron(II) chloride, and other halides too, form complexes with nitrogen, phosphorous and arsenic donor ligands which are usually of three general types : FeX_2L_2 (mostly tetrahedral), FeX_2L_4 (tetragonal) and $[FeL_6]^{2+}$ (octahedral). Complexes are also formed with alkali metal halides of the type $M[FeCl_3]$, (M = K, Rb) and $M_2[FeCl_4]$, (M = K, Pb, Cs). Some of these complexes are shown in the next page.



$FeBr_2$ (pale yellow) may be prepared by burning iron (in *excess*) in bromine vapour. A solution of iron in aqueous HBr deposits pale green crystals of $FeBr_2$, $6H_2O$ when cooled sufficiently.

FeI_2 (grey) is formed by heating iron with iodine. Aqueous solutions yield FeI_2, $6H_2O$ at lower temperatures and FeI_2, $4H_2O$ (green) at ordinary temperature.

Miscellaneous compounds

FeS, iron(II) sulphide (ferrous sulphide) is formed by melting iron with sulphur. The grey compound occurs in nature as ***pyrrhottite*** and is also formed by the action of H_2S on aqueous iron(II) in ammoniacal medium. FeS dissolves in dilute hydrochloric and sulphuric acids, liberating H_2S. It does not dissolve in alkali but is slightly soluble in yellow ammonium sulphide.

The compound is antiferromagnetic and is non-stoichiometric with a deficiency of iron.

FeS_2, iron(II) disulphide, a brassy yellow solid with metallic lustre, occurs as *pyrites* and *marcasite*. Both forms are diamagnetic and contain spin-paired Fe(II) — the pyrites structure has a rock-salt arrangement of Fe^{2+} and S_2^{2-} ions. Marcasite changes into the more stable pyrite structure above 450°C. Pyrite is also stable in moist air while marcasite is slowly oxidized to iron(II) sulphate under similar conditions. Pyrite cannot be processed for iron but is a secondary source of sulphur

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

$FeCO_3$, iron(II) carbonate, is formed as a white precipitate when sodium carbonate is added to a solution of iron(II) in complete absence of air. On exposure to air, it is oxidized ultimately to hydrated iron(III) oxide, first turning green and then brown. $FeCO_3$ dissolves in water containing carbon dioxide, forming $Fe(HCO_3)_2$; this is readily oxidized in air to brown iron(III) hydrous oxide.

$$4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2$$

$FeCO_3$ occurs in nature as ***siderite*** or ***spathic iron ore***.

$FeSO_4$, iron(II) sulphate forms green monoclinic crystals of the hepatahydrate ($FeSO_4$, $7H_2O$; green vitriol); the white monohydrate and the anhydrous salt may be obtained by heating the heptahydrate. The double salt $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$ (*Mohr's salt*) is widely used in volumetric analysis because of its greater stability against aerial oxidation both in the solid state and in acidic solution. Double salts are also formed with alkali metal sulphates : M_2SO_4, $FeSO_4$, $6H_2O$.

$FeSO_4$ is prepared by dissolving iron in dilute H_2SO_4 (or as a bye-product in the Kipp's apparatus for H_2S) followed by evaporation. It is readily oxidized in air to iron(III) sulphate :

It decomposes on heating to leave iron(III) oxide, ***rouge*** :

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

An aqueous solution of $FeSO_4$ absorbs nitric oxide to form brown $[Fe(NO)(H_2O)_5]^{2+}$, often encountered in the famous "ring test" for nitrates.

Iron(II) sulphate is used as a mordant in dyeing, in the manufacture of rouge (red pigment), as a weed-killer in agriculture, as a reducing agent and in medicine.

$Fe_3(PO_4)_2$, iron(II) phosphate is formed as a white precipitate when disodium hydrogen phosphate is added to aqueous iron(II), but it soon turns blue in air owing to partial oxidation. Blue monoclinic crystals of $Fe_3(PO_4)_2 \cdot 8H_2O$ occur in nature as *vivianite*.

$Fe(NO_3)_2$, iron(II) nitrate, is conveniently prepared by double decomposition between $FeSO_4$ and $Ba(NO_3)_2$. Crystallization at low temperature gives green crystals of $Fe(NO_3)_2 \cdot 6H_2O$ which readily passes to Fe(III).

Aqueous chemistry

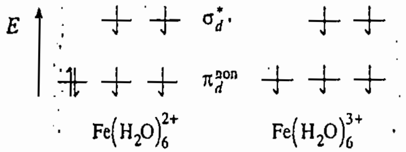
The pale green $Fe(H_2O)_6^{2+}$ ion is present in aqueous solutions of iron(II) and also in several crystalline salt hydrates like $FeSO_4 \cdot 7H_2O$ and Mohr's salt. The ion has a distorted octahedral environment of the coordinated water molecules, as exemplified by $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ with Fe-OH_2 distances 214, 188 and 185 pm.

The hexa-aqua ion is barely acidic (low charge on the metal), enabling precipitation of $FeCO_3$ and $Fe(OH)_2$, as noted earlier. $Fe(OH)_2$ is slightly soluble in concentrated alkali with the probable formation of $[Fe(OH)_4]^{2-}$ ion.

The hexaaqua ion, like most other complexes of iron(II), is paramagnetic which corresponds to the electron distribution

$$[\sigma]^{12}[\pi_d^{non}]^4[\sigma_{x^2-y^2}^*]^1[\sigma_{z^2}^*]^1$$

The ion is quite easily oxidized to iron(III) by the loss of one π_d^{non} electron :



The $Fe^{2+}(aq)$ ion is susceptible to oxidation by air according to the potentials

$$Fe^{3+}.aq + e \rightleftharpoons Fe^{2+}.aq ; \qquad E° = 0.77V$$

$$O_2 + 4H^+.aq + 4e \rightleftharpoons 2H_2O ; \qquad E° = 1.23 V$$

The oxidation is slow in acidic solution at room temperature in comparison to oxidation by other strong oxidizing agents like $Cr_2O_7^{=}$, MnO_4^- and H_2O_2. This forms the basis of volumetric estimation of iron. Oxidation of iron(II) becomes rapid in alkaline medium due to lower solubility of "$Fe(OH)_3$" (K_s $Fe(OH)_2$: ~ 10^{-14}; K_s $Fe(OH)_3$: ~ 10^{-36}) :

$$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2 + OH^- \qquad E° = -0.88 \text{ V}$$

This is why precipitates of $Fe(OH)_2$, initially white, rapidly turns brown on exposure to air.

The potential of the $Fe^{III} - Fe^{II}$ system is also markedly altered by the presence of other ligands, π-acceptor ligands stabilizing Fe(II). This is discussed under complexes.

Complex compounds

The Fe^{2+} ion forms a variety of complexes most of which are octahedral and high spin except with very strong ligands like 2, 2′-dipyridyl and 1, 10-phenanthroline.

[Sec. 28.7.5 *Iron(II)— Complexes*]

Though anhydrous iron(II) halides absorb ammonia gas to give the hexaammine, $[Fe(NH_3)_6]^{2+}$, this is readily decomposed in water :

$$[Fe(NH_3)_6]Cl_2 + 2H_2O \rightleftharpoons Fe(OH)_2 + 2NH_4Cl + 4NH_3$$

Chelating nitrogen donors form stable complexes which may be prepared from the aqua-ion; as an example, we observe the following formation constants :

$$[Fe(H_2O_6)]^{2+} + en \rightleftharpoons [Fe(H_2O)_4en]^{2+} + 2H_2O \qquad pK_1 = 4.3$$

$$[Fe(H_2O)_4en]^{2+} + en \rightleftharpoons [Fe(H_2O)_2(en)_2]^{2+} + 2H_2O \qquad pK_2 = 3.3$$

$$[Fe(H_2O)_2(en)_2]^{2+} + en \rightleftharpoons [Fe(en)_3]^{2+} + 2H_2O \qquad pK_3 = 2$$

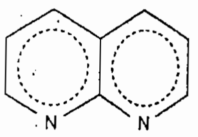
The effect of some chelating nitrogen-donor ligands on the Fe(III)-Fe(II) potential is noteworthy. The Fe^{2+} ion(d^6) is a good π-donor in comparison to Fe^{3+} which bears a higher charge on the metal. Accordingly, π-acceptor ligands like 2, 2′-dipyridyl and 1,10-phenanthroline (with low-lying π acceptor orbitals) greately stabilizes iron(II). Both oxidation states give rise to low-spin complexes where the potential [$E°$(aqueous) = 0.77 V] is modified as

$$[Fe(dipy)_3]^{3+} + e \rightleftharpoons [Fe(dipy)_3]^{2+} ; \qquad E° = 0.96 \text{ V}$$

$$[Fe(phen)_3]^{3+} + e \rightleftharpoons [Fe (phen)_3]^{2+} ; \qquad E° = 1.12 \text{ V}$$

The tris-(*o*-phenanthroline) iron(II) sulphate is widely used as a redox indicator under the name *ferroin*; the colour changes sharply from deep red to pale blue on oxidation.

An eight-coordinate dodecahedral complex is formed by 1, 8-naphthyridine (28-XVII) in $[Fe(naphthyridine)_4](ClO_4)_2$. Eight-coordination in a slightly twisted cubic environment is also present in the sandwich complex of crown (12-C-4) ether. Tetrahedral complexes are exemplified by the $[FeCl_4]^{2-}$ ion in salts with large counterions. Coordination number five in a distorted trigonal bipyramid arrangement is observed with tripod ligands like tris-(2-diphenylphosphinoethyl) amine, $N(CH_2CH_2PPh_2)_3$ (= NP_3), as in $[Fe(NP_3)X]^+$.



28-XVII

Acetylacetone (and other β-diketones) form neutral complexes with iron(II), especially in presence of nitrogen bases (which neutralize the proton liberated in the formation of the acetylacetonate ion). $Fe(acac)_2 \cdot py_2$ contains six-coordinate iron(II) in a high-spin configuration ($\mu_{eff} \simeq 5.4$ B.M). $[Fe(acac)_2]_4$ is formed as a tetramer in the solid with six-coordinate Fe(II) containing oxygen bridges and weak Fe—C bonds.

Haem (Fig. 26.3) is an extremely important complex of iron(II) present in the blood pigments haemoglobin and myoglobin. Prior to attachment of O_2, that is in deoxy-haemoglobin, the haem complex consists of a high-spin iron(II) bonded to four nitrogen atoms from pyrrole rings in a porphyrin system — the iron being about 70 pm above the plane on the globin side. The fifth coordination of the iron occurs through a nitrogen in globin (a protein) perpendicular to the porphyrin plane. The sixth coordination position of iron is occupied by a molecule of water which can be reversibly replaced by a molecule of dioxygen. The O_2 is coordinated at an FeOO angle about 120°, the iron atom now being in the plane of the porphyrin system. The resulting complex is diamagnetic and the

O-O stretching frequency is ~ 1106 cm^{-1}, comparable to that in the O_2^- (superoxide) ion. The system may be described in either of two ways : (i) a low-spin Fe(II) bonded to singlet O_2; (ii) low-spin Fe(III) bonded to O_2^-, together with antiferromagnetic interaction between the unpaired spins on both. It has also been suggested that a high-spin Fe(II) ion, with a single electron in the e_g level, being larger in comparison to both low-spin Fe(II) or Fe(III), cannot be accomodated in the porphyrin plane. The smaller ion formed on oxidation can now fit in the plane of the porphyrin ring. Steric congestion is thus primarily responsible for the reversible oxygenation process. In any case, the reversibility of the process forms an important step in the transport of oxygen by the red blood cells. In the lungs, the partial pressure of O_2 is high, binding this to the Fe(II) site; the oxygen is transported and liberated in the tissues where the oxygen pressure is low. The oxygen-site may also be occupied by CN^-, CO or PF_3 through strong irreversible coordination—leading to their poisonous nature. (However, these may also have other effects on the living system). Other important compounds of biological interest also contain iron, for example myoglobin (which is used to store oxygen in the muscles) and in various cytochrome pigments.

oxygenation by haem

The important iron-sulphur system present in ferredoxins has been mentioned before (Chapter 23).

Iron(II) forms a number of anionic complexes of which the halocomplexes have been mentioned earlier. The cyanocomplex $[Fe(CN)_6]^{4-}$ (hexacyanoferrate(II)) is formed readily from the aqua ion with CN^- ($K = 8 \times 10^{36}$). The low-spin complex substantially lowers the Fe^{III}-Fe^{II} potential

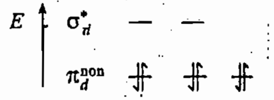
$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}; \quad E^\circ = 0.36\ V$$

The lower value of E° compared to phenanthroline and dipyridyl complexes (all π-bonding ligands) suggests that Fe(III) forms a more stable complex with CN^- than Fe(II). While the negative charge on CN^- disfavours metal-ligand back-bonding, the actual situation involves several other factors. Thermochemical data and study of E° at different temperatures show that the enthalpy term (ΔH°) for oxidation of $[Fe(CN)_6]^{4-}$ is actually more positive than that for the oxidation of $Fe^{2+}.aq$ ion, showing the same trend as for the oxidation of $[Fe(phen)_3]^{2+}$ ion. However, the higher charge on the $[Fe(CN)_6]^{4-}$ ion results in a very large negative entropy of hydration which may alter the ultimate E° value for the cyanide system as compared to the phenanthroline (and other) system. This idea gets further support from the Fe—C distances in the two cyano complexes : $[Fe(CN)_6]^{4-}$: 192 pm and $[Fe(CN)_6]^{3-}$: 195 pm. Since the C ≡ N bond lengths and stretching frequencies in these two species do not vary widely, the Fe—C distance may be taken as a support for stronger π-bonding in $[Fe(CN)_6]^{4-}$.

Electron distribution in the $[Fe(CN)_6]^{4-}$ ion may be described as

$$[\sigma]^{12}[\pi_d^{non}]^6$$

This explains its diamagnetic character :



As mentioned earlier, the $[Fe(CN)_6]^{4-}$ ion is kinetically inert toward substitution as shown by the absence of appreciable exchange with labelled CN^- ion. This is the main reason for its non-poisonous character in contrast to the iron(III) counterpart.

[**Sec. 28.7.5** *Iron(II)—complexes*]

$K_4[Fe(CN)_6]$, potassium hexacyanoferrate(II), (potassium ferrocyanide) is prepared by adding potassium cyanide to aqueous iron(II) sulphate until the initial brown precipitate redissolves :

$$FeSO_4 + 6KCN = K_4[Fe(CN)_6] + K_2SO_4$$

Pale yellow crystals of $K_4[Fe(CN)_6].3H_2O$ can be crystallized from the solution. The combined water is given up at 100°, forming a white hygroscopic powder.

It was formerly made by fusing organic substances (horn, hide etc) and scrap iron with potassium carbonate — the iron(II) sulphide and potassium cyanide formed reacted on leaching with water to form $K_4Fe(CN)_6$:

$$FeS + 6KCN = K_4[Fe(CN)_6] + K_2S.$$

$K_4[Fe(CN)_6]$ may also be obtained from the spent iron oxide from coal gas purification by boiling with milk of lime, followed by treatment with KCl and K_2CO_3.

Potassium ferrocyanide gives off carbon monoxide when heated with concentrated H_2SO_4 :

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Hexacyanoferrate(II) is oxidized by MnO_4^-, chlorine or electrolytically to hexacyanoferrate(III). The reaction with permanganate in dilute H_2SO_4 may be used for its volumetric estimation — the colour changes from greenish yellow to yellowish pink at the end point.

$$5[Fe(CN)_6]^{4-} + MnO_4^- + 3H^+ \longrightarrow 5[Fe(CN)_6]^{3-} + Mn^{2+} + 4H_2O$$

Except the barium salt, ferrocyanides of alkali and alkaline earth metals are soluble in water. Sodium ferrocyanide, $Na_4[Fe(CN)_6]$, $10H_2O$ is prepared in a similar way as used for the potassium salt. Others may be prepared by double decomposition. The hexacyanoferrates(II) of *d*-elements e.g., $Cu_2[Fe(CN)_6]$ have a coordination structure. The Fe and the other *d*-metal atom are linked in their crystals via CN groups. Most of them are poorly soluble in water and intensely coloured.

$H_4[Fe(CN)_6]$ is thrown as the etherate on adding ether to a strongly acidic solution containing $[Fe(CN)_6]^{4-}$ ion. The ether can be removed by heating gently (80°-90°C) in a stream of hydrogen. The free acid, a white powder, is soluble in water where it acts as a strong tetrabasic acid. In the solid, the protons appear to be bound to the N-atoms of the CN groups; intermolecular hydrogen bonding is also present.

Hexacyanoferrate(II) dissolves in liquid HF undergoing protonation to give $[Fe(CNH)_6]^{2+}$.

Prussian blue and Turnbull's blue

The $Fe(CN)_6^{4-}$ ion reacts with aqueous solutions of iron(III) in excess producing a deep blue precpitate called Prussian blue. Similarly, the $Fe(CN)_6^{3-}$ ion produces a blue precipitate with aqueous solutions of iron(II), known as Turnbull's blue. These have been used in inks and pigments since their discovery in early eighteenth century. The process of making "blue prints" (e.g. of building plans) involves the formation of these precipitates on sensitized paper.

It has now been established (X-ray and Mössbauer spectra) that both the blue substances are $Fe_4^{III}[Fe^{II}(CN)_6]_3 . xH_2O$ (x = 14 – 16). The basic structural motif of the solid consists of a cubic lattice with low-spin Fe(II) and high-spin Fe(III) joined by CN bridges lying along the edges. The cyanide coordinates strongly to Fe(II), giving an

$Fe^{II}C_6$ octahedral unit. The nitrogen of the cyanides and some of the interstitial water molecules present in the lattice interact with Fe(III). The intense colour of the compound arises from intravalence charge-transfer (Chapter 27) from Fe(II) to Fe(III).

Iron(III) hexacyanoferrate(II), i.e., Prussian blue is insoluble in water and dilute acids, but is readily decomposed by dilute alkali.

$$Fe_4[Fe(CN)_6]_3 + 12NaOH = 3Na_4[Fe(CN)_6] + 4Fe(OH)_3$$

It also decomposes on heating with yellow HgO, forming soluble mercury(II) cyanide and hydrous oxides of iron :

$$Fe_4[Fe(CN)_6]_3 + 9HgO + 9H_2O = 9Hg(CN)_2 + 4Fe(OH)_3 + 3Fe(OH)_2$$

Prussian blue dissolves in oxalic acid to give a deep blue solution which is used in making ink.

Soluble Prussian blue (α-form) is formed when $Fe^{3+}(aq)$ is slowly added to an excess of potassium ferrocyanide solution (1 : 1 molar proportions of each reactant). The deep blue precipitate has the composition $KFe^{III}[Fe^{II}(CN)_6]$ and is soluble in water to a blue colloidal solution. Electronic and Mössbauer spectra indicate that this also contains high-spin iron(III) octahedrally surrounded by six nitrogen atoms and low-spin iron(II) having six carbon atoms as nearest neighbours.

When $K_4Fe(CN)_6$ is distilled with dilute (1 : 12) H_2SO_4 (*caution* !), HCN is evolved and the solution yields a pale yellow residue of $K_2Fe^{II}[Fe^{II}(CN)_6]$ (*Everitt's salt*)

$$2K_4[Fe(CN)_6] + 3H_2SO_4 = K_2Fe[Fe(CN)_6] + 3K_2SO_4 + 6HCN$$

This is oxidized by nitric acid or H_2O_2 to $KFe[Fe(CN)_6]$, called *Williamson's violet.*

Oxidation of Prussian blue with dilute nitric acid gives a green precipitate of $Fe^{III}[Fe^{III}(CN)_6]$, (*Berlin Green*).

It may be noted that in both $K_2Fe^{II}[Fe^{II}(CN)_6]$ and $Fe^{III}[Fe^{III}(CN)_6]$ iron is present in only one oxidation state and hence no charge-transfer takes place; accordingly these compounds are not intensely coloured.

Many substitution products of $[Fe(CN)_6]^{4-}$ ion are known where one CN^- ion has been replaced by H_2O, CO, NO_2^- and NO^+. The nitroprusside ion, $[Fe(CN)_5NO]^{2-}$, is a prominent example in this category. It is diamagnetic and hence should formally contain Fe(II) and NO^+ (rather than Fe(III) and NO). This is consistent with N – O distance of 113 pm and a stretching vibration at 1947 cm^{-1} which is considerably higher than that for NO. Mössbauer studies indicate appreciable π-delocalization of charge from the iron to nitrosyl and cyanide groups. The ion gives an intense purple colour with sulphide ions in presence of alkali :

$$Na_2[Fe(CN)_5NO] + Na_2S = Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside also gives a rose-red coloration with sulphites, forming $Na_4[Fe(CN)_5(NO)SO_3]$. With alkali, a red nitro-complex is formed:

$$Na_2[Fe(CN)_5NO] + 2NaOH \longrightarrow Na_4[Fe(CN)_5NO_2] + H_2O$$

"Sodium nitroprusside", $Na_2[Fe(CN)_5NO]$, (sodium pentacyanonitrosyl ferrate(II)), may be prepared by heating $K_4Fe(CN)_6$ with 30% HNO_3. The brown solution obtained is cooled when KNO_3 separates first. The filtrate, on neutralization by Na_2CO_3, concentration and cooling, yields ruby-red rhombic crystals of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3^- \longrightarrow [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+$$

[Sec. 28.7.5 *Iron(II)—complexes*]

It may also be prepared by the action of $NaNO_2$:

$$[Fe(CN)_6]^{4-} + NO_2^- + H_2O \longrightarrow [Fe(CN)_5NO]^{2-} + CN^- + 2OH^-$$

Roussin's salts : These are nitrosyl thio complexes formed by Fe(II) with evidences for some direct Fe – Fe interaction. Roussin's red salts have the formula $M_2[Fe_2(NO)_4S_2]$ where M = Na^+, K^+ or NH_4^+ ; the corresponding esters $[Fe(NO)_2SR]_2$ (where R = ethyl, phenyl) are also known. Roussin's black salts have the general formula $M[Fe_4(NO)_7S_3]$ where M = Na^+, K^+, Rb^+, Cs^+, NH_4^+ and Tl^+.

The red salt $K_2[Fe_2(NO)_4S_2]$ may be prepared by passing NO into a suspension of FeS in a solution of alkali polysulphide. Iron nitrosyl halide also reacts with alkali sulphide to give Roussin's red salt; this may be treated with an alkyl halide to get the ester.

$$Fe(NO)_2I \xrightarrow{K_2S} K_2[Fe_2(NO)_4S_2] \xrightarrow{RX} [Fe(NO)_2SR]_2$$

The ester is also made by the action of mercaptan on iron nitrosyl carbonyl

$$Fe(NO)_2(CO)_2 \xrightarrow{RSH} [Fe(NO)_2SR]_2$$

Roussin's black salts may be prepared by passing NO into a suspension of precipitated FeS in a dilute solution of alkal sulphide. They may also be formed by reacting ferrous sulphate with a mixture of alkali nitrite and sulphide.

Roussin's red salts are less stable and they easily pass into the black salts. The black salts may be converted to the red salts by boiling with alkali.

Both classes of Roussin's salts are diamagnetic. The red salts contain two pseudo-tetrahedrally coordinated iron bridged by the S-atoms. The black salts contain a pyramid of four iron atoms — three faces of the pyramid have one sulphur above each, linked to all three iron atoms on that face. The Fe—Fe distance in the red salts lies around 272 pm while in the black salt the distance varies from 271 pm to 357 pm.

The spectral and magnetic behaviour of iron(II) complexes are relatively simple as the ^5D ground state from d^6 configuration splits into $^5T_2$ and ^5E states in octahedral and tetrahedral fields (Chapter 27). Only one spin-allowed transition is thus expected. In the high spin octahedral $Fe(H_2O)_6^{2+}$, the $^5T_{2g} \longrightarrow {}^5E_g$ transition occurs around 10,000 cm^{-1}; other complexes of this category also show this transition in the visible or near-ir region. The excited $t_{2g}^3 e_g^3$ configuration is Jahn-Teller degenerate; this makes the peaks broad. Magnetic moments lie around 5.2 B.M. with some orbital contribution.

In tetrahedral complexes, all high spin, the $^5E \longrightarrow {}^5T_2$ band appears around 4000 cm^{-1}. These also show magnetic moment corresponding to four unpaired electrons (5.0-5.2 B.M.).

As mentioned earlier, complexes of iron(II) with very strong π-acid ligands like CN^-, phenanthroline etc. are diamagnetic. In a strong crystal field, the $^1A_{1g}$ state falls sharply in energy and becomes the ground term (Tanabe-Sugano diagram) and high-spin low-spin transitions may be observed with suitable ligand combinations. The complex $[Fe(phen)_2(H_2O)_2]^{2+}$ is high-spin while the complex $[Fe(phen)_3]^{2+}$ is low-spin.

Spin-transitions have been observed with several complexes of the type $Fe(LL)_2X_2$ where LL = phen or dipy and X = NCS or NCSe. The compounds are almost diamagnetic below −125°C above which the magnetic moment rises to ~5 B.M. and higher at some temperature between −125°C and −75°C depending on the compound.

28.7.6 Lower oxidation states

Compounds of iron in oxidation states lower than +II are not very common and most of them are complexes with π-acceptor ligands like CO, NO, phosphines, dipyridyl etc. Iron(I) is represented by the nitrosyl complex $[Fe(H_2O)_5NO]^{2+}$ formed in the "brown ring test". Iron(0) is present mainly in carbonyls, nitrosyls and their derivatives and also in $[Fe(dipy)_3]^0$. Iron(−I) and −II are similarly present in derivatives like $Fe(CO)_4^{2-}$ and $Fe(CO)_2(NO)_2$. The carbonyls and phosphines will be discussed in connection with organometallic compounds.

Nitric oxide complexes

$Fe(NO)_4$, iron tetranitrosyl is formed in black crystals when $Fe(CO)_5$ is heated with NO at 45°. The involatile compound is highly reactive. N – O stretching frequencies recorded in the infrared spectrum occur at 1810, 1730 and 1140 cm^{-1} which cover both the NO^+ and NO^- regions. Hence the compound may be formulated as $Fe(NO^+)_3(NO^-)$. Other nitrosyl derivatives like the halide $Fe(NO)_3Cl$ and nitrosyl carbonyls (e.g. $Fe((NO)_2(CO)_2)$ are also known.

The classical "brown ring" compound involved in the ring test of nitrates is usually quoted as $[Fe^I(H_2O)_5(NO^+)]^{2+}$, consistent with a magnetic moment of 3.9 B.M. for three unpaired electrons (high-spin d^7). However, recent studies* on the kinetics and mechanism of the reaction of NO with Fe(II) (*aq*) and EPR and Mössbauer spectra of the reaction product $[Fe(H_2O)_5(NO)]^{2+}$ suggest that the complex ion is best described by the presence of high-spin Fe(III) coordinated by NO^-, i.e. as $[Fe^{III}(H_2O)_5(NO^-)]^{2+}$.

The observed spin-state ($S = \frac{3}{2}$) is explained on the basis of "antiferromagnetic coupling" of Fe(III) with NO^-, i.e. an arrangement in which the two unpaired electrons on NO^- have spins opposite to those of the five *d*-electrons in iron(III). Displacement of a coordinated water molecule from $[Fe^{II}(H_2O)_6]^{2+}$ by NO in the rate-determining step (I_d mechanism : dissociative interchange) is followed by a rapid intramolecular charge-redistribution process leading to formal oxidation of Fe^{II} to Fe^{III} and reduction of NO to NO^-. The IR spectrum shows a single peak at 1810 cm^{-1} (lower than that in NO, 1860 cm^{-1}), a value close to wavenumbers found around 1777 cm^{-1} in the Fe^{III}–edta–NO complex which is known to bind NO as Fe^{III}–NO^-. The assignment is further supported by EPR and Mössbauer spectra.

28.7.7 Organometallic compounds

Carbonyls

Three carbonyl compounds of iron are well-known : $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. When powdered iron is heated in a current of CO between 150°C and 200°C and a pressure $10^7 - 2 \times 10^7$ Pa, $Fe(CO)_5$ is formed as a volatile yellow gas (m.p. −20°C, b.p. 103°C), soluble in benzene and ether but insoluble in water. The molecule is trigonal bipyramidal.

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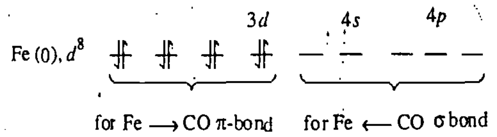
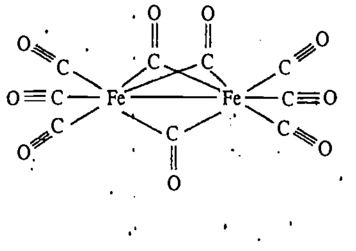
* Wanat. A. : Schneppensieper. T. : Stochel. G. : van Eldik. R. ; Bill. E. : Wieghardt. K. *Inorganic Chemistry*. 2002, 41, 4–10.

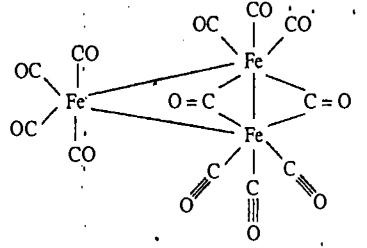


The reactions and bonding of carbonyls have been discussed later in a separate chapter.

Irradiation of $Fe(CO)_5$ with uv radiation gives dark yellow $Fe_2(CO)_9$ (m.p. 100°C). This is a dinuclear compound with direct Fe — Fe bridge (28-XVIII).



28-XVIII



28-XIX

Treatment of $Fe(CO)_5$ with aqueous triethylamine results in $[Et_3NH][Fe_3(CO)_{11}H]$. This is acidified and the carbonyl extracted into petroleum ether. $Fe_3(CO)_{12}$ separates from this extract as green diamagnetic crystals which decompose above 100°C. The structure is shown in Fig. 28-XIX.

In $Fe_2(CO)_9$, the environment of each iron atom is approximately octahedral. Metal-metal bond is invoked to explain the observed diamagnetism of the compound. $Fe_3(CO)_{12}$ shows the presence of two different types of iron atom through Mössbauer spectrum. Two of them are joined by bridging CO groups as in $Fe_2(CO)_9$. The structure is confirmed by x-ray.

The carbonyls are oxidized and reduced with partial or complete preservations of the CO groups. Thus, $Fe(CO)_5$ reacts with metallic sodium in liquid ammonia as

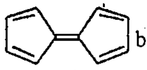
$$2Na + \overset{0}{Fe}(CO)_5 \longrightarrow Na_2[Fe^{-II}(CO)_4] + CO$$

Similar reduction is also effected by alkali in an alcoholic solution :

$$Fe(CO)_5 + 4KOH = K_2[Fe(CO)_4] + K_2CO_3 + 2H_2O$$

The reaction of aqueous alkali with $Fe(CO)_5$ gives yellow solutions containing the $[Fe(CO)_3H]^-$ anion; some $[Fe(CO)_4]^{2-}$ is also formed in this reaction. The latter ion is also formed in disproportionation reaction with other ligands :

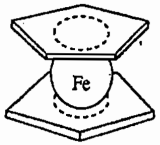
$$2Fe(CO)_5 + 3en \xrightarrow{145^\circ} [Fe(en)_3][Fe^{-II}(CO)_4] + 6CO$$

Ferrocene or bis(η^5-cyclopentadienyl)-iron, $Fe(\eta^5\text{-}C_5H_5)_2$, is a very interesting organometallic compound of iron. It was discovered accidentally in 1951 in an attempt to synthesize fulvalene  by the reaction of cyclopentadienyl magnesium bromide with $FeCl_3$ (Pauson and Kealy). The reaction produced an orange compound of empirical formula $C_{10}H_{10}Fe$ containing Fe(II). A similar compound was reported independently by Miller and others who passed cyclopentadiene and nitrogen over a heated iron catalyst. Characterization of the sandwich structure of the compound was pioneered by G. Wilkinson and E.Fischer who were awarded the 1973 Nobel Prize in chemistry.

Ferrocene is readily prepared by the reaction between sodium cyclopentadienide with iron(II) chloride in THF :

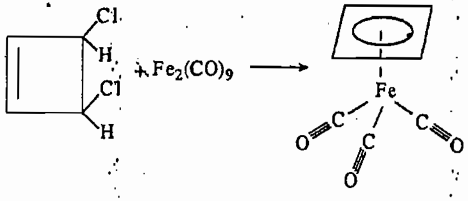
$$2NaC_5H_5 + FeCl_2 \longrightarrow Fe(C_5H_5)_2 + 2NaCl$$

It is an orange crystalline solid stable in air and water. It is soluble in organic solvents but insoluble in water. X-ray diffraction studies have confirmed its sandwich structure (28-XX) with staggered cyclopentadienyl rings. The bonding between the cyclopentadienide ions ($C_5H_5^-$) and Fe^{2+} essentially consists of π-interaction by overlap of the d_{xz} and d_{yz} orbitals on iron with the π-molecular orbitals of $C_5H_5^-$ rings having proper symmetry.



28-XX

An extensive organic chemistry of ferrocene is now established. These are in fact a general chemistry of similar "metallocenes" which will be discussed separately later (see 32.2.4). The major reactions of ferrocene are those of the aromatic rings : it undergoes Friedel-Crafts acylation and alkylation reactions though it does not undergo the Diels-Alder reaction characteristic of dienes. Ferrocene is oxidized to the ferricinium ion, $[Fe^{III}(\eta^5\text{-}C_5H_5)_2]^+$, and hence cannot be nitrated or halogenated. Other arene complexes of iron are also known, for example, $[Fe(C_6H_6)_2]^{2+}$ is isoelectronic with ferrocene. Cyclobutadiene forms a stable complex with carbon monoxide as co-ligand :



28.7.8 Detection and estimation

Iron(III) salts in solution are readily identified by the characteristic colours produced with aqueous ammonium thiocynate (blood red) or potassium ferrocyanide (prussian blue). Iron(II) salts may be similarly detected through the blue colour formed by potassium ferricyanide solution.

Iron is estimated volumetrically by titration of iron(II) with potassium dichromate or potassium permanganate. It may be precipitated as the hydrated oxide or by cupferron and weighed after ignition as Fe_2O_3.

28.8 COBALT

Co : [Ar] $3d^74s^2$	**Atomic number** : 27	**Atomic weight** : 58.94
M.P. : 1499°C	**B.P.** : 2900°C	**Density** : 8.9 g cm^{-3}

Even 5000 years ago a blue cobalt pigment was known in ceramics and glass making; in King Tutankhamen's tomb archaeologists found glass stained blue with cobalt salts. Glass of the same origin was also discovered in excavation sites in ancient Assyria and Babylonia.

28.8.1 Introduction

History : The methodology of making cobalt paints seems to have been lost with time since blue glasses in later civilizations (Byzantine, Alexandria and Rome) contained no cobalt but copper and were inferior to the early specimens. Glassmakers in Venice somehow mastered the art again in the late 17th-18th century.

The history of the discovery of cobalt may be started with its naming. Miners of medieval Saxony often came across a mineral with outward characteristics of silver ore but no silver could be extracted from it. Furthermore, roasting of the ores produced poisonous gases. So they called these ores "cobold" after the evil spirit who was assumed to inhabit the mineral (German *Kobold* = evil spirit, goblin).

In 1735 the Swedish chemist G. Brandt analysed some specimens of "cobold" and wrote about a new semi-metal which he named cobold. By semi-metals he meant compounds whose properties resembled those of known metals but the elements were not malleable. Brandt described six semi-metals : mercury, bismuth, zinc, antimony, cobalt and arsenic. But his discovery did not receive a hearty welcome from the scientists for many years. Even in 1776, many scientists believed that cobalt was a compound of iron and arsenic. The identity of cobalt as a new element was established around 1780 by T. Bergmann and other scientists.

Occurrence : Cobalt is less common than all other elements in the first transition series except scandium. Its position among the elements is thirtieth in order of abundance (29 ppm).

Cobalt occurs mainly associated with nickel and arsenic. The principal minerals (also ores) are arsenides and sulphides, e.g. *smaltite* (or *speiss cobalt*) : $CoAs_2$ or (Co, Ni, Fe)As_2; *erythrite* $Co_3(AsO_4)_2$. Besides arsenic, sulphur and iron, the minerals contain ~4-10% Co, ~2-8% Ni and varying amounts of silver (2-20%), copper and lead. The chief producers of the metal are Africa and Canada; small reserves are also present in Australia and the Russian countries. India has no good reserve of the metal; very small quantities of cobalt-nickel sulphide is found in the copper-mines of Khetri-Jaipur region. Some cobalt-ore deposits have been reported from Nepal.

Traces of cobalt occur in soils and as a constituent of vitamin B_{12}.

Cobalt has only one naturally occurring isotope — Co-59. When bombarded with thermal neutrons, this gives radioactive Co-60 which decays to Ni-60 through β and γ emission (5.271 y).

28.8.2 The element

Extraction

The extraction of cobalt involves separation of large amount of other metals commonly associated with it, namely copper, nickel, lead and silver. A general outline is as follows :

(i) *Concentration*. The oil-floatation method is commonly adopted.

(ii) *Roasting*. As_4O_6 is obtained as a by-product from arsenical ores.

(iii) *Smelting.* A flux of limestone or sand is used according to necessity. The molten product separates into three layers :

(a) a top layer of slag, mainly $FeSiO_3$.

(b) a middle layer (Speiss) of mixed oxides (and arsenides) of cobalt, nickel, copper and iron.

(c) a bottom layer of bullion containing easily reducible metals like silver and copper.

(iv) *Desilverization of speiss.* The speiss still contains some silver which is converted to chloride by roasting with common salt. Most of the arsenic is also driven out at this stage. Some of the cobalt, nickel and copper are extracted with water as chloride. The silver chloride is then removed with sodium thiosulphate solution.

Sometimes the entire operation has to be repeated.

(v) *Isolation of cobalt.* The desilverized speiss is again roasted with sodium nitrate and carbonate when the remaining arsenic is converted to sodium arsenate which is leached with water.

The residue containing oxides of cobalt, nickel and iron is digested with concentrated H_2SO_4 and finally agitated with water. Iron, arsenic and copper are removed by adding calcium carbonate and sodium carbonate. The filtrate containing cobalt and nickel is now treated with calculated quantity of bleaching powder (or sodium hypochlorite) so that only the cobalt gets precipitated as the "hydroxide".

$$2CoSO_4 + 2Ca(OH)_2 + Ca(OCl)Cl + H_2O = 2\,Co(OH)_3 + CaCl_2 + 2CaSO_4$$

The aqueous extract from desilverization may be treated with scrap iron to remove copper and the cobalt precipitated with bleaching powder.

(vi) *Reduction of hydrous cobalt(III) oxide.* The precipitate of hydrated cobalt(III) oxide may be ignited to produce Co_3O_4 which is used to prepare other cobalt compounds. The oxide may be reduced with coke in an electric arc furnace to get the metal :

$$Co_3O_4 + 4C = 3Co + 4CO$$

Reduction is also carried out with aluminium. The pure metal may be obtained by electrolysis of cobalt(II) sulphate solution containing ammonium sulphate.

A very reactive form of the metal may be prepared by reducing $CoCl_2$ with lithium naphthalenide in glyme (ethylene glycol dimethyl ether).

Properties

Cobalt is a lustrous silvery metal with a bluish tinge. It excels steel in hardness and tensile strength. It is ferromagnetic with a high curie temperature (1121°C). Some of its physical properties have been given in Table 28.2.

Finely divided metallic cobalt is pyrophoric like iron but the compact metal is not attacked by air or water at ordinary temperature. It burns in air above 300°C to form Co_3O_4 and CoO. Steam forms CoO at red heat.

Cobalt dissolves less readily than iron in mineral acids (E° for $Co^{2+} - Co = -0.277$ V). Concentrated nitric acid renders it passive. The metal is not attacked by aqueous alkali but is dissolved by fused KOH at 550°C.

The metal reacts on heating with halogens and other non-metals like B, C, P, As and S; H_2 and N_2 appear exceptions.

Uses

Large quantities of cobalt compounds are used in glass and ceramic industries. The light blue tint of cobalt compounds is used to complement the faint yellow colour arising from iron impurities so that the products appear perfect white. The compounds are also used in making blue pigments used in glass and ceramic industries and as artists' colour. Cobalt salts are also used to speed up the oxidation of oil-based paints and hence as a drying agent. Nearly 30% of the total production of cobalt (~ 10.000 tonnes per annum world wide) is used in this manner.

Almost the same quantity of cobalt is used in making tough alloys suitable for use in gas turbines and high speed tools. *Stelite* (~ 50% Co with chromium, tungsten and carbon) and *Widia metal* (~10% Co and 90% W_2C) are such examples. Cobalt-alloys are also used in making powerful magnets; *Alnico* (Al 10, Ni 18, Co 12.5, Fe 53.5 and Cu 6 per cent) is used in making powerful permanent magnets.

Radioactive Co-60 is used in the treatment of cancer.

Cobalt compounds are also used as catalysts in a number of organic reactions, like the oxo process and hydrogenation reactions.

General chemical features

The oxidation state-free energy diagram for cobalt (Fig. 28.44) is rather simple, containing the only important oxidation states II and III. It appears that in acidic aqueous medium, cobalt (II) is more stable than cobalt (III).

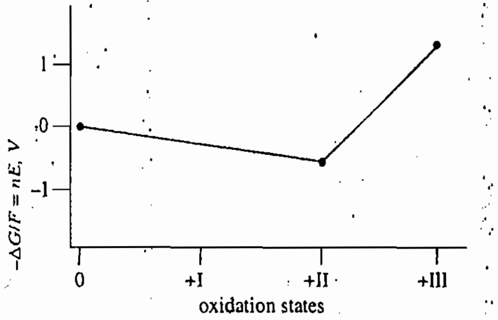


Fig. 28.43 Oxidation state-free energy diagram for cobalt. Co(II) is more stable than Co(III) in aqueous solutions (acid).

28.8.3 Oxidation states IV and V

Oxidation of aqueous Co(II) in alkaline medium (by Cl_2, O_2, O_3 etc) forms a black hydrous oxide CoO_2, but this is not well characterized. Several mixed oxide species containing Co(IV) are also reported, e.g. M_2CoO_3(M = K, Rb, Cs); Li_8CoO_6 and Ba_2CoO_4. The last compound has the same structure as K_2SO_4 and can be prepared by heating $Co(OH)_2$ with $Ba(OH)_2$ or $BaCO_3$ in oxygen at 1050°C :

$$Co(OH)_2 + 2BaCO_3 + \frac{1}{2}O_2 = Ba_2CoO_4 + 2CO_2 + H_2O.$$

Similarly, fusion of Co_3O_4 with NaO_2 produces Na_4CoO_4; this has the tetrahedral CoO_4 anion with Na^+ coordinated to the oxygen atoms. Cs_2CoF_6, prepared by fluorination of Cs_2CoCl_4, is isomorphous with Cs_2SiF_6 and has an octahedral coordination around Co(IV). The magnetic moment (2.97 BM at 294 K) is considerably higher than the spin-only value for a t_{2g}^5 configuration; large orbital contribution in the $^2T_{2g}$ ground state or partial population of the higher $^6A_{1g}$ state ($t_{2g}^3e_g^2$) has been suggested as a likely explanation.

The alkyl tetra(1-norbornyl)cobalt(IV) (Fig. 27-II) is reasonably stable to air and heat. The brown, paramagnetic, low-spin compound is prepared by reacting $CoCl_2$ and lithium norbornyl. Dithio carbamate complexes and organocobalt(IV) compounds with Schiff bases are also known.

Cobalt(V) is likely to be present in the materials having the stoichiometry $M^{I}_3CoO_4$, produced by heating the oxide mixtures in oxygen under pressure. The oxidation state is also present in the tetrahedral $[Co(1\text{-norbornyl})_4]^+$ obtained by oxidizing the Co(IV) - complex with $AgBF_4$. The compound is diamagnetic.

28.8.4 Compounds of cobalt(III), (d^6)

As mentioned earlier, this oxidation state of cobalt is strongly oxidizing in aqueous medium and as such there is no aqueous chemistry in this oxidation state. But there exists a wide range of coordination compounds with various ligands. Simple compounds like oxide, fluoride, sulphate and nitrate are also known which are also oxidizing in nature.

Oxides

Cobalt(III) oxide, Co_2O_3 is formed as a brown hydrated species of unknown structure when $Co(OH)_2$ is oxidized in alkaline medium. This may be represented as $Co_2O_3.aq$ which may be dried at 150°C to the composition $Co_2O_3.H_2O$. This is probably CoO(OH) — the dark-brown product is also formed when $Co(OH)_2$ is heated in air at 100°C. It forms Co_3O_4 on further heating in air. It has a layer structure having each cobalt surrounded octahedrally by six oxygen. The hydrous oxide is also present in the mineral *heterogenite*.Co_2O_3 dissolves in hydrochloric acid with the evolution of chlorine :

$$Co_2O_3 + 6HCl = 2CoCl_2 + Cl_2 + 2H_2O$$

Co_3O_4 is a black solid isomorphous with Fe_3O_4 and has a normal spinel structure (chapter 27). It is also formed by heating cobalt(II) oxide in air or cobalt(II) nitrate below 1000°C. The oxide loses oxygn above 900°C. The oxide loses oxygen above 900°C and passes into cobalt(II) oxide. It dissolves in acids with the evolution of oxygen; chlorine is evolved with HCl :

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4H_2O$$

Halides

Cobalt(III) fluoride, CoF_3 is obtained as a light-brown powder by heating CoF_2 or $CoCl_2$ in fluorine. It reacts violently with water, evolving oxygen. A green hydrate $CoF_3.3.5H_2O$ has been prepared by electrolytic oxidation of CoF_2 in 40% HF; it also oxidizes water.

CoF_3 is a strong fluorinating agent, and fluorinates hydrocarbons directly to fluorocarbons.

$$4CoF_3 + \rangle CH_2 \longrightarrow \rangle CF_2 + 4CoF_2 + 2HF$$

Since Co(III) is strongly oxidizing in nature other cobalt(III) halides are not known.

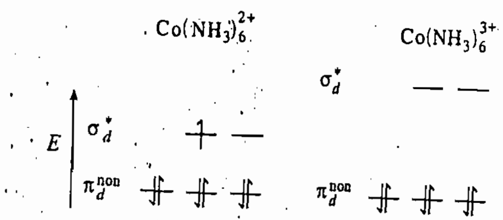
Simple salts

Cobalt(III) forms few simple salts, the most readily available one being **cobalt(III) sulphate;** $Co_2(SO_4)_3$, $18H_2O$ may be obtained as blue needle shaped crystals by oxidation of cobalt(II) sulphate in 8*M* H_2SO_4 either electrolytically or with F_2 or O_3. It is stable when dry but liberates oxygen from water. It dissolves in dilute sulphuric acid without appreciable decomposition. Dark blue alums $M^{I}Co(SO_4)_2$. $12H_2O$ (M = Na, K, Rb, Cs, NH_4) are known. These are reduced by water but can be washed with acetone and glacial acetic acid.

The alums and the hydrated sulphate are believed to contain $[Co(H_2O)_6]^{3+}$ ion which is strongly acidic and oxidizing in nature.

Complex compounds

We have already come across several complexes of cobalt(III) in chapter 27. The d^6 configuration readily gains the advantage of large CFSE with strong ligands (see diagram).



This is also reflected in the changing redox potentials for the Co(III) – Co(II) couple :

Ligand	H_2O	NH_3	CN^-
E^0 (V)	1.84	0.1	−0.8

The stabilization of Co(III) over Co(II) has been discussed in Chapter 27. We have also noted the slowness of Co(III) complexes toward substitution — one of the main reasons for their extensive study during the early development of coordination chemistry.

As noted in connection with Werner's work, cobalt(III) forms a series of ammine complexes. The orange hexaammine, $[Co(NH_3)_6]^{3+}$ is readily formed by aerial oxidation (charcoal acts as a catalyst) of aqueous cobalt(II) in presence of aqueous ammonia and ammonium salts :

$$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + O_2 \longrightarrow 4\,[Co(NH_3)_6]Cl_3 + 26H_2O.$$

Oxidation by H_2O_2 in absence of charcoal gives the red pentaamineaqua complex (*roseo cobaltic chloride*) as the major product :

$$2[Co(H_2O)_6]Cl_2 + 2NH_4Cl + 8NH_3 + H_2O_2 \longrightarrow 2[Co(NH_3)_5(H_2O)]Cl_3 + 12H_2O$$

The coordinated water is readily replaced by chlorine on treatment with concentrated HCl.

Co(III) shows great affinity for other nitrogen donors also, for example, amines, nitro and –NCS groups. The preparation of these complexes usually involves addition of the ligand to aqueous cobalt(II) followed by oxidation (air or H_2O_2). Ligand exchange reactions may also be used; for example the chelating ligand ethylenediamine readily forms $[Co(en)_3]Cl_3$ with the pentaamminechloro complex mentioned earlier. Presence of other ligands like water, halides, carbonate, hydroxide etc. with the nitrogen donors give rise to complexes with various stereoisomers which helped Werner greatly in establishing his theory of coordination compounds.

Complexes of cobalt(III) with oxygen donor ligands are also known, e.g., $[Co(ox)_3]^{3-}$ or $Co(acac)_3$. The latter compound (green) is insoluble in water but soluble in organic solvents as the monomer. Reduction of this with aluminium alkyls in presence of triphenylphosphine under nitrogen produces the orange dinitrogen complex $[Co^{I}H(N_2)(PPh_3)_3]$ (see low oxidation states : Fig. 28.44).

Uptake of oxygen by cobalt(II) — ammonia solutions also produces peroxobridged complexes.

The red or brown $[NH_3)_5Co—O—O—Co(NH_3)_5]^{4+}$ complexes are diamagnetic while the green complex $[(NH_3)_5\ Co(O_2)\ Co(NH_3)_5]^{5+}$ is paramagnetic with superoxide ion (O_2^-) and contains both Co(III) in octahedral coordination.

$K_3[Co(CN)_6]$, ("potassium cobalticyanide") potassium hexacyanocobaltate(III), is readily formed by adding excess KCN to a solution of cobalt(II) and boiling the resulting brown solution of $K_4[Co(CN)_6]$ preferably with a few drops of H_2O_2 or NaOCl or NaOBr.

$$2K_4[Co(CN)_6] + H_2O + O = 2K_3[Co(CN)_6] + 2KOH.$$

Pale yellow crystals of $K_3[Co(CN)_6]$ are isomorphous with $K_3[Fe(CN)_6]$. The low-spin, diamagnetic complex gives precipitates of hexacyanocobaltates(III) with heavy metals and are mostly inert to attack by reagents like chlorine, HCl and alkali.

$Na_3[Co(NO_2)_6]$, "sodium cobaltinitrite", [Sodium hexanitrito-κN-cobaltate(III)] is formed by passing a rapid stream of air through concentrated aqueous solutions of cobalt(II) nitrate and sodium nitrite at 40-50°C in presence of acetic acid :

$$2[Co(H_2O)_6](NO_3)_2 + 12NaNO_2 + 2CH_3COOH + \tfrac{1}{2}O_2 \longrightarrow$$
$$2Na_3[Co(NO_2)_6] + 2CH_3COONa + 4NaNO_3 + 13H_2O.$$

The dull red compound is precipitated by adding ethanol. It is readily soluble in water but the aqueous solution decomposes with the evolution of oxygen

$$2Na_3[Co(NO_2)_6] + H_2O = 6NaNO_2 + 2Co(NO_2)_2 + 2HNO_2 + \tfrac{1}{2}O_2$$

Its solution is used to detect potassium ion which forms the very sparingly soluble yellow precipitate of $K_3[Co(NO_2)_6]$ from acetic acid solution. "Potassium cobaltinitrite" (*Fischer's salt*) is stable to light and air and is used as a yellow pigment in water colour and in painting porcelain.

The fluorocomplexes $M_3^ICoF_6$ are obtained as blue solids from HF solutions of CoF_3 and MF (alkali metal fluoride). They are the rare examples of high spin complexes of cobalt(III) — the $t_{2g}^4e_g^2$ electron distribution gives rise to magnetic moments around 5.4 B.M. The occupancy of the t_{2g} level gives rise to slight J—T distortion showing two bands in the electronic spectra around 14500 cm^{-1} and 11800 cm^{-1} (Chapter 27). $[Co(H_2O)_3F_3]$ is also paramagnetic with four unpaired electrons.

The electronic spectrum of the Co^{3+} ion ($3d^6$) is expected to follow the same gross pattern of energy level diagram as found with Fe(II). But in this case the higher energy singlet $^1A_{1g}$ state of the free ion drops rapidly with increasing 10*Dq*, going below the $^5T_{2g}$ state at a very low value. Complexes of Co(III) are thus commonly diamagnetic except the fluoro complexes mentioned above. For regular octahedral complexes, two spin-allowed transition are expected, $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$. However, the $^1T_{1g}$ state is further split due to lower symmetry when the ligands are not all the same and three transitions are observed (Fig. 27.60).

28.8.5 Compounds of cobalt(II), d^7

Cobalt(II) is quite stable in simple compounds and salts and in complexes with weak ligands. With ligands stronger than water in the spectrochemical seris, Co(III) becomes the preferred state owing to the large gain in CFSE for the low-spin t_{2g}^6 configuration.

Oxide and hydroxide

Cobalt(II) oxide, CoO is formed when steam is passed over red-hot cobalt or cobalt(II) carbonate, nitrate etc. heated to 1000°C out of contact with air. It is also formed on heating $Co(OH)_2$.

The oxide is an olive-green solid stable upto 1000°C, but when heated in air it forms Co_3O_4. CoO is essentially a basic oxide, giving cobalt(II) salts with acids but it also dissolves in concentrated alkali to a deep blue solution containing the $[Co(OH)_4]^{2-}$ ion; this is readily oxidized by air to precipitate the black hydrated oxide.

CoO has the rock-salt structure but normally contains a slight excess of oxygen, behaving as a *p*-type semiconductor.

Cobalt(II) hydroxide, $Co(OH)_2$ is precipitated by adding ammonia or alkali metal hydroxides to aqueous solutions of cobalt(II) in cold. This usually gives the blue form which passes to the more stable pink form on standing or warming the suspension. The pink form is also formed when an aqueous solution of cobalt(II) is added to an alkali. $Co(OH)_2$ is amphoteric in nature. It dissolves in aqueous acids to cobalt(II) salts which may be crystallized as hydrates. Solution of $Co(OH)_2$ in excess alkali contains the blue $[Co(OH)_4]^{2-}$ ion. This, as well as a suspension of $Co(OH)_2$ in slightly alkaline solution are rapidly oxidized by air to brown CoO(OH). An excess of aqueous ammonia converts $Co(OH)_2$ to soluble ammine complexes such as $[Co(NH_3)_6]^{2+}$ which are rapidly oxidized in air to the Co(III) ammines.

CoO is largely used in ceramics to impart blue colour. It forms mixed oxides on fusion with aluminium, zinc and magnesium oxides having characteristic colours e.g., $CoAl_2O_4$ (*Thenard's blue*), $CoZnO_2$ (*Rinmann's green*); Co_2SnO_4 and $CoCr_2O_4$ are also green. Magnesium forms a pale pink mass. These colours were sometimes used to identify the metals by heating the sample with excess dry sodium carbonate on a cavity in charcoal, followed by heating the residual oxide with a drop of cobalt nitrate solution ("cobalt nitrate test").

Halides

CoF_2 is conveniently made by heating the double salt CoF_2, $2NH_4F$ or by the action of HF on $CoCl_2$. Other cobalt(II) halides are obtained by direct reaction between the elements. CoF_2 is pink, $CoCl_2$ blue, $CoBr_2$ green and CoI_2 is blue-black in colour.

The halides form various crystalline hydrates. $CoCl_2$. $6H_2O$ (pink) contains the cobalt surrounded by four water molecules at the corners of a distorted square while two chloride ions occupy the remaining positions of the distorted octahedral environment. The dark red deliquescent monoclinic crystals (m.p. 86°C) readily dissolve in water to a pink solution which turns violet to blue on gentle warming, depending on the condition.

The Magic Canvas : The well-known 16th century chemist and physician Paracelsus liked to demonstrate his "magic canvas". He would first show the audience a painting of a winter landscape with snow-covered trees and hills. After some time, he would turn the winter scenario into a summer : the trees covered with green foliages and white hills disappearing under green grass. A solution of cobalt(II) chloride with some nickel(II) chloride appears colourless. On gentle warming, it develops beautiful green colour. It is likely that Paracelsus used this chemistry in his magic; he would light a candle placed suitably behind his canvas and the rest followed very easily.

Aqueous solution chemistry

As mentioned earlier, the $[Co(H_2O)_6]^{2+}$ ion is thermodynamically very stable toward oxidation in absence of complexing agents :

$$[Co(H_2O)_6]^{3+} + e = [Co(H_2O)_6]^{2+}; \quad E^\circ = 1.84V$$

Oxidation is highly favoured in basic media as well as by the presence of complexing agents like NH_3, CN^- etc. which form stronger complexes with cobalt(III) :

$$CoO(OH)\ (s) + H_2O + e = Co(OH)_2\ (s) + OH^-; \quad E^\circ = 0.17\ V$$

$$[Co(NH_3)_6]^{3+} + e = [Co(NH_3)_6]^{2+}; \quad E^\circ = 0.1V$$

Aqueous solutions of cobalt(II) contain the pink hexaaqua ion $[Co(H_2O)_6]^{2+}$ together with small amounts of $[Co(H_2O)_4]^{2+}$; the hexaaqua ion is also present in several crystalline hydrates like $Co(NO_3)_2 . 6H_2O$; $CoSO_4.7H_2O$; $Co(ClO_4)_2.6H_2O$. Low cationic charge makes the aqua-ions barely acidic. Hence one can precipitate blue basic carbonates by adding alkali metal carbonate or bicarbonate solution to cobalt(II) solutions. The normal carbonate may be obtained as the pink hexahydrate, $CoCO_3$, $6H_2O$ from a solution of cobalt(II) with sodium bicarbonate solution under an atmosphere of carbon dioxide.

Cobalt(II) sulphate, $CoSO_4.7H_2O$ is obtained from solutions of cobalt(II) oxide or cobalt(II) carbonate in dilute H_2SO_4 on crystallization below 44°C. The red monoclinic crystals are isomorphous with $FeSO_4$. $7H_2O$ and $NiSO_4$. $7H_2O$. Between 44° and 77°C, $CoSO_4.6H_2O$ crystallizes; above 70°, the crystals are $CoSO_4$. H_2O. All the hydrates are pink.

The anhydrous sulphate is obtained as a red hygroscopic powder by heating the hydrate with concentrated H_2SO_4.

Red, monoclinic double sulphates $M_2SO_4.CoSO_4.6H_2O$ (M = K, Rb, Cs and NH_4) crystallize from solutions containing the two sulphate.

Cobalt(II) nitrate, $Co(NO_3)_2.6H_2O$ forms red deliquescent crystals from solutions of cobalt(II) in dilute nitric acid. A red double nitrate is formed with bismuth nitrate : $3Co(NO_3)_2, 2Bi(NO_3)_3, 24H_2O$.

Cobalt(II) sulphide, CoS deposits as a black precipitate on passing H_2S into an aqueous solution of cobalt(II) in acetic acid medium; the precipitate is difficultly soluble in dilute HCl. In group analysis, CoS is precipitated by H_2S from an ammoniacal solution of cobalt(II); the precipitate is insoluble in cold dilute HCl but readily dissolves in hot concentrated HNO_3 or aqua regia :

$$3CoS + 8HNO_3 = 3Co(NO_3)_2 + 2NO + 3S + 4H_2O.$$

Complex compounds

Numerous complexes of cobalt(II) are known, majority of which fall within the categories octahedral (pink) and tetrahedral (blue). Of course, there are many with other coordination numbers and stereochemistries and some for which the colours are reversed. For example, anhydrous $CoCl_2$ contains octahedrally coordinated cobalt(II) and is yet blue.

[**Sec. 28.8.5** *Cobalt(II)—complexes*]

As explained in connection with CFSE (Fig. 27.14), Co(II) , d^7, forms more tetrahedral complexes than any other transition metal ion. The small energy difference between octahedral and tetrahedral complexes of the same ligand often gives rise to an equilibrium between the two forms, as noted in case of the aqueous solution which always contains some $[Co(H_2O)_4]^{2+}$ ions in equilibrium with $[Co(H_2O)_6]^{2+}$. Similar equilibrium exists for other systems, for example the mixed pyridine halo (and thiocyanato) complexes mentioned later.

Tetrahedral complexes

Tetrahedral complexes of the type $[CoX_4]^{2-}$ are generally formed by monodentate ligands like Cl^-, Br^-, I^-, SCN^-, N_3^- and OH^- or their combination with neutral ligands, e.g. $CoCl_2py_2$. Solid $M_2^ICoX_4$ (X = Cl, Br, I) are readily formed from aqueous solutions of MX and CoX_2. The $CoCl_4^{2-}$ ion is tetrahedral with some angular distortion depending upon the cation. In acid concentrations below 3*M*, hydrochloric acid solutions of $CoCl_2$ contain $[Co(H_2O)_6]^{2+}$ and $[CoCl(H_2O)_5]^{2+}$ ions. In acid concentrations above 8*M*, the principal species are $[CoCl_3(H_2O)]^-$ and the $[CoCl_4]^{2-}$ (*deep blue*). Complex thiocyanates also resemble the complex halides. Addition of Hg(II) salt to a solution of cobalt(II) in excess thiocyanate almost quantitatively precipitates $HgCo(NCS)_4$. The blue crystalline solid contains Co(II) tetrahedrally coordinated by N-atoms of the thiocyanate group while the Hg(II) is coordinated by S-atoms, resulting in a polymeric structure. It is used as a calibrant in the determination of magnetic susceptibility by Gouy method.

Cobalt(II) chloride adds pyridine to form $CoCl_2(py)_2$ having two forms ; blue and violet. The blue form has a monomeric tetrahedral structure which is metastable at ordinary temperature. This passes to the stable violet form with chlorine-bridged octahedral coordination around cobalt. $CoBr_2$ and CoI_2 form only the tetrahedral complex CoX_2py_2 (X = Br, I); $Co(SCN)_2$ and $Co(SeCN)_2$ form only the octahedral form of CoX_2py_2 (X = SCN, SeCN). All these complexes are tetrahedral in organic solvents but they set up tetrahedral-octahedral equilibrium when excess pyridine is added :

$$CoX_2py_2 + 2py \rightleftharpoons CoX_2py_4$$

Bulky β-diketonate anions form tetrahedral complexes with Co(II) but these tend to polymerize to effect higher coordination number when the ligand is less hindered, e.g. $Co(acac)_2$ is tetrameric with six-coordination around each cobalt. Tetrahedral cationic complexes are also known, for example $[Co(OAsPh_3)_4]I_2$ and $[Co\{SC(NH_2)_2\}_4](ClO_4)_2$.

The electronic spectrum of Co(II)-complexes has been mentioned earlier (Fig. 27.53 and 27.54). Most tetrahedral complexes are intense blue, the highest energy transition corresponding to $^4A_2 \longrightarrow {}^4T_1(P)$. Another band corresponding to the transition $^4A_2 \longrightarrow {}^4T_1(F)$ is also expected, while the lowest energy band $^4A_2 \longrightarrow {}^4T_2$ usually lies in the infra-red region (1000 – 2000 nm). In $CoCl_4^{2-}$ the assignments are

$$^4A_2 \longrightarrow {}^4T_1\ (F)\ 5{,}800\ cm^{-1}; \quad {}^4A_2 \longrightarrow {}^4T_1\ (P)\ 15{,}000\ cm^{-1}$$

The $^4A_2 \longrightarrow {}^4T_2$ transition is calculated to be around 3300 cm^{-1}. The complex nature of the spectrum has been ascribed to a number of transitions to doublet excited states together with spin-orbit coupling.

- The tetrahedral complexes contain three unpaired electrons, the spin-only magnetic moment expected being 3.89 B.M. Theoretical considerations establish the relation

$$\mu_{obs} = 3.89 - \frac{15.59\lambda'}{\Delta_{tet}},$$

where λ′ is the spin-orbit coupling constant which is inherently negative and varies little from one complex to another. Hence the value of μ_{obs} increases as the magnitude of Δ_{tet} decreases, as exemplified by the tetrahalo complexes :

$$CoCl_4^{2-} . 4.59 \text{ B.M.}; CoBr_4^{2-} : 4.69 \text{ B.M.}; CoI_4^{2-} : 4.77 \text{ B.M.}$$

Octahedral complexes

Cobalt(II) forms both high spin and low-spin octahedral complexes. the change-over appears to come between NH_3 and NO_2^- in the spectrochemical series. Anhydrous cobalt(II) salts add ammonia to form octahedral ammine complexes of the type $[Co(NH_3)_6]X_2$ where X = Cl, Br, I, ClO_4, BF_4 etc. These may also be prepared in aqueous ammonia where they get readily oxidized; in pure water, the $[Co(NH_3)_6]^{2+}$ gets readily decomposed. Other bases are also known to form such octahedral complexes, for example, $[Co(N_2H_4)_6]^{2+}$ and $[Co(en)_3]^{2+}$. Auto-complex formation may sometimes occur in a donor solvent, for example

$$2CoCl_2 + 6Me_2SO \rightleftharpoons [Co(OSMe_2)_6]^{2+} + CoCl_4^{2-}$$

$$2CoI_2 + 6MeCN \rightleftharpoons [Co(NCMe)_6]^{2+} + CoI_4^{2-}.$$

An irregular structure with six-coordinate cobalt is found in the purple complex $[Co(NO_3)_2(Me_3PO)_2]$ where the nitrate ions are bidentate.

When KCN is added to aqueous Co(II), the initial red-brown precipitate of cobalt(II) cyanide dissolves in excess KCN to an olive-green solution which is rapidly oxidized by air. The principal species in the solution is probably $[Co(CN)_5(H_2O)]^{3-}$. Addition of ethanol to this solution gives a violet precipitate $K_6[Co_2(CN)_{10}].4H_2O$. The diamagentic solid contains the anion $[(CN)_5Co-Co(CN)_5]^{6-}$ which has been established in the purple barium salt. The green solution reacts with water to give $[Co(CN)_5H]^{3-}$, $[Co(CN)_5OH]^{3-}$ and other species. The solution has the remarkable property of absorbing molecular hydrogen, reducing it to the hydride ion :

$$2[Co(CN)_5]^{3-} + H_2 = 2[Co^{III}(CN)_5H]^{3-}.$$

This is in effect an activation of molecular hydrogen and has been taken advantage of in a variety of reduction processes. Solutions of $[Co(CN)_5]^{3-}$ are used as homogeneous catalysts in the hydrogenation of unsaturated organic compounds, for example, styrene (to ethylbenzene) and benzil (to benzoin). The ion reacts with C_2F_4, C_2H_2, SO_2 or $SnCl_2$ when these molecules are "inserted" between the two cobalt atoms :

$$[Co(CN)_5]^{3-} + C_2H_2 \longrightarrow [(CN)_5CoCH = CHCo(CN)_5]^{3-}.$$

The configuration about the double bond has been shown to be *trans*.

When oxygen is passed through the solution containing green $K_3[Co(CN)_5]$, the diamagnetic peroxoanion $[(CN)_5Co^{III}-O-O-Co^{III}(CN)_5]^{6-}$ is formed. This is oxidized by bromine and alkali to the red paramagnetic superoxo complex $[(CN)_5Co-O-O-Co(CN)_5]^{5-}$ ion.

The electroinc spectra of high-spin octahedral complexes of cobalt(II) have been mentioned in Chapter 27 (Fig. 27.53). The highest energy band corresponds to transitions from the ${}^4T_{1g}$ (*F*) ground term to ${}^4T_{1g}$ (*P*) and ${}^4A_{2g}$ both of which are close together. We recall that the ${}^4T_{1g}(F)$ ground term is derived from the electron distribution $t_{2g}^5 e_g^2$ and the ${}^4A_{2g}$ term from $t_{2g}^3 e_g^4$. Hence any transition between these two states is a two-electron process and hence about one-hundredth time weaker than the other transition. Another spin-alowed transition (${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}$.) occurs in the near-ir region.

Magnetic moments of the octahedral complexes appear in the range 4.7 to 5.2 B.M. at room temperature; these values are higher than the spin-only value owing to considerable orbital contribution. We recall that the ground state possesses inherent orbital angular momentum.

Low-spin octahedral complexes show Jahn-Teller distortion in keeping with the $t_{2g}^6 e_g^1$ configuration. Thus, the $[Co(C_6H_5NC)_6]^{2+}$ ion in solution is axially distorted. Since the ligand field required to bring about spin-pairing is also high (> 15,000 cm^{-1}), low-spin octahedral complexes of Co(II) show a tendency to form complexes with a lower coordination number.

Cobalt(II) forms few five-coordinated complexes; these may have the limiting geometries of square planar or trigonal bipyramidal and many intermediate structures are known. Square pyramid complexes may be represented by $[Co(CN)_5]^{3-}$ and $[Co(CNPh)_5]^{2+}$. As we have seen with the cyano species, these ions may be further coordinated weakly by a solvent molecule, completing C.N. six, in a distorted octahedral geometry. $CoBr_2(PMe_3)_3$ binds O_2 in its sixth coordination site. $[Co(Me_6tren)Br]^+$ is trigonal bipyramidal (*tren* = tris (2-aminoethyl)amine, $(NH_2CH_2CH_2)_3N$).The complexes may be both high-spin with three unpaired electrons and low-spin with one unpaired electron. Heavy atom donors (P, As, Br, S etc.) are usually found to favour spin-pairing.

Square planar complexes are formed by chelating ligands like dimethylglyoxime, salicylaldehyde, ethylenediamine, dithioacetylacetone and many others. Here also, further weak coordination cannot be completely ruled out, as for example, in $[Co(en)_2][AgI_2]_2$. All square planar complexes are low spin with magnetic moments lying in the range 2.2 — 2.7 B.M. at 300K, slightly higher than the spin-only value for a single unpaired electron.

28.8.6 Low oxidation states (I, 0, –I)

These low oxidation states are mostly found with strongly π-bonding ligands, CO, NO, CN^- etc. The carbonyls and nitrosyls have been discussed separately.

$K_3[Co(CN)_4]$ is formed by the reduction of $K_3[Co(CN)_6]$ with potassium in liquid ammonia in absence of air. The isocyanide complexes $[Co(CNR)_5]X$ may be separated as crystalline salts from solution obtained by heating Co(II) salt with the isocyanide in alcohol. These are also obtained by reduction of $CoCl_2(CNR)_4$ with, say, N_2H_4 or $S_2O_4^{2-}$. Disproportionation of $Co_2(CO)_8$ by RNC also produces the Co(I) species :

$$Co_2(CO)_8 + 5RNC \longrightarrow [Co(CNR)_5]^+[Co(CO)_4]^- + 4CO$$

The perchlorate salt of CH_3CN contains the Co(I) in a trigonal bipyramid environment but $[Co(NCPh)_5]ClO_4$ has the Co(I) in square pyramid distribution of the ligands. Co(II) - aqua ions also disproportionate to Co(I) and Co(III) when heated with strongly π-acidic polycylic phosphite ligands such as $P(OEt)_3$(L) :

$$2[Co^{II}(H_2O)_6]^{2+} + 11L \longrightarrow [Co^IL_5]^+ + [Co^{III}L_6]^{3+} + 12H_2O.$$

Several other complexes of Co(I) with phosphines or phosphite ligands alone or with other ligands are prepared by reduction reactions like

$$[\text{Co(acac)}_3] + \text{PR}_3 + \text{N}_2 \xrightarrow{\text{AlEt}_3} [\text{CoH(N}_2)_3(\text{PR}_3)_3]$$

$$\text{CoCl}_2 + 4\text{PMe}_3 \xrightarrow{\text{Na-Hg}} [\text{Co(PMe}_3)_4] + 2\text{NaCl}.$$

$[\text{CoH(N}_2)\ (\text{PPh}_3)_3]$ has the structure shown in Fig. 28.44; its structure was one of the first dinitrogen complexes to be determined.

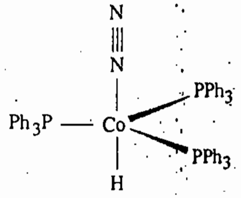


Fig. 28.44

Structure of $[\text{CoH(N}_2)\ (\text{PPh}_3)_3]$.

Co — N ≃ 180 pm(±3 pm)
Co — H ≃ 160 pm
<N – Co – P ≃ 97 ± 2°

Thus the Co is slightly raised above the plane of the three equatorial P - atoms.

Co(I) is also present in the hydrido complex ion $[\text{CoH}_5]^{4-}$ and CoLX where $\text{L} = \text{CH}_3\text{C(CH}_2\text{PPh}_2)_3$ and X = halogen.

$\text{K}_4[\text{Co(CN)}_4]$ may be obtained by reduction of $\text{K}_3[\text{Co(CN)}_6]$ in liquid ammonia by potassium. Quite a few complexes of cobalt(0) are formed by phosphine ligands, e.g. $[\text{Co(PMe}_3)_4]$. Dimeric Co(0) species are obtained by reacting the carbonyls with phosphines at about 0°C in benzene :

$$\text{Co}_2(\text{CO})_8 + 2\text{PPh}_3 \longrightarrow [\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2].$$

Co(–I) is present in complexes like $\text{K}[\text{Co(N}_2)(\text{PMe}_3)_3]$, $[\text{Co(CO)}_3\text{NO}]$ and $\text{H}[\text{Co(CO)}_4]$. The nitrosyls and carbonyls have been discussed separately.

Carbonyls and nitrosyls

Unlike iron and nickel, which combine with CO at atmospheric pressure and moderate temperatures (Fe 120°C, Ni 30°C), cobalt reacts with carbon monoxide at 150°C and 40 atm pressure. There is no mononuclear carbonyl of cobalt, as this would marginally miss the 18 - *e* configuration; in fact the Co(CO)_4 unit is a radical with 17 electrons which readily dimerizes to form the dinuclear carbonyl $\text{Co}_2(\text{CO})_8$. This is an orange diamagnetic solid, mp. 51°C, which is also formed when cobalt compounds are reduced in presence of CO :

$$2\text{CoCO}_3 + 8\text{CO} + 2\text{H}_2 \longrightarrow \text{Co}_2(\text{CO})_8 + 2\text{CO}_2 + 2\text{H}_2\text{O}$$

[250 — 300 atm pressure; 120° — 150°C]

Cobalt also forms two other binary carbonyls — $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_6(\text{CO})_{16}$. All three carbonyls are air-sensitive and undergo both substitution and disproportionation reactions with bases :

$$\text{Co}_2(\text{CO})_8 + 2\text{PPh}_3 \longrightarrow 2[\text{Co(CO)}_3(\text{PPh}_3)]_2 + 2\text{CO}.$$

$$\text{Co}_2(\text{CO})_8 + 12\text{NH}_3 \longrightarrow 2[\text{Co(NH}_3)_6][\text{Co(CO)}_4)] + 8\text{CO}.$$

The bridging CO groups are replaced by the ligands in the formation of the dimeric substitution products. The carbonyls are hydrolyzed in aqueous alkali forming the tetra carbonyl cobaltate(–I) ion $[\text{Co(CO)}_4]^-$; this is also formed by reducing the carbonyls with alkali metals in liquid ammonia or tetrahydrofuran. When these solutions are acidified, the yellow volatile cobalt carbonyl hydride HCo(CO)_4 is formed. This compound has been shown to be the active species in the "oxo process" for the conversion of alkenes to alcohols in presence of a cobalt catalyst :

$$\text{RCH} = \text{CH}_2 + \text{CO} + 2\text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{OH}$$

The likely course of the reaction involves *hydrometallation*, the insertion of H — Co into the double bond :

$$\text{RCH} = \text{CH}_2 + \text{HCo(CO)}_4 = \text{RCH}_2\text{CH}_2\text{Co(CO)}_4$$

A molecule of CO is now inserted between the reactive Co – C bond :

$$\text{RCH}_2\text{CH}_2\text{Co(CO)}_4 \xrightarrow{\text{CO}} \text{RCH}_2\text{CH}_2\text{COCo(CO)}_4$$

The acyl-cobalt compound may now lose one molecule of CO and get reduced by hydrogen via the aldehyde

$$\text{H}_2 + \text{RCH}_2\text{CH}_2\text{COCo(CO)}_4 \longrightarrow \text{RCH}_2\text{CH}_2\text{CHO} + \text{HCo(CO)}_4$$

The $[\text{Co(CO)}_4]^-$ ion also acts as a catalyst in the conversion of alkyl halides into esters :

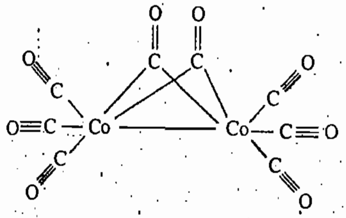
$$\text{RX} + \text{CO} + [\text{Co(CO)}_4]^- \longrightarrow \text{RCOCo(CO)}_4 + \text{X}^-$$

$$\text{RCOCo(CO)}_4 + \text{R'OH} \longrightarrow \text{RCOOR'} + \text{HCo(CO)}_4$$

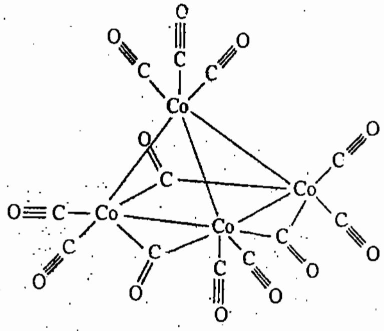
A tertiary amine is used to regenerate the $[\text{Co(CO)}_4]^-$ ion

$$\text{HCo(CO)}_4 + \text{R}_3\text{N} \longrightarrow [\text{R}_3\text{NH}]^+\ [\text{Co(CO)}_4]^-$$

The structure of solid $\text{Co}_2(\text{CO})_8$ (28-XXIa) has two bridge CO groups and a Co—Co bond. The infrared stretching bands for bridging carbonyls (1857 and 1886 cm^{-1}) disappear when $\text{Co}_2(\text{CO})_8$ is dissolved in hexane. Four terminal CO groups to each cobalt gives rise to a staggered geometry (D_{3d} symmetry).



28-XXI(a)



28-XXI(b)

In $\text{Co}_2(\text{CO})_8$, each cobalt forms six σ bonds, four of them through donor-acceptor interactions of electron pairs of four of the CO molecules and the free orbitals of cobalt. The fifth is formed by a *d* electron pair of the cobalt and a free π orbital of a CO molecule. The unpaired electrons of the two cobalt atoms form the sixth σ bond, the Co—Co bond. The molecule is stabilized by π bonds from filled 3*d* orbitals of cobalt.

$$\text{Co(0)},\ d^9\quad \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \overset{3d}{\uparrow\downarrow}}_{\pi\ \text{bond}}\ \underbrace{\uparrow\downarrow\ \uparrow\ \overset{4s}{-}\ \overset{4p}{-\ -\ -}}_{\sigma\text{-bond}}$$

$Co_2(CO)_8$ reacts with nitric oxide at ordinary temperature (40°C) to form the nitrosyl carbonyl $Co(NO)(CO)_3$, the reaction being practically quantitative :

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3NO + 2CO$$

The compound conforms to the 18-electron category taking NO as a 3-electron donor. It is monomeric in the vapour, having a tetrahedral structure. Reaction with donor molecules results in replacement of the CO. Other mixed nitrosyl complexes are also known, for example, $[Co(NO)_2X]_2$ (X = halogen); $[Co(NO)(CN)_5]^{3-}$ and $[Co(NO)(NH_3)_5]^{2+}$.

Cobalt also forms $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$. $Co_4(CO)_{12}$ is a black solid; its structure consists of a tetrahedron of cobalt atoms — three having two terminal CO groups while the fourth cobalt has three terminal CO groups (Fig. 28-XXIb). Each of the first three cobalt atoms have two bridge CO groups.

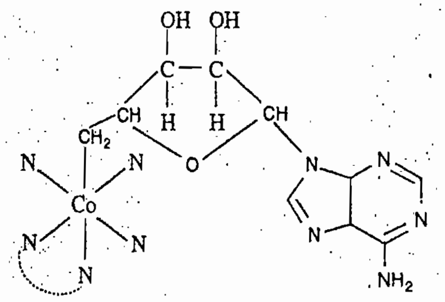
28.8.7 Organometallic chemistry

No simple alkyls or aryls of cobalt appear to be known, though these can be stabilized with π-bonding ligands like CO, CN^-, PR_3 or cyclopentadiene. Alkyl cobalt(I) carbonyls are made by the reactin

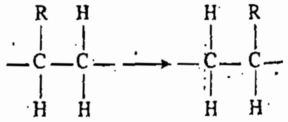
$$NaCo(CO)_4 + RI \longrightarrow RCo(CO)_4 + NaI.$$

We have already encountered similar organometallic compounds of cobalt which may be involved in reactions catalyzed by $Co_2(CO)_8$. Vitamin B_{12} presents a naturally occurring organometallic compound of cobalt.

The structure of Vitamin B_{12} (Fig. 26.2) consists of a cobalt(III) atom coordinated to 4 coplanar N-atoms of a "corrin" ring; The fifth coordination position is linked to an imidazole nitrogen. The sixth coordination position (which is either vacant or coordinated by an O_2 in haemoglobin) may be occupied by different groups. In the commonly isolated form of the vitamin, this position is occupied by a CN group, but in vivo this may be occupied by a loosely bound water molecule. The purple cobalt(III) species can be reduced to Co(II) (brown Vitamin B_{12}) by catalytic hydrogenation and other methods. Treatment with chromium(II) acetate (pH 9.5) or $NaBH_4$ causes further reduction to Co(I) in the green vitamin B_{12s} which has the sixth coordination site of cobalt vacant and is very reactive. Vitamin B_{12s} reacts with adenosine triphosphate making a coenzyme which contains a Co—C σ-bond (Fig. 28-XXIIa) and provides an example of a naturally occurring organometallic compound. The coenzyme is involved in various biological processes, mainly as a catalyst for 1, 2 rearrangements of the type which take place without any exchange of hydrogen with the solvent water (28-XXIIb). The nature of the R group may be varied — it may be a complex alkyl or acyl group or a relatively simple nucleophilic group like OH or NH_2.



28-XXII (a)



28-XXII (b)

The reduced vitamin B_{12} reduces ClO_3^- to Cl^- and NO_3^- to NH_4^+ in acid solution (pH 1.5-2.5).

Cobaloximes

Most of the reactions of vitamin B_{12} are not clearly understood. One way to study the chemistry of vitamin B_{12} is to study more tractable relatively simple cobalt complexes that mimic many of the reactions of vitamin B_{12}. Such model complexes, mostly formed by dimethylglyoxime and also other glyoximes, are collectively known as *cobaloximes* (Fig. 28.45).

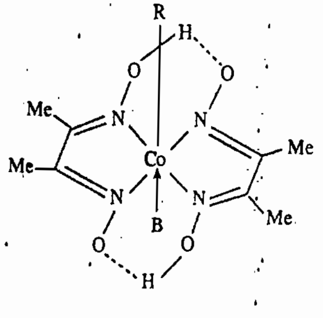


Fig. 28.45

A model cobaloxime formed by dimethylglyoxime
R = alkyl, aryl or acid anion
B = base, e.g., pyridine.

The main interest on the study of cobaloximes is centered on its reduction to a Co(I) species and their reactions. The cobalt exhibits four oxidation states, IV, III, II and I. Cobaloximes may be reduced similar to vitamin B_{12} forming blue or green Co(I) species which, in analogy to vitamin B_{12s}, are strong nucleophile and powerful reducing agents. They react with water to give hydridocobalt(III), specially in presence of tertiary phosphine ligands. They also undergo Michael additions and nucleophilic displacements to give complexes with alkyl groups directly bonded to Co(III).

Cobaltocene, $Co(\eta^5\text{-}C_5H_5)_2$, is paramagnetic. Arene complexes of cobalt are also known, for example $[Co(C_6Me_6)]^+$.

28.8.8 Detection and estimation

Cobalt may be detected conveniently by the deep blue colour produced in borax beads ($Co(BO_2)_2$) which remains unchanged in reducing flames. Solutions containing cobalt(II) produce a yellow precipitate with potassium nitrite solution in excess acetic acid medium (potasium "cobaltinitrite"). Co(II) salts in solution also produce a deep blue complex $[Co(SCN)_4]^{2-}$ with ammonium thiocyanate; the complex can be extracted into amyl alcohol or acetone. Interference of iron(III) may be avoided by adding F^- ions.

Cobalt may be estimated gravimetrically as $CoSO_4$ (fuming with conc. H_2SO_4) or as metallic cobalt after electrodeposition. Co(II) may be oxidized by H_2O_2 - alkali to $Co(OH)_3$. The precipitate is dissolved in acetic acid and treated with α-nitroso β-naphthol (L) when a red chelate of composition $CoL_3.2H_2O$ is precipitated. It is ignited to Co_3O_4 at 800°C and weighed. The method enables separation of cobalt from nickel. (Also see under nickel).

28.9 NICKEL

Ni : [Ar]$3d^84s^2$ **Atomic number : 28** **Atomic weight : 58.69**

M.P. : 1455°C B.P. : 2920°C **Density : 8.91 g cm^{-3}**

Back in the third century B.C., the Chinese made an alloy of copper, nickel, and zinc. Coins made from this alloy were used in the Central Asian state of Bactria.

28.9.1 Introduction

History : Nickel also derives its name from the German word for devil-spirit. In the late 17th century, a mineral having appearances of cuprite could not be smelted to obtain copper. Metallurgists decided that the ore was dominated by the evil spirit of the mountains and called it copper-devil or kupfer-nickel (actually nickel arsenide). Confusion persisted regarding the nature of this mineral until in 1751 A. Cronstedt (Sweden) succeeded in isolating crude nickel from it. Even for some time after this, some scientists believed that nickel was a mixture of cobalt, iron, arsenic and copper. Their doubts were finally removed by T. Bergmann in 1775.

Occurrence : Nickel is the twenty-second most abundant element in the earth's crust (99 ppm), seventh among the transition elements. It has five naturally occurring isotopes.

Nickel occurs both as oxide-silicate ores and as sulphides :

Garnierite : (Ni, Mg)$_6$Si$_4$O$_{10}$(OH)$_8$. These are rocky minerals containing 4.7% of Ni with iron oxides and silica.

Pentlandite : (Ni, Fe)$_9$S$_8$. These are usually mixed with *pyrrhotites* Fe_nS_{n+1}, $n = 5 - 16$ and contain about 2 - 4% nickel together with chalcopyrites.

Garnierite is found in New Caledonia, Cuba, Brazil and Queensland. The most important single deposit of nickel (pentlandite) occurs at Sudbury, Canada and also in Russia and South Africa.

There are no commercially significant deposit of nickel ores in India. Nickeliferrous iron sulphides containing 1.7% nickel, have been reported in Jammu and Kashmir (Ramsu) with possibilities of workable zones existing at depths. Some nickeliferrous minerals are also present in Karnataka (Hassan and Kolar) and Kerala but these are not of any mining significance. Similar small quantities of cobalt nickel sulphide also occur in the Khetri-Jaipur region in Rajasthan. Lately nickel-ore has been found in small but significant proportion associated with uranium ores in Singhbhum, Bihar.

28.9.2 The element

Extraction

Nickel is mainly extracted from the sulphide ore which contains about 3% Ni, 1.5% Cu, precious metals like Au, Ag and platinum metals together with chalcopyrites and other iron sulphides. The main steps in the extraction of nickel are as follows :

(i) *Concentration* : The ore is concentrated magnetically and by selective floatation.

(ii) *Roasting and smelting* : The concentrated sulphide ore is subjected to a series of roasting and smelting with the addition of silica and limestone. This removes iron and sulphur to a great extent. Sulphur is oxidized to SO$_2$ while the more basic metal iron (as sulphide) is oxidized to FeO which is removed as slag (FeSiO$_3$). The remaining FeS is oxidized in a Bessemer converter and removed as slag. The matte rich in nickel and copper sulphides is left to slow cooling when nickel sulphide and copper sulphide form separate solid phases. Nickel is next extracted by the *Mond Process* or *electrolytically*.

(iii) *The Mond carbonyl process* (developed by Mond in 1899)

(a) The nickel-copper sulphide is further roasted to oxidize the metals to their oxides. Leaching with hot dilute H$_2$SO$_4$ dissolves out most of the copper oxide. (CuSO$_4$ is a by-product).

(b) The oxide residue is now reduced with H$_2$ in water gas at about 300-350°C.

$$NiO + H_2 = Ni + H_2O; \quad CuO + H_2 = Cu + H_2O.$$

(c) The impure nickel is now converted to volatile nickel carbonyl, Ni(CO)$_4$, by the action of CO at atmospheric pressure around 50°C.

$$Ni + 4CO = Ni(CO)_4$$

Higher pressure and temperature (20 atm/150°C) are also used at present.

(d) The nickel tetracarbonyl vapour is decomposed at 230°C over pellets of nickel acting as nuclei. The nickel deposited is about 99.95% pure. The CO is recycled.

(iv) *The electrolytic process* : The nickel-copper matte is roasted in a multiple hearth roaster to form nickel and copper oxides. Most of the copper oxide is leached with hot dilute H$_2$SO$_4$ and the residue reduced with coke — the product containing about 65% Ni (together with 30% Cu, 3 - 8% S and a little iron) is cast into anodes. Electrolysis is carried out with nickel sulphate solution as electrolyte and nickel cathodes on which pure nickel is deposited. The anode is enclosed in canvas bags in which valuable metals like Au, Ag, Pt etc. are collected as *anode slime*.

Extraction from silicate ore

The silicate ores (e.g., Garnierite) are double silicates of nickel and magnesium containing about 5 - 8% Ni and no copper. The ore is smelted with limestone, coke and gypsum in small blast furnaces. Gypsum is reduced to CaS by coke; this undergoes double decomposition with nickel silicate :

$$CaSO_4 + 4C = CaS + 4CO; \quad CaS + NiSiO_3 = CaSiO_3 + NiS.$$

The slag of molten calcium, magnesium and iron silicates forms an upper layer above the nickel sulphide matte. The matte is roasted to oxide and finally reduced by coke. The crude nickel is purified electrolytically.

The nickel oxide may be used directly for steel making (see use).

Properties

Some properties of nickel have been listed in Table 28.2. Nickel is a hard, silvery metal which is very malleable and ductile and can be easily rolled, drawn, forged and polished. It is ferromagnetic, though less so than either iron or cobalt; the Curie point (375°C) is also lower. The metal normally forms face-centered cubic lattice.

Nickel is moderately electropositive :

$$Ni^{2+} + 2e = Ni; \quad E^\circ = -0.24 \text{ V}$$

The compact metal is quite resistant towards air and water at ordinary temperatures. Strong heating in air produces little oxide and steam is decomposed slowly at red heat. Nickel does not rust. The finely divided metal is however very reactive and may be even pyrophoric.

Nickel is only slowly attacked by dilute hydrochloric and sulphuric acids but it dissolves readily in dilute nitric acid and aqua regia. Concentrated nitric acid renders nickel passive.

The metal is practically unattacked by caustic alkalis, not even fused.

Nickel reacts only slowly with fluorine at ordinary temperature. Heated nickel catches fire in chlorine or bromine and also combines with phosphorus, arsenic or antimony.

Uses

Nickel is used mainly in the form of alloys with iron and other nonferrous metals. Small amounts of nickel in cast iron imparts hardness while a higher percentage (15 - 25%) provides corrosion resistance. Similarly, small (0.25 - 0.45%) amounts of nickel in steels gives good mechanical properties and toughness while 8-32% Ni imparts corrosion resistance specially when alloyed with chromium. We have earlier mentioned some alloys of iron and nickel, for example invar and platinite.

Some important alloys containing mainly nonferrous metals are mentiond below :

Monel metal : Ni 67%, Cu 20%, Fe, Mn. It is directly made from the nickel-copper matte by roasting followed by reduction. It is as strong as steel but resistant to attack by chemicals. including alkali. Hence its use in making diaphragms in alkali cells, turbine blades, valves etc.

Nickel silver : (or German Silver) Ni 10-30%, Cu 55-65%, rest Zn; used in tableware, often electroplated on other metals (EPNS = electroplated nickel silver).

Nichrome : Ni 60, Cr 40; used in electrical heating coils. Other similarly high resistance alloys are *constantan* (Ni 40, Cu 60), *manganin* (Cu 84, Mn 12, Ni 4), *platinoid* (Ni 14, Cu 60, Zn 24, W 2), *rheotan* (Ni 25, Cu 52, Zn 18, Fe 5) etc.

Alnico : used in making permanent magnets; *Hastealloy*, low expansion, high electrical resistance and high modulus of elasticity are other examples in this category.

Nickel is used in nickel plating. However, this often tarnishes in town air and is attacked by acids. Hence it has been largely replaced by chromium plating.

Nickel is also used in electric cells (like the alkaline iron-nickel and cadmium nickel cells) and as a catalyst for the hydrogenation of oils. The common catalyst for this purpose is *Raney nickel*, a highly active form of the metal; this is prepared by dissolving aluminium from the alloy $NiAl_3$ with alkali, leaving the nickel in a highly porous form.

General chemical features

Nickel has only one important oxidation state, +II. In continuation of the trend to disfavour higher oxidation states in the last lap of the transition series, the +III state becomes relatively unimportant (difference from Co). There are a few compounds of Ni(III) and Ni(IV) while the major chemistry involves Ni(II), $3d^8$.

28.9.3 Chemistry of Ni(III) and Ni(IV)

Oxidation states above II for nickel are known only in some poorly understood oxides and some complex compounds. The only important simple compound appears to be Ni_2O_3, $2H_2O$ or NiO(OH) which has two crystalline forms. No simple halides are also known, though nickel(III) fluoride has been prepared in the impure form which is marginally stable at 25°C.

A suspension of $Ni(OH)_2$ in alkali may be oxidized by chlorine, bromine, persulphate or electrolytically below 25°C to a black precipitate which is the common β-NiO(OH) — it decomposes at 140°C into NiO, oxygen and water vapour and is readily soluble in acids.

A separate phase γ-NiO(OH) is formed by adding nickel to a molten mixture of Na_2O_2 and NaOH at 600°C and treating the cooled melt with ice-water. The compound dissolves in sulphuric acid evolving oxygen.

Oxidation of nickel(II) by sodium hypochlorite in alkaline medium gives a black hydrated species with approximate composition $NiO_2 \cdot xH_2O$ which also is a powerful oxidizing agent.

NiO(OH) seems to be the principal species in the working of the Edison cell which uses nickel-iron electrodes with KOH as electrolyte :

$$Fe + 2NiO(OH) + 2H_2O \rightleftharpoons Fe(OH)_2 + 2Ni(OH)_2 \ (\sim 1.3\ V)$$

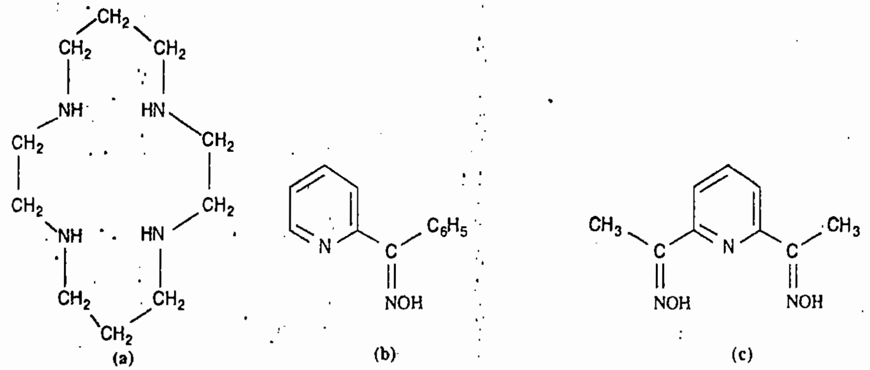
The reaction proceeds to right during discharging and vice-versa.

$NaNiO_2$ may be formed by bubbling oxygen through molten alkali metal hydroxides contained in nickel vessels at about 800°C.

Many complexes of Ni(III) are known. Oxidation of nickel(II) halo complexes like $NiX_2(PR_3)_2$ may give rise to complexes $NiX_3(PR_3)_2$. $NiBr_3(PEt_3)_2$ shows a room temperature magnetic moment of 1.72 B.M.and is probably trigonal bipyramidal. Fluorination of $KCl\text{-}NiCl_2$ melts forms violet K_3NiF_6 which evolves oxygen from water. It disproportionates in liquid HF.

$$2K_3NiF_6 \longrightarrow NiF_2 + NiF_6^{2-} + 4F^- + 6K^+$$

Macrocylic nitrogen ligands and peptides may stabilize Ni(III) (28-XXIIIa).



28-XXIII

Ligands (L) containing oxime groups [28-XXIII, (b) and (c)] are also known to stabilize Ni(III) in complexes of the type NiL_3. The green complex $[NiCl_2(en)_2]^+Cl^-$ also shows a magnetic moment consistent with one unpaired electron.

As expected for the lowspin d^7 configuration with $t_{2g}^6 e_g^1$ arrangement, Ni(III) complexes are susceptible to Jahn-Teller distortion. $[Nidipy_3]^{3+}$ and K_3NiF_6 both show tetragonal distortion having short axial bonds.

Ni(IV) is exemplified by oxo species like $BaNiO_3$ and the alkali salts of the hexafluoronickelate(IV) ion, M_2NiF_6. These are formed by fluorination of molten mixtures of $KCl\text{-}NiCl_2$ under moderate fluorine pressure. The salts are red or purple, forming bright red solution in HF. Oxygen is evolved from water while heating to 350°C in vacuum evolves F_2 :

$$3K_2NiF_6 \longrightarrow 2K_3NiF_6 + NiF_2 + F_2$$

K_2NiF_6 is diamagnetic, as expected for the low-spin t_{2g}^6 configuration. The purple compound $KNi(IO_6).nH_2O$ also contains Ni(IV). Ni(IV) is also known in complexes of the type NiL_2 where L is ligand shown in 28-XXIIIc. There are also octahedral complexes with dimethylglyoximate, $[Ni(dmg)_3]^{2-}$ and phosphine or arsine ligands, e.g., $[NiCl_2\ diphos_2]^{2+}$ (diphos = 1,2-bis(diphenylphosphino)ethane; also other chelating diphosphines).

28.9.4 Chemistry of nickel(II), $3d^8$

Ni(II) forms a wide range of simple as well as complex compounds.

Oxide and hydroxide

NiO is formed as a green solid in the thermal decomposition of the hydroxide, carbonate, oxalate or nitrate. It has the rock-salt structure and is readily soluble in acids.

$Ni(OH)_2$ is precipitated as a voluminous green gel by the addition of an alkali metal hydroxide solution to aqueous Ni(II). The precipitate turns crystalline on prolonged standing. From very concentrated solution of nickel(II), basic salts like $NiCl_2$. $Ni(OH)_2$ may be precipitated. $Ni(OH)_2$ dissolves readily in acids and also in ammonia forming soluble ammine complexes. A soluble $[Ni(OH)]_4^{4+}$ species is also likely to be formed when a concentrated alkali solution is added to a dilute solution of $Ni(ClO_4)_2$ in excess.

Halides

Nickel is the only element in the first transition series which forms halides in +II oxidation state only. All four anhydrous halides NiX_2 are known. Except NiF_2, all others may be prepared by direct reaction of the elements. NiF_2 is only moderately soluble in water, others being fairly so. From the solutions, $NiF_2 \cdot 3H_2O$ and $NiX_2 \cdot 6H_2O$ (X = Cl, Br, I) may be crystallized.

Nickel fluoride, NiF_2 : The yellow anhydrous salt (m.p. 1450°C) may be prepared by heating a mixture of nickel chloride and ammonium fluoride in a current of HF. A solution of $Ni(OH)_2$ or $NiCO_3$ in aqueous HF gives bluish green crystals of NiF_2, $3H_2O$. NiF_2 has a rutile structure.

Nickel chloride, $NiCl_2$: The yellow anhydrous salt (m.p. 1001°C) may be prepared by heating (i) powdered nickel in chlorine or (ii) the hydrated salt in a stream of HCl. Its layer structure gives rise to smooth scaly crystals (talc-like when touched) which readily sublime.

Grass-green, deliquescent, monoclinic prism crystals of $NiCl_2$, $6H_2O$ separate from solutions of NiO or $Ni(OH)_2$ in HCl. It loses water at 70°C to $NiCl_2$, $4H_2O$ and other lower.

Double salts with ammonium and alkali metal chlorides are known, e.g. $NH_4Cl \cdot NiCl_2 \cdot 6H_2O$ (green prisms) and $CsCl \cdot NiCl_2$ (yellow).

Nickel bromide, $NiBr_2$: The yellow anhydrous halide (m.p. 965°C), prepared by direct reaction, also possesses a layer structure. The hexahydrate obtained from solution is green.

Nickel iodide, NiI_2 : The anhydrous compound (Ni + I_2, heat) is black, m.p. 780°C. NiI_2, $6H_2O$ separates from solution as green crystals.

Other compounds

Direct reaction of nickel with various nonmetals like P, S, As, C, B etc. gives binary compounds containing nickel(II), but all these compounds may not be stoichiometric. Finely divided nickel absorbs large amount of hydrogen and a black hydride of formula NiH_2 is supposed to be formed when an ether solution of nickel(II) chloride is treated with hydrogen in presence of phenyl magnesium bromide.

Nickel sulphide, NiS. Found native as millerite, is formed as a black precipitate by the action of NH_3/NH_4HS on aqueous nickel(II). A dark brown colloidal solution formed initially coagulates on boiling — the precipitate is insoluble in dilute hydrochloric acid but dissolves in hot concentrated nitric acid or aqua regia.

$$3NiS + 8HNO_3 = 3Ni(NO_3)_2 + 2NO + 3S + 4H_2O.$$

The precipitate is actually nickel-deficient $Ni_{1-x}S$ with the NiAs structure. Other compositions like NiS_2 (pyrites structure), Ni_3S_4 (spinel structure) and Ni_3S_2 are also known.

Nickel carbonate, $NiCO_3 \cdot 6H_2O$. Addition of sodium carbonate solution to aqueous nickel(II) precipitates basic nickel carbonate. The normal carbonate is obtained as a green precipitate by adding sodium bicarbonate to aqueous solutions of nickel(II). Green double carbonates $M_2CO_3 \cdot NiCO_3 \cdot 4H_2O$ (M = Na, K) are also known.

Nickel cyanide, $Ni(CN)_2$. Addition of KCN solution to aqueous nickel(II) precipitates a pale blue hydrated cyanide which can be dehydrated between 180 - 200°C to yellow anhydrous $Ni(CN)_2$. The hydrated cyanide readily dissolves in excess cyanide to form the stable $[Ni(CN)_4]^{2-}$ ion which may be crystallized as $Na_2[Ni(CN)_4]$. $3H_2O$. Nickel(II) thiocyanate (yellow brown) also dissolves in excess SCN^- to $[Ni(NCS)_4]^{2-}$.

Nickel(II) cyanide shows the interesting property of forming clathrate (cage) compounds of the type $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ with aqueous ammonia and benzene. The pale-violet crystals contain the benzene molecule trapped inside a cage with sides made up of - Ni - C ≡ N - Ni units (Fig. 28.46). Many other organic molecules including pyridine, aniline, pyrrole and thiophene may be similarly trapped. The organic molecules show the same i.r. spectrum in the clathrates as in the free molecules, suggesting that no bonding occurs between the aromatic molecule and the nickel.

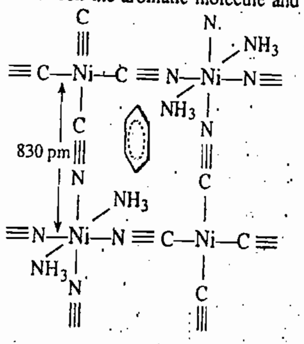


Fig. 28.46

Clathrate compound of $Ni(CN)_2$, NH_3 and C_6H_6.

The Ni and –CN groups form layers with NH_3 molecules bonded above and below the planes of the layers on alternate nickel atom. Half of the nickel are thus octahedrally coordinated to nitrogen and paramagnetic; the other-half coordinated to carbons in a square planar geometry and diamagnetic. The average magnetic moment per nickel atom is 2.2 B.M.

Aqueous solution chemistry

In absence of strong complexing agents, aqueous solutions of nickel(II) contain the green hexaaqua-ion $[Ni(H_2O)_6]^{2+}$. A number of hydrated salts also contain the ion, e.g. $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot nH_2O$ (n = 6, 7) and $Ni(ClO_4)_2 \cdot 6H_2O$. Ni^{2+} forms salts with even strongly oxidizing anions like ClO_2^- as well as with polarizable anions like CO_3^{2-}. We recall that Fe(II) and Co(II) are oxidized to the +III state by ClO_2^-.

Nickel sulphate, $NiSO_4 \cdot 7H_2O$ is isomorphous with Epsom salt. The emerald green rhombic crystals separate from a solution of NiO or $NiCO_3$ in dilute H_2SO_4 on evaporation; on prolonged exposure to air, this changes to the blue tetrahydrate. Crystallization above 54°C deposits green monoclinic crystals of $NiSO_4 \cdot 6H_2O$.

The hydrates partly lose water above 118°C to form the dihydrate, while anhydrous sulphate is formed above 280°C.

Double sulphates M_2SO_4, $NiSO_4 \cdot 6H_2O$ (M = NH_4 or alkali metal) are isomorphous with corresponding salts formed by bivalent Fe, Co, Zn and Mg. $(NH_4)_2SO_4$, $NiSO_4$, $6H_2O$ is used in electroplating baths in nickel plating.

Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ is isomorphous with $Co(NO_3)_2 \cdot 6H_2O$. The emerald green deliquescent monoclinic crystals are obtained from a solution of nickel, nickel carbonate or hydroxide in dilute nitric acid.

Complex compounds

Complexes of Ni(II) are numerous, and as pointed out earlier, they occur in a wide variety of geometry — octahedral, square planar, tetrahedral, square pyramidal as well as trigonal bipyramidal. As shown in Chapter 27, the energy difference between square planar, octahedral and tetrahedral geometry is not large and one complex may exist in more than one geometry, sometimes in an equilibrium mixture of different forms.

Trigonal planar 3-coordinate nickel is present in $[Ni(NPh_2)_3]^-$ and $Ni_2(NR_2)_4$. The latter has an Ni—Ni bond in addition to two μ—NR_2 groups. Tetrahedral complexes involve halogen ligands either in combination with large cations, e.g., $(Ph_4As^+)_2$ $[NiCl_4]$ or with phosphine or phosphine oxide type ligands, as in $(PPh_3)_2$ NiI_2 or $(Ph_3AsO)_2NiBr_2$. Cationic complexes of tetrahedral nickel are rare, but may occur with bulky ligands such as hexamethylphosphoramide (HMPA) : $[Ni(HMPA)_4]$ $(ClO_4)_2$.

Tetrahedral complexes of nickel are usually intensely blue in colour having absorption in the red end of the spectrum. They show magnetic moments around 3.5-4.1 B.M. corresponding to tetrahedral d^8 complexes.

Diamagnetic square planar Ni(II) complexes are formed with ligands of high field strength such as the $[Ni(CN)_4]^{2-}$ and the analytically important dimethyl glyoximate complex (Fig. 26-X). In the latter, planes containing the four nitrogen and nickel atoms are stacked one above another, alternate molcules being twisted through 90°; the nickel atoms thus appear in a chain with Ni—Ni distance ~ 325 pm, virtually achieving a tetragonal environment.

The $[Ni(CN)_4]^{2-}$ ion is formed with a high overall formation constant of about 10^{30} from solutions containing Ni^{2+} and excess CN^- ion. The potassium salt forms orange crystals $K_2[Ni(CN)_4]$. H_2O which are diamagnetic. Even bis(dimethylglyoximato) nickel(II) dissolves in excess KCN solution owing to the formation of the tetracyano complex.

Separation of cobalt and nickel

When excess KCN is added to a solution containing Co(II) and Ni(II) ions, soluble cyano complexes of both are formed :

$$CoCl_2 + 6KCN = K_4[Co(CN)_6] + 2KCl$$

$$NiCl_2 + 4KCN = K_2[Ni(CN)_4] + 2KCl.$$

On warming the solution with sodium hypobromite (Br_2 + NaOH), the nickel complex decomposes to the black hydrated oxide but the cobalt-complex remains in solution as hexacyanocobaltate(III) :

$$2K_2[Ni(CN)_4] + NaOBr + 4NaOH + H_2O = 2Ni(OH)_3 + 4KCN + 4NaCN + NaBr$$

$$2K_4[Co(CN)_6] + NaOBr + H_2O = 2K_3[Co(CN)_6] + 2KOH + NaBr.$$

The $[Ni(CN)_4]^{2-}$ ion may add one more CN^- ion to form $[Ni(CN)_5]^{3-}$ which may exist is both square pyramid and trigonal bipyramid structures.

Square planar complexes of Ni(II) are also known with phosphorus and arsenic donor ligands, e.g. $[Ni(diars)_2Cl_2]^+$ and $NiX_2(PR_3)_2$.

The green octahedral $Ni(H_2O)_6^{2+}$ ion turns violet on addition of excess concentrated ammonia when the $[Ni(NH_3)_6]^{2+}$ ion is formed; this may be precipitated with anions such as Br^- and I^-. The cationic chelates $[Ni(en)_3]^{2+}$ and $[Ni(dipy)_3]^{2+}$ are octahedral but $[Ni(en)_2(NO_2)]BF_4$ has a polymeric structure based on distorted octahedral cations with bridging NO_2 groups. Many other octahedral complexes are formed by direct reaction of donor molecules with nickel(II) salts. Thus pyridine combines with nickel(II) chloride to form the blue *trans*-$Ni(py)_4Cl_2$. In presence of weakly coordinating anions hexapyridine complexes are formed, for example nickel(II) nitrate gives $[Ni(py)_6](NO_3)_2$. Above 110°C, $Ni(py)_4Cl_2$ decomposes to yellow-green $Ni(py)_2Cl_2$ which loses further ligands at 170°C to form $Ni(py)Cl_2$. The coordination number of nickel in both these complexes are retained at 6.

The interconversion of nickel(II) complexes from one geometry to another may sometimes show temperature dependence, accompanied by a shift in the $d-d$ absorption band and the observed colour of the species (*thermochromism*). $(NR_xH_{4-x})_2NiCl_4$ complexes (x = 1, 2, 3) are yellow brown or green at low temperatures, with chlorine bridged octahedral Ni(II) but changes to blue tetrahedral complexes at high temperatures.

28.9.5 Lower oxidation states (+I, 0, –I)

Reduction of the $[Ni(CN)_4]^{2-}$ ion with potassium in liquid ammonia results in $K_4[Ni_2^{I}(CN)_6]$ (*Bellucci's salt*) and finally $K_4[Ni^{\circ}(CN)_4]$. The red diamagnetic Ni(I) complex with Ni – Ni bond may also be prepared by reduction of $K_2[Ni(CN)_4]$ in aqueous medium by sodium amalgam or hydrazine. Paramagnetic nickel(I) species are joined by phosphine and related ligands when Ni^{2+} is reduced electrolytically in MeCN in presence of such ligands; they are usually tetrahedral or trigonal bipyramidal. $Ni(PPh_3)_3X$ (X = Cl, Br, I) are all tetrahedral.

The final reduction product of $K_2[Ni(CN)_4]$ in liquid ammonia with potassium is the yellow species containing nickel(0), $K_4[Ni(CN)_4]$. The $[Ni(CN)_4]^{4-}$ ion is isoelectronic with $Ni(CO)_4$ and is believed to be tetrahedral. This may undergo substitution with other neutral ligands to give other nickel(0) compounds, e.g.

$$Ni(SbPh_3)_4 \xleftarrow{Ph_3Sb} K_4Ni(CN)_4 \xrightarrow{CO} K_2[Ni(CO)_2(CN)_2]$$

Other nickel(0) species include $Ni(CO)_4$, $Ni(PF_3)_4$, $Ni(PCl_2Me)_4$ and $Ni(Ph_2PCH_2CH_2PPh_2)_4$. Many of these can be prepared directly from the metal similar to $Ni(CO)_4$:

$$Ni + 4PF_3 \longrightarrow Ni(PF_3)_4 \text{ (100°C, 350 atm)}$$

Other ligands capable of stabilizing low oxidation states are also effective in forming compounds with Ni(0), for example 2, 2′-dipyridyl, 1,10-phenanthroline, acetylide ion and aryl isocyanides. Nickel carbonyl has been discussed separately below.

Ni(–I) is present in the carbonyl anion $[Ni_2(CO)_6]^{2-}$ formed in the disproportionation reaction

$$3Ni(CO)_4 + 6py \longrightarrow [Ni(py)_6][Ni_2(CO)_6] + 6CO.$$

Nickel carbonyls

Nickel tetracarbonyl, $Ni(CO)_4$, was the first metal carbonyl to be prepared (1890, Mond) and its ready volatility was used in the isolation and purification of nickel. As mentioned earlier, it is formed when carbon monoxide reacts with nickel at ordinary temperature (30°C), more readily under high pressure (~ 100 atmosphere).

$Ni(CO)_4$ is a colourless liquid with high refractive index, b.p. 42°C; m.p. –25°C. The liquid is immiscible with water but soluble in ether, benzene and chloroform. It burns in air with a bright luminous flame :

$$Ni(CO)_4 = Ni + 2CO_2 + 2C.$$

Its vapour is poisonous which explodes at 60°C. It is decomposed by halogens and their hydracids, specially HI.

$$Ni(CO)_4 + Br_2 = NiBr_2 + 4CO$$

$$Ni(CO)_4 + 2HI = NiI_2 + H_2 + 4CO.$$

Reduction of $Ni(CO)_4$ by alkali metals in tetrahydrofuran gives carbonylate anions like

$$4Ni(CO)_4 + 2Na \longrightarrow Na_2[Ni_4(CO)_9] + 7CO.$$

An unstable dimeric nickel carbonyl hydride may be isolated as a red ammoniate in liquid ammonia.

$$2Ni(CO)_4 + 2Na + 6NH_3 \longrightarrow [NiH(CO)_3]_2.4NH_3 + 2CO + 2NaNH_2.$$

The disproportionation of $Ni(CO)_4$ with pyridine has been mentioned before. Phosphines, arsines etc. give substitution products with $Ni(CO)_4$ which are stable with respect to disproportionation. For example, with PPh_3, we get

$$Ni(CO)_4 \longrightarrow Ni(CO)_3(PPh_3) \longrightarrow Ni(CO)_2(PPh_3)_2.$$

The $Ni(CO)_4$ molecule is tetrahedral with linear Ni-C-O bonds, as shown by electron diffraction studies on the vapour and X-ray studies on the solid. The Ni – C distance is 184 pm and C – O distance is ~ 115 pm.

Nitrosyl compounds

Nickel does not form any simple nitrosyl. $Ni(CO)_4$ reacts with NO as

$$Ni(CO)_4 + 4NO \longrightarrow Ni(NO)(NO_2) + 4CO + N_2O.$$

$Ni(NO)(NO_2)$ has a blue color. It ignites in contact with air. Substituted nickel carbonyls may be reacted with NO to form complexes like $Ni(NO)_2(PPh_3)_2$.

Reaction of nickel(II) halides with NO in presence of zinc (or other halogen acceptors) gives Ni(NO)X. These react with $Ni(CO)_4$ to give $Ni(NO)X_2$. The compounds contain the NO^+ group and are supposed to be polymeric.

28.9.6 Organometallic compounds

Simple alkyls and aryls of nickel are not very stable but may be stabilized by ligands. Yellow or brown diamagnetic compounds of the type $(R_3P)_2NiAr_2$ may be prepared by reacting square planar complexes $(R_3P)_2NiX_2$ with aryl Grignard reagents. Olefin, acetylene, cyclobuta-dienyl and cyclopentadienyl compounds of nickel are well established. Nickelocene, $Ni^{II}(\eta^5-C_5H_5)_2$, is a bright green reactive solid. This may be obtained by adding a solution of $NiCl_2$ in dmso (dimethylsulphoxide) to a solution of KC_5H_5 in 1,2-dimethoxyethane. The sandwich compound (c.f. ferrocene) is paramagnetic ($\mu \simeq 2.86$ BM), with two additional electrons over ferrocene which are accomodated in an antibonding orbital. It is readily oxidized to the orange-yellow cationic species $[Ni(\eta^5-C_5H_5)_2]^+$. Reaction of nickelocene with a Lewis acid such as BF_3 gives rise to a "double sandwich" or "triple-decker sandwich" cation (Fig. 28.47), $[Ni_2(\eta^5-C_5H_5)_3]^+$:

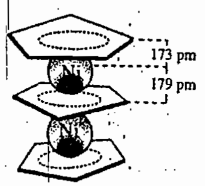
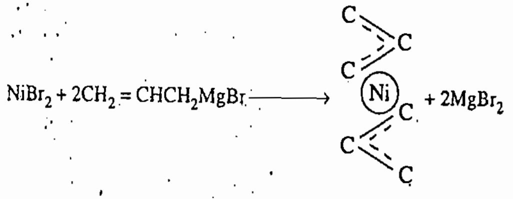
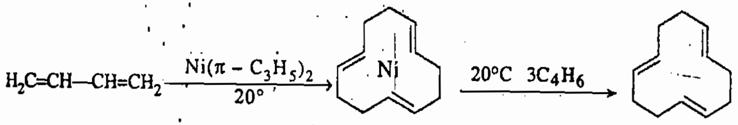


Fig. 28.47
The triple decker sandwich cation.
The C_5H_5 rings are in distorted staggered arrangement.

Bis-(π-allyl) nickel is another sandwich structured compound obtained by the reaction



The compound is pyrophoric in air but its ether solution is stable to deoxygenated water. It is a very active catalyst in the cyclotrimerization of butadiene to cyclododeca–1,5,9-triene :



28.9.7 Detection and estimation

In the *borax bead test*, nickel compounds form nickel metaborate $Ni(BO_2)_2$ or $Na_2[Ni(BO_2)_4]$ in the oxidizing flame, colouring the bead brown. In the reducing flame, the bead appears grey due to metallic nickel.

The most delicate test for nickel is the *dimethyl glyoxime test* (Tschugaeff, 1905) : an alcoholic solution of the reagent gives a bright red precipitate with a nickel salt solution made just ammoniacal or buffered with sodium acetate (to neutralise the proton liberated)

$$Ni^{2+} + 2dmgH = Ni(dmg)_2 + 2H^+$$

The precipitate is unaffected by acetic acid, ammonia or H_2S but mineral acids or KCN decompose it. Iron(II) forms a red but soluble complex with the reagent.

Diphenyl glyoxime is an even more sensitive reagent.

Nickel may be estimated conveniently by filtering the precipitate of nickel dimethyl glyoximate through a sintered glass crucible (Gooch crucible), drying at 110° — 120° and weighing as $Ni(C_4H_7O_2N_2)_2$.

28.10 COPPER

Cu : [Ar] $3d^{10}4s^1$ **Atomic number** : 29 **Atomic weight** : 63.57, 63.55

M.P. : 1083°C **B.P.** : 1570°C **Density** : 8.95 g cm^{-3}

Archaeological finds on the island of Crete dating back to about 3500 B.C. revealed not only copper but bronze articles as well. Among the copper mines of antiquity the particularly famous ones were those on the island of Cyprus to which, it has been suggested, copper derived its Latin name cuprum (via cyprium).

28.10.1 Introduction

History : Copper and its alloy with tin (bronze) marked a whole epoch in the history of mankind — the Bronze Age. This is because native copper was fairly abundant in nature and the metal could also be extracted relatively easily from its ores.

Occurrence : Copper is present to the extent of 68 ppm (0.007%) in the earth's crust, slightly less than that of nickel. The major ore is copper glance or *chalcopyrites*, $CuFeS_2$. Other common ores are *cuprite*, Cu_2O; *chalcocite*, Cu_2S; malachite, $CuCO_3.Cu(OH)_2$. Large deposits are found in the North and South America, Chile, Congo and the Russian countries.

In India, two main deposits of copper ore are present in Bihar and Rajasthan. In Singhbhum, sulphide ore assaying around 2.4 per cent of copper are found in a long belt extended over Mosaboni, Rakha, Surda and Dhobhani mines. The Rakha and Dhobhani workings have practically gone out of production. An ore reserve of about 3,497 million tonnes (~ 1.49% Cu) has been estimated at Mosaboni and Surda. Ores from these areas are processed by Indian Copper Corporation at Moubhandar (near Ghatsila). Small quantities of copper also occur at Chhota Nagpur, Hazaribag and Santhal Parganas.

Rajasthan still bears evidence of flourishing copper industry of India in the middle age at Alwar, Ajmer and Khetri. At present, the important occurrences of copper ore are those of Khetri, Babai and Daribo in Jhunjhunu and Alwar districts. The deposits at Khetri reveal a reserve of over 100 million tonnes of ore with less than one per cent copper.

Sporadic occurrences of copper ore are known at Kerala (*Vavathur*), Karnataka (*Chitradurga* and *Hassan*), Andhra Pradesh (*Yallambailu in Khammam*; also in Nellore and Krishna districts), Tamilnadu (*Mamandur* in South Arcot), Punjab (*Mothoka and Ghatsher* in Mahendragarh district), Uttar Pradesh (*Dandokhan* and Kandhara in Garhwal) and West Bengal (Darjeeling). Sikkim has workable deposits of ore with high copper content (~ 3 - 7%) in association with bismuth and antimony.

Copper is present in the *haemocyanin* of blood of cuttlefish which acts like haemoglobin as an oxygen carrier. Copper also helps the formation of haemoglobin in the body. Minute quantities of copper are also present in plants, particularly in green peas.

28.10.2 The element

Extraction

Copper is mainly extracted from the sulphide ore by self-reduction process. The ores are often low-grade (~ 0.5% Cu) and require prior concentration (up to 15 - 20% Cu). The main steps are as follows :

1. *Concentration* by froth-floatation.

2. *Roasting and smelting* (~ 1400°C) with addition of silica in a reverberatory furnace (since the ores are in a finely powdered form, blast furnaces are not suitable). FeS is preferentially oxidized prior to Cu_2S since iron is more basic.

$$2FeS + 3O_2 = 2FeO + 2SO_2.$$

The iron oxide forms slag with silica. The molten mass separates into a top layer of slag ($FeSiO_3$) and a lower layer of copper matte, containing mainly Cu_2S and FeS.

3. *Self reduction* : The molten matte is further oxidized by air blast in a converter (similar to the Bessemer converter) when the remaining iron is mainly oxidized. More silica is added which forms slag with the iron oxide. After removing the slag, the copper sulphide is partly oxidized by air to Cu_2O; this combines with the remaining Cu_2S producing copper.

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2; \quad 2Cu_2O + Cu_2S = 6Cu + SO_2$$

As the sulphur dioxide leaves, the metal during cooling, the crude copper obtained develops blisters and hence is called "blister copper".

4. The crude copper is refined electrolytically in a bath of acidified copper sulphate solution using crude copper as anode and pure copper cathode. The impurities from the anode are processed for the recovery of gold, silver and platinum.

Wet metallurgy

Low grade sulphide ores may be stacked in moist heaps in air when the iron and copper sulphides are slowly oxidizd to sulphates. The heaps are then leached with water and copper precipitated from the solution by scrap iron.

Alternatively, the burnt copper pyrites (from the manufacture of sulphuric acid) may be roasted with 10—15% common salt to convert the copper into soluble chloride. This is leached with water and copper precipitated by scrap iron.

Copper may also be electrodeposited from the copper sulphate solution obtained in the above processes.

Copper ores other than the sulphides may also be leached with dilute sulphuric acid and the copper electrodeposited. The oxide or carbonate ores may also be reduced with coke in a reverberatory furnace.

Biotechnology has opened a new possibility for extraction of copper from very low grade ores by the action of microbes — the method has already been adopted in the U.S.A.

Properties

Copper is a reddish-brown lustrous metal with high electrical and thermal conductivity. It is soft, tough, malleable and ductile (which can be easily rolled and hammered into thin sheets or drawn into fine wire). The metal forms an fcc lattice like nickel.

The colours of copper and its congeners silver and gold arise from the presence of a filled *d*-band just below the *s-p* conduction band. In copper, the bands are separated by ~ 220 kJ mol^{-1} or 2.3 eV $atom^{-1}$; excitation of electrons from the *d*-band to the *sp* band accompanies absorption of energy in the green and blue regions of the visible spectrum. In silver, the corresponding energy gap (~ 385 kJ mol^{-1}) is much higher, giving absorption in the uv region. For gold, the energy gap is again lowered, but being slightly greater than that in copper, absorption now takes place in the near uv and blue region of the spectrum, transmitting the characteristic golden yellow colour.

Copper slowly tarnishes in air owing to the formation of a thin film of oxide (and sulphide). On long exposure to air, copper articles get covered with a green basic sulphate $CuSO_4.3Cu(OH)_2$. In presence of carbon dioxide, basic copper carbonate is formed

$$2Cu + H_2O + CO_2 + O_2 = CuCO_3.Cu(OH)_2.$$

Being less electropositive than hydrogen, copper is not attacked by water or steam at red heat or cold non-oxidizing acids in absence of air. In presence of air, copper slowly dissolves in dilute H_2SO_4 or concentrated HCl.

$$2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O.$$

Hot concentrated nitric and sulphuric acids readily oxidize the metal; hot concentrated HCl slowly evolves hydrogen

$$2Cu + 8HCl = 2H_3[CuCl_4] + H_2$$

Copper also dissolves in aqueous ammonia in presence of air, forming a deep blue solution

$$2Cu + 8NH_3 + 2H_2O + O_2 = 2[Cu(NH_3)_4(OH)_2]$$

The metal also combines directly with chlorine and sulphur on heating. Less electropositive metals such as silver are displaced from solution by copper while more electropositive metals like zinc precipitate copper from solutions containing copper(II). Finely divided copper reduces a solution of Fe(III) to Fe(II) :

$$Fe_2(SO_4)_3 + Cu = CuSO_4 + 2FeSO_4$$

Uses

(i) The principal use of copper is in the electrical industry as a good conductor — copper is extensively used in making wires, cables and other contacts for various use in generators, transformers, motors and any electrical equipment. In certain cases, it is now getting replaced by cheaper aluminium.

(ii) Copper was also used in making utensils, pipes and coins but in these fields also, aluminium, stainless steel and other alloys are gaining popularity.

(iii) Copper alloys are extensively used in various domestic and industrial purposes. We have already mentioned a number of such alloys containing manganese and/or nickel, for example constantan, manganin and monel metal. Alloying improves the mechanical strength and corrosion resistance of the metal. Some alloys with non-ferrous metals are

Brasses : These contain from 57 to 97% Cu, the remainder being zinc and small quantities of other elements like Al, Sn, Ni, Mn and Pb which modify the mechanical and chemical properties. Examples : *Brass* (Cu 70 Zn 30), *Muntz metal* (Cu 60 Zn 40), *Delta metal* (Cu 55, Zn 40 Fe 5). Delta metal, nearly as hard as steel and resistant to sea water, is used in making ship's propellers, bearings etc.

Bronzes : These contain 4 — 25% tin and other elements like P(1 - 2%), Si (0.5%), Al (8 - 10%). These are hard and mechanically strong but cannot readily be worked. With tin contents below 8%, they were used in statues, coins etc. and those containing 10-20% Sn are used for bearings, gears and taps and fittings. *Gun metal* (Cu 85, Sn 5, Zn 10), *Bell metal* (Cu 80, Sn 20), *Bronze* (Cu 92 Sn 8) are examples.

Now-a-days, these are being gradually replaced by steel and cheaper and lighter aluminium base alloys. Overall, the traditional importance of brass and bronzes have greatly declined.

Cupronickels contain from 10 to 30% of nickel and possess high tensile strength and are resistant to chemical corrosion, rust and acids. These are used in chemical plant engineering, telephone systems, turbine blades etc. Monel metal (see nickel) belongs to this category. Silicon-copper (1.5 - 3% Si), aluminium copper (5 - 10% Al + small amounts of Fe, Ni, Si), chrome copper (0.1 — 1.0% Cr and a small amount of Si), beryllium copper (1.5 - 2% Be and also Cr) alloys have outstanding combinations of mechanical properties like workability, hardness, weldability and corrosion resistance etc.

General chemical features

In the early periodic table of Mendeleev, copper, together with silver and gold, were placed in Gr IB, by the alkali metals of Gr IA. But the physical as well as chemical properties of the elements in these two subgroups vary widely. The alkali metals are all soft, low metling, low density and highly electropositive metals while the "coinage metals" copper, silver and gold (from their extensive use in making coins) are relatively noble metals with high melting point and high density. The differences are naturally associated with the nature of the penultimate core — for alkali metals this is the s^2p^6 core while for copper etc. it is a d^{10} core; the latter is much less efficient in shielding the valence shell *s* electrons.

Gr. IB metals have higher first ionization energy and smaller ionic radii. Involvement of the *d*-electrons in metallic bonding imparts a higher melting point to copper. However, it is easier to involve a filled *d*-shell in valence participation than a filled s^2p^6 core of the noble gas type and the second and third ionization energies of copper are lower than those of corresponding alkali metals. This imparts the transition metal character to copper. Also, the sum of $I_1 + I_2$ is easily overcome by the gain in hydration energy of the smaller Cu^{+2} ion over the Cu^+ ion, favouring Cu(II) in solution. This leads to disproportionation of Cu(I) in aqueous solution to Cu(II) and Cu(0). In the solid state, copper(I) compounds are quite stable. As we shall see in the next chapter, the situation becomes somewhat different for silver and gold.

28.10.3 Copper(III), $3d^8$

Copper(III) is isoelectronic with nickel(II) but forms only a few compounds in this state. The increased nuclear charge and consequent higher value of the sum of ionization energies $I_1 + I_2 + I_3$ seem to be the main reason for this. There are no simple halides CuX_3 but pale green K_3CuF_6 may be obtained by fluorination of a mixture of KCl and $CuCl_2$ at 250°C. The compound shows a magnetic moment equal to 2.8 B.M., corresponding to the expected $t_{2g}^6 e_g^2$ configuration.

The square planar complex $CsCuF_4$ is obtained by reacting F_2 with $CsCuCl_3$.

Heating mixtures of CuO with alkali metal superoxides in oxygen produces solid cuprate(III) compounds, e.g. $KCuO_2$ — a steel blue diamagnetic solid. The suggested structure is linked square planar CuO_4 units. Oxidation of copper(II) salts in alkaline medium in presence of the alkali metal periodate or tellurate give $Na_7[Cu(IO_6)_2]$. $12H_2O$ and $Na_9[Cu(TeO_6)_2]$. $16H_2O$, both diamagnetic.

28.10.4 Chemistry of copper(II), $3d^9$

This is the main oxidation state of copper. The d^9 configuration suggests paramagnetism and Jahn-Teller distortion both in simple compounds and complexes.

Oxide and hydroxide

The black copper(II) oxide, CuO, is formed on heating copper in oxygen but is best prepared by thermal decompostion of the basic carbonate, nitrate or hydroxide.

It is readily reduced to copper by hydrogen or carbon monoxide around 300°C and is used as an oxidant in organic chemistry.

In the crystal lattice of the oxide, each copper is coordinated by four oxygen in a square planar environment while each oxygen has four copper atoms in tetrahedral coordination.

$Cu(OH)_2$ is obtained as a blue precipitate by adding alkali to aqueous copper(II). The precipitate darkens on standing due to dehydration to the oxide. It is soluble in concentrated alkali, forming $[Cu(OH)_4]^{2-}$ anion, and in ammonia solution, forming deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. This deep blue solution, known as *Schweizers reagent*, dissolves cellulose (e.g., cotton) and the solution is used in making cuprammonium rayon.

Halides

Only fluoride, chloride and bromides of Cu(II) are known. Iodide reduces copper(II) owing to the precipitation of Cu_2I_2 (Chapter 9) and hence CuI_2 is not formed. CuF_2 is a white hygroscopic solid, $CuCl_2$ is yellow while $CuBr_2$ is black. The anhydrous halides may be prepared by direct reaction. The hydrated halides $CuX_2.2H_2O$ may be obtained by dissolving $CuCO_3$ or $Cu(OH)_2$ in appropriate HX and crystallizing. $CuF_2.2H_2O$ is light blue; $CuCl_2.2H_2O$ forms emerald green crystals but $CuBr_2$ is almost black. The structure of the solid halides show Jahn-Teller distortion, for example,

CuF_2; 4 Cu – F 193 pm 2Cu – F 227 pm

$CuCl_2$; 4 Cu – Cl 230 pm 2Cu – Cl 295 pm

The crystal structure of $CuCl_2$ consists of infinite chains of planar $CuCl_4$ groups with chlorine bridges completing the elongated octahedra. $CuCl_2.2H_2O$ has a square planar arrangement of two Cl at 228 pm and two H_2O at 193 pm; two further chlorine atoms at 295 pm make the distorted octahedron.

Other compounds

Copper(II) sulphate, $CuSO_4.5H_2O$ is prepared by dissolving scrap copper in dilute H_2SO_4 in presence of air and crystallizing. The structure consists of four water molecules in a square plane around the copper with two oxygen atoms from two sulphate ions, completing the tetragonal structure (Fig. 17.11). The fifth water molecule is hydrogen bonded as shown.

The dark blue ammine-aqua complex $CuSO_4.4NH_3.H_2O$ can be crystallized from solutions of copper(II) sulphate saturated with ammonia. This has a square pyramidal environment around the copper which lies about 20 pm above the plane of the four nitrogen atoms. The violet pentaammine, $CuSO_4.5NH_3$ is formed with gaseous ammonia and $CuSO_4$ solution.

Copper nitrate is obtained as deep blue deliquescent crystals $Cu(NO_3)_2.3H_2O$ from nitric acid solutions of Cu(II). The anhydrous nitrate may be prepared by dissolving copper metal in liquid N_2O_4

$$Cu + 2N_2O_4 \longrightarrow Cu(NO_3)_2 + 2NO$$

The blue-green solid that separates has the composition $Cu(NO_3)_2.N_2O_4$. Heating in a vacuum at 120° leaves the blue anhydrous nitrate. This has two crystalline structures based on linking of the Cu(II) ions by nitrate ions. $Cu(NO_3)_2$ can be sublimed in vacuum at 200°C — the vapour has discrete monomeric $Cu(NO_3)_2$ molecules having copper atoms four-coordinated by oxygen atoms from the two bidentate nitrate groups.

Copper carbonate : The normal carbonate $CuCO_3$ does not exist but basic carbonates occur in nature, e.g. malachite. Basic copper carbonate is formed as a green precipitate from solutions of sodium carbonate and copper(II) sulphate (see below).

Copper(II) acetate : The acetate is dimeric and hydrated : $[Cu_2(OCOCH_3)_4].2H_2O$, having the same structure as its chromium analog (Fig. 28.34); the Cu – Cu distance of 264 pm is slightly longer than that in the metal (256 pm). In this compound, and in other carboxylates, weak Cu – Cu interaction results only in partial quenching of the spin magnetic moments of the ions (1.4 B.M. per Cu^{2+} ion.).

Aqueous chemistry

The tetragonally distorted blue hexaaqua ion $[Cu(H_2O)_6]^{2+}$ is present in solutions of copper(II) in water; the ion is mildly acidic, often causing precipitation of basic salts :

$$[Cu(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Cu(H_2O)_5(OH)]^+ + H_3O^+$$

$$2[Cu(H_2O)_5OH]^+ + CO_3^{2-} \rightleftharpoons [Cu(OH)(H_2O)_5]_2CO_3 \text{ or } CuCO_3.Cu(OH)_2$$

The hexaaqua ion is also present in $[Cu(H_2O)_6](ClO_4)_2$.

The Cu(II)-Cu(I) potential

$$Cu^{2+} + e \rightleftharpoons Cu^+; \quad E° = 0.15V$$

suggests that Cu(II) should be a mild oxidizing agent. As we have seen earlier (Ch. 9), insolubility of CuI thermodynamically drives the reaction

$$Cu^{2+} + 2I^- \longrightarrow CuI \downarrow + \tfrac{1}{2}I_2$$

almost to completion.

The Cu(II) — Cu(I) potential is also changed significantly in presence of CN^- when the Cu(I) bcomes more stabilized.

Many complexes of copper(II) may be prepared by substitution in the hexaaqua ion, e.g., the deep blue ions $[Cu(NH_3)_4(H_2O)_2]^{2+}$ or $[Cu(en)_2(H_2O)_2]$. $[Cu(en)_3]^{2+}$ is formed only with very high concentration of the ligand while $[Cu(NH_3)_6]^{2+}$ is formed in liquid ammonia. Ligands like hydrazine and methylhydrazine reduce Cu(II) in aqueous solution.

Complex compounds

We have already mentioned several complexes of copper (II), for example the aqua, ammine-aqua and ethylenediamine complexes. The d^9 configuration of Cu(II) is susceptible to Jahn-Teller distortion in regular octahedral and tetrahedral ligand fields and as discussed earlier (Ch. 27), the limiting case of distortion by elongation of the axial bonds leads to a virtually square planar geometry as in $[Cu(NH_3)_4(H_2O)_2]^{2+}$. There are also examples of complex compounds with other geometries.

Copper(II) readily forms chloro complexes in aqueous solution from which many salts of the stoichiometry M^ICuCl_3 (red) have been isolated. But the coordination number of copper in these complexes are not necessarily three. They mostly contain $Cu_2Cl_6^{2-}$ ions formed by two tetrahedra sharing an edge. For smaller cations like Li^+, the dimers appear to be linked by long Cu – Cl bonds forming infinite chains with five or six-coordinate copper(II). $CsCuCl_3$ forms infinite chains of distorted octahedra sharing opposite faces.

Copper(II) also forms chloro-complexes in coordination numbers four and five. The yellow $[CuCl_4]^{2-}$ ion, also formed from the $[Cu(H_2O)_6]^{2+}$ ion, is planar in $(NH_4)_2[CuCl_4]$ but with larger cations such as Cs^+, the complex anion is a flattened tetrahedron. Many complexes of copper(II) halides with other ligands are also known, for example the tetragonal pyridine complex $CuCl_2py_2$, and the tetrahedral phosphine oxide complexes $CuCl_2(Ph_3PO)_2$. 2,2′-dipyridyl forms $CuX_2(dipy)_2$ adducts which are actually examples of trigonal bipyramid coordination in the cation $[Cu(dipy)_2X]^+$. Other trigonal bipyramid complexes are $[CuCl_5]^{3-}$, $[CuBr_5]^{3-}$ and $[CuCl_2Br_3]^{3-}$ (axial Cl). These are usually stabilized in lattice by large cations like $[Cr(NH_3)_6]^{3+}$.

Cu(II) forms many other square planar complexes, particularly when the ligand field is strong. Addition of aqueous KCN to aqueous Cu(II) at room temperature causes reduction to colourless $[Cu^I(CN)_4]^{3-}$ with evolution of $(CN)_2$, but in aqueous methanol at low temperatures it is possible to characterize the violet $[Cu(CN)_4]^{2-}$ ion which has the square planar structure. $[Cupy_4]^{2+}$ is also square planar. There are also indications for the same compound occurring in two different structures (compare Ni^{II}). The complexes $CuCl_2L_2$, where L is an N-oxide (e.g. pyridine N-oxide, C_5H_5NO), have a yellow tetrahedral form and a green form, supposed to be *trans* square planar.

The deep blue solution obtained by mixing Fehling solutions no. 1 and 2 contain monomeric, dimeric and also polymeric tartrate complexes depending on pH. One of the dimers, $Na_2[Cu\{(\pm)tart\}]$. $5H_2O$ has Cu^{II} in square planar coordination with a Cu – Cu distance of 299 pm.

Six coordinate copper(II) complexes are mostly distorted but $K_2Pb[Cu(NO_2)_6]$ shows a *regular* octahedral environment of six nitrogen atoms around the copper at room temperature. We have already seen examples of distortion in CuF_2 and $CuCl_2$ which have octahedral environment of the halide ions. The $[Cu(H_2O)_6]^{2+}$ is similarly distorted.

The increasing Jahn-Teller distortion with increase in ligand field is nicely demonstrated by the ammine-aqua complexes of copper(II). Addition of ammonia to $Cu(H_2O)_6^{2+}$ gradually displaces the water molecules upto $[Cu(NH_3)_4(H_2O)_2]^{2+}$ but the fifth ammonia molecule adds only with extreme difficulty (extremely low formation constant) and the sixth water molecule can be displaced only in liquid ammonia. In $[Cu(H_2O)_2(NH_3)_4]^{2+}$ four nitrogens are at 205 pm while the oxygens are at 259 and 337 pm distance. Similarly, addition of ethylenediamine to aqueous Cu(II) readily gives rise to $[Cu(en)(H_2O)_4]^{2+}$ and $[Cu(en)_2(H_2O)_2]^{2+}$ but $[Cu(en)_3]^{2+}$ is formed only with very high concentrations of the ligand. We recall that in the trischelate distortion gives rise to a strained situation (Fig. 27.20).

An example of seven-coordinate pentagonal bipyramid complex of copper(II) is provided by $[Cu(H_2O)_2(DPS)]^{2+}$ where DPS = 2, 6-diacetylpyridine bis(semicarbazone).

A distorted dodecahedral structure containing 8-coordinate Cu(II) is found in $Ca[Cu(COOCH_3)_4]$. $6H_2O$.

The electronic spectra and magnetic properties of copper(II) complexes (d^9) are virtually equivalent to an one-electron case but complicacies arise owing to distortions. The complexes are usually blue or green due to presence of absorption bands around 600-900 nm. Exceptions arise when strong charge transfer bands tail into the blue end of the visible region, and the colour appears red or brown. Solutions containing $[Cu(H_2O)_6]^{2+}$ are light blue which become intense blue on adding ammonia or ethylenediamine (Fig. 27.35 and 27.36). The aqua ion absorbs weakly around 800 nm; as the ligand field increases, absorption maxima shifts to about 600 nm in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and the molar absorbance also shows nearly five fold increase in keeping with increased distortion. In $[Cu(NH_3)_5(H_2O)]^{2+}$, however, the fifth ammonia molecule is only weakly bound and the absorption maximum again shifts to a lower wavelength (~ 700 nm).

In absence of Cu – Cu interaction, the magnetic moments of copper(II) complexes fall in the range 1.75 — 2.20 B.M. for all stereochemistry. The value is practically independent of temperature except below 5K.

28.10.5 Copper (I), $3d^{10}$

Copper(I) has the closed shell $3d^{10}$ configuration highly stabilized by exchange energy. In solid compounds, this state is often thermodynamically stable one at moderate temperatures. Thus Cu_2O is formed at high temperatures from CuO and $CuBr_2$ decomposes on heating to CuBr. There are a large number of both simple and complex compounds of Cu(I). As expected, they are all diamagnetic and colourless, except when in combination with coloured counter ions or having CT bands in the visible range.

Oxide

Copper(I) oxide or cuprous oxide, Cu_2O(red) is formed when alkaline solutions of copper(II) are reduced by mild reducing agents like glucose. In Fehling's solution, tartrate ions prevent the precipitation of $Cu(OH)_2$ by forming a soluble complex.

Red Cu_2O is also precipitated by boiling copper sulphate solution with sodium carbonate and sodium sulphite :

$$2CuSO_4 + 2Na_2CO_3 + Na_2SO_3 = Cu_2O + 3Na_2SO_4 + 2CO_2$$

The oxide is also the stable oxide of copper at high temperatures but when heated in air below 1000°C, it forms CuO.

Cu_2O is insoluble in water, but dissolves in concentrated HCl forming a colourless solution :

$$Cu_2O + 6HCl = 2H_2[CuCl_3] + H_2O$$

In absence of air, Cu_2O also dissolves in strong ammonia solution to a colourless solution; otherwise, the blue $Cu(NH_3)_4^{2+}$ ion is formed. The oxide disproportionates in dilute H_2SO_4

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

It is a reducing agent :

$$3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O$$

$$Cu_2O + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + H_2O.$$

Cu_2O occurs in nature as cuprite. The oxide imparts a deep red colour to glass and is used in making *ruby glass.*

Halides

CuF is not well characteristized; the other halides are all colourless solids insoluble in water. CuCl is readily prepared by reducing Cu(II) with copper metal or sulphur dioxide in hydrochloric acid. We have seen CuI precipitated during the titration of Cu(II) iodimetrically.

In the solid halides, the halide ions tetrahedrally surround the Cu^+ ions. In the vapour, CuCl is present mainly as a trimer with puckered cyclic structure.

Though insoluble in water, the halides dissolve readily in solutions of ligands like Cl^-, CN^-, NH_3 and $S_2O_3^{2-}$. Thus, CuCl dissolves in HCl to give $CuCl_2^-$, $CuCl_3^{2-}$ or $CuCl_4^{3-}$ ions depending on the concentration of Cl^-.

Copper(I) chloride, CuCl. It was first prepared by Robert Boyle (1666) by heating $HgCl_2$ with copper. It is formed by thermal decomposition of cupric chloride or reduction of copper (II) :

(i) $Cu + CuO + 2HCl = 2CuCl + H_2O$

The mixture is boiled with concentrated HCl, then poured in large excess of cold water to decompose the chloro complex. The water should be boiled previously to expel dissolved oxygen which may oxidize copper(I). The precipitate of CuCl is filtered out and washed.

(ii) $2CuCl_2 + SO_2 + 2H_2O = 2CuCl\downarrow + H_2SO_4 + 2HCl$

$$2CuSO_4 + 2NaCl + 2H_2O + SO_2 = 2CuCl\downarrow + 2NaHSO_4 + H_2SO_4.$$

The precipitate is filtered and washed.

CuCl is a white powder (m.p. 422°C) which gradually turns green in moist air owing to slow oxidation to basic chloride, $CuCl_2.Cu(OH)_2$. The ammoniacal solution gives a red precipitate with acetylene.

CuBr is formed by adding NaBr to a solution of $CuSO_4$ in presence of excess SO_2.

$$2CuSO_4 + 2NaBr + SO_2 + 2H_2O = 2CuBr + 2NaHSO_4 + H_2SO_4$$

CuI is readily precipitated on adding KI to $CuSO_4$ solution.

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$$

The iodine may be reduced by SO_2 or $FeSO_4$.

CuI turns red, then black on heating, but becomes white again on cooling. It also dissolves in aqueous ammonia or solutions of thiosulphate, cyanide etc.

Other Compounds

Cuprous sulphate, Cu_2SO_4 is obtained as a white powder by heating copper(I) oxide with dimethyl sulphate :

$$Cu_2O + (CH_3)_2SO_4 = Cu_2SO_4 + (CH_3)_2O$$

It readily disproportionates in water to Cu° and Cu(II).

Cuprous cyanide, CuCN is formed as a white precipitate on slow addition of KCN solution to a solution of copper(II).

$$2CuSO_4 + 4KCN = 2CuCN + (CN)_2 + 2K_2SO_4$$

It dissolves in excess KCN to $K_3[Cu(CN)_4]$.

Cuprous thiocyanate, CuCNS is also obtained as a white precipitate by adding potassium or ammonium thiocyanate to aqueous copper(II) in presence of sulphurous acid :

$$CuSO_4 + 2NH_4CNS = \underset{\text{black}}{Cu(SCN)_2} + (NH_4)_2SO_4$$

$$2Cu(SCN)_2 + H_2SO_3 + H_2O = 2CuSCN + 2HCN + H_2SO_4$$

The precipitation is quantitative and was used for gravimetric estimation of copper.

Aqueous solution chemistry

The +I state for copper is not stable in aqueous solution owing to disproportionation.

$$2Cu^{I} \rightleftharpoons Cu^{\circ} + Cu^{II}$$

From the standard potentials (Chapter 9), it has been shown that for the process

$$2Cu^{+}(aq) \rightleftharpoons Cu^{\circ} + Cu^{2+}(aq)$$

$E^{\circ} = 0.37$ V, whence $K = [Cu^{2+}]/[Cu^{+}]^2 \simeq 10^6$.

This suggests that the concentration of $[Cu^{2+}]$ will be very large in comparison to $[Cu^{+}]$.

The marked instability of the Cu^{+} ion in water, in spite of its d^{10} configuration with high exchange energy, may be largely attributed to the smaller size and higher charge density of the Cu^{2+} ion. This makes the hydration energy of Cu^{+} much lower than that for Cu^{2+}. In fact the energy of interaction of water dipoles with the Cu^{+} ion should be still less if we expect that the Cu^{+} ion is 2-coordinate in water also, as it is in a number of complexes like the diammine, $Cu(NH_3)_2^{+}$. The Cu^{2+} ion, on the other hand, is six coordinate, with four stronger and two weaker interactions from water molecules. (However, on passing to silver, we shall find that this trend may be reversed, making Ag^{2+} highly unstable; Chapter 29). Only insoluble or nonionic compounds of copper(I) may exist in contact with water, for example CuCl, CuI or CuCN. Cu_2SO_4, on the other hand, will immediately disproportionate in water :

$$Cu_2SO_4 + 6H_2O \longrightarrow Cu + Cu(H_2O)_6^{2+} + SO_4^{=}$$

However, the equilibrium may be shifted in either direction by the use of suitable complexing agents. Thus, copper(I) is formed by the reaction of copper(II) with soft anions like CN^-, I^-, Me_2S etc. On the other hand, with chelating ligands (e.g., en), or, anions that cannot establish covalent bonds or bridges (e.g., ClO_4^-), the + II state is favoured, as in the following reaction in aqueous KCl.

$$2CuCl\ (s) + 2en = [Cu(en)_2]^{2+} + Cu^{\circ} + 2Cl^{-} \ldots\ldots K \simeq 10^5$$

For nonchelating amine ligands, for example pentamethylene diamine, the value of K falls drastically to ~ 10^{-2}. With ammonia, in absence of air, the reaction

$$[Cu(NH_3)_4(H_2O)_2]^{2+} + Cu = 2[Cu(NH_3)_4]^{+}$$

has a K value of ~ 50 at 25°C.

The nature of the solvent may also affect the Cu^{II}–Cu^{I} equilibrium. Acetonitrile (CH_3CN) effectively solvates the Cu^{+} ion, dissolving the copper(I) halides which are almost insoluble in water. This makes Cu(II) a stronger oxidizing agent in acetonitrile. The ion $[Cu(CH_3CN)_4]^{+}$ is tetrahedral and can be isolated as salts with large anions like ClO_4^- and PF_6^-.

Q. 28.8 *Why does KCN reduce Cu(II) to Cu(I)?*

Hint : CN^- acts as a π-acid ligand and stabilizes +1 state. The difference in hydration energy between Cu(II) and Cu(I) is not large as the CN^- ion is large and polarizable.

Q. 28.9 *In aqueous solution, Cu(II) is not reduced to Cu(I) in presence of ethylenediamine but is reduced in presence of 2,2′-dipyridyl. Comment.*

Complex compounds

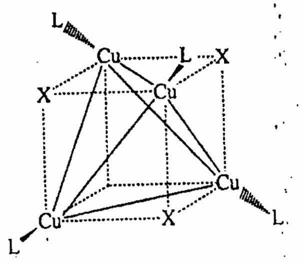
These have complex structures having little resemblance to their formula and may be mononuclear, dinuclear or polynuclear species with copper in a variety of coordination numbers (2, 3, 4) or forming infinite chains.

The $CuCl_2^-$ ion has a linear structure with 2 - coordinate copper which exists as a discrete halogeno species. Planar 3-cordination is present in $KCu(CN)_2$ (Ch. 26) which forms a spiral chain with bridging CN groups. Infinite chains of $CuCl_4$ tetrahedral units sharing corners are present in K_2CuCl_3.

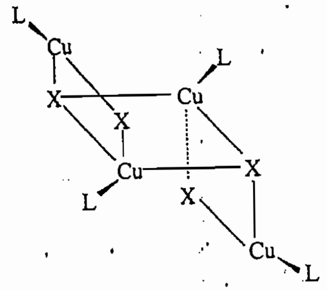
Copper(I) acetate is formed as a white air-sensitive crystalline compound when copper(II) acetate is reduced with copper in pyridine or acetonitrile. It has a planar chain structure. Copper(I) trifluoroacetate and benzoates are tetrameric with bridging carboxylate group.

4-coordinate complexes of copper(I) are mostly tetrahedral, e.g., $[Cu(CN)_4]^{3-}$, $[Cupy_4]^+$ and $[Cu(CH_3CN)_4]^+$. A distorted planar structure is found with a macrocyclic N_4 anionic ligand.

Polymeric complexes of Cu(I) are known of the type $(CuXL)_4$ where X = halogen (or SR) and L = R_3P (phosphines), arsine or py. These form two main structural types (a) *the cubane structure* has a tetrahedron of Cu-atoms, each attached to a ligand; the halogens form the other four corners of a cube in a triply bridging role (28 - XXIV).



28-XXIV



28-XXV

(b) *the step form* (28 - XXV) has both double and triply bridging halogens with two tetrahedrally coordinated copper atoms and two trigonally coordinated copper atoms.

28.10.6 Organometallic compounds

Carbonyls

Copper does not form any binary carbonyl at normal temperatures; some carbonyls [e.g., $Cu(CO)_3$, $Cu(CO)_2$ and Cu(CO)] have been reported to be formed by condensation of copper vapour with CO at 6 ÷ 15 K. Copper also forms an unstable carbonyl halide when CO is bubbled through a solution of CuCl in concentrated HCl or aqueous ammonia. The halogenbridged dimer $[CuCl(CO)]_2$ can be isolated as colourless crystals.

Other compounds

Copper alkyls and aryls may be prepared by the action of LiR or a Grignard reagent on CuX.

$$CuX + LiR \longrightarrow CuR + LiX.$$

$$CuX + RMgX \longrightarrow CuR + MgX_2$$

The alkyls and aryls are thermally unstable and often polymeric. Thus $CuCH_3$ is a yellow polymeric solid which tends to explode in air; CuC_6H_5, white and also polymeric is somewhat more stable but sensitive to air and water. A σ-cyclopentadienyl complex $Cu(\eta^1\text{-}C_5H_5)(PEt_3)$ prepared by the reaction of CuO with PEt_3 and cyclopentadiene in petroleum ether is more stable.

Solutions of copper(I) halides in HCl absorb acetylene forming complexes of the type $CuCl.C_2H_2$ and $[CuCl_2(C_2H_2)]^-$. Ammoniacal solutions of CuCl give the explosive orange diamagnetic solid $Cu - C \equiv C - Cu$; this may also be formed using potassium acetylide in liquid NH_3. Similar complexes are also known for other alkynes and alkenes. Copper(I)-olefin complexes are prepared by reducing alcoholic solutions of copper(II) halides with SO_2 in presence of the olefins. The compounds are labile, often decomposing when isolated. Chelating diolefins like cyclo-octa-1, 5-diene and norbornadiene give the most stable complexes. In the complex of cycloocta -1,5-diene $[C_8H_{12}CuCl]$, each copper is surrounded tetrahedrally by two bridge chlorine atoms and two olefinic double bonds.

Lithium dialkylcuprate, R_2CuLi has been extensively used in the synthesis of alkanes in high yield (Corey, Posner, Whitesides and House). The overall scheme may be represented schematically as .

$$R\text{—}X \xrightarrow{Li/Et_2O} RLi \xrightarrow{CuI} R_2CuLi \xrightarrow{R'X} R\text{—}R' + RCu + LiX$$

R′ may be a methyl, 1° alkyl or 2° cycloakyl halide. The R-group of the lithium dialkylcuprate may be methyl, 1°, 2° (or 3° with special techniques). The method is superior to the Wurtz reaction since a single alkane is always produced.

28.10.7 Detection and estimation

Copper salts may be detected through their characteristic blue flame in the conventional 'flame test'; the borax bead test (green when hot, blue on cooling); the deep blue colouration produced by aqueous ammonia and the chocolate colour developed by potassium ferrocyanide in acetic acid medium.

Volumetrically, copper is most readily titrated iodometrically. It may be estimated by weighing as copper(I) thiocyanate by precipitation with ammonium thiocyanate in presence of sulfurous acid.

SUMMARY

The *d*-block elements differ from the *s*- and *p*-block elements mainly due to the following reasons :

(i) poorer penetration of $(n-1)d$ orbitals compared to that of *ns* or *np* orbitals into the inner electron core;

(ii) highly directional character of the *d*-orbitals;

(iii) the pronounced effect of ionic charge, effective nuclear charge on the radial distribution of the *d*-orbitals. Among the first members in each *d*-series (e.g., Sc in 3*d*-) the $(n-1)d$ orbital is energetically very close to the *ns* orbital and the common oxidation state of these elements involve the *ns* and $(n-1)d$ – electrons $(2 + 1 = 3)$. As one proceeds along any *d*-series, the effect of increasing nuclear charge and poor screening of the *d*-electrons gradually binds the *d*-electrons tightly forming a core and the last elements (Zn, Cd, Hg) in each *d*-series do not involve these *d*-electrons in their stable oxidation state (+2).

Formally, the transition elements should contain an incomplete *d*-shell in the ground states of their atoms or in any of their principal oxidation states.

General Periodic Trend : Among the *d*-block elements, the vertical relation among the three elements in each group is not so prominent as in the *p*-block. The expected increase in size between a 4*d*- and a 5*d*-transition element is nearly cancelled by the effect of lanthanide contraction. As a result the second and third members in any vertical group in the *d*-block have almost identical radii. Such similarity in size results in many similar characteristics among these members, like ionization energies, solvation energies of ions, redox behaviour etc. Thus, each group in the *d*-block is essentially divided into two parts — (i) the first member $(3d^n)$ with its individual chemistry and (ii) the second and third elements having nearly similar chemistry.

The main difference between the first and the heavier members in a group are those of size and relative stabilities of different oxidation states. The heavier elements also have a tendency to attain higher coordination number and to show greater stability in higher oxidation states. This is readily shown by the strongly oxidizing nature of Cr(VI) while Mo(VI) and W(VI) are quite stable.

Among the earlier members in each row (up to d^5), all the *d*- and *s*-electrons take part in valence, but once the d^5 configuration is crossed, the highest oxidation state is often less than the sum of *d*- and *s*- electrons. Where the group oxidation state is attained, the properties of the elements involving all valence electrons show certain similarities with the main group elements having the same number of valence electrons (sulfates and chromates, for example, are isostructural).

Towards the right of the *d*-block, the similarity in chemistry between the two heavier elements in a group gradually disappears. The simple size relation is overruled by more intricate penetration effects and crystal field stabilization effects. In the early groups headed by Ti and V, the lower members Zr-Hf and Nb-Ta are quite similar in properties within the pair. But silver and gold have more dissimilatities than similarities.

High oxidation states of transition elements are mostly stabilized in combination with small, hard ligands with strong σ-donor properties (e.g., F^-, O^{2-}). Other factors may also contribute to such stability.

Low oxidation states are usually stabilized by large saturated ligands which are good reducing agents (e.g. I^-, S^{2-}) and ligands with π-acceptor capacity.

EXERCISE

1. *Comment/Explain*

   (*a*) *CCl_4 vapour reacts with V_2O_5 at red heat to give VCl_4.*

   (*b*) *VCl_3 forms VCl_4 on heating in excess chlorine and VCl_2 on heating in vacuo.*

   [**Hint :** Two equilibria are involved :

$$2VCl_3 \rightleftharpoons VCl_2 + VCl_4; \quad VCl_4 \rightleftharpoons VCl_3 + \tfrac{1}{2}Cl_2$$

   In excess chlorine, the second equilibrium is forced to left. In vacuo, the chlorine is pumped out, and VCl_4 is fully converted to VCl_3 which disproportionates to VCl_2 and VCl_4. The latter again gives VCl_3 and so on.]

   (*c*) *The magnetic moment of copper(II) acetate, 1.4 B.M. per Cu^{2+} at 25°C, is considerably less than that expected for one unpaired electron. The copper(II) salt of diazoaminobenzene, $Cu(NPh—N—NPh)_2$ is diamagnetic.*

   (*d*) *E^0 for $Ti(IV) + e \rightleftharpoons Ti(III)$ is 0.1 V in aqueous solution. But $TiCl_3$ evolves hydrogen on being heated with concentrated aqueous NaOH.*

   [**Hint :** TiO_2 is extremely insoluble and H_2 escapes readily as soon as formed.]

   (*e*) *Zinc amalgam reduces vanadates to vanadium(II) and niobates to niobium(III), but tantalates are not reduced.*

   (*f*) *An acidified solution of vanadate gives a deep blue solution on heating with SO_2. A similar quantity of the vanadate solution gives a violet solution when reduced with zinc amalgam. A green solution is formed on mixing the blue and violet solutions.*

   [Blue : VO^{2+}; Violet : V^{2+}; Green V^{3+}]

   (*g*) *"Chromic acid" is used to clean laboratory glassware.*

2. *Barium diphenylamine sulfonate (BDS) has E^0 value of 0.85 V. What will be your expected observations if ceric sulfate solution is run into solutions containing*

   (*a*) *ferrous sulfate and BDS?*

   (*b*) *ferrous sulfate, BDS and phosphoric acid?*

   (*c*) *ferrous sulfate and tris (o-phenanthroline) iron(II) sulfate?*

   $E^0 : (Fe^{3+} - Fe^{2+}) = 0.77V; ([Fe(phen)_3]^{3+} - [Fe(phen)_3]^{2+}) = 1.12\ V;$

   $Ce^{4+}—Ce^{3+} = 1.70V.$

3. *How would you prepare*

   (*a*) *$TiCl_3$ (anhydrous) from TiO_2;*

   (*b*) *$TiCl_3$ (aqueous) from TiO_2;*

   (*c*) *Ti(III) sulfate from Ti;*

   (*d*) *Co(III) sulfate (anhydrous) from Co;*

   (*e*) *Al_2CoO_4 from cobalt(II) nitrate;*

   (*f*) *$Ni(CO)_4$ from Ni;*

   (*g*) *Ni_2O_3 from Ni;*

   (*h*) *cuprous bromide from $CuSO_4$?*

4. *How would you prepare the following compounds from chromium trioxide?*

   (*a*) $K_2Cr_2O_7$
   (*b*) K_2CrO_4
   (*c*) CrO_2F_2
   (*d*) $CrO_5.py$
   (*e*) $KCrO_3Br$.

5. *How would you obtain the following complex species?*

   (*a*) $[Co(NH_3)_6]^{3+}$
   (*b*) $[CoCl_4]^{2-}$
   (*c*) $[Co(CN)_6]^{3-}$
   (*d*) $[Co(C_2O_4)_3]^{3-}$
   (*e*) $[Ni(CN)_3]^{2-}$.

6. *Answer the following questions for which the following E^0 values may serve as a guideline :*

$$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(e) \qquad -0.7\ V$$
$$Cr^{3+}(aq) + e \rightleftharpoons Cr^{3+}(aq) \qquad -0.41\ V$$
$$Hg_2^{2+}(aq) + 2e \rightleftharpoons 2Hg\ (l) \qquad 0.79\ V$$

   (*a*) *What happens when chromium is added to dilute hydrochloric acid?*

   (*b*) *How would you prepare anhydrous chromium(II) chloride from chromium?*

   (*c*) *How are Cr(II) solutions prepared from Cr(III) solutions?*

   (*d*) *What would be the result of adding mercurous nitrate solution to a solution of chromium(II) perchlorate?*

   [(b) : Cr + 2HCl (c) : Zn – Hg (d) : 2Hg (grey) + Cr^{3+} (green)]

7. *What do you expect to observe when*

   (*a*) *Chromium metal is added to a solution of zinc salt?*

   (*b*) *Air is blown through a solution of manganese(II) solution in presence of excess cyanide?*

   (*c*) *MnO_2 is added to a concentrated solution of KOH?*

   (*d*) *A little $KMnO_4$ is added to conc. H_2SO_4?*

[**Hints :** (b) red $[Mn(CN)_6]^{3-}$ (c) blue solution probably containing Mn(III) and Mn(V). (d) green solution, probably containing the permanganyl ion, MnO_3^+.]

   (*e*) *Chromyl chloride is added to a saturated solution of potassium chloride?*

   (*f*) *Precipitated MnO_2 is heated with conc. H_2SO_4?*

   (*g*) *Chlorine is passed into a suspension of hydrated ferric oxide in hot concentrated KOH?*

   (*h*) *Potassium ferrocyanide is heated with 50 per cent nitric acid, the solution cooled, filtered and the filtrate neutralized with sodium carbonate?* *[Sodium nitroprusside]*

   (*i*) *Potassium cobalticyanide is added to potassium in liquid ammonia?*

   (*j*) *A solution of nickel(II) sulfate is oxidized with potassium persulfate in presence of KIO_4?*

   (*k*) *KCN is gradually added to an aqueous solution of $CoCl_2$ and $NiCl_2$ until the initial precipitate just dissolves and the solution is boiled with bromine and caustic soda?*

8. *In presence of cyanide ion, Co(II) salts are readily oxidized to the Co(III) state while Cu(II) salts are reduced to the Cu(I) state. Comment.*

Also contrast the effect of addition of NH_3, Cl^- and SCN^- to Co(II) and Cu(II) separately in aqueous solution.

9. *Though the Co^{3+}—Co^{2+} couple normally liberates oxygen from water, it liberates hydrogen in presence of cyanide ion.—Explain.*

10. *The first five ionization energies of vanadium ($kJ\ mol^{-1}$) are 650, 1414, 2832, 4632, 6272 and 12450 respectively.*

    (a) *What is the significance of the large increase from I_5 to I_6?*

    (b) *What is the highest charge commonly attained by a simple vanadium cation in aqueous solution?*

    (c) *Do you expect niobium to form cations in aqueous solution more or less readily than vanadium?*

11. (a) *Atomic radii of V, Nb and Ta are 122, 134 and 134 pm respectively. Comment.*

    (b) *The ionic radius of V^{2+} is 88 pm, comparable to the radii of Ca^{2+} and Cd^{2+}. Does this fact lead to any valid comparison of the chemistry of these ions?*

    [**Hint :** Consider reducing power and ploarizing power.]

12. *Identify the substances marked A—F.*

    On opening a bottle of $TiCl_4$, a white smoke (A) was produced. The contents were then added to concentrated HCl when a colourless solution (B) was formed. A violet solution (C) resulted when zinc metal was added to B. Aqueous alkali was added slowly to C until alkaline. A purple precipitate (D) appeared which was filtered out and treated first with nitric acid and then with dilute aqueous alkali. A while solid (E) was formed. This was dried and fused with an equimolar quantity of magnesium oxide forming a complex oxide (F). [$F = MgTiO_3$]

13. *Write complete equations for reactions between the following chemical species (or write no reaction).*

    (a) $V^{2+} + I_2$ (b) $Cu_2O + MnO_4^-$ (neutral) (c) Cu_2O + dil HCl (d) Cu_2O + conc. HCl.
    (e) $Cr^{2+} + H_2O_2$ (acid) (f) $Cr_2O_7^{2-} + H_2O_2$ (acid) (g) $Co^{2+}(aq) + Na_2EDTA$. (h) $NaHCO_3$ + $Fe^{2+}(aq)$ (i) $Ti^{3+} + H_2O_2$ (j) Mn^{3+} + water.

14. *What happens when a solution of potassium dichromate reacts with the following in solution :*

    (a) F^- (b) Cl^- (c) Br^- (d) I^- (e) NO_2^- (f) H_2O_2.

15. *Explain why freshly prepared hydroxide of Co^{2+} is blue but turns pink on warming.*

16. (a) *How are Ti(–1) and Ti(0) states stabilized? Why are they stabilized?*

    (b) *Starting from pyrolusite, how will you prepare pure (i) $KMnO_4$ (ii) hydrated manganese(II) sulfate?*

    (c) *Starting from chromite, how will you prepare (i) potassium chromate (ii) chrome alum?*

17. *Give one example for each of the following types of complexes—mention the ligands :*

    (i) *Tetrahedral Ni(II) (ii) Octahedral Mn(III) (iii) Square pyramidal V(IV).*

    Justify the ligands used in your examples with regard to their position in the spectrochemical series.

CHAPTER TWENTYNINE

THE TRANSITION ELEMENTS (4*d*, 5*d* and 6*d*)

Zr—Ag; Hf—Au; 104—112

OBJECTIVES

29.1 Introduction
29.2 Zirconium and Hafnium
29.3 Niobium and Tantalum
29.4 Molybdenum and Tungsten
29.5 Technetium and Rhenium
29.6 The Platinum metals
29.7 Silver and Gold
29.8 Elements of the 6*d*-series (104—112)

29

THE TRANSITION ELEMENTS
(*4d*, *5d* and *6d*)

29.1 INTRODUCTION

We may begin this section with a brief recapitulation of the general characteristics of *d*-block elements as outlined in the last chapter. We have seen that the second and third elements in any vertical group in the *d*-block are very similar in their chemistry while they differ significantly from the first member in the group. The salient features in their chemistry are summarized below :

(i) ***Electron configuration*** **:** The energy separations between *nd* and $(n + 1)s$ orbitals are *less* when $n = 4$ or 5 than when $n = 3$. Consequently, the ground state electron configurations of the *4d* - and *5d* - transition series elements often differ from those of the corresponding *3d* - transition element (Table 29.1). The *overall* energy for the configuration adopted is the primary concern in determining such configurations, not the isolated orbital energies. The electron configurations of the ions formed by the heavier transition elements are often uncertain.

TABLE 29.1

(a) Electron configuration (ground state) and
(b) Metallic radii* of transition elements

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
(a) 3 *d* 4 *s*	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$
(b)	147	135	129	137	126	125	125	128
	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
(a) 4 *d* 5 s	d^2s^2	d^4s^1	d^5s^1	d^5s^2	d^7s^1	d^8s^1	d^{10}	$d^{10}s^1$
(b)	160	147	140	135	134	134	137	144
	Hf	Ta	W	Re	Os	Ir	Pt	Au
(a) 5*d* 6*s*	d^2s^2	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^9s^1	$d^{10}s^1$
(b)	159	147	141	137	135	136	139	144

(ii) ***Atomic radii and related properties*** **:** The atomic radii (metallic radii, Table 29.1) of the elements in *4d* - and *5d* - series remain practically the same when we move downward in any particular group, though an increase is observed from the *3d* - series to the *4d* - series in the same group.

This is a consequence of the poor shielding by the *4f* electrons with a consequent steady increase in effective nuclear charge and decrease in atomic size along the lanthanide elements (*lanthanide contraction*). Hence the expected size increase in moving from the *4d*- to *5d*-transition series is not observed. The effect is relayed to the covalent radii and ionic radii of these elements. Thus atomic, ionic and covalent radii of second and third transition series elements are closely similar in each vertical group, though they are larger than the corresponding elements in the first transition series. We expect a similar trend in those properties of the elements which are primarily size-related, for example, lattice energies, solvation energies, formation constants of complexes and the like. This is partly responsible for the chemical similarities between the two heavier transition elements in a group. First ionization energies of the *5d* - series elements are somewhat higher than those of corresponding *4d* elements since their atomic number differ by 32. Removal of further electrons may, however, show different trends. The larger sizes of the second and third transition series elements also enable them to attain a higher coordination number than their *3d* - analogue. Thus, compounds of the heavier transition metals having the element in coordination numbers seven, eight and nine are quite common.

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* 12 - coordinate metallic radii, pm.

(iii) ***The Relativistic effect*** **:** This effect arises from the relativistic variation of the mass of an electron with its velocity. The effect is most marked with elements having $Z \simeq 80$ or higher where the radial velocity of inner electrons rises to a significant fraction of the speed of light, thereby increasing the mass of the electron in accordance with the special theory of relativity. This, in turn, results in some contraction of the inner orbitals in space.

It is possible to obtain some idea about the relativistic contraction of inner orbitals of heavy atoms from the simple Bohr model. We recall the relativistic variation of the mass m of a body with its velocity v according to the relation

$$m = m_0 / \sqrt{1 - v^2/c_0^2}$$

where m_0 is its rest mass and c_0 the speed of light in vacuum.

According to the Bohr model, the radial velocity v of an electron in an atom is given by

$$v = Ze^2/2\,\varepsilon_0 nh$$

For the 1*s* orbital in hydrogen, we put $Z = 1$ and $n = 1$, when we get $v = 2.19 \times 10^6$ ms^{-1}, or $v/c_0 = 0.0073$. This gives $m \simeq m_0$.

Now we repeat the calculation for Hg ($Z = 80$). v now becomes 80 times greater than the above value, giving $v/c_0 \simeq 0.58$; roughly v is 60 per cent of the speed of light. This gives $m \simeq 1.2m_0$, or a 20 per cent increase in the mass of an electron in the 1*s* orbital. Consequently there will be a small but significant contraction in the radius of the orbit, given by the Bohr relation

$$r = Ze^2/4\pi\varepsilon_0 mv^2$$

We may carry these findings on to the orbital description of the atom as well, when we come to the conclusion that in heavy atoms, the inner orbitals will undergo some sort of relativistic contraction. Since v is inversely proportional to n (see above), the effect will be most pronounced with orbitals having electron density closer to the nucleus.

Summarily, the high velocity of electrons in the inner core of heavy atoms causes a small but significant increase in the mass of the electron, which, in turn, gives rise to some contraction of the orbitals. The effect is most pronounced for *s*-orbitals; the *p*-orbitals are less affected as they have low electron density near the nucleus. For the *d*- and *f*-orbitals, the situation is somewhat different. The contracted *s*-orbital now provides better screening for these outer orbitals; as a consequence the *d*- and *f*-orbitals undergo slight expansion.

The consequences of relativistic contraction may be varied. Primarily, this will stabilize the *s*-orbitals and reduce their overlap with orbitals of other atoms. The poor contribution of the 6*s* orbitals to metallic bonding in mercury may be related to such effects resulting in very low melting and boiling points. The ionization energies of mercury are similarly much higher in comparison to its group members. Similar considerations apply to other heavy elements also, e.g., Au, Tl, Pb and Bi.

The relativistic effect also contributes, at least partly, to the close similarity between the earlier members of the $4d$ and $5d$ series. As we move toward right along the $5d$ series, we find increasing disparity with the corresponding $4d$ element. This may also be partly ascribed to the relativistic effect which lowers the binding on the $5d$ electrons (better shielded) and hence favours their better participation in bonding. Thus, Pd(IV) or Ag(III) are much less stable than Pt(IV) or Au(III) respectively while Pt(VI) and Au(V) have no Pd or Ag counterpart.

Along the $5d$ series, the relativistic effect increases remarkably as the $5d$ shell gets filled and the maximum effect is observed at Au, followed by a decline to Bi. It then changes slowly along the $5f$-series. Effects comparable to Au are seen to operate around Fm. At Lw, the effect may be sufficient to place the $6d$ level above the $7p$, giving the alternative configuration with the last electron in $7p$ rather than the $6d$.

(iv) ***Oxidation states*** : (See Table 28.5) Higher oxidation states are generally more stable among the heavier transition elements. Thus CrF_6 is highly unstable while WF_6 and WCl_6 are stable. Also, CrO_3 and other Cr(VI) compounds are strongly oxidizing but MoO_3, WO_3 and other compounds containing Mo(VI) and W(VI) are not so. The maximum range of oxidation states appears in the middle of the block — the VIII state of osmium and ruthenium being highest. It is likely that ease of promotion to attain the higher valence state as well as better overlap by higher d-orbitals are both responsible for the greater stability of higher oxidation states by the heavier transition elements. Side by side with this increased stability of higher oxidation states, many lower oxidation states become less frequent or less stable among the heavier transition elements. Thus W(II) is virtually non-existent (Cr(II), also reducing, forms quite a few compounds); a compound with the empirical formula WCl_2 is actually a cluster compound of W_6 octahedron forming the $[W_6Cl_8]^{4+}$ ion. Similarly, Zr(III) is strongly reducing in nature (compare Ti(III)) and so also is Nb(IV) (compare V(IV)).

(v) ***Aqueous chemistry*** : Unlike their $3d$ analogues, many of the heavier transition elements do not have a simple aqueous chemistry and only a few electrode systems involving them are reversible. Other thermochemical data are also equally uncertain, making predictive use of solubility products, complex formation constants etc. restricted in most cases. In fact, aqua ions involving the metals in lower oxidation states are often unimportant for the heavier transition metals, and some, like Zr, Hf and Re, do not form any simple cationic complex, too. These facts, together with frequent occurrence of metal-metal bonding and wide range of geometries with comparable energy make straightcut application of the simple crystal field theory to these complexes extremely difficult. However, some of the heavy metals like Ru, Rh, Pd and Pt form some cationic complexes in aqueous solutions. Others are known mainly as anionic oxo and halo complexes.

(vi) ***Metal - metal bonding*** : Whereas the first member of any transition metal group forms few or no species with metal-metal bonds, the heavier members often form such species, commonly referred to as metal cluster compounds. Greater spatial extension of the higher d-orbitals and the high enthalpy of atomisation of the heavier transition metals may be partly responsible for such metal-metal bond formation. We have already mentioned the differences between $CrCl_2$ and WCl_2; it seems that in the latter, formation of the $[W_6Cl_8]^{4+}$ ion with W_6 cluster requires fewer metal-metal bonds to be broken. In this same group, W_3^{IV} and Mo_3^{IV} oxoclusters are also known with no chromium analogue; a similar trend is a common feature in most groups, particularly in low oxidation states. Mononuclear compounds are often formed by these very metals in a higher oxidation state, for example, WF_6 and WCl_6 in case of tungsten.

(vii) ***Magnetic properties*** : Since the heavier transition metals ensure a higher crystal-field splitting than their $3d$ counterparts (Δ_0 increases largely from $3d \rightarrow 4d \rightarrow 5d$), their complexes are mostly low-spin. Spin-orbit coupling constants are also much larger for the second and third transition series elements and hence the few paramagnetic complexes known rarely conform to the spin-only magnetic moment. Thus simple use of magnetic criterion as a predictive tool is not permitted for most heavier transition metals.

Yittrium and lanthanum, the first elements in the $4d$ and $5d$ series, occur in nature with the lanthanides (see f - block elements) and also resemble them closely in chemical behaviour. Hence these metals will be discussed in connection with the lanthanides.

29.2 ZIRCONIUM [$4d^35s^2$] and HAFNIUM [$5d^36s^2$]

Zr : Atomic number : 40 Atomic weight : 91.22 M.P. : 1855°C
Hf : Atomic number : 72 Atomic weight : 178.49 M.P. : 2222°C

29.2.1 Introduction

The mineral zircon (from Arabic *zarqun* = golden) occurs in a beautiful range of colours like golden, orange and pink and has been appreciated as a gemstone as early as the epoch of Alexander the Great. It occurs in two main forms : hyacinth and jargon. Early analysis of these minerals, however, showed only the presence of oxides of silicon, iron, aluminium and calcium. It was only in 1789 that the German chemist Klaproth discovered the new element zirconium in zircon (hence the name). But the crude metal was first extracted by Berzelius in 1824; the pure metal was obtained by decomposition of the iodide (1925; van Arkel).

Hafnium remained undiscovered till 1923 when the Dutch spectroscopist D. Coster and Hungarian radiochemist G. Hevesy discovered it in zircon, after about 130 years since the discovery of zirconium in this same mineral. In fact, Niels Bohr convincingly advised Coster and Hevesy to look for the element, atomic number 72, for which there was a vacant place in the Mendeleev periodic table. In honour of Bohr, the element was named after his native land Copenhagen, whose old name was Hafnia. Elemental hafnium was obtained by sodium reduction of its complex fluoride, separated from zirconium by repeated crystallization.

Zirconium comprises 0.016% of the earths crust (162 ppm) and is quite abundant, ranking aftr Fe, Ti and Mn among the transition elements. Hafnium occupies a much lower rank (2.8 ppm), but is as common as cesium and bromine.

Zirconium and Hafnium occur chiefly as *Zircon* ($ZrSiO_4$) and Baddeleyite (ZrO_2), found mainly in USA, Australia and Brazil.

In India, zircons occur in the alluvial soils in Ranchi and Hazaribagh districts in Bihar, in U.P. and some other places, but they lack the high degree of transparency required for a gem. The transparent red variety, *hyacinth*, is said to be found at Kedarnath (Garhwal). The ilmenite beach sands, particularly at the Kerala coast, contain about 6 per cent zircon. The total reserve is estimated to exceed 10 million tonnes.

29.2.2 The Element

Extraction

Zirconium is produced by the Kroll process (see Ti) : the minerals are converted to chloride by heating with carbon and chlorine. The tetrachloride is reduced with molten magnesium.

Very pure zirconium is produced by the van Arkel process : the metal is heated with iodine in an evacuated vessel (200°C) — the ZrI_4 formed volatilizes which is allowed to decompose on an electrically heated filament (1300°C). For use in nuclear reactors, the hafnium content has to be reduced below 100 ppm which can be achieved by solvent extraction or ion exchange. For example, the tetrachlorides may be absorbed on a silica gel column from methanolic solution. Elution by methanol-HCl extracts the zirconium first.

Hafnium is also produed from zirconium minerals by the same procedure as that for zirconium — finally the metal is obtained by sodium reduction of K_2HfF_6.

$$K_2HfF_6 + 4Na = Hf + 2KF + 4NaF.$$

HfF_4 may also be decomposed on a hot tungsten filament to deposit pure hafnium.

Properties

Both the metals are silvery white, hard and high melting.

	Zr	Hf
Density g cm^{-3}	6.5	13.3
M.P./(B.P.), °C	1855(4200)	2222(4450)
Electrical resistivity (at 20°C; μohm cm)	40	35

They are fairly electropositive — form dioxides on heating in oxygen. Zirconiun also reacts more readily with nitrogen and hence burns in air to give a mixture of oxide, nitride and an oxide nitride Zr_2ON_2. The massive metals at room temperature are resistant to corrosion. Zirconium is only slowly attacked by cold acids — it dissolves in hot concentrated H_2SO_4, aqua regia and HF.

$$Zr + 6HF = H_2[ZrF_6] + 2H_2$$

Hot aqueous alkali does not attack the metals.

Uses

Zirconium is used in making bullet-proof alloy steels and other corrosion-resistant alloys. In many chemical plants, it is preferred over Ti, Ta or stainless steel. A major use of zirconium is in the form of an alloy with 1.5% tin — the corrosion resistance and mechanical properties make it highly suitable as a cladding material for uranium dioxide rods in water-cooled nuclear reactors. Zirconium has a very low absorption of thermal neutrons but it must be free from traces of hafnium which absorbs neutrons 600 times more.

The Nuclear Fuel Complex (NFC) of India has recently (March 1999) developed "Zircaloy-4" as an import-substitute for use in nuclear reactors as a challenge to post-Pokhran sanctions. The annual production of nuclear grade hafnium-free zirconium sponge is at an all-time high of 165 tonnes and is used to manufacture seamless coolant tubes for eight heavy water reactors and Zircaloy-4 square channels for the two boiling water reactors at Tarapur.

Zirconium is also used as a scavenger in steel industry — it removes dissolved O_2 and N_2.

29.2.3 *Chemistry of the metals in +IV state*

The most common oxidation state of zirconium and hafnium is IV — lower oxidation states are not common. Zr^{III} and Hf^{III} are strongly reducing in nature and reduce water; hence they have no aqueous chemistry, only the trihalides and their derivatives being known.

The M^{4+} - M potentials for Ti, Zr and Hf indicate the greater reducing power of Zr and Hf :

	Ti	Zr	Hf
$E°$(V)	−0.89	−1.56	− 1.70

The IV state is known in solution and in a variety of solids.

Oxides

The dioxides MO_2 are high melting white solids :

	ZrO_2	HfO_2
M.P. °C	2850	2900
$\Delta H_f^0 / \Delta G_f^0$, kJ mol^{-1}	−1100/−1043	−1118/−1061

These are insoluble in water, cold dilute acids (except HF) and alkalis, but react slowly with acids only when heated for a long time and with alkali on fusion.

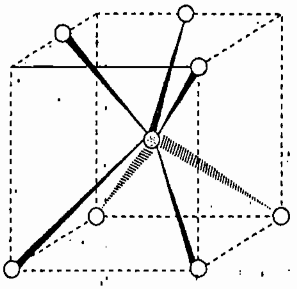


Fig. 29.1

Coordination geometry in ZrO_2 (baddeyleite).

The monoclinic form of ZrO_2, stable at room temperature (baddeyleite), has a structure containing 7-coordinate zirconium. One form of HfO_2 is isomorphous with this.

The 4 lower O atoms are each tetrahedrally coordinated by 4 Zr atoms. The 3 upper O atoms are each coordinated by 3 Zr atoms in a plane.

Q. 29.1 *The specific gravity of HfO_2 (9.68) is much higher than that of ZrO_2 (5.73). Comment.*

Hint : Both have nearly equal cell dimensions but the mass of an Hf atom is nearly twice that of a Zr atom.

ZrO_2 is used in making refractory crucibles and furnace linings.

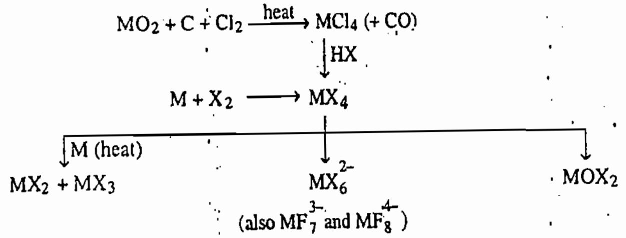
The "hydroxides" $M(OH)_4$ are obtained as white gelatinous precipitates on adding alkali to M(IV) solutions and actually have variable compositions MO_2, nH_2O; these give the dioxide on strong heating. Fresh precipitates (α - form) have a relatively large number of OH groups and are more soluble in acids than the aged ones (β form) in which the OH groups (-ol) are replaced by (—O—) groups (oxo-). In contrast to Ti(IV) hydroxide, these hydroxides practically do not react with alkali. During the reaction of the oxides or hydroxides with acids, the products are usually the oxocompounds MOX_2 (X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$) (see aqueous chemistry).

Mixed metal oxides like $CaZrO_3$, K_2ZrO_3 and others may be obtained by heating strongly the dioxide or hydroxides of zirconium with similar compounds of other metals. These are often called zirconates but no discrete zirconate ions are known. K_2ZrO_3 actually contains infinite chains of square pyramidal ZrO_5 units.

ZrS_2 and HfS_2 and other chalcogenides have layered structure and are intrinsic semiconductors.

Halides

All four tetrahalides MX_4 are known and may be prepared by standard procedures. They show the expected reactions as outlined below :



All the halides are white solids — the fluorides are involatile except at high temperatures (e.g., ZrF_4 sublimes at 903°C) but other halides sublime on heating between 320 — 430°C. The unit cell of solid ZrF_4 involves 2 : 8 coordination where each Zr atom is surrounded by eight F^- ions in a square antiprism configuration. $ZrCl_4$ has a zigzag chain of edge-shared $ZrCl_6$ octahedra. Vapours of all these halides consist of tetrahedral monomers.

The tetrahalides are vigorously hydrolyzed, hydrolysis at room temperature giving the oxohalides which are stable to further hydrolysis.

$$ZrCl_4 + 9H_2O \longrightarrow ZrOCl_2 . 8H_2O + 2HCl$$

$ZrF_4 . H_2O$ and $ZrF_4 . 3H_2O$ can be crystallized from HF - HNO_3 solutions. In $ZrF_4 . 3H_2O$, the Zr has an 8-coordination with two bridging fluorides.

The tetrahalides may add further halides or other neutral donor molecules Fluorides form the most stable anionic complexes e.g., ZrF_6^{2-} (octahedral, Li_2ZrF_6); ZrF_7^{3-} (pentagonal bipyramid, Na_3ZrF_7 and Na_3HfF_7); ZrF_8^{4-} (Fig. 29.2 (a) Na_4ZrF_8, Na_4HfF_8, Ca_2ZrF_8).

The structures adopted may be different with different cation combination, for example $(NH_4)_3ZrF_7$ has the structure in Fig. 29.2(b) based on a trigonal prism. Similarly the ZrF_8^{2-} ion is found in an antiprismatic form when the alkali metals are replaced by $[Cu(H_2O)_6]^{2+}$.

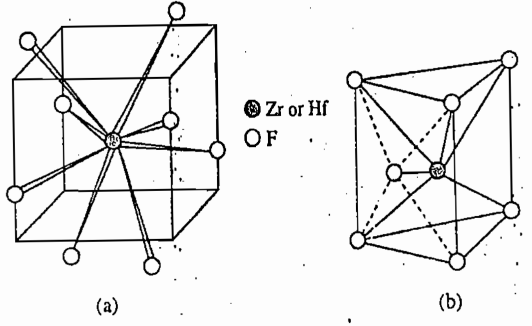


Fig. 29.2 (a) : The coordination geometry of ZrF_8^{4-} and HfF_8^{4-}.

29.2(b) : The coordination geometry of the ZrF_7^{3-} ion in $(NH_4)_3ZrF_7$: trigonal prism with an extra ligand attached on one face.

Aqueous solution chemistry

The electrode potentials for M^{4+} - M have been mentioned before. In solution Zr(IV) and Hf(IV) hydrolyze less extensively than Ti(IV). The main species in aqueous solution are frequently written as the ZrO^{2+}/HfO^{2+} ions, but existence of these simple species is doubtful. Though tracer experiment indicates the presence of Zr^{4+} ions in low concentration and highly acidic medium, the principal species appears to be $M(OH)_n^{(4-n)-}$ and trimeric or tetrameric species. As the concentration increases and acidity decreases, the condensed species become more important. For example, $ZrOCl_2$, $8H_2O$ actually consists of the tetrameric ion $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (Fig. 29.3) ion.

Strong polarizing nature of the M^{4+} ion also disfavours the formation of simple ionic compounds with this cation. Like the tetrahalides, other compounds like $Zr(OOCCH_3)_4$ are also covalent in nature, not salts.

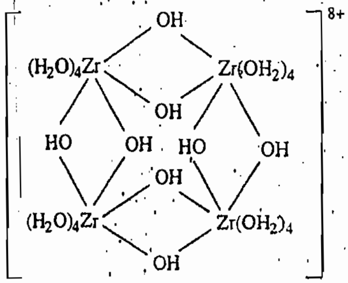


Fig. 29.3

Schematic arrangement of the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ion.

The Zr atoms lie approximately at the corners of a square and are eight coordinated. The O-atoms of the water and of the –OH groups are located at the apieces of a square antiprism.

Other compounds and complexes

Zirconium(IV) nitrate, sulphate etc. salts are actually basic salts. The sulphate, formed by dissolving ZrO_2 in hot concentrated sulphuric acid, crystallizes with the composition $Zr(NO_3)_4 . 5H_2O$ from acidic solutions. The anhydrous nitrate may be prepared by reacting N_2O_5 on $ZrCl_4$, as a sublimable white solid having structural similarity with $Ti(NO_3)_4$. Hafnium nitrate, prepared similarly, sublimes as the adduct $Hf(NO_3)_4 . N_2O_4$.

Zirconium also forms a basic zirconyl nitrate, $ZrO(NO_3)_2$, $2H_2O$. A solution of this in *N* nitric acid gives a white gelatinous precipitate with solutions containing phosphate ion in acidic solution.

$$ZrO(NO_3)_2 + Na_2HPO_4 = ZrO(HPO_4) + 2NaNO_3$$

The reaction is used in the separation of phosphates in routine group analysis of cations.

Zirconium and hafnium form volatile borohydrides $M(BH_4)_4$ in which each BH_4 group is linked to the M atoms through three shared H-atoms, making the coordination number of metals equal to 12. A tetranuclear peroxo complex of Zr(IV) is also known with the tentative formulation $[Zr_4(O_2)_2(OH)_4]^{8+}$.

The relatively large Zr^{4+} ion allows high coordination numbers shown in a great variety of coordination polyhedra. Six-coordinate complexes include the previously mentioned ZrF_6^{2-} ion (Li_2ZrF_6) and $Zr(acac)_2Cl_2$. Seven-coordination is observed in ZrF_7^{3-} (and HfF_7^{3-}) which is pentagonal bipyramidal in sodium salts but a capped trigonal prism in the ammonium salt (Fig. 29.2). Eight-coordinate structures may be square antiprism as in ZrF_8^{4-} (Fig. 29.2), $Zr(acac)_4$ and $Zr(SO_4)_2 . 4H_2O$; or dodecahedral as in $[Zr(ox)_4]^{4-}$, $[ZrX_4(diars)_2]$ and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ion (Fig. 29.3). Other fluoro-anions are also known, for example, the $Zr_2F_{12}^{4-}$ ion formed by edge-sharing of petagonal bipyramids and the $Zr_2F_{14}^{6-}$ ion formed by edge-sharing of square antiprisms.

29.2.4 *Lower oxidation states*

The lower oxidation states of zirconium and hafnium are very strongly reducing and does not exist in aqueous solution. The di- and tri-halides (Cl. Br, I) may be obtained by reduction of the tetrahalides with (i) the metal, (ii) with H_2 at 400 - 500°C or (iii) Al or Zn in molten AlX_3. The reduction of $HfCl_4$ occurs much more slowly, allowing separation from zirconium. Reduction of a mixture of $ZrCl_4$ and $HfCl_4$ with zirconium metal leavs $HfCl_4$ intact which may be sublimed out from the $ZrCl_3$ formed. $HfCl_3$ is formed by reducing $HfCl_4$ with Hf.

The trihalides have layer structures involving infinite parallel chains of MX_6 octahedra sharing opposite faces. The halides tend to be non-stoichiometric MX_n where $n = 2.9 - 3.4$.

The strongly reducing nature of the III state is shown by the reduction of KNH_2 in liquid NH_3 to K which forms a blue solution :

$$ZrCl_3 + 4KNH_2 \longrightarrow Zr(NH_2)_4 + K + 3KCl$$

Complexes of Zr(III) are not well characterized. $Zr_2Cl_6(PBu_3)_4$ has octahedral Zr atoms with a Zr – Zr bond and is diamagnetic.

$ZrCl_2$, $ZrBr_2$ and ZrI_2 may be prepared by reduction of ZrX_4 with zirconium metal at high temperatures in sealed inert tubes. They form layer structures with zigzag chains of Zr atoms.

ZrCl and ZrBr (and their hafnium analogues) are also formed in the reduction of MCl_4 with M at 800-850°C. The solids are metallic conductors with sheets of metal and halogen atoms in the stacking sequence ...... XMMX ...... XMMX ..... The Cl......Cl interlayer separation in the chloride is ~ 360 pm, representing normal van der Waal contact. ZrCl and ZrBr react with hydrogen or oxygen when H or O atoms are inserted between the double layer of metal atoms.

Zr(0) and Hf(0) are known mostly in organometallic compounds. Reduction of $ZrCl_4$ with lithium in ether in presence of dipyridyl gives the violet octahedral dipyridyl complex $Zr(dipy)_3$. $M_5[Zr(CN)_5]$ has been reported to be formed by the action of MCN on $ZrCl_3$ in liquid ammonia (M = K, Rb).

29.2.5 Organometallic compounds

A few unstable alkyl derivatives like $Li_2[Zr(Me)_6]$ have been isolated from reaction of LiMe and $ZrCl_4$ at low temperatures. $Zr(benzyl)_4$ is stable and may act as a homogeneous catalyst in the Ziegler-Natta process. Cyclopentadiene (Cp) forms a number of important compounds comparable to those of titanium : $ZrCp_4$, $Zr(\eta^1 - Cp)_2(\eta^5 - Cp)_2$ is also a promising homogeneous catalyst like $Zr(benzyl)_4$. Cp_2MXY (M = Zr, Hf; X, Y = R, Ar, Cl, Br, H) compounds are formed by Zr(IV)/Hf(IV).

29.2.6 Detection and estimation

Zirconium is precipitated in GrIIIA in routine qualitative analysis as ZrO_2, xH_2O in absence of phosphates. The residue is dissolved in HCl and boiled to expel chlorine. The resulting solution is treated with Na_2HPO_4 solution and 40-vol H_2O_2. A white precipitate indicates the presence of zirconium. The H_2O_2 helps to keep any titanium present in solution as an orange peroxo complex.

Alizarin S gives a red precipitate with solutions of zirconium in strongly acid medium. The colour is discharged by fluorides (formation of ZrF_6^{2-}).

29.3 NIOBIUM [$4d^45s^1$] and TANTALUM [$5d^36s^2$]

Nb : Atomic number : 41 Atomic weight : 92.91 M.P. : 2468°C
Ta : Atomic number : 73 Atomic weight : 180.95 M.P. : 2980°C

29.3.1 Introduction

In the year 1801, Ch. Hatchelt (Britain) claimed the discovery of a new element in a mineral from North America; he named the mineral *columbite* (from Columbia, the former name of America) and the element *columbium*. In 1802, A. Ekeberg of Sweden described the discovery of an oxide of a new metal which could not be dissolved in any acid. From the observed failure of the oxide to "absorb" any acid, he named the metal *tantalum* after Tantalus who was punished to stand immersed upto the chin in water but could not drink any. In 1809, the English chemist V. Wollaston announced that columbium and tantalum were the same elements. The dispute lasted for three decades until Rose established that both columbium and tantalum were new elements which were chemically very similar and hence always occurred together. He renamed columbium as *niobium* (Niobe was the daughter of Tantalus), which was adopted by IUPAC in 1950. In 1865, the Swiss chemist Marignac observed the difference in the solubilities of potassium fluorotantalate and fluoroniobate in HF. Pure samples of the metals were first obtained in 1907 (W. von Bolton) by reduction of the fluorometallates by sodium.

Niobium occurs in the earth's crust to the extent of 20 ppm while the abundance of tantalum is 1.7 ppm. Owing to their great chemical similarity, the elements occur together, the chief mineral being columbite or tantalite (according to dominance) with the composition (Fe, Mn) M_2O_6, M = Nb, Ta. The metals are obtained mainly as byproduct in the extraction of tin in Malayasia and Nigeria.

In India, Columbite generally occurs in rocks of the Dharwar system. In association with beryl in pegmatites traversing mica belts, columbite-tantalites are found in Bihar (Gaya), Rājasthan, Tamil Nadu (Nellore), Karnataka and Kerala. Some occurrences are also reported in Tiruchirapalli and the mica mines of Salem and Coimbatore.

29.3.2 The Element

Extraction

The minerals are generally fused with potassium carbonate and extracted with water — insoluble hydroxides of iron and manganese are thereby largely eliminated.

The aqueous extract containing K_3NbO_4 and K_3TaO_4 is treated with CO_2 to precipitate the pentoxides of the metals. This is dissolved in concentrated HF-KF when niobium forms the more soluble K_2NbOF_5 and tantalum forms the less soluble K_2TaF_7. These are separated by fractional crystallization.

Reduction of $K_2[NbOF_5]$ by aluminium gives niobium. Electrolysis of molten K_2TaF_7 gives tantalum.

Now-a-days, the metals are conveniently obtained by solvent extraction. From dilute aqueous HF, tantalum is first extracted by methyl isobutyl ketone; niobium is extracted next from more acidic aqueous phase. From these extracts, the metals may be obtained by sodium or carbon reduction of their oxides or by the electrolysis of their fused fluorides.

Uses

Niobium is used as an alloying metal in stainless steel for use at high temperature. Niobium-zirconium wires are used in superconducting magnets.

Tantalum is used as a liner in chemical plants owing to its very high corrosion resistance. It is widely used in the manufacture of capacitors and as a filament in lamps. Being completely inert to body fluids, tantalum is highly suitable for making plates, screws and wires used in orthopaedic surgery.

Properties

Both niobium and tantalum are silvery white bright metals with high melting points. They form bcc structures and are malleable and ductile when pure. The high melting and boiling points are consequences of participation by larger number of *d* - electrons in metallic bonding. The elements are relatively unreactive and resistant to acids except HF. They are oxidized on heating in air and dissolve in fused alkali.

General chemical features

The effect of lanthanide contraction makes the metallic and ionic radii of the two elements same and a close similarity follows in their chemical properties, undisturbed by the different ground state electron configurations. The elements present a normal oxidation state of V but also show a wider range of lower oxidation states; these states are not so unstable as they are for Zr and Hf. Of course, they are less stable than the group oxidation state V and strongly reducing in nature. Standard potentials (V) for these elements in acidic solution are

$$\underset{+V}{Nb_2O_5} \xrightarrow{-0.1} \underset{+III}{Nb^{3+}} \xrightarrow{-1.1} \underset{0}{Nb} \quad (Nb_2O_5 \xrightarrow{-0.65} Nb) \qquad \underset{+V}{Ta_2O_5} \xrightarrow{-0.81} \underset{0}{Ta}$$

However, the elements show little cationic chemistry and form a large number of anionic species. The halides and oxohalides appear to be the most important compounds of the elements; these are mostly volatile and get readily hydrolyzed. Numerous metal atom cluster compounds are known in the lower oxidation states of the metals.

29.3.3 Compounds of Nb(V) and Ta(V)

Oxides

The stabilities of the oxides increase from V-Nb-Ta, as shown by the Gibbs energy changes

	V_2O_5 (c)	Nb_2O_5 (c)	Ta_2O_5 (c)	
ΔG_f^0, 298K	−1427	−1776	−1908	kJ mol^{-1}

While vanadium(V) forms only V_2O_5 and fluoride VF_5, all other halides MX_5 are known for Nb(V) and Ta(V).

Nb_2O_5 and Ta_2O_5 are obtained by dehydrating the hydrous oxides or by heating the metals or their suitable compounds in oxygen. These are white, high melting solids (Nb_2O_5 : m.p. 1490°C; Ta_2O_5 : m.p. 1870°C). with unit cells consisting of MO_6 octahedra. They are chemically inert, practically insoluble in water and acids, attackable only by concentrated HF or by fusion with alkali metal hydrogen sulphate, carbonate or hydroxide.

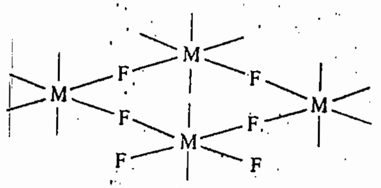
The various "niobates" and "tantalates" are actually mixed oxides providing octahedral coordination around the metal. The metaniobates and metatantalates M^INbO_3 and M^ITaO_3 have perovskite structures. A number of more complex species are also known with 2, 5 or 6 metal atoms, like $M^I_4Nb_2O_7$ or $M^I_8Ta_6O_{19}$. Other polyanions are also known both in solution and in the solid state. Gelatinous hydrous oxides of the metals are formed when solutions containing these oxyanions are neutralized with acids or by hydrolysis of the halides.

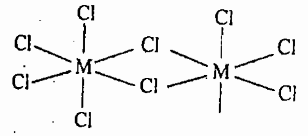
Halides

NbF_5 and TaF_5 may be obtained by reacting the metals, their oxides or pentachlorides with fluorine (also HF on MCl_5). These are white solids : NbF_5 : m.p. 80°C, b.p. 235°C; TaF_5 m.p. 95°C, b.p. 229°C. Other pentahalides, obtained by direct reaction of the metals with excess halogens or other standard method, are yellow to brown or purple red solids. They are soluble in organic solvents like ether, carbon tetrachloride etc. They are readily hydrolyzed to gelatinous hydrous oxides.

$$2NbCl_5 + 5H_2O \longrightarrow Nb_2O_5 + 10HCl.$$

The pentafluorides are tetrameric in the solid with MF_6 units and one bridge fluoride ion between each pair of metal atoms (29-I). The pentachlorides and pentabromides consist of dimeric molecules (29-II). Their vapours are monomeric.

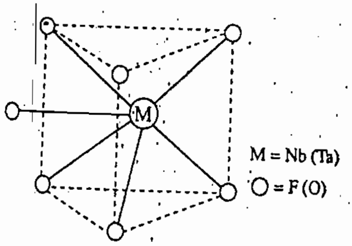

29-I


29-II

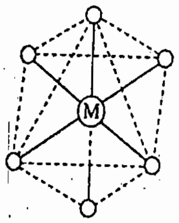
Fluorocomplexes are formed by the pentafluorides with F^- and also by dissolving the pentoxide in HF. NbF_6^- and TaF_6^- ions are formed at moderate F^--ion concentrations but with higher concentration of F^-, species like NbF_7^{2-}, TaF_7^{2-}, $NbOF_5^{2-}$, $NbOF_6^{3-}$ and TaF_8^{3-} are formed.

$$2KF + TaF_5 = K_2[TaF_7]; \quad 3KF + NbOF_3 = K_3[NbOF_6].$$

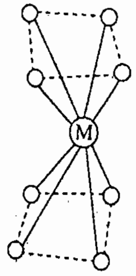
The MF_7^{2-} ions are based on trigonal prism (29-III) while $NbOF_5^{2-}$ is octahedral. $NbOF_6^{3-}$ is also based on an octahedral structure with the seventh ligand at the center of a triangular face (29-IV). The TaF_8^{3-} ion is square antiprismatic (29-V).



29-III



29-IV



29-V

The oxohalides are also formed by reaction of the pentahalides with oxygen. With HF, M_2O_5 gives MO_2F; on progressive heating, this gives MOF_3 and then M_3O_7F. The series MOX_3, MO_2X and M_3O_7X is known for both Nb and Ta with all halogens. The oxohalides are monomeric in the vapour but polymeric in the solid. For example, $NbOCl_3$ consists of chains of planar binuclear $Cl_2Nb{<}^{Cl}_{Cl}{>}NbCl_2$ units linked by oxygen bridges between Nb atoms.

Even for niobium and tantalum, the group oxidation state (V) is too high to favour the formation of simple ionic salts. The trend observed in vanadium to form oxovanadium species is maintained and we have only a few ill-defined salts and double salts like $MO(NO_3)_3$ and $(NH_4)_6Nb_2O(SO_4)_7$. These are hydrolyzed extremely rapidly.

Like vanadium(V), niobium and tantalum also form colourless peroxocomplexes $[Nb(O_2)_4]^{3-}$ and $[Ta(O_2)_4]^{3-}$ by the action of H_2O_2 on the pentoxides in alkaline medium.

$$M_2O_5 + 8H_2O_2 + 6KOH = 2K_3[M(O_2)_4] + 11H_2O$$

$K_3Nb(O_2)_4$ is pale yellow and $K_3Ta(O_2)_4$ is white.

These compounds are stable in the solid state. Action of acids convert them to corresponding "peracids" of composition HMO_4.

The pentahalides also act as Lewis acid forming complexes with O, S, N, P and As donor ligands (L). Most of these MX_5L type complexes are octahedral, where L = R_2O, R_2S, $POCl_3$, 2, 2′-dipyridyl etc.

29.3.4 Oxidation state IV

The bluish-black oxide NbO_2 is formed by high temperature reduction of Nb_2O_5 with hydrogen. It has a distorted rutile structure. Both the oxides show a tendency to disproportionate. They dissolve only in hot alkali.

The chlorides, bromides and iodides of Nb(IV) and Ta(IV) are stable diamagnetic compounds. NbF_4(black) is a nonvolatile paramagnetic solid (dec > 350°C); TaF_4 is unknown.

The chlorides and bromides may be obtained by reduction of the pentahalides with H_2, Al or the metals (Nb/Ta) at high temperatures. These are brown-black or black solids which disproportionate on heating.

$$2TaCl_4 \xrightarrow{400°C} TaCl_3 + TaCl_5$$

Hydrolysis of $TaCl_4$ also gives a precipitate of Ta_2O_5 and a green solution containing Ta(III) which is fairly stable at ordinary temperature. Crystalline $NbCl_4$ has linear chains of edge-linked $NbCl_6$ octahedra in which the Nb atoms are off the centre (Fig. 29.4) and linked in pairs.

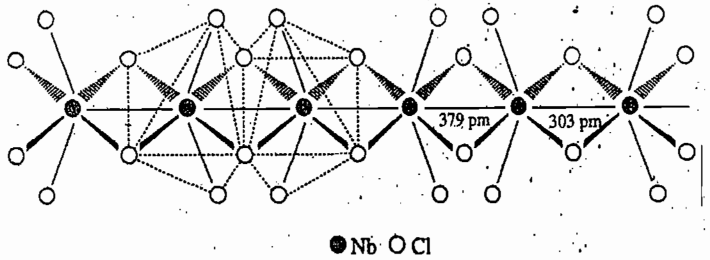


Fig. 29.4
Structural pattern of $NbCl_4$.

NbI_4 may be obtained by prolonged heating of NbI_5 at 300°C. TaI_4 is easily made by heating TaI_5 with Ta. Alternatively, TaI_5 may be reacted with excess pyridine to give $TaI_4(py)_2$; this gives TaI_4 on heating. Both these iodides are also diamagnetic volatile solids with structures similar to that shown in Fig. 29.4. The diamagnetism arises because of pairing of the unpaired spin on each metal through metal-metal bonds.

Oxohalides of the type MOX_2 are known for X = Cl, Br, I for both Nb and Ta. Electrolytic reduction of Nb(V) in 13M HCl results in an orange solution which probably contains the $NbOCl_4^{2-}$ anion. The complex $(Me_3P)_4M_2(Cl)_4(\mu - Cl)_4$ contains the metal in 9-coordination.— each metal is surrounded by two phosphines, two terminal chlorines, four bridge chlorines and the other metal atom.

29.3.5 Lower oxidation states

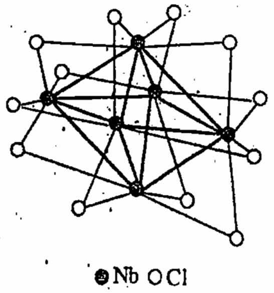
The trihalides are known for F, Cl and Br. When NbI_5 is heated at 430°C, the product contains Nb in mixed oxidation states, as in Nb_3I_8. Other trihalides of Nb are made by reducing NbX_5 with H_2 at about 500°C. $TaCl_3$ results from the disproportionation of $TaCl_5$. Most of these compounds are brown or black in colour and strongly reducing in nature. Solutions containing the metals in III state are yellow or blue under different conditions. Reduction of MX_5 (pentahalides) with sodium amalgam in presence of ligands (L) give several binuclear complexes, e.g., $M_2Cl_6L_3$ when L = tetrahydrothiophene (THT or SC_4H_8), SMe_2 or $M_2Cl_6L_4$ when L = PMe_3. These compounds are capable of entering a large number of substitution, oxidative addition, cluster formation and coupling reactions with ≡ C–. The dinuclear complexes usually possess an M≡M double bond with typical bond distances around 270 pm.

Reduction of $Ta_2Cl_6(THT)_3$ with sodium amalgam gives the bright red species $[Cl_3Ta^{II}(\mu\ THT)_3Ta^{II}Cl_3]^{2-}$containing Ta ≡ Ta (distance 263 pm.). The compound is stable towards water.

The only simple dihalide of Ta(II) is $TaCl_2$; the green-black non-stoichiometric solid results from the disproportionation of $TaCl_3$ at 600°C. It is much more reactive than $TaCl_3$ and reacts with water under all conditions. Nb(II) does not appear to be well-established. The volatility of the compounds drop from the tetrahalide to the trihalide to the dihalide, suggesting polymeric structures of varying degree. Sodium amalgam reduction of higher chlorides in presence of ligands L gives paramagnetic octahedral complexes MX_2L_4 where X may be Cl and L may be PMe_3.

The lower oxidation states of Nb and Ta are marked by their strong tendency to form *cluster compounds* based on poly-centered metal-metal bonding. Thus, reduction of the pentahalides with sodium amalgam (or cadmium at red heat followed by precipitation of CdS) produces a number of halides with representative formula M_6X_{14} (X = Cl, Br, I) as well as Nb_6F_{15}, Ta_6Cl_{15}, Ta_6Br_{15} and Ta_6Br_{17}. The compounds are soluble in water and alcohol. When treated with Ag^+, a solution of M_6X_{14} precipitates only one-seventh of the total halogen as AgX, suggesting the presence of the complex cation $M_6X_{12}^{2+}$.

$$[M_6X_{12}]^{2+}Cl_2 + 2Ag^+ \longrightarrow [M_6X_{12}]^{2+} + 2AgCl$$



29-VI

The structure of the $M_6X_{12}^{2+}$ ion has been determined by X-ray studies : it consists of an octahedron formed by the metal atoms with M—M bonds as well as bridging halogen atoms (Fig. 29-VI). Additional terminal M—X groups to this central skeleton may give rise to other ionic species like $M_6X_{18}^{4-}$.

Formal oxidation states 0. I and –1 for the elements are known only in complexes, specially carboxyls and cyanides.

29.3.6 Complex compounds

We have already mentioned some complex compounds of Nb and Ta, mainly the peroxo and halo complexes. In Table 29.2 we mention some of the main complex species in different oxidation states. Other geometries and coordination numbers are also known.

TABLE 29.2

Complex compounds of Niobium and Tantalum

Oxidation State	Co-ordination Number	Geometry	Example
V	6	*Octahedral*	$NbCl_5.OPCl_3$; TaF_6^-; $TaCl_5.SMe_2$.
		Trigonal prism	$[M(S_2C_6H_4)_3]^-$ (benzenedithiolato)
	7	*Capped trigonal prism*	MF_7^{2-}
	8	*Square antiprism*	TaF_8^{3-}
IV	6	*Octahedral*	MCl_6^{2-}; MBr_6^{2-}; $TaCl_4py_2$
	7	*Pentagonal bipyramid (distorted)*	NbF_7^{3-}
	8	*Dodecahedral*	MCl_4 (diars)$_2$; $K_4[Nb(CN)_8].2H_2O$ (crystal)
		Square antiprism	Nb (β-diketonate)$_4$ $[Nb(CN)_8]^{4-}$ (solution)
III	6	*Octahedral*	$Nb_2Cl_9^{3-}$, $M_2Cl_6(SMe_2)_3$
	8	*Dodecahedral*	K_5 $[Nb(CN)_8]$ (solid).

Niobium and tantalum do not form simple carbonyls. The $M(CO)_6^-$ ion contains the metals in their formal oxidation state –I. The –III state is formally present in the $M(CO)_5^{3-}$ ion (tbp). The $M(CO)_6^-$ species are now prepared by reduction of the pentahalides in pyridine with Zn/Mg under an atmosphere of carbon monoxide at ordinary pressure. The yellow octahedral $M(CO)_6^-$ ion is rather inert to displacement of CO. It may be further reduced by sodium in liquid NH_3 at –78°C to $M(CO)_5^{3-}$ which is stable only at low temperature.

29.3.7 Organometallic compounds

Niobium and tantalum have an extensive chemistry involving M—C σ-bonds, η-C_5H_5 and cyclooctatetraene. Niobium and tantalum methyls are stable compounds prepared by reduction of the pentahalides :

$$2TaCl_5 + 3ZnMe_2 \xrightarrow{\text{ether}} 3ZnCl_2 + 2TaCl_2Me_3$$

$$2TaCl_2Me_3 + 2LiMe \xrightarrow{\text{ether}} TaMe_5 + 2LiCl.$$

$TaMe_5$ may explode spontaneously at room temperature. The alkyls act as Lewis bases, adding neutral ligands or forming anions.

Zerovalent Nb and Ta compounds like $M(arene)_2$ have been prepared by metal vapour synthesis.

Niobium and tantalum form a number of cyclopentadiene (Cp) complexes :

$M(\eta^5-Cp)_2(\eta^1-Cp)_2$; $[M(\eta^5-Cp)_2X_3]$ and $[M(\eta^5-Cp)_2X_2]$ where X = Cl, Br. These are not true sandwich compounds. The two cyclopentadiene rings are often not parallel.

29.4 MOLYBDENUM AND TUNGSTEN

Mo :	$[Kr]4d^55s^1$	**Atomic number : 42**	**Atomic weight : 95.94**	**M.P. : 1620°C**
W :	$[Xe]4f^{14}5d^46s^2$	**Atomic number : 74**	**Atomic weight : 183.85**	**M.P. : 3380°C**

29.4.1 Introduction

History : Molybdenum derived its name from the Greek word *molybdos* for lead because of the similarity of its soft black mineral molybdenite (MoS_2) which would be used for writing. The mineral was first studied by the Swedish minerologist A. Cronstedt in 1754 and following him Scheele prepared molybdenum oxide from the mineral in 1778. In 1790 P. Hjelm prepared molybdenum by redcuing the oxide with carbon. Pure molybdenum was prepared by Berzelius in 1817 by reducing the oxide with hydrogen.

The mineral "tungsten" (Swedish *heavy stone*; $CaWO_4$) was studied by Cronstedt in 1751; later Scheele (and Bergmann) isolated a new oxide from this. Two years later the Spanish chemists F. and H. D'Egluar (brothers), separated the same oxide from the mineral known as "wolframite" and reduced it to the metal by heating with charcoal. The mineral wolframite was so named because medieval miners observed that in smelting of tin from these ores, a part of smelted metal was permanently lost; they believed that tin was "eaten up" by the mineral present in the ores like a sheep is eaten up by a wolf. Tungsten derived its symbol W from the name Wolfram which is still used in some literature.

Abundance & Occurrence : Both molybdenum and tungsten are rare (~1.2 ppm). The most important ore of molybdenum is *molybdenite*, MoS_2, found in Colorado (USA), Canada and Chile. Other minerals are *wolfenite* $PbMoO_4$ and *molybdite* MoO_3. Tungsten occurs as *scheelite* (calcium tungstate, $CaWO_4$) and *wolframite* (Fe, Mn)WO_4 — the main reserves are placed in China, followed by the USA, South Korea, Bolivia, Portugal and Russia.

In India, small deposits of molybdenite are found in the Khasi Hills (Meghalaya), Hazaribagh (Bihar), Godavari district (A.P.) and Madura (T.Nadu). Wolframite occurs sparingly in Jodhpur, Nagaur and Sirohi districts in Rajasthan.

Trace quantities of molybdenum occur in enzymes involved in the conversion of atmospheric nitrogen to NH_3 (*nitrogenase*) and other related biological systems.

29.4.2 The Element

Extraction

Molybdenite, concentrated by foam floatation, is roasted to MoO_3. Owing to its volatility at 1000°C, it is first reduced to MoO_2 by heating with H_2 at 500°C. In the second step, MoO_2 is reduced by H_2 at 1100°C to Mo. MoO_3 may also be reduced by aluminium. Pure molybdenum is obtained by H_2-reduction of ammonium molybdate, obtained by dissolving the MoO_3 in aqueous ammonia and crystallizing. Carbon-reduction of MoO_3 gives mostly carbides.

MoO_3 may also be used directly or as ferromolybdenum in steel-making.

Ferromolybdenum is prepared by reducing molybdenite with iron and coke in an electric furnace or by reducing a mixture of molybdenum and iron oxides with aluminium (thermite reaction).

Tungsten ores, being magnetic, are easily concentrated by magnetic separation. The ore is then fused with caustic soda or sodium carbonate in air and the cooled melt is leached with water. The solution of sodium tungstate deposits hydrous WO_3 ("tungstic acid") on acidification which is dehydrated by heating. Metallic tungsten is prepared by reduction of WO_3 with H_2 or carbon at red heat.

Since both the metals have very high melting points, they are obtained initially in the form of powders which are converted to the massive state by compression under hydrogen at high temperatures.

Properties

Some main properties of the elements are shown in Table 29.3.

TABLE 29.3

Some properties of Mo/W

	Mo	W
Density g cm^{-3}	10.28	19.3
M.P. °C	1620	(3380)
B.P. °C	4650	(5500)
Ionic radii(VI), pm	59	60

The metals are lustrous and silvery with high melting and boiling points—tungsten has the highest melting point of all metals and stands second only to carbon among all elements. It appears that it is the last element in the third transition series in which all *d*-electrons participate in metallic bonding. This is because the *d*-electrons in the third series enter the core rather slowly. The elements have typically metallic bcc structures—they are hard and relatively unreactive due to a protective surface film of oxides.

The metals are only slightly attacked by weak acids or alkalis. Both of them dissolve in HNO_3-HF mixtures and in fused alkalis.

$$W + 2HNO_3 + 8HF = H_2[WF_8] + 2NO + 4H_2O$$

$$W + 3NaNO_3 + 2NaOH = Na_2WO_4 + 3NaNO_2 + H_2O$$

On heating in air, they form the trioxides MoO_3 and WO_3 (Cr gives Cr_2O_3).

$$2Cr + \frac{3}{2}O_2 = Cr_2O_3 \qquad \Delta \overset{\circ}{G}_{298} = -1059 \text{ kJ mol}^{-1}$$

$$Mo(W) + \frac{3}{2}O_2 = MoO_3(WO_3) \qquad \Delta \overset{\circ}{G}_{298} = -668(-767 \text{ kJ mol}^{-1})$$

The oxides are acidic but the salts derived from these acids are complex polyanions. On heating in chlorine, the metals give WCl_6/$MoCl_6$ (Cr gives $CrCl_3$).

Uses

The main consumption of molybdenum is in the manufacture of stainless steel and alloy steels used in high-speed tools. The oxide MoO_3 or ferromolybdenum is directly used for this purpose. Ni–Mo steel is used for making gun-barrels and propeller shafts. Cr–Mo steel tubes are used in air-craft construction. Pure molybdenum metal (with added cobalt, supported on Al_2O_3) is used to treat crude petroleum with H_2 when sulphur containing organics are converted to H_2S and also to hydrogenate olefinic bonds. MoS_2 may be formed in situ in the catalytic process. The metal is also used as a catalyst. MoS_2, having a layer lattice, finds use as a high temperature lubricant (*Molyslip;* see Sec. 29.4.5).

Tungsten is largely used as tungsten carbide, WC, used in tool-tips owing to its extreme hardness. The pure metal is largely used in making filaments for electric lamps and anticathodes in X-ray tubes. Tungsten is also an important alloying metal in high speed tool steel. It forms several very hard alloys such as *stellite* (Co, Cr, W) and *Widia metal* (WC + 10% Co).

General Properties

In spite of their close resemblance, Mo and W also show some distinct differences in their chemistry, as we shall shortly encounter. The standard reduction potentials(V) are given below :

Acidic solution

+VI   +V   +IV   +III   0

$$\overbrace{H_2MoO_4\,(aq) \xrightarrow{0.5} Mo_2O_4^{2+} \xrightarrow{0.17} Mo_2O_2^{4+} \xrightarrow{0.0} Mo_2(OH)_2^{4+} \xrightarrow{0.005} Mo}^{0.114}$$

$$H_2MoO_4\,(aq) \xrightarrow{0.65} MoO_2 \xrightarrow{-0.01} Mo^{3+} \xrightarrow{-0.2} Mo$$

$$\underbrace{WO_3 \xrightarrow{-0.03} W_2O_5 \xrightarrow{-0.03} WO_2}_{-0.09} \xrightarrow{-0.12} W$$

Basic solution

+VI   +IV   0

$$\underbrace{MoO_4^{2-} \xrightarrow{-0.78} MoO_2 \xrightarrow{-0.98} Mo}_{-0.91}$$

$$\underbrace{WO_4^{2-} \xrightarrow{-1.26} WO_2 \xrightarrow{-0.98} W}_{-1.07}$$

The corresponding oxidation state-free energy diagram (Fig. 29.5) suggests that the Group state VI is the most stable, but the V and IV states will also be well represented. Strong reducing properties are not met with before oxidation states III and II. The greater relative stability of the lower oxidation states of Mo is also apparent.

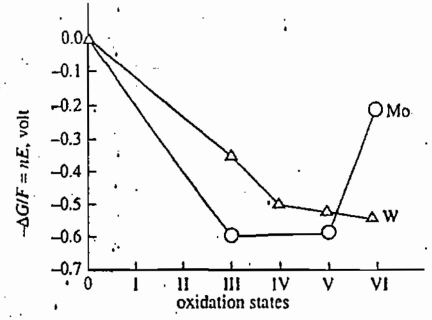


Fig. 29.5
Oxidation state-free energy diagram for Mo/W.

The two elements also show a contrast with chromium— Cr(III) is quite stable while Cr(VI) is oxidizing in nature; for the heavier elements, the III state is very unstable and the VI state is quite stable. The II state, which is well defined for Cr, is uncommon among Mo/W except some M—M bonded compounds.

29.4.3 Oxidation state VI

The oxides, hexafluorides and hexachlorides for both metals are established; tungsten also forms WBr_6. There is a close similarity with uranium(VI) which also forms volatile hexafluoride, oxide, hexachloride and hexabromide.

In the Cr(VI) – Mo(VI) – W (VI) series, there is a marked increase in the stability of similar compounds, as shown by the ΔG_f^0 values (kJ mol^{-1}) :

CrO_3 (c) :	−506	MoO_3 (c) :	−668	WO_3 (c) :	−764
CrO_2Cl_2 (l) :	−524	MoO_2Cl_2 (l) :	−623	WO_2Cl_2 (c) :	−753
CrO_4^{2-} (aq) :	−730	MoO_4^{2-} (aq) :	−916	WO_4^{2-} (aq) :	−920

MoO_3 (white) and WO_3 (yellow) are the end-products of heating other compounds of these elements in air. MoO_3 (mp 801°C) consists of MO_6 unit cells and passes into the gaseous state without decomposition. Insoluble in water, they dissolve in alkalis.

$$2KOH + MoO_3 = K_2MoO_4 + H_2O$$

The MO_4^{2-} ions are tetrahedral.

The oxomolybdates(VI) and oxotungstates(VI) of Group I elements, Tl^+, NH_4^+ and also Mg^{2+} and Ca^{2+} are water soluble forming colorless solutions.

MoO_3 also dissolves in acids to give oxy-cations or related hydrolyzed species but WO_3 is insoluble in acids.

Neutralization of the alkaline solutions containing the MO_4^{2-} ions precipitates the hydrated oxides, $MoO_3.2H_2O$ (yellow) and $WO_3.\ 2H_2O$ (off-white) from strongly acidic media. These are often called molybdic acid or tungstic acid but they are not the hydrated acids H_2MO_4, H_2O. $MoO_3.2H_2O$ contains sheets of MoO_6 octahedra sharing corners.

The simple mononuclear oxyanion found in strongly basic solutions give rise to various condensed aggregates when the solution is made weakly acidic. These are discussed separately. (see "Polyacids" or iso- and hetero-polymetallates).

The hexahalides are prepared by direct reaction. MoF_6, a colourless liquid (b.p. 34°C) and WF_6, a colourless gas (b.p. 17°C) are much more stable. In contrast to SF_6, they are quite reactive : they react readily with oxygen and moisture to form oxohalides and HF. The acidic nature of MF_6 is shown in their interaction with basic fluorides

$$MF_6 + KF = KMF_7$$

WBr_6 is unstable—decomposes on gentle warming. The oxohalides are of two types :

MOX_4 (X = F, Cl; for W, X = Br also); MO_2X_2 (X = F, Cl, Br; for W, X = I also).

These are also volatile covalent compounds, usually solids, hyrolyzing to give MO_3, MoX_4 compounds more rapidly than MO_2X_2 compounds. WO_2Cl_2 (yellow) decomposes above 200°C to WO_3 and red $WOCl_4$. The MOX_4 molecules in gas phase are based on square pyramidal structure with the metal above the plane of four halogen atoms. $WSCl_4$ and $WSeCl_4$, also volatile solids, have similar structures in gas phase.

The sulphides MS_3 are precipitated by H_2S from slightly acid solutions of M(VI). In strong acid medium reduction occurs to IV state, precipitating MS_2. The MS_3 compounds are best prepared by thermal decomposition of the thiosalts $(NH_4)_2MS_4$. Many sulphur containing polyanions are also known.

Some compounds of the elements in oxidation states between VI and V states are worth mention. When the trioxides are reduced with mild reducing agent, intense blue oxides are formed having composition between M_2O_5 and MO_3. Even when powdered molybdenum is kept long in contact with a suspension of MoO_3 in water, a deep blue colloidal solution is formed (*Molybdenum blue*; also formed on reducing an acidified molybdate solution with H_2S, SO_2, glucose etc.).

The blue oxides contain M^V and M^{VI} in an oxide lattice and the intense colour appears due to charge-transfer between the metal atoms in two different oxidation states.

Reduction of sodium tungstate, Na_nWO_3 (*n* lies between 0 and 1), for example by heating with W or H_2, gives intensely coloured inert materials with bronze-like appearance. These are known as *tungsten bronzes*. The colour of these materials vary from yellow to blue-violet as *n* varies from 0.9 to 0.3. They possess good lustre and are conductors of electricity. They are insoluble in water and resistant to all acids except HF. In alkaline medium, these are exidized by oxygen to tungstate(VI). Their structure is based on that of ReO_3 (Fig. 29.6) and is related to the perovskite.

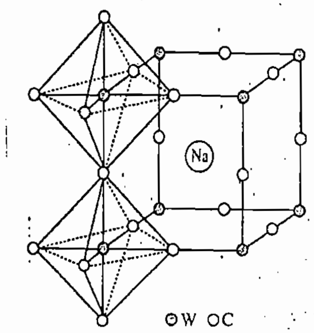


Fig. 29.6

The structure of tungsten bronze (the ReO_3 structure except the Na).

The W (or Re) atoms lie at the corners of the cube while O-atoms lie at edge centres. If all the body centres were occupied by Na^+ ions, the structure would represent the *perovskite*. In the bronzes, Na^+ ions occur at random. The metallic lustre and conductivity of the bronzes arise from delocalization of the valence electron of sodium over the structure.

Isopoly and heteropoly oxometallates (Iso- and hetero-polyacids and salts)

The MO_4^{2-} ions of Mo(VI) and W(VI) show a prominent tendency to condense in strongly basic medium forming various polyoxoanions in solution as well as in the solid state. This tendency is shown to a limited extent by V(V), Nb(V), Ta(V) and U(VI) but is almost negligible for Cr(VI). These polyoxometallates and their corresponding protonated species are conventionally called isopolyacids and their salts : here the condensed moiety contains only one kind of oxometal ion. Species formed by condensation of these oxometal ions with another oxo-ion (e.g., PO_4^{3-}, SiO_4^{4-}) are called heteropolyacids and their salts. At present, it has been possible to ascertain the exact structures of the large aggregates by X-ray crystallography; the nature of the species existing in solution is also known directly by ^{17}O nmr studies. It is now established that the polyoxometallate aggregates are mostly built up of MO_6 octahedra sharing vertices or edges (not faces), occasionally with additional MO_4 units.

The principal isopolyoxometallates for Mo(VI) and W(VI) in solution are

$$Mo_7O_{24}^{6-}\ (pH \approx 6)\ ;\quad Mo_8O_{26}^{4-}\ (pH < 6)$$

$$H_2W_6O_{22}^{6-}\ ;\ W_7O_{24}^{6-}\ \text{ and }\ H_2W_{12}O_{42}^{10-}.$$

In the solid state, the $Mo_2O_7^{2-}$ ion, (analogous to the $Cr_2O_7^{2-}$ ion) is also known — $(NH_4)_2Mo_2O_7$ has an infinite chain of MoO_6 octahedral and MoO_4 tetrahedral units. In solution it readily rearranges to $Mo_7O_{24}^{6-}$. The principal equilibria are

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O \qquad (29\text{-I})$$

$$Mo_7O_{24}^{6-} + 3H^+ + HMoO_4^- \rightleftharpoons Mo_8O_{26}^{4-} + 2H_2O \qquad (29\text{-II})$$

In strongly basic solution, the principal species for Mo(VI) is MoO_4^{2-} (tetrahedral). On slowly adding acids, the following types of equilibria are established :

$$MoO_4^{2-} + H^+ \rightleftharpoons HMoO_4^- \qquad (29\text{-III})$$

$$HMoO_4^- + H^+ + 2H_2O \rightleftharpoons Mo(OH)_6 \qquad (29\text{-IV})$$

$$Mo(OH)_6 + HMoO_4^- \rightleftharpoons (HO)_5Mo(OMoO_3)^- + H_2O \qquad (29\text{-V})$$

$$(OH)_5Mo(OMoO_3)^- + HMoO_4^- \rightleftharpoons (HO)_4Mo(OMoO_3)_2^{2-} + H_2O \qquad (29\text{-VI})$$

$$\downarrow$$

$$Mo(OMoO_3)_6^{6-}$$

$$Mo(OMoO_3)_6^{6-} \longrightarrow Mo_7O_{24}^{6-} \qquad (29\text{-VII})$$

The final $Mo_7O_{24}^{6-}$ moiety consists of MoO_6 octahedral units as shown in Figure 29.7. The octahedral units are, however, not regular.

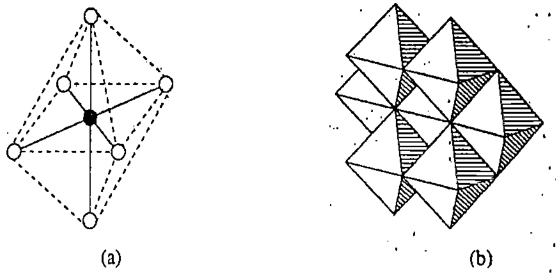

(a) (b)

Fig. 29.7
(a) The MoO_6 octahedral unit (b) The $Mo_7O_{24}^{6-}$ ion.

Heteropoly oxometallates are readily formed by cocondensation of the two oxoanions, as we have seen in the test for phosphates with ammonium molybdate solution :

$$HPO_4^{2-} + MoO_4^{2-} \xrightarrow{H^+} [PO_4.\ 12MoO_3]^{3-}$$

The formula of the Mo(VI) ion is simplified—the actual species may be the $Mo_7O_{24}^{6-}$ ion. Similar heteropoly anions are also formed by W. Many of these anions may be protonated to form the heteropolyacids in solution as well as in hydrated crystals. These also consist of MO_6 octahedra surrounding a central $M'O_4$ tetrahedron (M' is the heteroatom) or $M'O_6$ octahedron. In the latter type represented by the general formula $[M'M_6O_{24}]^{(12-x)-}$ where x is the formal positive charge on the heteroatom M'. M' may be I^{7+}, Te^{6+}, Co^{3+}, Al^{3+} etc. The structure is a ring of six linked MO_6 octahedra with a central octahedral hole for M' (Fig. 29.8).

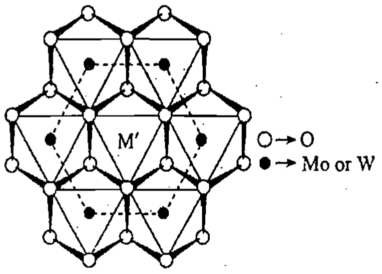


Fig. 29.8
The structure of $M'M_6O_{24}^{(12-x)-}$.

In the heteropolyanions $M'M_9O_{32}^{(10-x)-}$, the structure consists of three sets of clusters of three M [illegible] groups giving a central hole for M' (Mn^{4+}, Ni^{4+}).

In the heteropolyanions centered around $M'O_4$ tetrahedron, the phosphomolybdate ion $[PMo_{12}O_{40}]^{3-}$ is a typical example, corresponding to the general formula $[M'M_{12}O_{40}]^{(8-x)-}$ where M' may be P^V, As^V, Si^{IV}, Ge^{IV}, Ti^{IV}, Zr^{IV} and Sn^{IV}. The structure contains four sets of three MO_6 octahedra joined by edges and forming a central tetrahedral hole. The heteropolyoxometallates provide a rich and varied field of condensed structures comparable to those of silicates. These, together with the isopoly oxometallates, are now attracting fresh attention as they provide a variety of uncommon environments which may stabilize unusual oxidation states (e.g., Ni^{IV}) and may find use as catalysts.

Ammonium molybdate is prepared by dissolving MoO_3 in excess aqueous ammonia — the solution may be evaporated to deposit crystals of ammonium molybdate $(NH_4)_6[Mo_7O_{24}]$. $4H_2O$. A solution of ammonium molybdate in dilute HNO_3 slowly deposits yellow MoO_3. $2H_2O$ ("molybdic acid") which forms a colloidal solution in water. A solution of ammonium molybdate in dilute HNO_3 is used to detect phosphate (see Group V, 15).

29.4.4 Oxidation state V

The oxide Mo_2O_5 reported earlier is actually non-stoichiometric. Heating MoO_3 with Mo at 700°C or WO_3 with W at 1000°C produces a large number of oxides of variable composition MO_x, $2 < x < 3$. These substances are intensely blue or purple. Mo_2S_5 is precipitated by the action of H_2S on Mo^V solutions.

Pentahalides MF_5 and MCl_5 are known for both Mo and W, together with WBr_5. MoF_5 is a yellow volatile solid (m.p. 67°C, b.p. 213°C) prepared in the reactions

$$Mo + F_2\,(\text{dilute}) \xrightarrow{400°C} MoF_5$$

$$Mo + 5MoF_6 \longrightarrow 6MoF_5$$

$$5MoF_6 + Mo(CO)_6 \xrightarrow{25°C} 6MoF_5 + 6CO$$

WF_5 is formed by reduction of WF_6 with W at 500 — 800°C and quenching the products. The yellow solid disproportionates above 30°C to WF_4 and WF_6. Both MoF_5 and WF_5 have tetrameric structures in the solid like NbF_5.

$MoCl_5$ (black, mp 194°C) and WCl_5 (green black, mp 242°C) are obtained by direct reaction. The solids are dimeric but are paramagnetic with no M—M bonds. The vapours are mainly monomeric as also their solutions in many organic media. They are highly reactive, being hydrolyzed by water. Solid $(MoCl_5)_2$ dissolves in fused KCl to give $MoCl_6^-$ but with KCl in ICl, $MoCl_6^{2-}$ is formed.

Oxohalides MOX_3 (X = Cl, Br) are known for both Mo and W; the latter also forms WO_2I.

The complexes formed by Mo(V) and W(V) are mostly formed by halogens, pseudohalogens and oxohalide groups. M^IMoF_6 and M_3MoF_8 are formed by reaction of $Mo(CO)_6$ in liquid IF_5 in presene of alkali fluoride (MF); the W-compounds may be prepared similarly. Oxohalide complexes MOX_5^{2-} and MOX_4^- (X = Cl, Br, CNS) are formed by reduction of M(VI). The cyanocomplexes $M(CN)_8^{3-}$ are known for both and may be prepared by strong oxidation of the M(IV) cyanocomplexes (see Mo(IV)).

The "aqua ion" of Mo(V), $Mo_2O_4^{2+}$ is actually a dimeric, diamagnetic species with Mo—Mo bond in which two octahedral $Mo(H_2O)_3(O)$ units are joined by two O-bridges.

29.4.5 Oxidation state IV

Both the dioxides MO_2 may be prepared by reducing the trioxides with H_2 or NH_3 below 470°C above which reduction may occur to the metal. MoO_2 may also be obtained from reaction of the metal with steam at 800°C. The oxides are insoluble in nonoxidizing mineral acids but dissolve in concentrated HNO_3 with oxidation to M(VI). They have a highly distorted rutile structure containing M—M bonds.

MoS_2 is the most stable sulphide of molybdenum and occurs naturally as molybdenite. It is formed by direct reaction of the elements. It may also be prepared from MoO_3 by heating in H_2S or fusing with sulphur and potassium carbonate. MoS_2 is attacked only by aqua regia and hot concentrated H_2SO_4. It has a layer structure in which the metal atoms are surrounded by six sulphur atoms at the corners of a trigonal prism. The outer planes (of S-atoms) in neighbouring layers are weakly cross-linked, making it a solid lubricant (*Molyslip*).

The tetrahalides MX_4 are known for X = F, Cl and Br. The tetrafluorides may be prepared by reducing the hexafluorides with benzene or other hydrocarbons. MoF_4 is also formed (plus MoF_5) in the disproportionation of Mo_2F_9, obtained by reacting $Mo(CO)_6$ with $F_2(+N_2)$ at -75°C. On heating to 150°C, MoF_5 volatilises, leaving light green nonvolatile MoF_4. Red-brown WF_4 is similarly nonvolatile.

$MoCl_4$ (dark red) exists in three forms. α-$MoCl_4$ is obtained by reduction of $MoCl_5$ by refluxing in benzene. It gets readily oxidized and hydrolyzed and tend to disproportionate :

$$2MoCl_4 \longrightarrow MoCl_3 + MoCl_5$$

α-$MoCl_4$ has a polymeric structure involving octahedrally coordinated Mo atoms linked into chains by sharing Cl-atoms. The Mo-Mo distance suggests some metal-metal bonding with partial spin pairing.

On heating to 250°C, α-$MoCl_4$ passes to the β form having larger Mo-Mo distance (367 pm), too long for any significant metal-metal bonding. The third form is obtained by heating MoO_2 with carbon and CCl_4-N_2 vapour; it has a magnetic moment of ~ 1.9 B.M.

WCl_4 is similar but is more readily prepared by reducing WCl_6 with $W(CO)_6$ in boiling chlorobenzene. It is somewhat more stable than $MoCl_4$. It also disproportionates at 500°C :

$$3WCl_4 = WCl_2 + 2WCl_5$$

The Mo(IV) aqua ion is the trinuclear $[Mo_3O_4(H_2O)_9]^{4+}$ ion which gives rise to many complexes of $Mo_3O_4^{4+}$, for example, $[Mo_3O_4F_9]^{5-}$ and $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$. There are also analogous complexes of the $W_3O_4^{4+}$ (*aq*) ion. In $[Mo_3O_4F_9]^{5-}$ and its W(IV) analogue, three Mo or W atoms form the triangular base of a tetrahedron with an O atom at the vertex — the $M_3O_4^{4+}$ unit is completed by a bridge O-atom on each M-M edge; three terminal F-atoms are now linked to each M atom.

The octacyano complexes formed by both the metals in IV and V oxidation states are interesting as they adopt variable structures depending upon the environment. The $M(CN)_8^{4-}$ ion is extremely stable, being attacked only by very strong oxidizing agents like MnO_4^- or Ce(IV) which oxidize it to the M(V)-octacyano complex. Solid $K_4M(CN)_8.2H_2O$ has a dodecahedral structure [Fig 29.2(a)]. The nature of crystal field splitting for this arrangement is shown in Fig. 29.9.

[Sec. 29.4.6
Mo, W—low ox. states]

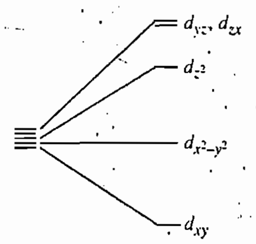


Fig. 29.9

Nature of crystal field splitting for dodecahedral ligand field.

The d_{xy} orbital is largely stabilized in comparison to the rest, providing large crystal field stabilization for d^1 and d^2 complexes, more so when the ligand field is strong. Thus, CFSE may be thought to contribute significantly to the stability of such species as $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$.

The $[M(CN)_8]^{3-}$ ions obtained by oxidation of $[M(CN)_8]^{4-}$ are also dodecahedral. However, small energy difference with other structures also give rise to the square antiprism coordination in combination with large cations. The $[Mo(CN)_8]^{4-}$ ion with $[Cd(N_2H_4)_2]^{2+}$ cation and also in $K_4Mo(CN)_8.6H_2O$ are square antiprismatic. Similarly both Mo and W complexes of $[M(CN)_8]^{3-}$ type are square antiprism with $[Co(NH_3)_6]^{3+}$.

29.4.6 Lower oxidation states

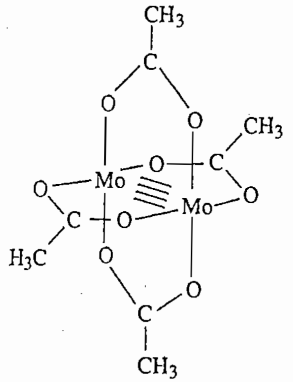
The low oxidation states of Mo and W are unstable and strongly reducing. The $[Mo(H_2O)_6]^{3+}$ ion can be obtained in aqueous CF_3SO_3H by dissolving $[MoCl_6]^{3-}$ or $[MoCl_5(H_2O)]^{2-}$ and separating from the Cl^- ion on a cation-exchange resin. The ion shows a magnetic moment of 3.7 B.M. and has been confirmed by X-ray study on an alum. There is no W(III) analogue. The oxide Mo_2O_3 is not known, but a sulfide Mo_2S_3 is known. All four trihalides of Mo(III) are known, but W(III) forms only WCl_3 and WBr_3. MoF_3 is formed as a yellow brown nonvolatile solid by reduction of MoF_6 with Mo at ~ 400°C. Other trihalides are also formed by strong reduction or disproportionation of higher halides. $MoCl_3$ (dark red) is only slowly hydrolyzed by water and slowly oxidized in air. It contains the Mo atoms in octahedral holes of Cl atoms which may be in either *hcp* or *ccp* array and there is appreciable metal-metal bond between Mo atoms in adjacent holes. Tungsten(III) is comparatively unstable, WCl_3, WBr_3 and some chloro complexes being the main representatives. WCl_3 consists of the cluster $W_6Cl_{12}^{6+}$ and Cl^- ions while WBr_3 consists of $W_6Br_6^{6+}$ with Br_4^{2-} — it is a polybromide. Several halocomplexes like MoX_6^{3-} (where X = Cl, F, SCN etc.) are also known.

Mo(III) forms a cyano complex $K_4[Mo(CN)_7].2H_2O$ with μ_{eff} = 1.75 B.M. at room temperature. Some cationic complexes like $[Mo(dipy)_3]^{3+}$ and $[Mo(phen)_3]^{3+}$ and neutral complexes like $Mo(acac)_3$ are also known.

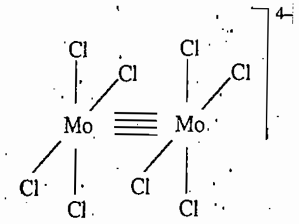
The II state is known in fewer compounds. The aqua ion $Mo_2^{4+}(aq)$ is formed in dilute CF_3SO_3H by interaction between $K_4[Mo_2(SO_4)_4]$ with $Ba(CF_3SO_3)_2$. The ion contains quadruply bonded $[Mo \equiv Mo]^{4+}$ unit which is thermally stable at room temperature but is a strong reducing agent. There are many other compounds containing the Mo-Mo quadruple bond. When $Mo(CO)_6$ is treated with excess acetic acid in refluxig diglyme, one gets $Mo_2(CH_3COO)_4$ (29-VIIa). This is also obtained by reducing $MoCl_6^{3-}$ with zinc in acetic acid. The tetraacetate may be dissolved in 12M HCl at 0°C to form $Mo_2Cl_8^{4-}$ (29-VIIb) which can be isolated in a number of air-stable salts. These undergo many ligand exchange reactions maintaining the Mo_2^{4+} unit intact.

Q. 29.2 *$K_3[W_2Cl_9]$ is diamagnetic whereas $K_3[Cr_2Cl_9]$ is strongly paramagnetic.*

Hint : W ≡ W but no Cr—Cr bond.



29-VII (a)



29-VII (b)

Complex halides of Mo(II) and W(II) of the type M_6X_{12} (X = Cl, Br, I) are also cluster compounds — $(M_6X_8)^{4+}X_4^-$, the six M atoms forming a cluster at the corners of an octahedron and the faces are bridged by the chlorine atoms. Oxidation of Mo_6Cl_{12} stops at $[Mo_6Cl_{12}]^{3+}$ though $W_6Cl_8^{4+}$ can be oxidized to $W_6Cl_{12}^{6+}$. The cyanocomplex of Mo(II), $[Mo(CN)_7]^{5-}$ may be prepared by reducing the Mo(IV) complex; it has a pentagonal bipyramid structure.

Mo(I) is known in $[Mo(C_6H_6)_2]^+$ and $[C_5H_5Mo(CO)_3]_2$

Oxidation states 0 and lower are observed in the carbonyls and related complexes, for example $Mo(CO)_6$, $W(CO)_6$, $Mo(CO)_5I^-$ and $M(CO)_5^{2-}$.

29.5 TECHNETIUM AND RHENIUM

Tc : [Kr] $4d^65s^1$; **Atomic number : 43 , Atomic weight : 98.91 M.P. : 2200**

Re : [Xe] $4f^{14}5d^56s^2$ **Atomic number : 75 Atomic weight : 186.21 M.P. : 3180**

29.5.1 Introduction

The discovery of the elements was initiated by the vacant places left below manganese in the Mendeleev periodic table. The vacancies at atomic numbers 43 and 75 were confirmed by Moseley's work and search for them continued until W. Noddack, I. Tacke and O. Berg of Germany spectroscopically identified the element of atomic number 75 in 1925. This was named rhenium after the river Rhine. It took at least another three years for the scientific community to accept their discoveries.

These three scientists also claimed the discovery of element number 43 and named it masurium after the state Masuren in Prussia. However, their claim did not survive subsequent check-ups. The element 43 was later discovered in 1937 by Perrier and Segre (Italy) after bombarding molybdenum nuclei with accelerated deuterons from a cyclotron. The element was named technetium from the Greek work for artificial. This is regarded by many as the first manmade element though minute traces of ^{99}Tc occur in nature from fission of uranium. All isotopes of the element decay by β-emission or electron capture; three isotopes having half-lives of the order of a million years are Tc-97 : 2.6 × 10^6 y; Tc-98 : 4.2 × 10^6 y; Tc-99 : 2.13 × 10^5 y. The atomic weight mentioned in the beginning of this topic refers to Tc-99, the only isotope isolated on a macro scale.

The concentration of rhenium in the earth's crust is also very small, 0.0007 ppm; also no large deposits are known. It occurs to a small extent in some molybdenites.

29.5.2 The element

Isolation

Technetium is recovered from wastes of uranium fission plants after removal of strongly radioactive products. It is separated from other fission products by oxidation, followed by distillation of volatile Tc_2O_7. Separation of accompanying Re (Re_2O_7 is also volatile) is achieved by precipitation with H_2S from acid concentration above 8*M* HCl when only Re_2S_7 is precipitated. The TcO_4^- may be carried with $[Ph_4As]^+ ClO_4^-$ as $[Ph_4As]^+ TcO_4^-$. At present, solvent extraction and ion-exchange processes have replaced the old procedures. The metal is obtained by reduction of Tc_2S_7 or NH_4TcO_4 with H_2. Technetium for nuclear medicine is also obtained by neutron irradiation of molybdenum (see use).

Rhenium is recovered mainly from the flue dust of roasting molybdenum sulfide ores and the residue from the smelting of certain copper ores. The volatile Re_2O_7 is converted to NH_4ReO_4 which may be reduced to the metal by H_2 (heat) :

$$2NH_4ReO_4 + 4H_2 = 2Re + N_2 + 8H_2O$$

Uses

The main use of technetium is in nuclear medicine as an imaging agent for disorder in physiological systems. Though Tc-99 is a weak β-emitter, it has a metastable isotope Tc-99m which is a mild γ-emitter ($t_{\frac{1}{2}}$ = 6 hours). This is obtained by neutron irradiation of ^{98}Mo

$$^{98}Mo\ (n, \beta)\ ^{99m}Tc \xrightarrow[6\ hrs]{\gamma} {}^{99}Tc$$

The γ-ray emitted by Tc-99m is weak and harmless but can be detected by photography. The isotope is administered to the patient in the form of a suitable compound which is carried to specific organs and an image of the organ is obtained with γ-ray scanning device. Different compounds are used in the study of different organs, for example TcO_4^- to examine the blood brain barrier, Tc(III) complexes of the type $TcL_2X_2^+$ (L = diphosphine or diarsine) to study the heart and phosphonate complex anions in imaging bones.

Technetium compounds, e.g. ammonium pertechnetate has been shown to act as a good corrosion inhibitor even in traces.

The use of rhenium is limited by its scarcity. Most of it is used in making alloys like Pt-Re catalysts used in reforming of petroleum. It is also used in making mass spectrometer filaments, thermocouples etc.

Properties

Technetium (mp 2200°C) and rhenium (mp 3180°C) form *hcp* metallic lattice and are less reactive than manganese. They are not oxidized in air at ordinary temperatures but form volatile heptoxides M_2O_7 when heated in oxygen. The sulphide MS_2 may also be formed by direct reaction. The metals dissolve in HNO_3, conc. H_2SO_4 or bromine-water to form HMO_4 — "pertechnetic"/"perrhenic" acids.

$$3Tc + 7HNO_3 = 3HTcO_4 + 7NO + 2H_2O$$

Fluorine reacts with Tc to give TcF_5 + TcF_6 and with Re to give ReF_6 + ReF_7.

General chemical features

The elements resemble one another closely, but both deviate appreciably from manganese. While manganese presents a large cation chemistry in oxidation state II, Tc and Re form few compounds in this oxidation state which is strongly reducing in nature. On the other hand, the elements are particularly stable in the VII oxidation state, being only weakly oxidizing, while Mn(VII) is strongly oxidizing. Among the lower states, the V and VI states are les common and tend to disproportionate. Tc(III) and Re(III, IV) are quite stable (Fig. 29.10).

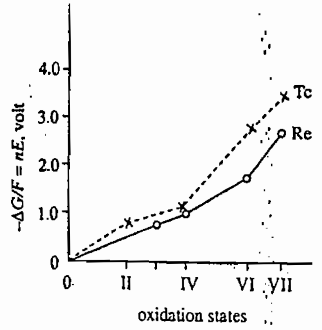


Fig. 29.10
Oxidation state-free energy diagram for Tc and Re.

Rhenium and to a limited extent technetium, show marked tendency to form metal-metal bonds which are not known for manganese. This tendency is very prominent in Re(III) halides and other compounds in low oxidation states, at least up to IV.

29.5.3 Oxidation state VII

The increasing stability of this oxidation state in the series Mn(VII) — Tc(VII) — Re(VII) is shown by comparing the ΔG_f^0 and ΔH_f^0 values for similar compounds, e.g.,

	Mn_2O_7(c)	Tc_2O_7(c)	Re_2O_7(c)	$MnO_4^-(aq)$	$TcO_4^-(aq)$	$ReO_4^-(aq)$
ΔG_f^0,	−544	−938	−1098	−449	−630	−699

Tc_2O_7 ($\Delta H_f^0 = -1115$ kJ mol^{-1}) and Re_2O_7 ($\Delta H_f^0 = -1272$ kJ mol^{-1}) are stable yellow crystalline solids. They are obtained by direct oxidation of the metals by O_2. Tc_2O_7 (m.p. 120°C) is stable up to its boiling point, 310°C. Re_2O_7 sublimes on heating. Vapours of both consist of $O_3M{-}O{-}MO_3$ molecules with tetrahedral coordination around M. Tc_2O_7 solid has the same structure with a linear Tc—O—Tc bridge but Re_2O_7 solid consists of ReO_6 octahedra and ReO_4 tetrahedra, a likely formulation being $ReO_3^+ ReO_4^-$.

The oxides form colourless solutions of acids in water. $HTcO_4$, pertechnic acid, can be obtained as dark red crystals by evaporating the solution but solid $HReO_4$ cannot be obtained in this manner. However, the yellow-green concentrated solution shows Raman spectra characteristic of the acid. The aqueous acids or their salts are also obtained by oxidation of all compounds of the elements by nitric acid, H_2O_2 and similar strong oxidizing agents.

The HMO_4 compounds are strong acids, liberating H_2 with metals like Zn, Fe or Mg. Acid strength slightly diminishes in the order $HMnO_4$—$HTcO_4$—$HReO_4$.

The tetrahedral TcO_4^- and ReO_4^- ions form insoluble precipitates with $Ph_4As^+Cl^-$ and nitron. The solubilites of alkali metal salts resemble those of the perchlorates, salts of K^+, Rb^+ and Cs^+ being much less soluble. The solubility also decreases from $KTcO_4$ to $KReO_4$. These are still called pertechnetates and perrhenates (actually technetate (VII) and rhenate (VII)). The salts $KTcO_4$ and $KReO_4$ are highly stable and can be distilled without decomposition at 1000°C.

The technetate(VII) and rhenate(VII) ions are quite stable in alkaline solutions also. In acid solution, they are milder reducing agents than permanganate :

$$TcO_4^- + 8H^+ + 5e \rightleftharpoons Tc^{2+}(aq) + 4H_2O \qquad E^\circ = 0.50\text{ V}$$

$$ReO_4^- + 8H^+ + 4e \rightleftharpoons Re^{3+}(aq) + 4H_2O \qquad E^\circ = 0.42\text{ V}$$

In strong acid media, the ions are reduced by Sn^{II}, Fe^{II}, Ti^{III} and I^-.

The TcO_4^- and ReO_4^- ions appear colourless as their charge transfer bands lie in the uv region. The red colour of crystalline $HTcO_4$ may arise due to distortion of the tetrahedral strcuture giving some absorption in the blue end of the visible range.

Perrhenic acid has another form H_3ReO_5, salts of which are formed in basic media :

$$ReO_4^- + K^+ + OH^- \longrightarrow K_3ReO_5\text{ (red)}$$

Such salts are also formed on fusing rhenates (VII) with alkali. Fusion with basic oxides also gives salts like $Ba_5(ReO_6)_2$.

The ReO_4^- ion can function as a ligand which coordinates less strongly than Cl^- or Br^- but more strongly than ClO_4^-.

The only binary halide in oxidation state VII is ReF_7, a pale yellow solid (mp 48°C) formed by direct reaction. A wide range of oxyhalides are known for Re, and some for Tc : $ReOF_5$, ReO_2F_3 (TcO_2F_3), ReO_3F(TcO_3F), ReO_3Cl (TcO_3Cl) and ReO_3Br. The rhenium oxyfluorides may be prepared by the action of water on ReF_7. Others may be obtained from halogenation of the oxides.

Treatment of perrhenate with potassium in ethylenediamine or alcoholic solution gives a water soluble rhenium species which contains the ReH_9^{2-} ion (Fig. 29.11).

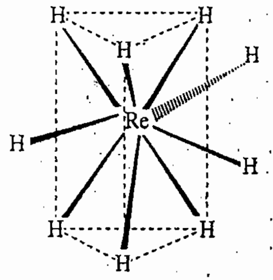


Fig. 29.11
Structure of the ReH_9^{2-} ion—tri-capped trigonal prism.
The Re-atom is at the center of a trigonal prism of six H atoms. Three more hydrogens are linked along rectangular face centers. The Re-Re distance is too large for any metal-metal bonding. A single sharp line in the proton magnetic resonance spectrum suggests rapid intramolecular site-exchange.
There is a similar compound of Tc, which is isostructural.

29.5.4 Oxidation state VI

Re(VI) and Tc(VI) tend to disproportionate, particularly in aqueous solution. There are a few compounds like ReO_3, ReF_6(TcF_6), $ReCl_6$($TcCl_6$) and some oxohalides.

ReO_3 (red) is formed by the action of Re on Re_2O_7. It disproportionates in vacuum at 300°C into ReO_2 and Re_2O_7. In the solid, each metal atom lies at the center of an octahedron of O-atoms — the unit cell consists of Re-atoms at the corners of a cube with O-atoms at edge-centers. ReO_3 (m.p. 160°C) does not react with acids or bases in non-oxidizing conditions but rhenate(VI), ReO_4^{2-}, may be obtained by fusing ReO_2 with rhenate(VII) (perrhenate). The green rhenate(VI) ion can exist in aqueous solutions with a great excess of alkali; otherwise they disproportionate :

$$3ReO_4^{2-} + 2H_2O = 2ReO_4^- + ReO_2 + 4OH^-$$

TcO_4^{2-} shows less tendency to disproportionate and pink $BaTcO_4$ may be precipitated. The MO_4^{2-} ions are readily oxidized by oxygen in the atmosphere :

$$4K_2MO_4 + O_2 + 2H_2O = 4KMO_4 + 4KOH$$

The ions also result from controlled cathodic reduction of the MO_4^- ions.

ReF_6, a pale yellow volatile liquid (m.p. 19°C, b.p. 34°C), may be prepared by direct combination (120°C); it is freed from ReF_7 by heating with the metal. Similar fluorination of Tc at 400°C gives TcF_6 (mp 37°C). Both undergo hydrolysis to hydrated MO_2. Liquid ReF_6 readily accepts fluoride ions to form the pink ReF_8^{2-} ion with square prismatic structure :

$$2KF + ReF_6 = K_2[ReF_8]$$

The reaction is carried out in an inert PTFE vessel.

There is a range of oxohalides $ReOX_4$ (X = F, Cl, Br). $TcOX_4$ (X = F, Cl) as well as anions like $ReO_2F_4^{2-}$, $ReOCl_6^{2-}$ etc. $ReOF_4$ (blue) results from the reaction of ReF_6 with rhenium carbonyl. This has an infinite chain structure involving fluorine-bridged octahedra. The blue form of $TcOF_4$ has this structure but another green form contains trimers of octahedra. $ReOCl_4$ is formed by the action of SO_2Cl_2 on Re metal (350°C). This, and also other oxyhalides may be prepared by the action of air/oxygen on the halides. $ReOCl_4$ is monomeric in the solid with a square pyramid structure.

The green crystalline diphenyldithiolate complex $[Re(S_2C_2Ph_2)_3]$ was the first authentic example of trigonal prismatic structure in coordination number six.

29.5.5 Oxidation state V

This oxidation state is also susceptible to disproportionation to M^{IV} and M^{VI}. It is represented by a few compounds like an oxide Re_2O_5, the halides ReX_5 (X = F, Cl, Br), TcF_5 and a few oxohalides and complexes,

Greenish yellow ReF_5 (m.p. 48°C) is obtained by reducing ReF_6 with hydrogen in liquid HF at 25°C. $ReCl_5$ (dark red, m.p. 261°C) is actually a dimer and is a common starting material for rhenium compounds. It is prepared by direct reaction of Re with Cl_2 at ~ 600°C. The compound is rapidly hydrolyzed by water

$$3ReCl_5 + 16OH^- = 2ReO_2.2H_2O + ReO_4^- + 15Cl^- + 4H_2O.$$

The solid consists of edge-sharing octahedral units. It decomposes on heating to Re_3Cl_9.

A number of complex compounds in this oxidation state appear interesting. $[Re(CN)_8]^{3-}$, isoelectronic with the Mo(IV) analogue, has a dodecahedral structure. It may be oxidized to $[Re(CN)_8]^{2-}$. Both Tc(V) and Re(V) form stable complexes with diarsine like $[M(diars)_2Cl_4]^+$ (eight-coordinated). Diarsine also stabilizes oxidation states II and III of these metals. There are also a number of hydrido complexes. $ReH_7(PR_3)_2$ has been shown to be a dihydrogen complex, $ReH_5(H_2)(PR_3)_2$, where the dihydrogen unit bonds sideways on to the metal. There are also a number of oxotechnetium(V) complexes of Schiff base ligands, amine oximes, dimercaptosuccinic acid or its esters and similar ligands.

29.5.6 Oxidation State IV

This important oxidation state of the elements is represented by several compounds of the type MO_2, MS_2, MX_4 and MX_6^{2-}. The derivatives of Tc(IV) are relatively more stable than similar Mn(IV) or Re(IV) analogues.

The oxides MO_2 may be prepared direct from the metal by controlled oxidation or by reduction of M_2O_7. ReO_2 dissolves in fused alkali to give rhenate(IV) (rhenite), ReO_3^{2-}. The oxides also dissolve in the hydrogen halides. Both the dioxides have distorted rutile structure. Hydrated ReO_2 and TcO_2 are formed by hydrolysis of ReO_3^{2-} or MCl_6^{2-}.

All four tetrahalides for Re are known while only $TcCl_4$ and $TcBr_4$ are reported. Hexahalocomplexes are known for both the metals with all four halogens. These are readily formed by dissolving ReO_2 in the halogen acids. $ReCl_6^{2-}$ is also obtained by reduction of $KReO_4$ with HCl and KI. Rhenium also forms the complex $Re_2X_9^-$ (X = Cl, Br) in which ReX_6 octahedra are linked by three Cl-atoms by sharing a face. TcI_6^{2-}, on treatment with methanolic KCN, gives $[Tc^{IV}(CN)_6]^{2-}$, while ReI_6^{2-} on similar treatment gives $Re^V(CN)_8^{3-}$. Referring to Fig. 29.9, we find that an eight-coordinate complex (dodecahedral) should be more favoured for d^2 metal ions like Tc(V) and Re(V) over d^3 ions like Tc(IV) or Re(IV). The difference in behaviour of the two metals may have other reasons, including steric crowding in eight-coordinate Tc.

Reduction of $ReCl_5$ with $LiAlH_4$ in presence of phosphine gives a dimeric hydride $Re_2^{IV}H_8(PR_3)_2$ with a Re—Re bond at 253 pm.

29.5.7 Lower oxidation states

The black hydrous oxide $Re_2O_3.xH_2O$ is formed by hydrolysis of $ReCl_3$. The trihalides are actually trimers Re_3X_3 (X = Cl, Br, I) formed by heating the pentahalides in an inert gas. The chloride and bromide are dark red while Re_3I_9 is black. The basic Re_3X_3 unit consists of a triangle of three Re atoms bridged along each side by a halogen atom; there are two more halogen atoms joined to each Re. Addition of terminal halogen atoms to this unit gives haloanions like $Re_3Cl_{10}^-$, $Re_3Cl_{11}^{2-}$ and $Re_3Cl_{12}^{3-}$. The Re_3X_9 halides may also add neutral ligands to give complexes of the type $Re_3X_3L_3$. Dinuclear complexes containing Re(III) are also known e.g., diamagnetic $Re_2Cl_8^{2-}/Br_8^{2-}$ and $Re_2Br_8^{2-}$ and $Re_2Cl_6(PEt_3)_2$. Hydrides containing Re(III) are $(C_5H_5)_2ReH$ and $(C_5H_5)_2ReH_2^+$. The $ReCl_4$ units in the $[Re_2Cl_8]^{2-}$ anion are in eclipsed configuration relative to one another to facilitate δ-bond formation in the Re ≣ Re bonding.

In lower oxidation states, only ReI_2 is known among the halides, though many complexes of the MX_2 halides with donor ligands are known e.g., py_2ReI_2 and $(diars)_2TcCl_2$.

Re(I) forms a stable dinitrogen complex in presence of other ligands, e.g., $ReX(N_2)(PR_3)_4$, $ReX(N_2)(CO)_2(PR_3)_2$ and $ReX(N_2)(diphos)_2$. These are oxidized by Ag^+ or Fe^{3+} to the Re(II) species e.g., $ReCl(N_2)L_4^+$. Both Tc(I) and Re(I) form cyano-complexes $K_5M(CN)_6$ and other complexes like $Re(PF_3)_4Cl$.

$Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ have the same structure as the manganese compound. Re(–I) is present in the anion $Re(CO)_5^-$ formed with alkali metals.

29.6 THE PLATINUM METALS

	Ru	Rh	Pd	Os	Ir	Pt
Atomic Number	44	45	46	76	77	78
Outer electron configuration	$4d^75s^1$	$4d^85s^1$	$4d^{10}$	$5d^66s^2$	$5d^76s^2$	$5d^96s^1$
Atomic weight	101.07	102.91	106.42	190.2	192.22	195.08

29.6.1 Introduction

The triads of periods 5 and 6 under Group VIII of Mendeleev's periodic table (Groups 8—10) are commonly known as the platinum metals. The elements, ruthenium, osmium, rhodium, iridium, palladium and platinum, occur together as the metals or in sulphide ores of copper and nickel, alongwith gold and silver. Platinum is the oldest known among the six elements and also the most abundant among them; hence the family is known by its name. The metals have several features in common justifying their inclusion into a family. However, there are also substantial differences in the individual chemistry of the elements, including stabilities of different oxidation states. In this section, we shall review the common features of the elements; individual groups of metals will be discussed in subsequent sections as per convention followed earlier in the chapter.

History

Platinum was found in the Tomb of Queen Shapenapit (7th century B.C.) but its use and mention were scarce owing probably to its high melting point. In 1748, the Spanish expeditionist Antonio de Ulloa first mentioned having seen in Colombia certain minerals which were difficult to process and contained a metal of very high melting point. It was called *platina* (little silver in spanish). Subsequent investigators — H. Scheffer, von Sickingen and P. Chabeneau to name only a few, independently studied and developed methods for isolation of the metal platinum which was variously known as "the eighth metal" (after Au, Ag, Hg, Cu, Fe, Sn, Pb), "white gold" (now this is used for a Au-Pd alloy) etc.

The second platinum metal discovered was palladium (1803) — the English chemist W. Wollaston isolated and identified it during his investigation on crude platinum. He called the metal palladium after the asteroid *Pallas* discovered a year earlier (W. Olbers) and itself named after the Greek goddess of wisdom.

Wollaston discovered the third platinum metal in the same year (1803) from crude platinum and named it rhodium from the rose-red colour of the solution of its salts (Greek *rhodos* = rose).

The quick discovery of palladium and rhodium from crude platinum prompted other scientists to further investigations for more new metals. The English chemist S. Tennant studied some crude platinum when he found a black residue after treatment with aqua regia. From this he discovered two new metals (reported 1804) : one was named iridium from the variety of colours of its salts (rainbow is the sign of the Greek goddess Iris); the other was named osmium after the pungent smell of its volatile oxide (Greek *osme* = odour).

The last platinum metal was discovered nearly forty years later in 1844 by K. Klaus of Russia, again from residues of crude platinum. The name ruthenium was derived from Ruthenia, the Latin name for Russia.

29.6.2 The elements

Abundance and occurrence.

The platinum metals are all rare, their abundances in the earth's crust are all 0.01 ppm or less : Ru & Rh : 10^{-4} ppm each; Os : 0.005 ppm; Ir : 0.001 ppm; Pd : 0.015 ppm; Pt : 0.01 ppm.

The elements occur together, mostly as sulphides and arsenides associated with Cu, Ag and Au. A few minerals are *braggite* (Pd, Pt, Ni)S; *sperrylite* $PtAs_2$; *cooperite* PtS. Native metals are also available — individually or as alloys like osmiridium in combination with copper, gold, iron etc.

The chief sources of the metals are South Africa, Canada, Russia, Brazil, Columbia etc.

Extraction

The platinum metals are mostly obtained from nickel-copper ores. The ores are concentrated by gravity and oil-floatation and nickel-copper sulfide matte is prepared by smelting and bessemerization. These mattes are now directly cast into anodes and electrolyzed in sulphuric acid. Copper deposits at the cathode while nickel remains in solution; the platinum metals, together with gold and silver enter the anode sludge. Recovery of the platinum metals from the anode sludge is complicated and the methods vary in details. The main steps are summarised below. The residue from Mond carbonyl process for nickel extraction may also be treated in the same gross procedure.

Step I : Treatment of the anode slime with aqua regia removes Pt, Pd and Au as soluble $PtCl_6^{2-}$, $PdCl_4^{2-}$ and $AuCl_4^-$.

Step II : The residue of insoluble chlorides of Os, Ru, Rh, Ir and Ag is fused with $PbCO_3$ followed by dissolution in nitric acid. Silver passes into solution as silver nitrate.

Step III : The insoluble residue after removal of silver is fused with $NaHSO_4$ and leached with water. Rhodium passes into solution as $Rh_2(SO_4)_3$ (see below for Rh).

Step IV : The insoluble residue is fused with sodium peroxide and leached with water. Ru and Os pass into solution as RuO_4^{2-} and $[OsO_4(OH)_2]^{2-}$. Iridium is left as a residue of IrO_2 (see below for Ir).

Step V : Chlorine is passed into the solution containing ruthenium and osmium. On heating volatile OsO_4 and RuO_4 are evolved which are absorbed in HCl. On heating this solution, OsO_4 vaporises which is collected in alcoholic NaOH to form $[OsO_2(OH)_4]^{2-}$. This is treated with NH_4Cl to precipitate $OsO_2(NH_3)_4Cl_2$. The precipitate is ignited in H_2 to obtain osmium metal.

Step VI : The solution after expulsion of OsO_4 contains H_3RuCl_6 from which $(NH_4)_3RuCl_6$ is precipitated by NH_4Cl. The precipitate is reduced by heating with H_2 to ruthenium metal.

Recovery of platinum metals from anode slime of nickel refining.

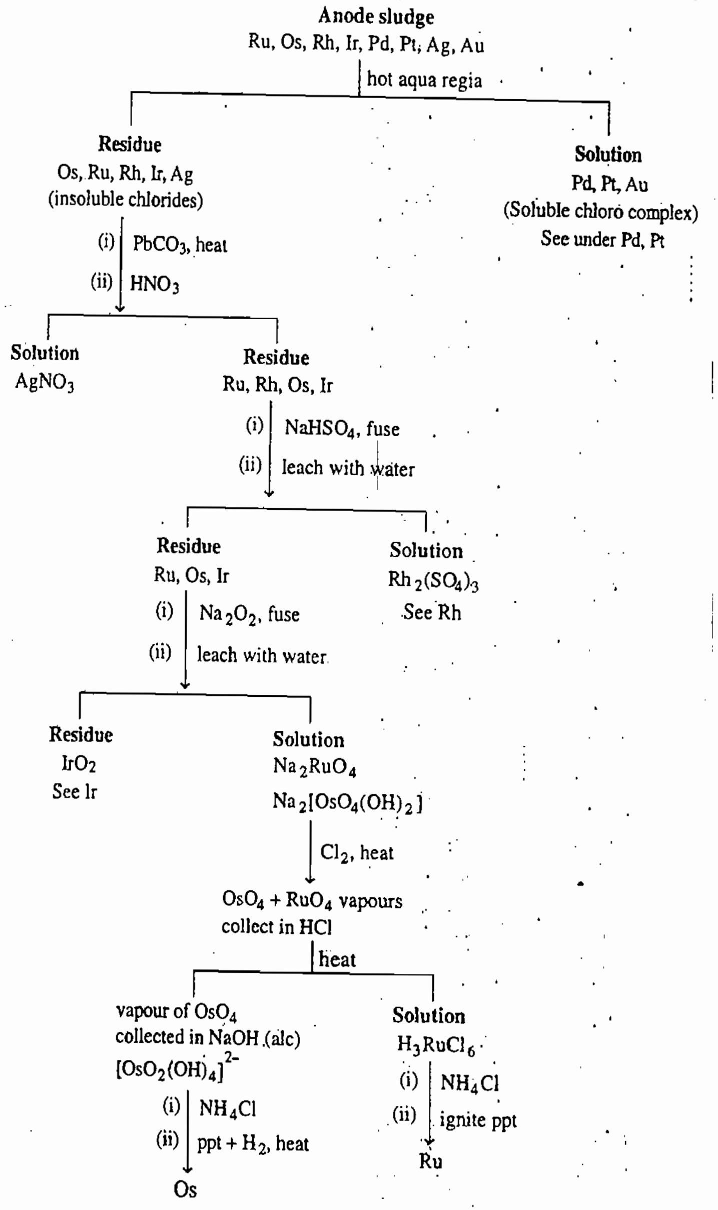


Fig. 29.12

Preparation of rhodium

The solution of Rhodium(III) sulphate (step III) precipitates $Rh(OH)_3$ with aqueous NaOH. The precipitate dissolves in HCl to give $H_3[RhCl_6]$. From this solution, addition of $NaNO_2$ and then NH_4Cl precipitates $(NH_4)_3[Rh(NO_2)_6]$. When this is digested in HCl, the soluble chlorocomplex $(NH_4)_3[RhCl_6]$ is formed. The solution is evaporated and the salt ignited in H_2 to produce rhodium metal.

Preparation of iridium

The residue of IrO_2 (step IV) is dissolved in aqua regia and the iridium precipitated as $(NH_4)_3[IrCl_6]$. This is purified by crystallization and ignited in H_2 to obtain iridium.

Extraction of Palladium and Platinum

Platinum and palladium are collected from the anode slime by aqua regia treatment — the metals, together with gold, form soluble chloro complexes : $HAuCl_4$, H_2PdCl_4 and H_2PtCl_6. From this, gold is precipitated by $FeSO_4$.

The solution containing $PdCl_4^{2-}$ and $PtCl_6^{2-}$ is treated with NH_4Cl to precipitate $(NH_4)_2PtCl_6$. This is ignited to obtain impure spongy platinum. This is again dissolved in aqua regia and the solution evaporated with NaCl. From the solution of Na_2PtCl_6 so obtained, Rh/Ir if any, is removed as their hydroxides by adding $NaBrO_3$. $(NH_4)_2PtCl_6$ is now reprecipitated with NH_4Cl and ignited to platinum metal.

The solution of H_2PdCl_4 left after precipitation of platinum is treated with excess aqueous ammonia followed by HCl. The precipitate of $[Pd(NH_3)_2]Cl_2$ is purified by reprecipitation and ignited to obtain palladium.

All the metals are obtained in the form of powder or sponge. These are made compact by powder metallurgical techniques.

At present, the metals are mostly isolated by ion exchange or solvent extraction.

Properties

The platinum metals generally have high melting point and density (Table 29.4). The gradual entry of $(n-1)d$ electrons into the inner core is reflected in the slowly decreasing trend along each horizontal series.

TABLE 29.4

Melting point and density of the platinum metals

	Ru	Rh	Pd	Os	Ir	Pt
M.P. (°C)	2546	1960	1552	3045	2443	1769
Density g cm^{-3}	12.41	12.39	11.99	22.57	22.61	21.41

Except Rh and Ir which are silvery white, all others are gray white. Palladium and platinum are lustrous and malleable; Rh is ductile. Others are relatively hard and brittle.

Chemically, the platinum metals are relatively noble. Almost all compounds of the metals decompose to yield the metal when heated. Chemically, the platinum metals, specially in the massive form, are relatively inert to attack by mineral acids and air or water under ordinary conditions (noble character). While non-oxidizing acids practically have no action on any of these metals, Ru, and particularly Rh and Ir, are even inert to aqua regia. Osmium and palladium dissolve slowly in oxidizing acids; even finely powdered rhodium can be dissolved in hot concentrated H_2SO_4 or aqua regia.

Osmium and palladium dissolve slowly in oxidizing acids; even finely powdered rhodium can be dissolved in hot concentrated H_2SO_4 or aqua regia. The metals also dissolve in concentrated HCl under pressure of oxygen or in presence of $NaClO_3$ at 125° — 150°C.

The metals may also be brought into solution by fusion with $NaHSO_4$ or with alkali plus sodium peroxide (or $KClO_3$). Non-metals like halogens and oxygen react with the metals at high temperatures. Platinum also combines readily with most non-metals like C, P, Si, Pb, As, Sb, S on heating — hence the metal is attacked by these elements when their compounds are heated in platinum crucibles under reducing conditions.

Palladium and platinum have the remarkable property of absorbing molecular hydrogen in large volumes.

Uses

The platinum metals are now largely used as catalysts in a variety of chemical processes. Platinum is largely used in the reforming of hydrocarbons, and other processes like the oxidation of NH_3 to NO. Other platinum metals are also good catalytic agents, for example, rhodium in hydroformylation reaction and in the synthesis of acetic acid.

In their role as catalysts, the metals are generally used as gauze or in a finely divided form supported on charcoal or alumina. For this purpose, the metals are formed in situ by reducing the metal salts (usually the ammonium hexachlorometallates) on the inert support.

Platinised asbestos is made by soaking asbestos fibres in chloroplatinic acid solution, drying and heating with a little NH_4Cl. The platinum is deposited in a finely divided state.

$$(NH_4)_2PtCl_6 = Pt + 2NH_3 + 2HCl + 2Cl_2$$

Platinum black is formed as a fine black powder by reducing chloroplatinic acid with zinc or sodium formate solution.

$$H_2PtCl_6 + 3Zn = Pt + 3ZnCl_2 + H_2$$

It is also obtained by adding ethanol to a solution of $PtCl_2$ in aqueous KOH and warming. A mixture of hydrogen and oxygen explode in contact with platinum black.

Colloidal platinum is obtained as a brown solution by reducing chloroplatinic acid with hydrazine in ammoniacal solution.

$$(NH_4)_2PtCl_6 + N_2H_4 + 4NH_3 = Pt + 6NH_4Cl + N_2$$

Platinum sponge is obtained as a grey porous mass by heating ammonium chloroplatinate.

Platinum is also used in making laboratory apparatus like crucible, boat etc. and as contacts in electrical apparatus and resistance wires in electrical furnaces. At present, it is largely used in car exhaust converters to reduce the proportion of pollutant gases.

Cis-$Pt(NH_3)_2Cl_2$ (*cisplatin*) is an effective anti-tumour drug (see later).

Palladium is also used as a catalyst, in jewellery (it is not blackened by H_2S), in dental filling and similar numerous purposes.

Rhodium is used as an alloying element with platinum and as a plating on silver to prevent tarnishing. Pt-Rh catalyst is used in the manufacture of nitric acid from ammonia. It is also used as a catalyst in car exhausts to minimize pollution. In the form of phosphine complexes, it is used as a catalyst in hydrogenation and hydroformylation reactions.

Iridium is remarkable for its hardness and is used in making hard alloys.

Ruthenium is also used mainly as an alloying element with platinum and palladium for imparting hardness.

Osmium was used before tungsten for making filaments of electric lamps. It is also used in making very hard alloys. OsO_4 is used in histology for staining tissue.

[**Sec. 29.6.2** *Platinum etc.- properties*]

Platinum compounds in cancer chemotherapy

A very high rate of success has been reported by the use of *cis* - $Pt(NH_3)_2Cl_2$ (*cisplatin*) in the treatment of solid tumours, particularly of the genito-urinary tract. The corresponding trans isomer is ineffective. The mode of action of cisplatin seems to proceed by substitution at the N(7) site of guanosine(G) in DNA in the place of the chlorine. The $(NH_3)_2Pt$ unit bridges across two nearby G-moiety and interrupts the reproduction of the DNA of the tumour cell. The role of chlorine as a leaving group is optimum — more easily displaced groups result in hydrolysis to produce hydroxy-Pt species which are toxic; more firmly bound groups do not allow binding to N(7) site. However, cisplatin is also quite toxic and attempts are on to find suitable substituents for NH_3 and Cl. The amine groups need at least one H-atom, suggesting the importance of hydrogen bonding. The most promising substitute seems to be diamines such as 1 : 2 - $C_6H_{10}(NH_2)_2$. In "carboplatin", the *cis*-chlorides are replaced by the *O*-chelate, cyclobutanedicarboxylate.

General chemical features

In addition to their general noble character and catalytic behaviour, the platinum metals present several common features in their chemistry.

(i) All of them form a wide variety of binary compounds like oxides, sulfides and specially halides.

(ii) Their chemistry is almost entirely that of complexes, simple cations being practically unknown. Aqua ions are known for Ru(II, III), Rh(III), Ir(III), Pd(II) and Pt(II), but complex ions are formed readily with anions such as ClO_4^-, BF_4^- and *p*-toluenesulfonate. Water soluble complexes are formed by many ligands, e.g., halides and nitrogen donors which have been extensively studied in connection with exchange reactions, substitutions and electron-transfer processes.

(iii) Hydrido complexes are formed readily, for example when the metal halides in high oxidation states are reduced, often aided by the presence of other ligands like tertiary phosphines.

(iv) Numerous complexes are formed with π-acid ligands such as CO, NO, PMe_3 (R_3P, in general, where R is alkyl or aryl group), along with R_3As and R_2S. The elements also show a strong tendency to form complexes with alkenes and alkynes. Pt(II, IV) and to a less extent Pd(II) readily form M—C σ bonds. Many stable organometallic compounds are also known.

(v) Compounds of the same formula type of the platinum metals almost always have the same structure. Compounds of the pairs of elements in the vertical group (Ru, Os; Rh, Ir and Pd, Pt) have almost the same dimensions as expected from their similarity in size. For example, the M—Cl distances in K_2PdCl_4 and K_2PtCl_4 are 231.8 pm and 231.6 pm respectively.

(vi) The normal mode of coordination for d^8 ions (e.g. Rh^I, Pd^{II}, Pt^{II}) is square planar. Unlike other metals in the second and third transition series, the platinum metals rarely show coordination numbers greater than six.

However, the platinum metals show substantial difference in the stability of various oxidation states;

Ru : III, IV, VI　　**Rh** : III　　**Pd** : II

Os : IV, VI, VIII　　**Ir** : III, IV　　**Pt** : II, IV

Principal similarities of the metals occur with the corresponding first transition series element in each vertical group. We shall deal with them in pairs as we have done previously in this chapter.

29.6.3 Ruthenium and Osmium

These first two members of the platinum metals are quite unreactive or noble as we have noted earlier. The metals (and also xenon) show the highest observed oxidation state VIII, the most stable states being, however VI and IV. Oxidation states range downward to –II, Ru being most stable in III state, Os in IV state.

Both metals form volatile tetroxides MO_4. OsO_4 is readily formed by burning the metal in air or by oxidation of any of its compounds by other oxidants like nitric acid. RuO_4 is obtained by oxidation of Ru(VI) in acid solution with BrO_3^-, MnO_4^-, Cl_2 etc.

$$Na_2RuO_4 + Cl_2 = RuO_4 + 2NaCl$$

Oxidation state VIII

RuO_4 (orange yellow, mp 25°C) and OsO_4 (colourless, m.p. 40°C) are both volatile molecular solids with ozone like odour. They are only slightly soluble in water from which they may be extracted by CCl_4. The molecules are regular tetrahedral.

RuO_4 decomposes explosively at 180°C to RuO_2 (and O_2) and is strongly oxidizing in nature. It dissolves in alkali evolving oxygen.

$$2RuO_4 + 4NaOH = 2Na_2RuO_4 + 2H_2O + O_2$$

K_2RuO_4 is also obtained by fusion of the metal with KNO_3 and KOH. With concentrated alkali, OsO_4 yields osmate(VIII) ions, *trans*-$[OsO_4(OH)_2]^{2-}$, which is reduced by ethanol to osmate(VI), *trans*-$[OsO_2(OH)_4]^{2-}$.

$$OsO_4 + 2KOH = K_2[OsO_4(OH)_2]$$

With KF, OsO_4 gives red brown $K_2[OsO_4F_2]$. Simultaneous action of concentrated KOH and NH_3 on OsO_4 gives the yellow crystalline nitrido complex $K[OsO_3N]$

$$OsO_4 + KOH + NH_3 = K[OsO_3N] + 2H_2O$$

The ir spectrum of the $[OsO_3N]^-$ ion shows bands corresponding to Os=O (871, 897 cm^{-1}) and Os ≡ N (1021 cm^{-1}).

Osmium tetroxide is a useful oxidizing agent in organic chemistry, converting, for example, alkenes to *cis*-diols; it is also used as a biological stain. It is readily reduced to the metal. This fact, together with its ready volatility, makes OsO_4 very dangerous to the eyes.

RuO_4 is also a strong oxidant, oxidizing, for example, concentrated HCl.

Ru(VII) and Os(VII) are present in the RuO_4^- (RuO_4 + OH^-; unstable) and OsO_4^- ions (Os + Na_2O_2, fusion). These readily pass to the +VI state.

Oxidation state VI

Ru(VI) and Os(VI) are present in the hexafluorides — RuF_6 (brown, m.p. 54°C), OsF_6 (yellow green, m.p. 33°C). The normal product of reaction between Ru and F_2 is RuF_5 but RuF_6 may be formed by reaction with fluorine under pressure and quenching the vapour. The ultimate product of fluorination of osmium is OsF_7 which decomposes in absence of excess fluorine to OsF_6. $OsOX_4$ (X = F, Cl) are square pyramidal in the gas phase with axial oxygen, similar to the rhenium and tungsten analogues.

Ruthenium(VI) forms the tetrahedral RuO_4^{2-} ion while Os(VI) forms the octahedral $[OsO_2(OH)_4]^{2-}$ ion when the metals or their compounds are oxidized in strongly alkaline medium e.g., fusion with KNO_3 and KOH. The Os(VI) species is also formed when $[OsO_4(OH)_2]^{2-}$ is reduced by ethanol. The orange oxyruthenate(VI) oxidizes concentrated HCl. The pink hydroxodioxyosmate(VI) is qui... readily oxidized to OsO_4.

$$2K_2[OsO_2(OH)_4] + O_2 = 2OsO_4 + 4KOH + 2H_2O.$$

Ru(VI), Os(VI)]

The acids H_2MO_4 and oxides MO_3 have not been obtained. The oxometallates(VI) decompose by the action of acids :

$$2Na_2RuO_4 + 2H_2SO_4 = 2RuO_2 + 2Na_2SO_4 + 2H_2O + O_2$$

$M_2^I[OsO_2X_4]$ and $M_2^I[OsNX_5]$ and their ruthenium analogs have also been reported.

In the unstable V state, no oxygen compounds are known. Both metals form the pentafluoride and its anion. Ruthenium burns in fluorine to form RuF_5 which is tetrameric, like NbF_5, with Ru-F-Ru bridges. OsF_5, formed by mild reduction of OsF_6, is also tetrameric. $OsCl_5$, isomorphous with $ReCl_5$, has a dimeric structure with chlorine bridges. The pentafluorides add more fluoride ions to form complex hexafluoro species, MF_6^-. Alkali converts them to MF_6^{2-} (plus O_2).

Oxidation state IV

The oxidation state IV of Ru and Os is quite stable. Ruthenium burns in air directly to form RuO_2 (blue-black) while OsO_4 requires only mild reduction to form copper coloured OsO_2. Both the dioxides are stable solids with rutile structure, insoluble in water.

Ru(IV) forms only yellow solid RuF_4 when RuF_5 is reduced with I_2. The compound is probably polymeric. Os(IV) forms OsF_4 (yellow, m.p. 230°C) when OsF_6 is reduced with $W(CO)_6$. Black solid $OsCl_4$ and $OsBr_4$ are obtained by heating the elements with the halogens under pressure. The tetrahalides are rapidly hydrolyzed by water :

$$3RuF_4 + 2H_2O = RuO_2 + 2H_2RuF_6$$

Complex haloanions are also formed by reacting the dioxides with excess halogen hydracids, e.g.,

$$MO_2 + 6HCl = H_2[MCl_6] + 2H_2O$$

K_2RuCl_6 has a room-temperature magnetic moment (2.8 B.M.) corresponding to lowspin d^4 configuration. K_2OsCl_6 has a still lower moment (1.5 B.M.) owing to greater spin-orbit coupling.

Oxidation state III

In the oxidation state III, no oxides are known, but OH^- ions precipitate black $Ru_2O_3.xH_2O$ from solutions containing Ru(III). This is readily oxidized by air to approximately $RuO_{2+x}.yH_2O$. RuF_3 (brown) is best made by reduction of RuF_5 :

$$5RuF_5 + 2Ir \xrightarrow{250°C} 5RuF_3 + 2IrF_5$$

Chlorides, bromides and iodides are known for both Ru(III) and Os(III). Heating ruthenium metal with chlorine and CO at 370°C gives brown β-$RuCl_3$. When heated further at 450°C with Cl_2, this givs the black α-$RuCl_3$ having a layer structure.

The common source of Ru(III) is the dark red deliquescent $RuCl_3.3H_2O$ obtained by evaporation of a solution of RuO_4 in concentrated HCl. This consists of mainly Ru(IV) complexes with some $RuCl_3(H_2O)_3$. The material dissolves in water, ethanol and acetone giving a convenient source of Ru(III). A full range of complexes – $[RuCl(H_2O)_5]^{2+}$ to $[RuCl_6]^{3-}$, are known. Os(III)also forms $OsCl_6^{3-}$ but only Ru(III) forms other hexahalo complexes. Addition of KI to a solution of $RuCl_3$. $3H_2O$ precipitates black RuI_3, but it probably contains –OH bridges in the lattice as shown by strong ir bands:

There are also a large number of complex compounds of both metals in this oxidation state. Both Ru and Os form hexaammines $M(NH_3)_6^{3+}$, while Ru also forms mixed amminehalo complexes like $Ru(NH_3)_3X_3$.

When $RuCl_3 . 3H_2O$ is reduced with zinc dust in strongly ammoniacal solution, $[Ru(NH_3)_6]^{2+}$ is formed which is oxidized by air to $[Ru(NH_3)_6]^{3+}$.

$$[Ru(NH_3)_6]^{3+} + e \rightleftharpoons [Ru(NH_3)_6]^{2+} \qquad E^\circ = 0.24V$$

The process is fast, consistent with an outersphere electron transfer between the lowspin species. The Ru—N distances in the +III and +II hexaammines are 210.4 and 214.4 pm respectively.

Addition of aqueous ammonia to a solution of $RuCl_3$ in air slowly forms an intense red solution from which a diamagnetic solid can be isolated; this can be represented as a mixed valence compound :

$$[(NH_3)_5 Ru^{III}—O—Ru^{IV}(NH_3)_4—O—Ru^{III}(NH_3)_5]^{6+}$$

The diamagnetism has been explained by assuming π-overlap forming polycentric m.o.s.

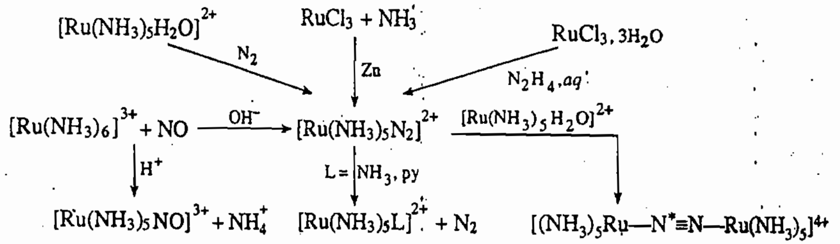
The ion is stable in acid or alkali but a trace of mild oxidizing agent (like Fe^{III}) oxidizes it to a yellow paramagnetic ion, which makes a sensitive test for oxidizing agents.

Since the metals Ru and Os lie on the hard-soft border line, the thiocyanate group can bind through either N end (hard donor) or through the S end (soft donor), giving complexes of the type $[M(NCS)_n(SCN)_{6-n}]^{3-}$, where $n = 1 — 4$ for Ru and $2 — 4$ for Os.

The hexaaquaruthenium(III) ion, $[Ru(H_2O)_6]^{3+}$ can be obtained by reduction of RuO_4 by Pb in H_2SiF_6 solution followed by removal of Pb^{2+} as $PbSO_4$. The ion can be reduced to $Ru(H_2O)_6^{2+}$ ($E^\circ = +0.23V$). The alum $Cs_2Ru^{III}(SO_4)_2 . 12H_2O$ has been prepared.

Oxidation state II

There are few simple compounds in the II state but both Ru(II) and Os(II) form numerous complexes, such as $M(dipy)_3^{2+}$, $M(CN)_6^{4-}$ and the ammine and arsine complexes. These are formed by reduction of the metals in IV or III state in presence of the ligands. Reduction of "$RuCl_3$" with hydrazine or zinc-amalgam in presence of ammonia gives the dinitrogen complex $[Ru(NH_3)_5N_2]^{2+}$, the first compound reported to contain coordinated dinitrogen.



*The Ru—N≡N—Ru group is nearly linear and the N—N distance is only slightly longer than in N_2 (112.4 pm vs 109.8 pm).

The action of HNO_2 on $[Ru(NH_3)_6]^{2+}$ produces the nitrosyl complex $[Ru(NH_3)_5NO]^{3+}$. Other nitrosyl complexes like $[Ru(NO)X_5]^{2-}$ are also known, where X = halogen, OH, CN etc.

The complex $[Ru(dipy)_3]^{2+}$ is extensively used as a photosensitizer and is being studied for the utilization of solar energy.

Low oxidation states

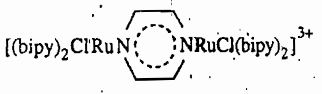
The carbonyls $M(CO)_5$ and $M_3(CO)_{12}$ contain the metals in oxidation state 0. The trinuclear carbonyls are the simplest metal cluster compounds of these metals. There are also many complex carbonyls, for example $Ru_6C(CO)_{17}$ in which an isolated carbon atom is octahedrally surrounded by a cluster of 6Ru — the Ru_6C cluster involving delocalized polycentered bonding. Four of the Ru atoms contain three terminal CO groups each and the other two Ru atoms have two terminal CO groups each and are bridged by the seventeenth CO group. There are also a number of other complexes in lower oxidation states of the metals, e.g., $Os^I(NH_3)_6Br$ and $Os^0(NH_3)_6$. $Ru(CO)_4^{2-}$ formally contains Ru(−II).

Mixed Valence compounds

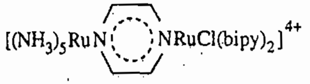
Some complexes containing two Ru atoms in different formal oxidation states have provided an interesting field of studying electron transfer processes across the ligands. The *Creutz-Taube complex* (29-VIII), named after its discoverer, is formally a mixed-valence complex (Ru^{II} and Ru^{III}).

29-VIII

The Ru atoms are indistinguishable and the ion appears symmetrical in crystal structure studies on salts isolated with large anions like perchlorate and dithionate. If the Ru(II) and Ru(III) were fixed at their respective ends, differences in Ru^{II} – N and Ru^{III} – N bond lengths would have made the ion slightly unsymmetrical. ^{99}Ru Mössbauer spectra and epr spectra suggest extensive delocalization of electron over the entire skeleton with strong metal-to-bridge coupling. However, there are also examples (29-IX and 29-X) in which the valences of Ru are localized on each individual atom ("trapped valence"). In 29-X, the Ru(III) is localized at the pentaammine end.



29-IX



29-X

Detection

Ruthenium salt solutions (a) produce a dark brown precipitate with yellow ammonium sulphide (b) turns azure blue on reduction with zinc, then becomes colourless with precipitation of the metal.

A concentrated solution of K_2OsO_4 gives orange yellow precipitate of $OsO_2(NH_3)_4Cl_2$ with NH_4Cl.

When a solution of an osmium salt in dil HNO_3 is distilled and the vapours collected in dilute NaOH solution, Na_2OsO_4 is formed. Heating with concentrated acid now gives off OsO_4 with a penetrating odour (**care!** protect eyes); a solution of OsO_4 in alcohol forms a green colour with KI which passes on to an ether layer on shaking.

29.6.4 Rhodium and Iridium

As compared with the previous pair of heavy transition elements (Ru, Os), Rh and Ir show less tendency to attain higher oxidation states. Though the highest state found is VI, the most stable states for Ir are IV and III and for Rh, only III.

The oxidation state VI is found in the hexafluorides MF_6, formed by direct reaction under pressure of fluorine. No oxygen species exists in this state and the reported oxide IrO_3 is probably a peroxide.

RhF_6 (red-brown, m.p. 70°C) and IrF_6 (yellow, m.p. 44°C, b.p. 53°C) are unstable and oxidize water vigorously

$$2IrF_6 + 10H_2O = 2Ir(OH)_4 + 12HF + O_2.$$

In absence of water, they even oxidize free chlorine and NO :

Oxidation states VI, V

$$2RhF_6 + 3Cl_2 = 2RhF_3 + 6ClF$$

$$NO + IrF_6 = NO^+[IrF_6]^-$$

As in the previous group, IrF_6 is more stable than RhF_6.

The normal products of fluorination of Rh and Ir at 300—400°C are the tetrameric pentafluorides Rh_4F_{20} and Ir_4F_{20}, isostructural with the Ru and Os analogs. Complexes like $CsMF_6$ may be prepared by fluorinating mixtures of the trihalides with alkali fluorides in BrF_3 solution. $KIrO_3$ and related salts also contain Ir(V); in strong base, the ion $Ir^VO_6^{7-}$ is formed with higher coordination number. The hydride $IrH_5(PR_3)_2$ is also formally Ir(V).

Rhodium has only a few compounds in oxidation state IV but Ir(IV) is fairly stable. On heating in air, Rh forms Rh_2O_3 but Ir forms black IrO_2. RhO_2 can, however, be made by strong oxidation of Rh(III) in alkaline solution and dehydrating under a high pressure of oxygen. The tetrafluorides and some hexa-halo complexes are other compounds of interest in this oxidation state. RhF_4 (purple) is prepared by the action of BrF_3 on $RhCl_3$.

Oxidation state IV

"IrF_4" had long been misrepresented by a compound which was later (1965) identified as IrF_5. IrF_4 (dark-brown) has been prepared later(1974) by reducing IrF_5 with iridium black at 400°C. It disproportionates above 400°C into IrF_5 and IrF_3. The complex anions RhF_6^{2-} and $RhCl_6^{2-}$ may be obtained by the reactions

$$RhCl_3 + 2KCl \xrightarrow{BrF_3} K_2[RhF_6]$$

$$RhCl_6^{3-} + CsCl \xrightarrow{Cl_2} Cs_2[RhCl_6]$$

Both are hydrolyzed by water to RhO_2. Iridium forms hexahalo anions IrX_6^{2-} where X = F, Cl, Br.

$M_2^IIrCl_6$ may be prepared by the interaction of IrO_2 and MCl in HCl or by chlorinating a mixture of iridium powder and sodium chloride :

$$IrO_2 + 4HCl + 2NaCl = Na_2[IrCl_6] + 2H_2O$$

The formation of poorly soluble $(NH_4)_2IrCl_6$ is used to separate iridium from other platinum metals. $Ir(C_2O_4)_4^{2-}$ can be resolved into optical isomers.

Oxidation state III

In the oxidation state III, both elements form oxides M_2O_3, halides MX_3(X = F, Cl, Br, I) and a large number of complex compounds. Dark grey Rh_2O_3 is formed by heating Rh metal in oxygen at 600°C. It is also formed by heating $RhCl_3$ or $Rh(NO_3)_3$. It has a corundum structure. Ir_2O_3 can be obtained in the hydrated form by adding alkali to aqueous $IrCl_6^{3-}$ under CO_2. The oxide is also said to be formed by igniting K_2IrCl_6 with Na_2CO_3. It is readily oxidized in air to IrO_2.

Rh(III) trihalides except iodide may be prepared by direct reaction. RhI_3 is obtained by adding aqueous KI on the tribromide. They are red or red-brown except RhI_3 which is black. The anhydrous trihalides are usually insoluble in water but water-soluble hydrates may be prepared by dissolving the hydrous oxide in appropriate HX. $RhCl_3 . 3H_2O$, the red deliquescent compound which is the common source of Rh(III), is prepared by heating the spongy metal with KCl in a stream of chlorine. The solution of $K_2[Rh(H_2O)Cl_5]$ is treated with KOH and the precipitated $Rh_2O_3.xH_2O$ is dissolved in HCl.

$Rh_2O_3 . xH_2O$ dissolves in acids to form the yellow $Rh(H_2O)_6^{3+}$ ion which forms alums structurally similar to those of $Co(H_2O)_6^{3+}$, but more stable to reduction.

Anhydrous IrF_3 is prepared by reducing IrF_6 with iridium metal; $IrCl_3$ and $IrBr_3$ are obtained by direct reaction while IrI_3 is obtained by heating the hydrated compound in vacuum. The anhydrous halides are insoluble in water. The hydrated halides, again prepared from appropriate HX acids, are water-soluble. $IrCl_3.3H_2O$ is also a convenient starting material for Ir(III) compounds. There are also salts of the type $M_2(SO_4)_3$ and $Rh(NO_3)_3$.

Complexes of Rh(III) are generally octahedral, for example the aqua ion $Rh(H_2O)_6^{3+}$, the ammine $Rh(NH_3)_6^{3+}$, haloammines etc. The formation of insoluble $Rh(NH_3)_3Cl_3$ is used to separate Rh from other platinum metals. It gives the metal on heating in a current of H_2.

There are many stable anionic complexes like $[M(CN)_6]^{3-}$, $[M(NO_2)_6]^{3-}$ and MX_6^{3-} together with RhX_5^{2-} and RhX_7^{4-}, specially with X = Br. The dinuclear complex $Rh_2Cl_9^{3-}$ is formed by face-sharing octahedral units with three bridge Cl. The acid $H_3[RhCl_6]$, obtained from $RhCl_3$ and HCl, yields bright red salts while the salts of $IrCl_6^{3-}$ are green. Na_3IrCl_6, obtained by reducing Na_2IrCl_6 with SO_2, is the common source of Ir(III). The $Ir(H_2O)_6^{3+}$ ion, produced similar to $Rh(H_2O)_6^{3+}$ ion, is very easily oxidized.

Rh(III)-complexes are relatively inert to substitution, thus permitting isolation of isomers, e.g. *cis*-$[Rh(en)_2Cl_2]^+$ has been resolved into the optical isomers.

The hydrides $(R_3P)_3M(H)_n(Cl)_{3-n}$ are known for both, with $n = 1$ and 2 for Rh and $n = 1$, 2 and 3 for Ir. The carbonyls $(R_3P)_2Rh(H)Cl_2(CO)$ and $(R_3P)_2Ir(H)_3(CO)$ are also known.

Lower oxidation states

The oxidation state II is not common for Rh and Ir. There is no established oxide or halide. Complexes like $[Rh(dipy)_2Cl]^+$, $[Ph_3PRh(OCOCH_3)_2]_2$, $Ir(CN)_6^{4-}$ and $Ir(NH_3)_4Cl_2$ are known. The dimeric acetate of Rh(II) is obtained by heating $RhCl_3.3H_2O$ with a methanolic solution of sodium acetate. This contains metal-metal bonding : the Rh — Rh distance in the Rh_2^{4+} ion is 239 pm, as expected for a single bond. The diamagnetic species has a structure like that of Cr(II) and Mo(II) acetates.

The oxidation state I for Rh and Ir is stabilized by π-acid ligands like CO, PPh_3 (PR_3), alkenes and arenes. The complexes are mainly square planar, though tetrahedral and five-coordinate examples are also known. These complexes are readily prepared by reduction of compounds like $RhCl_3.3H_2O$ and K_2IrCl_6 in presence of the ligands — the ligand itself or alcoholic solvents are often sufficient to bring about the reduction, e.g.

$$RhCl_3 . 3H_2O \xrightarrow[\text{alcohol;reflux}]{\text{excess } PPh_3} RhCl(PPh_3)_3 \xrightarrow{PPh_3,N_2H_4} RhH(PPh_3)_4$$

$$IrCl_3 \xrightarrow[\text{2-methoxyethanol}]{Ph_3P \text{ in}} trans\text{-}[IrCl(CO)(PPh_3)_2] \text{ (Vaska's compound)}$$

In the second reaction, the solvent 2-methoxyethanol acts as the reducing agent and supplier of CO.

Both $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$ are square planar. These, and other complexes of Rh(I) and Ir(I) undergo oxidative addition reactions with neutral molecules to give octahedral complexes in the oxidation state III, e.g.,

$$IrCl(CO)(PPh_3)_2 + XY = IrXY(Cl)(CO)(PPh_3)_2$$

where XY = HCl, CH_3I, $HgCl_2(Cl - HgCl)$ etc. Even O_2, H_2 or SO_2 may be reversibly added in the process.

Many of these complexes have been developed into useful catalysts. For example, the red-violet complex $RhCl(PPh_3)_3$, whose synthesis has been mentioned above, is known as *Wilkinson's catalyst*; it is highly effective for selective hydrogenation of complicated organic molecules. It enabled the first rapid homogeneous hydrogenation of double bonds at ordinary temperature and pressure.

The initial step probably involves oxidative addition of H_2 — the oxidation state of the metal increases to III taking the two hydrogen atoms as hydridic.

Another catalyst developed in this connection is *trans*-$[Rh(CO)H(PPh_3)_3]$ which selectively catalyzes 1-alkenes and has been used in ***hydroformylation*** of alkenes, (addition of H and a formyl group, CHO). The process, also known as "oxo process" since it introduces oxygen into a hydrocarbon, has immense industrial application in converting 1-alkenes into aldehydes and then to alcohols in the manufacture of polyvinyl chloride, polyalkenes and other longchain alcohols required in making synthetic detergents. The rhodium catalyst works at lower temperature and pressure than conventional cobalt carbonyl catalyst and produces straight-chain products. The key-point to the catalytic activity lies in the fact that rhodium can easily change its coordination number and it has nearly equal stability in the oxidation states I and III.

The yellow *Vaska's compound*, *trans* - $[IrCl(CO)(PPh_3)_2]$, whose synthesis has also been outlined above, is remarkable for its reversible uptake of dioxygen; as explained earlier (section 23.3.8), this is also an oxidative addition process.

The 0 oxidation state is present in the carbonyl $M_2(CO)_8$. $Rh_6(CO)_{16}$ has an octahedron of Rh, each having two terminal CO groups; other four carbonyl groups are found in the middle of opposite faces. This is also an example of Rh_6 cluster with delocalized metal-metal bonding. $Ir(NH_3)_5$ and $Ir(en)_3$, which may be prepared by reduction in liquid NH_3, also contain Ir(0).

$Rh(CO)_4^-$ contains Rh in the formal oxidation state −1 which is also present in $KIr(PF_3)_4$. This is oxidized by iodine to $Ir^I(PF_3)_4I$.

Rhodium salt solutions produce a brown colloidal solution on boiling with stannous chloride; the colour soon changes to crimson.

When a solution of Na_3RhCl_6 is warmed with KNO_2, an orange-yellow precipitate of $K_3Rh(NO_2)_6$ is produced; it is soluble in HCl.

A solution of Na_2IrCl_6 turns olive green when treated with KNO_2; the solution turns yellow on boiling and a yellowish white precipitate is formed, $K_3IrCl_6 . 3K_3Ir(NO_2)_6$, which is sparingly soluble in HCl.

29.6.5 Palladium and Platinum

In continuation of the trends observed earlier, these elements are also reluctant to attain high oxidation states — particularly palladium. The states VI and V have only a few compounds of platinum. The oxidation state IV is common to both elements, followed by the state II.

Oxidation states above IV

Pt(VIII) may be present in the compound $PtF_8(CO)_2$ which is reported to be formed by CO under pressure on PtF_4. The highest authenticated oxidation state is VI, represented by PtF_6. This may be prepared by heating the metal in fluorine under pressure (4 — 6 atm; 600°C) and rapidly quenching the vapour. It may be purified by vacuum distillation.

PtF_6 is a dark red, volatile unstable solid (m.p. 61.3°C; b.p. 69.1°C). The stability of the hexafluorides among the *5d* transition metals decrease in the order W > Re> Os> Ir> Pt. PtF_6 is highly reactive and corrosive, reacting with glass even when dry and is handled in apparatus made of Ni, quartz or monel metal. It is one of the most powerful oxidizing agents, oxidizing dioxygen to $O_2^+PtF_6^-$ and xenon to $Xe(PtF_6)_n$ (Chapter 25).

The oxidation state V is also limited to the tetrameric fluoride $(PtF_5)_4$, formed by fluorination of $PtCl_2$ at 350°C. The red compound (mp 80°C) is isostructural with Ru_4F_{20}. The oxidation state is also present in the ion PtF_6^- in O_2PtF_6.

Oxidation state IV

The highest oxidation state for palladium is IV which is also the most stable one for platinum. PdF_4(brick red) is the only tetrahalide of palladium in this state, formed by the elements at 300°C. Fluorination of $K_2[PdCl_4]$ gives K_2PdF_6. The anion PdF_6^{2-} is thermodynamically unstable to hydrolysis and is decomposed even by atmospheric moisture. The diamagnetic anion is also present in the paramagnetic compound of empirical formula PdF_3 which is actually $Pd^{II}[Pd^{IV}F_6]$. The $PdCl_6^{2-}$ ion, formed by oxidation of $PdCl_4^{2-}$ by excess chlorine, readily reverts to the Pd(II) species on heating the solution. $PdBr_6^{2-}$ is also known, as also the haloamines $Pd(am)_2X_4$ where am = ammonia, pyridine or related ligands.

Platinum forms all four tetrahalides. Yellow-brown PtF_4 is the major product of fluorination of platinum. Other tetrahalides may be obtained by direct reaction, though $PtCl_4$ is commonly prepared by heating H_2PtCl_6 in Cl_2 at 300°C. It can also be prepared by reacting platinum metal with SO_2Cl_2. The red-brown crystals dissolve in water to give ions having the likely composition $[PtCl_4(OH)_2]^{2-}$. The heavier tetrahalides are also quite stable, brown-black PtI_4 decomposing above180°C to PtI_2 and iodine. The structure of solid PtI_4 consists of PtI_6 octahedra linked by iodide bridges.

Pt(IV) forms a large number of octahedral complexes which are stable and inert toward substitution. Many of these may be readily obtained from the square planar Pt(II) complex by adding a ligand which is also oxidizing, e.g.,

$$Pt^{II}L_4 + Br_2 \longrightarrow trans - PtL_4Br_2.$$

Whole series of complex compounds ranging from $[Pt(am)_6]^{4+}$ (am = ammonia and variety amines) to $[PtX_6]^{2-}$ (X = halogen, OH, CNS, NO_2 etc.) are sometimes known, for example,

$[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_5Cl]Cl_3$, ... $[Pt(NH_3)_2Cl_4]$ ...... $K[Pt(NH_3)Cl_5]$, $K_2[PtCl_6]$.

The fluoride is, however, found only in PtF_6^{2-}. The gradual change in electrical conductance of these compounds and the number of chloride ions prcipitated by $AgNO_3$ solution provided strong support to Werner's coordination theory.

Addition of $AgNO_3$ solution to a solution of hexachloroplatinate(IV) yields a pale brown precipitate of Ag_2PtCl_6. Na_2PtCl_6 is soluble in water but the salts of K^+, Rb^+, Cs^+, and NH_4^+ are sparingly soluble. The pale yellow precipitates may be used to detct the $PtCl_6^{2-}$ anion.

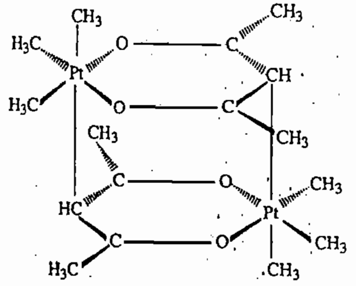
$H_2PtCl_6 \cdot 6H_2O$ can be obtained as red-brown deliquescent crystals by evaporating the solution obtained by dissolving Pt in aqua regia or reacting $PtCl_4$ with HCl. The crystals are soluble in water, alcohol and ether.

PtO_2 is the most stable oxide of platinum which is obtained in the hydrated form by the action of carbonate on Pt(IV) solution. It dissolves in both acids and alkalis in this form

$$Na_2[Pt(OH)_6] \xleftarrow{NaOH} \text{“}Pt(OH)_4\text{”} \xrightarrow{HCl} H_2[PtCl_6]$$

The hydrated oxide may be dehydrated by careful heating when it becomes insoluble. PtO_2 decomposes to the metal above 200°C.

The dimer of of trimethylplatinum(IV) acetylacetonate (29-XI) formed in non-coordinating solvent is an interesting example of Pt(IV) attaining six-coordination through the central carbon of acetylacetone which now functions as a tridentate ligand.



29-XI

Oxidation state III

Though a number of species are known to contain Pt(III) and Pd(III), many compounds apparently belonging to this oxidation state are actually mixed valence compounds. PdF_3(and PtX_3) is actually $Pd^{2+}PdF_6^{2-}$. Pt_3I_3 consists of two octahedral $Pt^{IV}I_6$ units linked to a central square planar $Pt^{II}I_4$ unit by sharing edges. The hydrated oxide in this state is also not well characterized. Similarly, the deep green complexes with composition $Pt(en)Br_3$ or $Pt(NH_3)_2Br_3$ are not complexes of Pt(III); they consist of chains built up of $Pt^{II}(NH_3)_2Br_2$ and $Pt^{IV}(NH_3)_2Br_4$ units (Fig. 29.13).

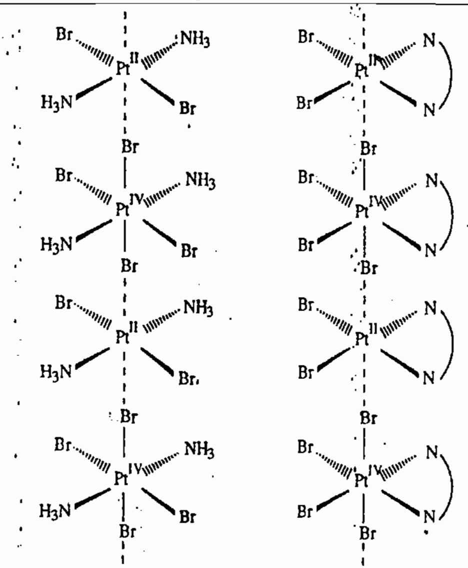


Fig. 29.13

Structures of $Pt(NH_3)_2Br_3$ and $Pt(en)Br_3$.

The structures consist of alternate square planar and octahedral units. Pt^{IV}—Br (vertical) = 250 pm; Pt^{II}—Br (vertical) = 310 pm.

Pd(III) is present in $Na^+[PdF_4^-]$ and Ag_3PdF_6. The PdF_6^{3-} ion shows four shorter Pd—F distances (195 pm) and two longer Pd — F distances (214 pm), as expected for a low-spin d^7 complex. There are also some complexes with metal — metal bonds.

Oxidation state II

The oxidation state II is by far the most important one for both the metals, offering oxides, sulphides, halides except PtF_2 and a large number of complex compounds.

PdO (black) can be prepared by heating palladium in oxygen. It dissociates above 875°C and is insoluble in all acids. A gelatinous dark yellow precipitate of the hydrous oxide $PdO \cdot xH_2O$ may be obtained by adding alkali to aqueous $Pd(NO_3)_2$. It is soluble in acids but cannot be completely dehydrated without loss of oxygen.

PtO is not well characterized. Alkali precipitates an unstable hydrous oxide from solutions of $PtCl_4^{2-}$, which can be dried in CO_2 at 120 — 150°C to an approximate $Pt(OH)_2$. It gives PtO_2 and Pt at higher temperatures.

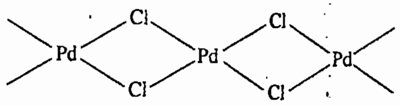
Brown PdS can be precipitated by H_2S from aqueous solutions of Pd(II); on heating with excess S this gives grey PdS_2. Green PtS may be similarly precipitated by H_2S from solutions of $PtCl_4^{2-}$ but it is best prepared by heating $PtCl_2$ with Na_2CO_3 and S.

All the dihalides except PtF_2 are known. Pale violet PdF_2 is obtained by refluxing "PdF_3" with SeF_4:

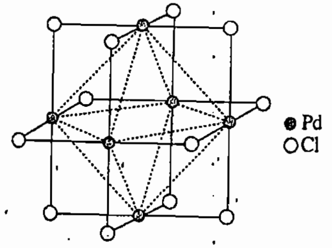
$$Pd^{II}[Pd^{IV}F_6] + SeF_4 \longrightarrow 2PdF_2 + SeF_6.$$

The compound is paramagnetic, corresponding to $t_{2g}^6 e_g^2$ configuration of octahedral Pd(II) in a rutile-type structure. The remaining halides are covalent, molecular or polymeric and diamagnetic in nature. $PdCl_2$ and $PtCl_2$ have two forms : the common α-forms are dark-red and olivegreen respectively and have chains of square planar units.

Heating Pd metal in Cl_2 above 550°C produces α-$PdCl_2$ which slowly transforms into β-$PdCl_2$. The latter is also obtained direct by heating Pd in Cl_2 below 550°C. The α-form has infinite planar chain structure (29-XII); but the β-form consists of an octahedral array of Pd atoms with Cl atoms off each edge of the octahedron (Fig. 29-XIII) making a square planar environment around each Pd. The whole unit corresponds to molecular Pd_6Cl_{12} but there is no indication of Pd—Pd bonding. $PdCl_2$ (red) is soluble in water and accepts further chloride ions to form $PdCl_4^{2-}$. From this, Cl^- may be replaced by Br^- or NH_3. Red-black $PdBr_2$ may be obtained by the action of bromine on palladium while PdI_2 (black) is formed by adding KI to aqueous $PdCl_2$. Both are insoluble in water and add further halide ions to form PdX_4^{2-}.



29-XII



29-XIII

$PtCl_2$ is obtained in the α-form when platinum metal is heated in chlorine at about 650°C. Thermal decomposition of $PtCl_4$ at 350°C produces β-$PtCl_2$ which slowly passes to the α-form at 500°C. The olive-green α-$PtCl_2$ is insoluble in water but dissolves in HCl forming $PtCl_4^{2-}$. The dark-red β-form is isomorphous with β-$PdCl_2$ and consists of Pt_6Cl_{12} unit (Fig. 29-XIII) which is also present in benzene solution. Brown $PtBr_2$ and black PtI_2 are obtained by thermal decomposition of the tetrahalides.

$Pd(H_2O)_4^{2+}$ is obtained by treating K_2PtCl_4 with $AgClO_4$. Palladium forms a number of hydrated salts like $Pd(ClO_4)_2 \cdot 2H_2O$; $Pd(NO_3)_2 \cdot 2H_2O$; $PdCl_2 \cdot 2H_2O$ and $PdSO_4 \cdot 2H_2O$.

Both Pd(II) and Pt(II) form numerous complexes which are diamagnetic and mostly square planar. As expected, they show little affinity for F and O donor ligands—besides the aqua ions one may name the polymeric acetates $[Pd(CH_3COO)_2]_3$ and $[Pt(CH_3COO)_2]_4$. The trimer is obtained as brown crystals from a solution of palladium sponge in acetic acid containing nitric acid. The Pd-atoms form a triangle with bridging acetate groups. As a b-class metal the majority of complexes involve soft donors like P, S, alkenes, alkynes, CN^- etc.

Complexes of the type MX_4^{2-} are formed by both metals with X = Cl, Br, I, SCN, CN and may be isolated as crystalline ammonium and alkali metal salts. The MCl_4^{2-} complexes may be used as the starting material for many other complexes as illustrated earlier (Chapter 27). The stability of the halo complexes increases from Cl^-—Br^-—I^-, as shown by the approximate stability constants : (log K) :

$[PdCl_4]^{2-}$	$[PdBr_4]^{2-}$	$[PdI_4]^{2-}$	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$
15.5	13.1	~25	16.0	20.5	~30

Increasing M→halogen dative π-bonding with increasing size of halogen *d*-orbitals and from Pd(II) to Pt(II) may provide some rationale for the observed trend.

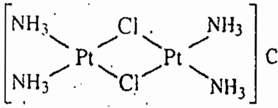
The thiocyanate ion normally coordinates through the soft S-end but in presence of strong π-acceptor ligands (e.g. PR_3), coordination occurs through the nitrogen end.

The chloride ions from the chlorocomplexes can be easily replaced by other ligands. Thus, shaking a solution of K_2PtCl_4 in dilute HCl with C_2H_4 gives the complex $K[PtCl_3(C_2H_4)]$ (*Zeise's salt*). The platinum ammines and mixed haloammines were some of the early complex compounds studied.

The synthesis of *cis* and *trans* $[Pt(NH_3)_2Cl_2]$ has been given earlier. *Magnus's green salt*, $[Pt(NH_3)_4][PtCl_4]$ is prepared by adding pink $PtCl_4^{2-}$ to colourless $[Pt(NH_3)_4]^{2+}$. In this compound, the square cations and anions stack over one another forming a linear chain of Pt atoms 325 pm apart. The short Pt—Pt distance gives rise to some intermetallic interaction which shifts the *d*—*d* absorption region of $PtCl_4^{2-}$ from green to the red region, transmitting the green colour observed. The effect of metal-metal interaction along the chain also results in marked dichroism with high absorption of light polarized in the direction of the metal chain and enhanced electrical conductivity along the chain. The Pt-Pt interaction is prevented by the presence of bulky ligands : for example $[Pt(EtNH_2)_4][PtCl_4]$ has a pink colour, the sum of the colours of the constituent ions (Et = ethyl).

Red $[Pd(NH_3)_4][PdCl_4]$ has also been obtained.

In addition to $[Pt(NH_3)_4][PtCl_4]$ and the haloammines, polynuclear complexes containing ammoia and chlorine are also known, e.g.,



The planar tetracyanocomplexes of Pd^{II} and Pt^{II} are very stable, K_{stab} for $[Pt(CN)_4]^{2-} \simeq 1 \times 10^{41}$. The discrete anion is found in certain compounds, for example, $K_2[Pt(CN)_4] \cdot 3H_2O$ (colourless) but in many the $Pt(CN)_4^{2-}$ ions are stacked one over another in a staggered arrangement (Fig. 29.14) giving rise to metal-metal interaction and a consequent shift in absorption band, imparting colour, for example $Ba[Pt(CN)_4] \cdot 4H_2O$ (yellow-green) and $Sr[Pt(CN)_4] \cdot 3H_2O$ (violet). The Pt — Pt distances in these compounds are 332 and 309 pm respectively.

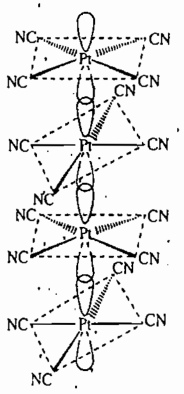


Fig. 29.14
The nature of stacking of $[Pt(CN)_4]^{2-}$ units in $Ba[Pt(CN)_4] \cdot 4H_2O$ (schematic).

Partial oxidation of $K_2[Pt(CN)_4]$ with chlorine or bromine forms bronze coloured compounds having compositions like $K_2[Pt(CN)_4]X_{0.3}\cdot 2.5H_2O$ i.e., 0.3 mol of X^- per mol of $K_2[Pt(CN)_4]$, coresponding to ~ 15% of the platinum in IV state. The halide ions occur outside the stack of $[Pt(CN)_4]^{2-}$ ions, the Pt — Pt distance in the stacks being ~288 pm, only 10% greater than that in the metal itself. Strong metal-metal interaction along the chain makes these compounds one-dimensional metallic conductors like polymeric sulfur nitrides. Similar compounds have been prepared using oxalates replacing the cyanides.

$K_2Pt(CN)_4\cdot 3H_2O$ crystallizes in yellow needles from a solution of spongy platinum in KCN or one obtained by adding KCN to a solution of Pt(II) chloride.

Barium tetracyanoplatinate(II), $Ba[Pt(CN)_4]\cdot 4H_2O$ is obtained as lemon-yellow crystals from a solution obtained by reducing H_2PtCl_6 with SO_2 in presence of baryta and HCN

$$H_2PtCl_6 + 5Ba(OH)_2 + 4HCN + SO_2 = Ba[Pt(CN)_4] + BaSO_4 + 3BaCl_2 + 8H_2O$$

The platinocyanides show two different colours depending on the direction of the incident light (*dichroic*) : $K_2Pt(CN)_4$ yellow and blue; $Ba[Pt(CN)_4]$ yellow and green; $Mg[Pt(CN)_4]$ red and green. $Ba[Pt(CN)_4]$ becomes brightly fluorescent on exposure to X-rays and hence is used in fluorescent screens.

Examples of complexes in coordination numbers higher than four are limited, a few examples being trigonal bipyramidal $[Pd(diars)_2Cl]^+$ and $[Pt(SnCl_3)_5]^{3-}$; square pyramidal $[PtI(PMe_3)_4]^+$ and octahedral PdF_2 (rutile type), $[Pt(NO)Cl_5]^{2-}$, $Pd(diars)_2I_2$ and $Pd(dmgH)_2$. the last compound has four coplanar N atoms wth weak Pd— Pd bonding forming a distorted octahedron.

The oxidation state I is not very common among these elements. Pd(I) is present in $[Pd_2(CN)_6]^{4-}$, analogous to the nickel complex. A square planar N_4-macrocyclic complex of Pd(I) is also known. Pt(I) is present in the dimeric anion $[PtCl_2(CO)]_2^{2-}$ which contains a Pt—Pt bond at 258 pm. It is prepared by the action of CO on $PtCl_4^{2-}$.

In the zero oxidation state Pd and Pt form no simple carbonyls. The oxidation state is found in the complexes of the type $M(PR_3)_4$ prepared by reduction of M(II) complexes by hydrazine or $NaBH_4$ in ethanol solution.

$$K_2MCl_4 + 4PPh_3 \xrightarrow{N_2H_4} M(PPh_3)_4$$

$Pt(PPh_3)_4$ is an air-stable yellow solid. $Pt(PF_3)_4$ is also stable but $Pd(PF_3)_4$ decomposes above −20°C. The $M(PR_3)_4$ compounds readily dissociate in solution to form 3-coordinate planar $M(PR_3)_3$, together with $M(PR_3)_2$. They also undergo a wide range of oxidative addition reactions, e.g.,

$$Pt(PPh_3)_4 + CH_3I \longrightarrow Pt(I)(CH_3)(PPh_3)_2 + 2PPh_3$$

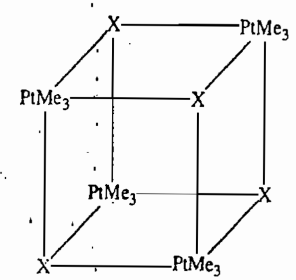
The oxidation state is also claimed to be present in $M(CN)_4^{4-}$ ions and carbonyl derivatives such as $Pt(CO)_n(PR_3)_{4-n}$ (n = 1, 2). $Pt(NH_3)_5$ and $Pt(en)_2$, analogous to the iridium compounds, have also been reported.

Platinum forms a number of clusters containing CO. Polymetallic 2-carbonyl anions of the general type $[Pt_3(CO)_6]_n^{2-}$ consist of a Pt_3 triangle with one terminal CO on each and one bridging CO group between each pair of Pt. The Pt_3 triangles stack one over another in twisted trigonal prisms. Species with n up to six have been reported. In the cluster $Pt_4(PR_3)_4(CO)_5$, the Pt_4 unit forms a tetrahedron with five bridging CO groups along five out of six edges; each Pt carries a terminal PR_3 group.

Organo-metallic compounds

The organometallic compounds of Pt and Pd are plentiful. Barring the cyanides, the first organometallic compound synthesized was $[Pt(C_2H_4)Cl_2]_2$ (Zeise, 1827). Zcise also synthesized the salt $K[Pt(C_2H_4)Cl_3].H_2O$ (1831) known after his name.

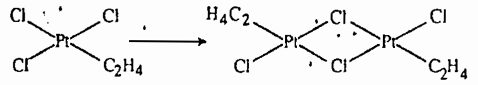
[**Sec. 29.6.5** *Pd(II), Pt(II) complexes*]



29-XIV

The platinum methyls (e.g., $(Me_3PtI)_4$ were also among the first known transition metal alkyls (Pope and Peachy, 1907). These are obtained by treating $PtCl_4$ with MeMgX in benzene. The 4 Pt atoms form a cube with I atoms which are triply bidging (29-XIV).

Pd and Pt form a number of alkene and alkyne complexes of which mention has been made of Zeise's salt. These are mainly formed in oxidation state II, Pt(II) forming the most numerous and stable compounds of the general type $[PtCl_3Alk]^-$, $[PtCl_2Alk]_2$ and $[PtCl_2Alk_2]$. $K[PtCl_3C_2H_4]$ (Zeise's salt) is produced by the action C_2H_4 on K_2PtCl_4 in dilute HCl, often speeded up by a small amount of $SnCl_2$. When an alcoholic solution of this is treated with concentrated HCl, an orange dimer (29-XV) is formed.



29-XV

The coordinated alkenes are very susceptible to attack by nucleophiles like OH^-, OMe^-, Cl^- etc. The dimeric $(C_2H_4PdCl_2)_2$ gives CH_3CHO and Pd with water. The palladium may be reoxidized by $CuCl_2$ and together this provides the basis for the *Wacker process* for converting ethylene (ethene) to acetaldehyde (ethanal).

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

$$Pd + CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

[In the slightly acidic solution CuCl is reoxidized to $CuCl_2$ by passing oxygen.]

The crucial step in the process appears to be the nucleophilic attack by water (or OH^-) on the coordinated C_2H_4 to give σ-bonded $-CH_2CH_2OH$ which undergoes rearrangement and is eventually eliminated with loss of a proton to form CH_3CHO. Since the reaction between Pd and $CuCl_2$ is quantitative, only low concentrations of Pd are actually required in the process, making it economically viable.

Detection

Palladium(II) chloride forms with aqueous ammonia a light red precipitate of $Pd(NH_3)_2Cl_2$. It dissolves in excess NH_3 to form a colourless solution from which it is reprecipitated by HCl.

Palladium (II) forms a yellow precipitate with dimethylglyoxime which is soluble in NH_3 (difference from Ni(II)) but insoluble in dilute acids.

A solution of H_2PtCl_6 produces yellow precipitates of K_2PtCl_6 or $(NH_4)_2PtCl_6$ when treated with K^+/NH_4^+ ions. H_2PtCl_6 also liberates I_2 from KI and gives a deep reddish-yellow precipitate with $Hg_2(NO_3)_2$. Reducing agents like Zn, N_2H_4 or HCHO reduce it to platinum metal.

29.7 SILVER AND GOLD

Ag: $[Kr]4d^{10}5s^1$ **Atomic number**: 47 **Atomic weight**: 107.88 **M.P.**: 961°C

Au: $[Xe]4f^{14}5d^{10}6s^1$ **Atomic number**: 79 **Atomic weight**: 197.2 **M.P.**: 1064°C

29.7.1 Introduction

Both silver and gold have been known from ancient ages; their use in jewellery and coinage has been traced to the third millenium B.C. The name silver stems from Assyrian *serpu* or Gothic *silbur* meaning white. The Latin name *argentum* also means shiny white (from Sanskrit *arganta* (?) and Greek *argos*). Gold derives its name from old English *geolu* (= yellow); the latin name aurum comes from *aurora* (dawn).

The relative abundance of silver in the earth's crust is ~ 0.08 ppm while that of gold is ~ 0.004 ppm. Silver is widely distributed in nature as sulfide ores, e.g. *silver glance* (argentite) Ag_2S. Native silver is also sometimes associated with such ores. *Horn silver*, AgCl is found in some deposits in Chile and New South Wales, probably formed by the action of salt water. Silver is now largely obtained as a byproduct in the extraction of copper and lead. The chief silver producing countries are USA, Mexico, Peru, Canada, Bolivia and New South Wales.

Gold is widely distributed in nature. Native gold occurs in two forms— (a) *reef gold* (gold which is still in its primary deposit as fine particles dispersed in quartz veins, often in deep mines) and (b) *alluvial gold* (gold removed from its primary deposit by geological action and redeposited in alluvial sands and gravel usually as fine grains.) This is also known as *placer gold*. Gold is also found combined in a few minerals, for example *calaverite* $AuTe_2$ and *sylvanite* $(Ag, Au)Te_2$. The chief gold producing countries with their annual production in tonnes for the year 1995 are South Africa (522); USA (320); Australia (253); Canada (150); China (140); Russia (133); Ghana (52); Philippines (27); Colombia (21); Mexico (20); Zaire (9.5).

Gold is also present in sea-water to the extent of about 10^{-3} ppm but uptil now no practical method for its exploitation has been developed.

In India, silver is obtained from the Kolar gold mines and as a by-product from the smelting of Zawar lead ores. Native silver occurs in Himachal Pradesh about 3 km east of Chargaon in the Sutlej valley in Bushaher, at an altitutde of about 3,300 meters, but the place is not accessible.

Gold occurs in India in both quartz reefs traversing the Dharwar rocks of Kolar district in Karnataka and in some other places. The distribution of alluvial gold is much wider — many of the rivers flowing through crystalline and metamorphic tracts are reputed to have auriferous sands but they hardly have any commercial importance. The annual yield of gold from the Kolar gold fields once averaged around 9.5 tonnes but for the last few years production has declined sharply mainly due to increasing depths (>3,000 meters). A promising gold vein has been spotted at Kolari in Maharastra.

29.7.2 The element

Extraction

Silver is now obtained mostly as a byproduct from the extraction of copper, lead and zinc. The anode slime collected in electrolytic extraction or refining of copper is partly freed from more basic metals by washing with hot dilute H_2SO_4 and air followed by fusion with a flux of lime or silica. This removes most of the basic metals as slag and the enriched anode slime is now electrolyzed in ~ 6% $AgNO_3$ solution containing little HNO_3. Pure silver deposits at the cathode, leaving gold and other noble metals as anode slime.

Silver is extracted from its ores by leaching the finely powdered ore with dilute (~ 0.4%) sodium cyanide solution when the sludge is agitated well with air. The free metal and its sulphide and chloride pass into solution as cyano complex :

(i) $4Ag + 8NaCN + O_2 + 2H_2O = 4Na[Ag(CN)_2] + 4NaOH$

(ii) $Ag_2S + 4NaCN = 2Na[Ag(CN)_2] + Na_2S$

(iii) $AgCl + 2NaCN = Na[Ag(CN)_2] + NaCl$.

The Na_2S is oxidized by aeration, otherwise it would tend to reverse reaction (ii). The sludge is removed by filtration and from the filtrate silver is precipitated by zinc or aluminium

$$2Na[Ag(CN)_2] + Zn = 2Ag + Na_2[Zn(CN)_4]$$

The precipitated silver is washed and melted with a flux of nitre to oxidize any excess of zinc.

The sulphide ore may also be roasted at 850°C to soluble silver sulfate and the silver precipitated by copper. Alternatively, the ore is roasted with NaCl to transform it to AgCl which is extracted by sodium thiosulphate solution.

Galena (PbS) contains about 0.01 to 0.1% Ag_2S. The silver accompanies lead; from this silver is extracted by molten zinc (*Parke's process*) in which it is 300 times more soluble than it is soluble in molten lead. The Ag-Zn-Pb alloy is also lighter with a higher melting point and hence may be separated easily from the molten lead. The silver-zinc alloy is heated in a fire clay retort (with a little C to reduce any ZnO formed) when zinc distills off leaving an alloy of lead and silver. This is melted in a shallow dish of boneash or cement (*cupel*, hence the name *cupellation*; a process more than 200 yrs. old) in the hearth of a reverberatory furnace. The lead is oxidized to PbO which is blown away by the air blast and its last portions are absorbed by the porous plate. The silver so obtained is ~ 99.5% pure.

Gold is also extracted mainly by the cyanide process. The finely powdered rock is thoroughly agitated with dilute sodium cyanide solution made alkaline with lime — presence of air is ensured to cause oxidation :

$$4Au + 8NaCN + 2H_2O + O_2 = 4Na[Au(CN)_2] + 4NaOH$$

The solution is filtered and gold deposited from the filtrate by zinc shavings.

$$Zn + 2Na[Au(CN)_2] = 2Au + Na_2[Zn(CN)_4]$$

The accompanying zinc is dissolved out by dilute H_2SO_4 and the dried residue of gold is melted under borax.

Crude gold contains copper, silver and sometimes lead. If any lead is present it is removed by cupellation. Copper is removed by oxidative fusion with borax and nitre. Silver may be removed by boiling with concentrated H_2SO_4 when only silver dissolves (provided it is present to the extent of at least 75%; if not, silver is added from outside). The best method seems to be electrolytic refining using a solution of $HAuCl_4$ and crude gold as anode.

Amalgamation is also used to separate native gold from alluvial sand and gravel deposits. The finely crushed rocks are passed with a stream of water over copper plates amalgamated with mercury when the fine particles of gold are arrested. The amalgam is scraped and the mercury distilled out in iron retorts. The residue is finally cupelled to obtain the gold. Very fine particles of gold escape amalgamation; these may be recovered from the tailings by the cyanide process.

Properties of the metals

Some physical properties of the elements are given in Table 29.5. Relevant figures for copper are also included for ready comparison.

TABLE 29.5

Some properties of Copper, Silver and Gold

	Cu	Ag	Au
M.P. °C	1083	961	1064
B.P. °C	2570	2155	2808
ΔH atomisation, kJ mol^{-1}	339	286	380
Density g cm^{-3}	8.95	10.49	19.32
Electrical resistivity, 20°C (μ ohm cm)	1.67	1.59	2.35
Electronegativity	1.9	1.9	2.4
Ionization energy kJ mol^{-1}, 1st	745	731	890
2nd	1958	2073	1973
3rd	3578	3360	(2895)

The metals form FCC structure in the solid which are known for their characteristic colours. The characteristic "golden yellow" colour of gold arises from absorption in the near uv and blue region of the spectrum corresponding to excitation of electrons from the filled *d*-band to *s-p* conduction band. For silver, this gap is larger (~385 kJ mol^{-1}), shifting the absorption to uv region and resulting in the silvery white colour. In copper, the gap is further less than that of gold, (about 220 kJ mol^{-1}, causing absorption in the green and blue region of the spectrum and transmitting the typical reddish colour. The melting point, boiling point and electrical resistivity are minimum for silver while the density rises uniformly from Cu-Ag-Au, gold having a very high density of 19.32 g cm^{-3}, a fact utilized by Archimedes in ascertaining the purity of a gold crown.

Gold is also the most electronegative of all metals and extremely malleable and ductile; it can be beaten out into sheets of about 5×10^{-5} mm thickness (1 g into 1 m^2).

Chemically, the metals are quite unreactive.

Silver dissolves in water to the extent of 0.037 mg L^{-1} in presence of dissolved oxygen :

$$2Ag + H_2O + \tfrac{1}{2}O_2 = 2Ag^+ + 2OH^-$$

It is also tarnished by atmospheric sulphur compounds, mainly H_2S. Non-oxidizing acids hardly attack silver and gold, though silver is slowly attacked by hot and concentrated HCl when the AgCl formed dissolves in the concentrated acid. Silver dissolves in hot concentrated H_2SO_4 and HNO_3 at all concentrations. It liberates H_2 from hot concentrated HI forming a stable iodo complex. Gold dissolves in selenic acid and also in concentrated HCl in presence of an oxidizing agent like Cl_2 :

$$2Au + 6H_2SeO_4 = Au_2(SeO_4)_3 + 3SeO_2 + 6H_2O$$

$$2Au + 3Cl_2 + 2HCl = 2H[AuCl_4]$$

Gold also dissolves in liquid BrF_3 forming $[BrF_2]^+[AuF_4]^-$.

Uses

Silver-salts are used in photography and for silvering mirrors. Silver is also used in silverware, jewellery and in high capacity electrical cells (Ag-Zn, Ag-Cd). Gold is used in jewellery, dentistry and also in making corrosion-free contacts in electronic industry : similar minor uses. It is still considered an internationally common material for exchange of wealth.

[Sec. 29.7.2 *Ag & Au—oxidation states*]

The purity of gold is expressed in *carats*. Pure gold is 24 *carat*; it is alloyed, usually with copper, to make it harder. Common ornaments are made of 22 carat gold (22 parts by weight of Au + 2 parts by weight of Cu); but lower carats are used in jewel-setting. For precious stones, the carat is used as a measure of the mass (= 200 mg) and not the purity.

In western countries, the price of gold is still stated per troy ounce :

1 troy ounce = 31.1035 g.

Gold and its compounds are extensively used in medicine — in our age-old Ayurveda as well as in modern allopathy, particularly in the treatment of rheumatoid arthritis.

Purple of Cassius, a purple powder containing colloidal gold absorbed on hydrated tin(IV) oxide is used in making ruby glass. It is prepared by reducing gold(III) chloride with $SnCl_2$:

$$2AuCl_3 + 3SnCl_2 + 6H_2O = 2Au + 3SnO_2 + 12HCl$$

General chemical trend

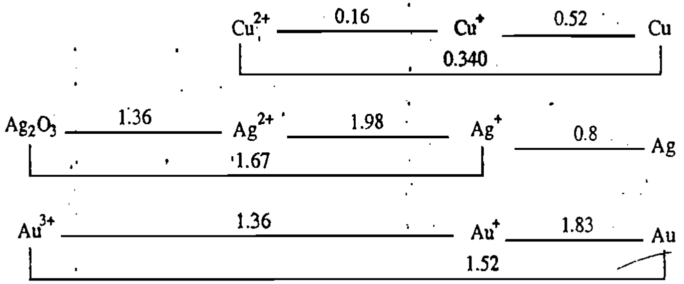
There are only a few intra-group resemblances between the chemistry of Cu, Ag and Au, Au being widely different from the other two in many respect. While copper is predominantly present as Cu(II), the only one stable oxidation state for silver is Ag(I). Oxidation states II and higher are known, but they are all strongly oxidizing in nature. For gold, the most stable state is Au(III), Au(I) being unstable with respect to disproportionation under all conditions. The chemistry of gold also covers a wider range than the others, from –I to III, V and perhaps even VII.

As noted earlier, one direct consequence of the higher effective nuclear charge (or ionic potential) is the predominantly covalent character of the compounds of silver and gold. In fact, the only stable aqua ion of silver is $Ag^+(aq)$; $Ag^{2+}(aq)$ is strongly oxidizing in nature. Au^+ disproportionates readily :

$$3Au^+(aq) = Au^{3+}(aq) + 2Au(s) \qquad K \simeq 10^{10}$$

But there is no evidence for a definite $[Au(H_2O)_4]^{3+}$ ion.

The standard reduction potentials(V) for Cu, Ag and Au are as follows :



The strongly oxidizing nature of higher oxidation states (Ag : II, III; Au . III) and the tendency of Cu^+ and Au^+ to disproportionate are clearly indicated (see Chapter 9).

Though the exact reasons for varying stabilities of different oxidation states of the elements in aqueous solution i.e., +II for Cu, +I for Ag and +III for Au, are not clearly understood, attempts have been made to correlate this fact with other more fundamental properties of these elements. First of all, we note the ionization energies (kJ mol^{-1}) of the elements (Table 29.4).

	Cu	Ag	Au
I_1	745	731	890
$I_1 + I_2$	2703	2804	2863
$I_1 + I_2 + I_3$	6281	6164	5758

It is interesting to observe that the I_1 is lowest for silver, the sum $(I_1 + I_2)$ is lowest for copper and $(I_1 + I_2 + I_3)$ is lowest for Au. The erratic sequence reflects the complicated nature of shielding provided to the last electron by inner electron cores which are different for the three metals. The order remains unchanged when we add to them the respective enthalpies of atomisation(Table 29.4) which is lower for Ag than with Cu.

The sizes of the ions and the consequent effect on their enthalpies of hydration are also important in deciding the fate of the aqua ion. Cu^{II} has a much higher enthalpy of hydration than that of Cu^{I} (– 2100 and –580 kJ mol^{-1} respectively) and the difference appears to overcome the second I.E. of Cu, rendering $Cu^{2+}(aq)$ more stable than $Cu^{+}(aq)$. For silver, the ionic radii are themselves much larger and the supposed gain of hydration energy cannot stabilize Ag(II) over Ag(I). For gold, enthalpies of atomization, ionization and hydration must be in favour of Au(III), though the $Au^{3+}(aq)$ ion is not known as such. The balance toward Au(III) is pushed further by the large gain in CFSE for the d^8 configuration of Au(III) over Au(II) in square planar environment (Fig. 29.15).

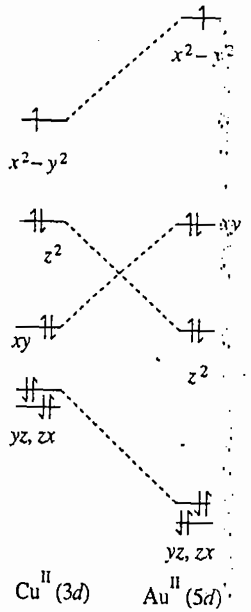


Fig. 29.15

Nature of crystal field splitting (not to scale) expected for Cu(II) and Au(II) in strongly distorted tetragonal fields.

Since gold belongs to the 5d series, $10Dq$ is nearly 80% greater than that for Cu(II), other conditions remaining the same. The last d electron in Au(II) would be highly destabilized, favouring square planar Au(III).

There are, however, some similarities within the group as follows :

(i) All the metals crystallize with FCC lattice.

(ii) Cu_2O and Ag_2O have the same structure (bcc; see later).

(iii) Both Cu(I) and Ag(I) show the same sequence of stability constants for their complexes with halide ions : $I^- > Br^- > Cl^- > F^-$. They also form many compounds and ions of the same type e.g., MCl_2^- and K_2MCl_3. Au^I also behaves similarly in a few cases.

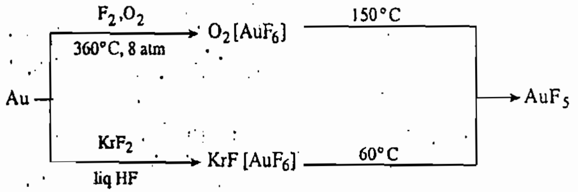
(iv) Cu^{II} and Ag^{II} form many isomorphous complexes. The complexes of all three metals in III state are also similar.

A formal comparison of Cu, Ag and Au (Gr IB of Mendeleev Table) with the alkali metals (Gr IA) is again centered around the difference in the penultimate shell of each : $(n-1)d^{10}$ for Cu, Ag and Au and $(n-1)s^2p^6$ for the alkali metals. Since the filled p-orbitals provide much better shielding effects, the last electron (ns^1) in the alkali metals are rather loosely held, resulting in their lower ionization energy, low melting and boiling point, lower density and strong electropositive character. The poorer shielding provided by the d^{10} core and consequent higher Z_{eff} makes the coinage metals denser, high melting and noble; they obviously have much higher ionization energies than corresponding alkali metals. The coinage metals are also much less soluble in liquid ammonia and their compounds are mostly covalent. Again, it is easier to disrupt a d^{10} configuration than a p^6 configuration — a fact leading to lower values of second and third ionization energies for the coinage metals. Consequently, it is easier to involve the penultimate core in the valence of the coinage metals whereas the alkali metals are uniformly univalent. However, both sodium and gold form solvated M^- anion in liquid ammonia.

29.7.3 Oxidation states above III

AuF_7 is said to be formed by the action of atomic fluorine on AuF_5; not much is known about it.

AuF_5(red) may be prepared by decomposition of the AuF_6^- complex anion according to the following reaction scheme



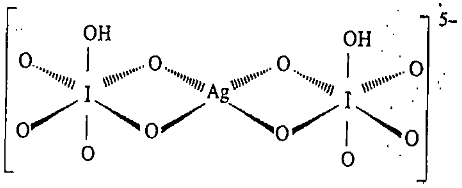
The compound is diamagnetic and gets very rapidly hydrolyzed by water. It is a violent fluorinating agent. At 200°C, it decomposes to AuF_3 and F_2. Oxidation of AuF_3 with F_2 and XeF_2 produces $Xe_2F_{11}^+ [AuF_6]^-$ in which the AuF_6^- ion is a slightly distorted octahedron linked by long weak Au – F ...... Xe bonds to the xenon atoms in the cation. KrF_2AuF_6 is similarly described as $FKr - FAuF_5$ with greater covalent character. Salts of AuF_6^- with larger alkali metals are also known. AuF_5 forms an adduct $BrF_5.AuF_5$ which is oxidized by KrF_2 to BrF_7. AuF_5 (BrF_7 does not exist free).

No compound of Ag(V) is definitely known, but Cs_2AgF_6 (orange) (formed by high-temperature fluorination of CsF + AgF) is weakly paramagnetic which may be due to the presence of Ag(III) and Ag(V). Similarly, $Cs_2Ga_{0.5}Ag_{0.5}F_6$ (diamagnetic) is supposed to contain Ag(V).

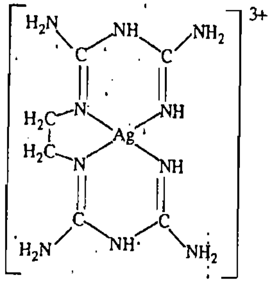
29.7.4 Oxidation state III

Compounds of Ag(III) are very few. Ag_2O_3 is obtained by anodic oxidation of Ag(I) salts in alkaline solution. It has a network of square planar AgO_4 units linked by shared corners. Au_2O_3 has the same structure. The yellow square planar $Ag(OH)_4^-$ ion is similarly obtained by anodic oxidation of silver metal in strong alkali. It is unstable, decomposing into AgO and O_2, which is slowed down in concentrated alkali ($t_{1/2} \simeq 100$ min in 1.2 M NaOH).

Fluorination of a mixture of alkali and silver halides (300°C) gives yellow fluoro complexes like $KAgF_4$ or Cs_2KAgF_6. The unstable compounds fume in moist air and attack glass. Direct oxidation of Ag(I) in alkaline solution by $K_2S_2O_8$ in presence of periodate or tellurate gives Ag^{III}-complexes like $\{Ag[IO_5(OH)]_2\}^{5-}$ (29-XVI) and $\{Ag[TeO_4(OH_2)_2\}^{5-}$. Stable complexes of Ag(III) are formed by ethylenebisbiguanide (29-XVII) by oxidation of Ag_2SO_4 with $K_2S_2O_8$ in presence of the ligand. Besides the red sulphate salt, hydroxide, nitrate and perchlorates of this cation have also been prepared by double decomposition. The diamagnetic compounds are all oxidizing.



29-XVI



29-XVII

Gold (III) is the most common oxidation state of gold offering a number of binary compounds and complexes. Some of the simple compounds are :

	$Au_2O_3(c)$	$Au(OH)_3(c)$	$AuF_3(c)$	$AuCl_3(c)$	$AuBr_3(c)$	$Au_2S_3(c)$
	Black-brown	Red-brown	Orange	Red	Dark-brown	Black
ΔG^0_f, 298K kJ mol^{-1}	+79	−350	−297	−54	−25	—

Amorphous brown $Au_2O_3 . H_2O$ is precipitated by alkali from solutions containing $AuCl_4^-$. It is amphoteric in nature, dissolving in excess alkali or acid to anionic complexes :

$$Au(OH)_3 + NaOH = Na[Au(OH)_4]$$

$$Au(OH)_3 + 4HNO_3 = H[Au(NO_3)_4] + 3H_2O$$

The anhydrous oxide may be obtained by drying the hydrated compound over P_4O_{10} followed by careful heating. It decomposes above 160°C to Au_2O and Au. The crystal structure consists of AuO_4 square planar groups sharing oxygen.

Fulminating gold is an olive-green explosive powder obtained by careful digestion of Au_2O_3 or its hydrate with ammonia. The dry powder explodes with flash (fulminates) on striking or heating and has the probable composition $HN = Au - NH_2 . 1.5H_2O$.

Au_2S_3 cannot be obtained from aqueous solution as it is decomposed by water. It is prepared by passing H_2S over dry $LiAuCl_4 . 2H_2O$ at −10°C.

$$2LiAuCl_4 + 3H_2S = Au_2S_3 + 2LiCl + 6HCl$$

The LiCl may be separated by extracting with alcohol and the black powder is dried at 70°C. It dissolves in a solution of Na_2S to $Na[AuS_2]$ which at once decomposes to $Na[Au^IS]$ and Na_2S_2. $Na[AuS_2]$ is also formed on fusing gold with sulphur and Na_2S.

Gold(III) selenides and tellurides are also known.

Gold(III) fluoride is made by the action of F_2 on Au_2Cl_6 at 300°C.

It is also obtained by the reaction sequences :

$$Au \xrightarrow{BrF_3} [BrF_2][AuF_4] \xrightarrow[150°C]{heat} AuF_3$$

The orange crystals decompose at 500°C to Au and F_2. It consists of square planar AuF_4 units linked into a helical chain by cis F atoms. The bridge Au-F distances are slightly longer (204 pm) than terminal Au-F distances (191 pm).

Au_2Cl_6 (red) and Au_2Br_6 (red brown) are obtained by direct reaction (200°C) but the chloride is best prepared by refluxing $HAuCl_4$ with thionyl chloride :

$$2H_3O^+AuCl_4^- + 2SOCl_2 = Au_2Cl_6 + 2SO_2 + 6HCl.$$

Both compounds decompose on heating (>150°C) first to AuX and then to Au. They dissolve in water with hydrolysis.

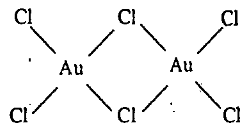
$$Au_2Cl_6 + 2H_2O = 2H[Au(OH)Cl_3]$$

$$Au_2Cl_6 + 2H_2O = 2H_2[AuOCl_3]$$

The $AuOCl_3$ unit is quite stable as Ag^+ ions precipitate the sparingly soluble salt $Ag_2[AuOCl_3]$ rather than AgCl. The $[AuCl_3OH]^-$ ion can be extracted from dilute HCl solutions into organic solvents like diethyl ether or ethyl acetate in which the partition coefficient is high. From these solutions, gold is readily precipitated by SO_2.

The halides dissolve in excess HX to form AuX_4^-. They are strong oxidizing agents.

The diamagnetic compounds form dimeric planar molecules (29-XVIII) in the solid as well as in vapour.



Au—Cl (bridge) : 234 pm
Au—Cl (terminal) : 224 pm

29-XVIII

Au_2Cl_6 dissolves in HCl to form "chloroauric acid", $HAuCl_4$ which on evaporation gives yellow crystals of $H_3O^+AuCl_4^- . 3H_2O$. Salts like $NaAuCl_4 . 2H_2O$ and $KAuCl_4$ are readily soluble in water. The $[AuBr_4]^-$ ion is also quite stable but AuI_4^- decomposes in solution into I_2 and AuI_2^-. AuX_4^- type complexes are also known with X = SCN^- (S-bonded), N_3^- and CN^-.

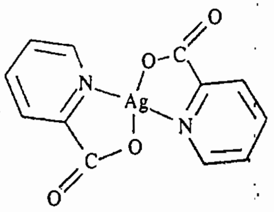
Planar adducts are formed by AuX_3 with R_3Y (Y = P, As, Sb) e.g., $Et_3P.AuCl_3$. $[Au(diars)_2I]^{2+}$ has a tbp structure while coordination number six is shown in $AuBr_6^{3-}$ and $[Auen_2Cl_2]^+$ (distorted).

29.7.5 Oxidation state II

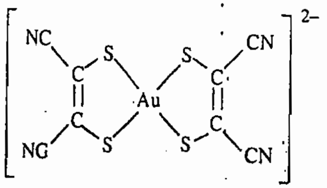
AgF_2 is the only simple compound of Ag(II). This is formed by the action of fluorine on AgF (or other silver compounds) or Ag at 250°C. The dark-brown solid is rapidly hydrolyzed by water and is a good fluorinating agent. It is antiferromagnetic; the magnetic moment at room temperature is much below the value expected from a d^9 configuration.

A black oxide of composition AgO is formed by persulphate or O_3 oxidation of Ag_2O or by electrolysis of 2*M* $AgNO_3$ solution. The compound is stable to heat upto 100°C and dissolves in acid to give Ag^+ and Ag^{2+}, evolving O_2. It is also strongly oxidizing in nature, for example, oxidizing Mn(II) to MnO_4^- in acid solution. Its diamagnetism suggests that it is not a compound of Ag^{II} (d^9). The compound is actually formulated as $Ag^I Ag^{III} O_2$. Neutron diffraction study shows the presence of two units in the lattice; a linear O—Ag—O common for Ag^I (d^{10}) and a square planar AgO_4 expected for Ag^{III} (d^8).

The $[Ag(H_2O)_4]^{2+}$ ion is obtained by dissolving AgO in aqueous $HClO_4$ or by ozone-oxidation of Ag^+. $E°$ for Ag^{2+}–Ag^+ couple is 2.0 V in 4*M* $HClO_4$, making Ag^{2+} a strong oxidizing agent. Ag(II) also forms a large number of complex compounds, mostly prepared by oxidation of Ag(I) with $S_2O_8^{=}$ in presence of the ligand. $[Ag(py)_4]^{2+}$ (red), $[Ag(dipy)_2]^{2+}$, $[Ag(phen)_2]^{2+}$ cations are stable in presence of non-reducing anions such as nitrate, perchlorate or persulphate with which they form crystalline salts. Examples of neutral complexes are $[Ag(pic)_2]$ (29-XIX) (where picH = picolinic acid, pyridine 2-carboxylic acid) and $Ag(MF_6)_2$ (M = Nb, Ta).



29-XIX



29-XX

The $Ag(MF_6)_2$ complexes consist of a central AgF_6 octahedron sharing three *cis*-F with MF_6 octahedra. The AgF_6 octahedron is marked by J-T distortion (d^9) and has two long and four short Ag — F distances.

$[Ag(py)_4]S_2O_8$ and $Ag(pic)_2$ are isomorphous with corresponding Cu(II) analogues. The magnetic moments of the Ag(II) complexes (1.75-2.2 B.M.) and their electronic spectra are consistent with square planar d^9 complexes.

Ag(II) compounds are obtained by direct oxidation — the disproportionation

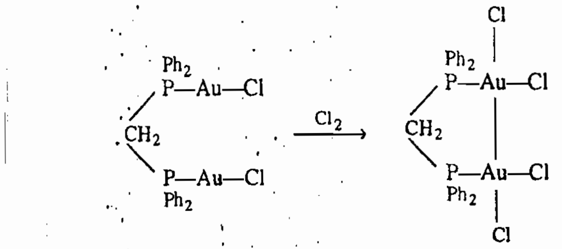
$$2Ag^+ \rightleftharpoons Ag + Ag^{2+}$$

being extremely unfavourable ($K \simeq 10^{-20}$) owing to the low heat of hydration of Ag^{2+}. However, it has been possible to drive the equilibrium to the right using a macrocylic ligand (L) which forms a stable paramagnetic complex AgL^{2+} in water as well as CN^- solutions.

As already explained, Au(II) is an unfavourable oxidation state for gold in comparison to Au(I) and Au(III). Genuine Au(II)compounds are thus rare, one example being the maleonitriledithiolato (mnt) complex (29-XX), $[Au(mnt)_2]^{2-}$:

Many compounds containing apparently Au(II) are actually mixed valence compounds e.g., $Au_2(SO_4)_2$ is $Au^IAu^{III}(SO_4)_2$; "$CsAuCl_3$" is $Cs_2[Au^ICl_2]$ $[Au^{III}Cl_4]$. Au_4Cl_8 similarly has a chair conformation with Au(I) and Au(III).

Formal Au^{II} is present in dinuclear compounds with Au—Au bonds which may be obtained by oxidative addition to Au^I compounds, for example,



The short "bite" of the bidentate phosphine ligands holds the two gold atoms close in a rigid conformation. Addition of further halogen oxidizes Au^{II} to Au^{III} when the Au—Au bond is ruptured.

29.7.6 Oxidation state I

This is the most common oxidation state for silver, offering the oxide, sulfide, halides and a number of oxoacid salts. The salts are primarily ionic and quite soluble in water, though Ag_2SO_4 and CH_3COOAg are only sparingly soluble. The halides except AgF are largely covalent, consistent with Fajan's rules (Ch. 7).

Compounds of Ag(I)

Ag_2O is obtained as a dark brown precipitate by adding alkali to aqueous Ag^+.

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$$

Its aqueous suspension is alkaline

$$\tfrac{1}{2}Ag_2O\,(s) + \tfrac{1}{2}H_2O = AgOH \qquad K \simeq 1.8 \times 10^{-6}$$

The suspension absorbs CO_2 from air forming Ag_2CO_3. Ag_2O decomposes above ~ 160°C. It is more soluble in alkali than in pure water owing to the formation of $Ag(OH)_2^-$. Ag_2O also dissolves in ammonia, producing $[Ag(NH_3)_2]OH$ — the solution on exposure to air deposits the black explosive silver nitride Ag_3N, also called *fulminating silver*.

Ag_2O is readily reduced to metallic silver. Moist Ag_2O is used as a mild oxidizing agent in organic chemistry.

On passing chlorine into a suspension of Ag_2O in water HOCl is produced :

$$Ag_2O + 2Cl_2 + H_2O = 2AgCl + 2HOCl$$

The "hypochlorous acid" (chloric(I) acid) dissolves excess Ag_2O giving a solution of AgOCl which rapidly deposits AgCl, leaving $AgClO_3$ in soluton.

$$3AgOCl = 2AgCl + AgClO_3$$

$AgClO_3$ may be crystallized from the solution and dried at 150°C.

Ag_2S is readily formed by heating the elements or by the action of H_2S on silver or Ag^+ in solution. It occurs naturally as argentite. Ag_2S (black) is insoluble in dilute acids, sodium thiosulfate and ammonia but it dissolves in KCN solution. The black coating on exposed silver surfaces due to the formation of the sulfide may be removed by KCN solution or by contact with aluminium in dilute sodium carbonate solution.

"Oxidized" silver articles are made by dipping the articles in a solution of sodium sulphide when their surface gets a pleasant grey coating of silver sulfide which protects the metal from tarnishing in air.

Silver(I) *halides* are quite familiar to the students in the detection of halides. As we already know, only AgF is soluble in water, while solubility decreases from AgCl to AgI with increasing covalence. All except AgI have the rock-salt structure.

AgI is polymorphic — it has the zinc blende structure at room temperature (γ-AgI). Between 136°C and 146°C, the stable form has a wurtzite structure (β-AgI). This structure being closely related to that of hexagonal ice crystals, it has been used in seeding rain-clouds. Above 146°C AgI adopts a cubic structure (α-AgI) when its electrical conductivity rises by a factor nearly 4000. Here the I^- ions form a nearly body-centered cubic lattice in which the small Ag^+ ion can move rather freely. Ag_2HgI_4 also becomes a fast ion conductor above 51°C.

AgF is prepared by dissolving Ag_2O in HF — crystallization gives yellow hydrates like AgF. $4H_2O$. (AgF is the only silver halide to form a hydrate). The anhydrous salt (mp 435°C) is hygroscopic; it can absorb 300 times its own volume of NH_3. Acid fluorides $AgHF_2$ and AgH_3F_4 are known. AgF is sensitive only to uv radiation.

AgCl occurs native as *horn silver*. AgCl, AgBr and AgI are all prepared easily by precipitation of Ag^+ with appropriate halide ions. They dissolve in solutions containing thiosulfate and cyanide; AgCl and AgBr are also soluble in aqueous ammonia, AgBr with difficulty.

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl$$

$$AgCl + 2KCN = K[Ag(CN)_2] + KCl$$

$$AgCl + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaCl$$

AgCl also dissolves in boiling concentrated H_2SO_4 :

$$2AgCl + H_2SO_4 = Ag_2SO_4 + 2HCl$$

The halides are sensitive to light — a fact used in photography (see later). They are readily reduced to the metal, e.g., by fusing with sodium carbonate or by heating in hydrogen.

$$4AgCl + 2Na_2CO_3 = 4Ag + 4NaCl + 2CO_2 + O_2$$

The darkening of silver halides in light is owing to photochemical decomposition into silver and the halogen. If the silver is not allowed to form aggregate and kept in close proximity with the halogen, recombination to the silver halide may take place when the light is cut off. This forms the basis of photochromic spectacles which automatically turn dark in sunlight.

Photography

Photography is also based on the light-sensitivity of silver halides. The photographic plate/film consists of an emulsion of fine grain silver halide (diameter <1 μm) on a transparent medium like glass or celluloid. The silver halide is usually AgBr with some AgCl and organic dyes; AgI is used for very fast films. The organic dye acts as a photosensitizer — helping light absorption over the entire visible band.

The chemistry involved in producing a photograph may now be considered under the following main steps :

(i) *Exposure* to the object, forming a latent image on the film. A halide ion excited by a photon loses its electron which subsequently reduces a silver ion to silver atom :

$$X^- \xrightarrow{h\nu} X + e\ ;\ Ag^+ + e \longrightarrow Ag.$$

A greater intensity of photon deposits more grains of silver and thus a *latent image* of fine layer of silver atoms is formed. The X atoms form X_2 which is absorbed by the gelatine.

(ii) *Developing* intensifies the latent image by depositing more silver atoms on the latent image. A mild reducing agent (e.g. hydroquinone) is used which reduces only the exposed parts of the AgX, that is which contain grains of silver atoms :

$$C_6H_4(OH)_2 + 2AgBr = 2Ag + C_6H_4O_2 + 2HBr$$

(iii) *Fixing* is done by dissolving out the unchanged silver halide by washing with sodium thiosulphate (hypo) :

$$AgX + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaX$$

A "negative" is thus produced.

(iv) *Printing* is done from the negative on a photosensitive printing paper by repeating steps i — iii.

Silver nitrate ($AgNO_3$, *lunar caustic*) is prepared by crystallization from a concentrated solution of silver in hot dilute HNO_3.

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O$$

Old silver coins or other silver articles containing some copper may be dissolved in dilute HNO_3 and evaporated to a residue of $AgNO_3$ and $Cu(NO_3)_2$. On heating to 250°C, copper nitrate decomposes to black copper(II) oxide while $AgNO_3$ remains unchanged. It may now be extracted with water and crystallized.

$AgNO_3$ forms transparent rhombic crystals (m.p. 17°C), which are highly soluble in water. The aqueous solution slowly darkens on expoure to light. The solid can absorb ammonia gas, forming $AgNO_3.3NH_3$. The aqueous solution is a familiar laboratory reagent. It produces brown precipitate of Ag_2O with aqueous ammonia which dissolves in excess ammonia to colourless $[Ag(NH_3)_2]OH$.

$AgNO_3$ decomposes on heating, first forming $AgNO_2$ and then Ag.

$$2AgNO_3 = 2AgNO_2 + O_2;\ 2AgNO_2 = 2Ag + 2NO + O_2.$$

It has a strong corrosive action on organic tissues (caustic action; hence the name lunar caustic, lunar relating to silver for its shine); consequently the silver(I) is reduced to fine metallic silver which leaves a permanent black stain on the skin.

Silver sulfate, (Ag_2SO_4) is made by heating finely divided silver in hot concentrated H_2SO_4 and crystallization of the solution. It also forms rhombic crystals which are sparingly soluble in water. It decomposes on strong heating :

$$Ag_2SO_4 = 2Ag + SO_2 + O_2$$

Silver thiosulfate, $Ag_2S_2O_3$ is formed as a white precipitate on adding a solution of sodium thiosulphate to silver(I) solution. The unstable precipitate decomposes on standing, rapidly on warming to black Ag_2S, the colour changing through yellow and brown. The precipitate dissolves in excess of sodium thiosulfate solution :

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

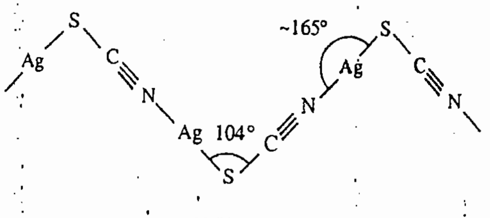
$$Ag_2S_2O_3 + 3Na_2S_2O_3 = 2Na_3[Ag(S_2O_3)_2]$$

AgCN (white) is precipitated by limited addition of KCN solution to aqueous Ag^+; the precipitate dissolves in ammonia solution and also in excess KCN. It has a linear chain structure (29-XXI).

AgSCN (white) also forms a curdy white precipitate from solutions of Ag^+ and SCN^-— the precipitate is insoluble in dilute HNO_3 but soluble in aqueous ammonia. On boiling with ~1*N* NaCl solution, it is converted to AgCl, with liberation of NaSCN in solution which may be detected by Fe(III). AgSCN also has a zig-zag chain structure (29-XXII).

—Ag—C≡N—Ag—C≡N—

29-XXI



29-XXII

Compounds of Au(I)

Simple compounds of Au(I) are practically restricted to the chloride, bromide and iodide. The light violet-grey "Au_2O", reportedly obtained by dehydrating AuOH (alkali + $AuCl_3$ + SO_2), is not well authenticated and may be a mixture of Au_2O_3 + Au. AuO contains Au(I) with Au(III).

Au_2S appears as a dark brown precipitate by saturating a solution of $KAu(CN)_2$ with H_2S, followed by addition of HCl. It is insoluble in water and dilute acids but dissolves in aqua regia and aqueous KCN. It also dissolves in excess of sodium sulfide solution, forming Na[AuS] and $Na_3[AuS_2]$. Large cluster anions like $Au_{12}S_8^{4-}$ are also present in such systems. Gold (I) - sulphur compounds are used as photosensitizers of silver halides in photography.

AuCl and AuBr are prepared by controlled thermal decomposition of respective trihalides :

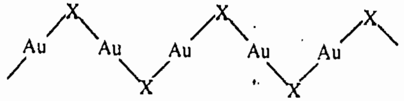
$$AuCl_3 = AuCl + Cl_2\ (175°C)$$

$$AuBr_3 = AuBr + Br_2\ (115°C)$$

AuI may be prepared by heating the metal with iodine or by adding an iodide solution to a solution of $AuCl_3$:

$$AuCl_3 + 3I^- = AuI + I_2 + 3Cl^-$$

The halides decompose on strong heating to the elements, AuCl above ~420°C, others at lower temperature. They dissolve in alkali halide solutions, forming AuX_2^-. AuCl and AuI have zig-zag chain structures (29-XXIII).



In AuI, ∠Au—I—Au = 72°

Au—I = 262 pm

29-XXIII

AuCN is formed as a yellow solid by heating $K[Au(CN)_2]$ with HCl at 50°C. It is highly insoluble in water and is not decomposed by it. It dissolves in aqueous alkali cyanide or thiosulfate solutions.

Complexes

Both Ag(I) and Au(I) form mainly two-coordinate complexes, though examples of other coordination numbers are also known. With increasing Z_{eff}, the differences between *s*- and d_{z^2} orbitals on the metals become sufficiently small to allow $s - d_{z^2}$ hybridization. The $d_{z^2} + s$ hybrid orbitals can further interact with p_z orbital of the metal to facilitate two-fold coordination along the z-axis. Examples of linear 2-coordinate complexes of Ag(I) are $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, AgX_2^- and $[Ag(NCO)_2]^-$. Silver halides dissolve in solutions containing excess halide ion or Ag^+ ion :

[**Sec. 29.7.7** *Ag & Au— low ox. states*]

$$AgI + I^- \rightleftharpoons [AgI_2]^-$$

$$AgI + Ag^+ \rightleftharpoons Ag_2I^+$$

Aqueous pyridine and substituted pyridines form 2-coordinate $[Ag(py)_2]^+$ complex ions but in nonaqueous media ($CHCl_3$ + pyridine), the tetrahedral $[Ag(py)_4]ClO_4$ complex may be obtained. $Ag(SCN)_4^{3-}$ and $[Ag(PPh_3)_4]ClO_4$ are other examples of tetrahedral complexes.

> **Q. 29.3** *AgI dissolves in a saturated aqueous solution of $AgNO_3$ but AgCl does not.*
>
> **Hint :** A class-b metal, Ag^+ forms stronger complex with I^- than with Cl^-. Ag_2I^+ is more stable than Ag_2Cl^+.

The diphosphine and diarsine complexes are also almost tetrahedral. The phosphine and arsine halides e.g., R_3PAgX are often tetrameric with cubane and chair forms (c.f. Cu(I) analogues : 28-XXIV and 28-XXV); $[Ph_3PAgI]_4$ can exist in both forms.

In general, ligands which do not π-bond mostly show coordination number two, while π-bonding ligands show coordination numbers of both 2 and 4. Three coordination is found with very strongly π-bonding ligands. The core of the $[Ag_4(S—R—S)_3]^{2-}$ ion (R = *o*-xylyl) contains an octahedron of six S-atoms with the silver atoms at the center of alternate faces, attaining planar 3-coordination.

Gold (I) forms mainly symmetrical linear complexes of the type $[AuX_2]^-$ where X = halogen, cyanide etc. The ions are known in crystalline solids and also in solution where $[AuCl_2]^-$ and $[AuBr_2]^-$ are stable only in presence of excess halide ions; otherwise they tend to disproportionate into Au and the Au(III)-complex :

$$3[AuX_2]^- = [AuX_4]^- + 2Au + 2X^-$$

A large number of complexes of the type LAuX are also known where L may be R_3P or R_2S and X may be a halogen or pseudo-halogen. These are readily formed from Au(III) :

$$R_3P + [AuCl_4]^- \xrightarrow{\text{alcohol}} R_3PAuCl$$

The R_2S complexes provide an easy route to other gold(I) complexes. Tetrahedral coordination is attained with higher concentrations of R_3P ligands, as in $(Ph_3P)_3AuCl$ and $(Ph_3P)_3AuSCN$. Planar three-coordinate Au(I) is found in $(Ph_3P)_2AuCl$.

Gold compounds used in the treatment of rheumatoid arthritis are mostly Au(I) species with sulfur ligands, presumably with RS-Au-SR units. Later drugs have linear phosphine complexes: The R groups are chosen to enhance lipid solubility, facilitating distribution through the body.

29.7.7 Lower oxidation states

A formal oxidation state of $\frac{1}{2}$ is present in the yellow-green solid Ag_2F. The compound, which decomposes above 100°C, is metallic in properties having a layer-lattice with Ag—Ag distance comparable to that in metallic silver. Gold in formal oxidation state <1 is present in cluster compounds (see below).

The oxidation state zero is not common for these elements; some unstable carbonyls are, however formed at extremely low temperatures (10 – 30 K), e.g., $Ag(CO)_3$.

Au(–I) is present in CsAu which does not show metallic properites and hence is not considered to be an alloy. The ion is also present in liquid ammonia in the ammoniated form and may be isolated with large cations like M(crypt)$^+$.

> Q. 29.4 *Explain why Au alone forms Au$^-$, but not Cu and Ag.*
> Hint : *f*-block contraction is operative only in Au.

Gold cluster compounds

Reduction of gold phosphine halides (R_3PAuX) with $NaBH_4$ yields various coloured gold cluster compounds, e.g. yellow $[Au_6(PR_3)_6]^{2+}$ ($R = p$ - C_6H_4-Me) containing an octahedron of six gold atoms, each containing one terminal phosphine ligand. Similar clusters with larger number of gold atoms (7, 8, 9, 11 and 13) are known, e.g., $Au_9L_8^{3+}$, $Au_{11}L_7^{3+}$ and $Au_{13}L_{12}^{3+}$ where L may be phosphines and halides, for example $[Au_{13}(PMe_2Ph)_{10}Cl_2]$ $(PF_6)_3$. The Au_{13} - cluster has one Au atom at the center of an Au_{12} icosahedron. The largest known metal cluster $Au_{55}(PPh_3)_{12}Cl_6$ has been obtained by reduction of Ph_3PAuCl with B_2H_6; it contains an inner Au_{13} icosahedron surrounded by Au, Au – P and Au – Cl units. Large mixed gold-silver clusters are also known. "*Liquid gold*" made by reaction of gold(III) chloro complexes with sulfurized terpenes or resins are probably some thiolate gold aggregates; very soluble in organic solvents, they are used for decorating photoframes, China and glass articles. When heated, liquid gold decomposes to leave a thin film of gold.

Organometallic compounds

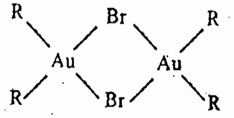
Silver forms many alkene and alkyne complexes of the type MLX but gold does so less readily and only with large olefins. Ag$^+$ forms "silver acetylide" with acetylenes; this contains Ag— C σ-bonds :

$$C_2H_2 + 2Ag^+ = Ag - C \equiv C - Ag + 2H^+.$$

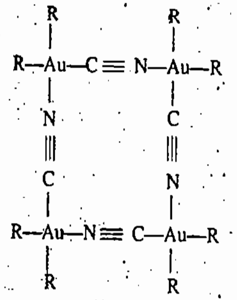
Simple alkyls and aryls of silver(I) are less stable than corresponding Cu(I) compounds while Au(I) forms such compounds only in presence of a ligand like phosphine.

$$Au(PEt_3)X + LiR \longrightarrow LiX + [Au(PEt_3)R]$$

Gold(III) forms several alkyl and aryl derivatives. $AuMe_3$ decomposes above –35°C but $AuMe_3(PPh_3)$ is stable. Alkyls of the type AuR_2X are most stable where X = Br$^-$, Cl$^-$, CN$^-$ and SO_3^{2-}. These are generally prepared by the action of a Grignard reagent on $AuBr_3$. The coordination geometry around Au(III) is square planar both in the dimeric halides and tetrameric cyanides :



29-XXIV



29-XXV

Aryl gold(III) compounds containing $C_6F_5^-$ groups are particularly stable.

29.7.8 Detection and estimation

Silver salts in aqueous solution produce a curdy white precipitate of AgCl with chloride ion — the precipitate is insoluble in nitric acid but readily dissolves in aqueous ammonia; silver ion also forms a red precipitate (Ag_2CrO_4) with potassium chromate solution which is insoluble in acetic acid. All silver compounds produce a lustrous white malleable bead of silver on heating with sodium carbonate on charcoal; the bead may be dissolved in nitric acid and tested with HCl.

Silver may be estimated gravimetrically as the chloride or by electrodeposition (coulometry). Volumetrically, it is determined by titration with standard solutions of sodium chloride or ammonium thiocyanate as follows.

In *Mohr's method*, a known volume of standard sodium chloride solution is titrated with silver nitrate solution using potassium chromate as indicator. Since silver chromate is more soluble than silver chloride, no persistent red precipitate of silver chromate is formed until all the chloride ion is removed. The appearance of red silver chromate thus indicates the end-point of titration.

In *Volhard's method*, the silver nitrate is titrated by running into it a standard potassium (or ammonium) thiocyanate solution using ferric alum as indicator. The Ag$^+$ ions form a white precipitate of AgSCN; when the concentration of Ag$^+$ falls below the solubility product limit, the thiocyanate ions produce a blood red colouration with ferric ion.

Gold may be detected by the characteristic purple colour produced by $SnCl_2$ on gold salts. Gold salt solutions also deposit gold as a fine brown powder when reduced with for example, sulfur dioxide, oxalic acid, hydroquinone, hydrazine, iron(II) sulfate etc. Estimation of gold is also done readily by gravimetry — the precipitated gold formed on reduction is filtered, dried and weighed.

29.8 ELEMENTS OF THE FOURTH TRANSITION SERIES (6*d*) : THE TRANS-ACTINIDE ELEMENTS.

The actinide series ends at Lawrencium, Z = 103. The following elements, Z = 104—112, have been synthesized ("discovered"!) and characterized rather recently. They formally belong to the fourth transition series, the last electrons entering the 6*d* level. The overall trend established so far indicates that the elements are indeed congeners of respective transition elements in periodic groups 4 to 12 (18 group table), element 104 belonging to group 4 (Ti group), 105 to group 5 (V group) and so on.

Transuranium elements up to Z = 106 were mostly synthesized by bombarding accelerated light atoms (e.g., $_5B$, $_6C$ etc.) on suitable target nuclei like $_{92}U$, $_{94}Pu$, $_{98}Cf$ etc. (see Chapter 14). The method does not suit still heavier elements since the compound nucleus formed acquires a very high excitation energy and becomes unstable. A more effective "cold fusion" technique involves bombardment of stable nuclei (close to magic number) like $_{82}Pb$ with moderately heavy ions which also have nearly closed nuclear shells (e.g., $_{24}Cr$, $_{26}Fe$ etc.). The energy of the bombarding particle is also kept low (just above the coulomb barrier)so that the compound nucleus does not acquire high excitation energy. The reaction recoils are separated in flight by a sophisticated velocity filter technique using an intricate combination of electric and magnetic fields (SHIP ≡ separated heavy ion reaction products). The method can locate even a single atom in position-sensitive solid-state detectors. The trapped atom is next characterized by following the successive radioactive decay products in a genetically related chain. The elements 104—112 are listed in Table 29.6.

TABLE 29.6

Elements of the *6d* transition series (104—112)

Atomic No/ (Year of synthesis)	Name, Symbol* (Previous names)	Mass No/ (No. of isotopes)	Half-life
104 (1969)	**Rutherfordium, Rf** (Kurchatovium, Dubnium)	253-262 (9, 10?)	7 ms-65 s
105 (1970)	**Dubnium, Db** (Nielsbohrium, Hahnium, Joliotium)	255-263 (7)	1.3 s-35 s
106 (1974)	**Seaborgium, Sg** (Rutherfordium)	259-266 (6)	3.6 ms-30 s
107 (1981)	**Bohrium, Bh** (Nielsbohrium)	261-264 (3)	12 ms-0.44 s
108 (1984)	**Hassium, Hs** (Hahnium)	264, 265, 269 (3)	80 µs-19.7 s
109 (1982)	**Meitnerium, Mt**	266, 268 (2)	3.4 ms-70 ms
110 (1994)	Ununnilium, Uun	269, 271, 273 (3)	0.1 ms-0.2 ms
111 (1994)	Unununium, Uuu	272 (1)	1.5 ms
112 (1996)	Ununbium, Uub	277 (1)	0.28 ms

* Names in bold are accepted by IUPAC 1997. Earlier suggested names given in parentheses.

For elements 110—112, systematic names (IUPAC 1977) are given (see Ch. 14).

Element 104, Rf, has been synthesized by reactions like

$^{242}Pu\ (^{22}Ne,\ 4n)\ ^{260}Rf;\ ^{249}Cf\ (^{12}C,\ 4n)\ ^{257}Rf;\ ^{248}Cm\ (^{16}O,\ 6n)\ ^{258}Rf.$

It forms a volatile chloride which may be arrested by a capillary containing KCl presumably owing to the formation of $K_2[RfCl_6]$. Aqueous solution chemistry resembles that of Zr and Hf.

Element 105, Db was synthesized by reactions like 1, 2 (Dubna) and 3 (Berkeley) :

1. $^{243}Am\ (^{22}Ne,\ 4n)\ ^{261}Db$ 2. $^{243}Am\ (^{22}Ne,\ 5n)\ ^{260}Db$
3. $^{249}Cf\ (^{15}N,\ 4n)\ ^{260}Db$.

The element resembles the group 5 elements Nb and Ta, sometimes closer to Nb.

Element 106, Sg, was first synthesized in Berkeley (1974) by the reaction $^{249}Cf\ (^{18}O,\ 4n)$. The Dubna group prepared it by cold fusion reactions like $_{82}Pb + {}_{24}Cr$. Only a few atoms of the element have so far been prepared.

Elements 107, 108 and 109 (Bh, Hs, Mt) were prepared at GSI, Darmstadt by the cold fusion method. Five atoms of ^{262}Bh were synthesized (1981) by fusing ^{54}Cr with ^{209}Bi (Half-life ≈ 102 ms). Three atoms of ^{265}Hs were synthesized (1984) by fusing ^{208}Pb with ^{58}Fe. It is also formed in reactions like $^{209}Bi\ (^{55}Mn,\ n)\ ^{263}Hs;\ ^{207}Pb\ (^{58}Fe,\ n)\ ^{264}Hs$ etc. The name hassium derives from Hesse, the region of Germany where Darmstadt GSI is situated.

Just one atom of ^{266}Mt was detected (1982) in the reaction $^{209}Bi\ (^{58}Fe,\ n)$; further two atoms were synthesized in 1988.

Elements 110, 111 and 112 were also synthesized at GSI, Darmstadt (1994-96) by reactions like

$^{208}Pb\ (^{62}Ni,\ n)\ ^{269}Uun;\ ^{209}Bi\ (^{64}Ni,\ n)\ ^{272}Uuu;\ ^{208}Pb\ (^{70}Zn,\ n)\ ^{277}Uub.$

Element 112 completes the *6d*-series.

SUMMARY

Introduction : The energy separations between *nd* and $(n + 1)s$ orbitals are less when $n = 4$ or 5 than when $n = 3$. Consequently, the ground state electron configurations of the *4d*- and *5d*- transition series elements often differ from those of the corresponding *3d*-transition series elements. Poor shielding by the *4f* electrons results in nearly equal atomic radii for the corresponding elements in the 2nd and 3rd transition series and we expect a similar trend in those properties which are size-related, for example, lattice and solvation energies, formation constants of complexes etc. The larger sizes of the elements also enable them to attain a higher coordination number than their *3d*-counterpart.

The relativistic effect : Calculation for the relativistic variation of the mass of an electron shows that for elements around $z = 80$, the relativistic mass of the electron is nearly 20% greater than its rest mass. This, in turn, causes a contraction of the size of the orbitals which is most pronounced for the *s*-orbitals, followed by the *p*-orbitals. The *d*- and *f*-orbitals, however, get better shielding from the contracted *s*- and *p*-orbitals and thus experience some relativistic expansion.

Oxidation states : Higher oxidation states are generally found to be more stable among the heavier transition elements. Thus CrF_6 is unstable but WF_6 and WCl_6 are stable. The maximum range of oxidation states appear in the middle of the block — the VIII state of osmium and ruthenium being highest. Many lower oxidation states become stable among the heavier elements. Thus, Mo(II) is virtually non-existent while Cr(II) forms a few compounds. WCl_2 is actually a cluster compound having the $[W_6Cl_8]^{4+}$ ion based on a W_6 octahedron. Similar instability of the heavier members is exemplified by the pairs $Ti^{III}—Zr^{III}$ and $Nb^{IV}—V^{IV}$.

Aqueous chemistry : Aqua ions involving the metals in lower oxidation states are often unimportant. Many elements do not have a simple aqueous chemistry though Ru, Rh, Pd and Pt etc. form some cationic complexes in aqueous solution. Anionic oxo and halo complexes are known for others.

Cluster compounds : The heavier transition elements are notable for their tendency to form clusters having metal-metal bonds, for example the $W_6Cl_8^{4+}$ cluster in "WCl_2".

Magnetic properties : A higher crystal field splitting (than their *3d* counterparts) mostly gives rise to low-spin complexes of the heavier transition metals. Spin-orbit coupling constants are also much larger for the second and third transition series elements and hence the few paramagnetic complexes known do not conform to the spin-only formula.

EXERCISE

1. *How do the elements of the first transition series differ from those in the second and third transition series with respect to (a) atomic and ionic radii, (b) oxidation states, (c) formation of metal-metal bonds, (d) stereochemistry and (e) magnetic properties?*
2. *Compare and contrast the chemistry of copper with that of silver and gold.*
3. *Compare the chemistry of Ni(II) with that of Pt(II).*
4. *Give balanced equations for the following processes :*
   - (a) *Leaching of metallic gold by cyanide in presence of* O_2.
   - (b) *Dissolution of silver in water in presence of* O_2.
   - (c) *Gold dissolves in selenic acid.*
   - (d) *Washing of AgI on photographic plates by 'hypo' (fixing).*
   - (e) *Reaction of* K_2PtCl_4 *in dilute HCl solution with ethylene.*
   - (f) *Thermal decomposition of* $(NH_4)_2PtCl_6$ *on asbestos fibre.*
   - (g) *Reaction of* $S_2O_8^{2-}$ *with silver nitrate solution in presence of excess pyridine.*
   - (h) *Zirconium dissolves in HF.*

5. *Give short answers/explanations :*
   - (i) *What is the true nature of "WCl_2"?*
   - (ii) *A green solution is obtained by mixing a colourless solution of $[Pt(NH_3)_4]^{2+}$ with a pink solution of $[PtCl_4]^{2-}$.*
   - (iii) *Name the most important silver salt soluble in water.*
   - (iv) *Au(II) disproportionates readily in solution.*
   - (v) *What is the structure of α-$PdCl_2$?*
   - (vi) *What is the nature of the product obtained by dissolving spongy palladium metal in acetic acid in presence of HNO_3, followed by crystallization?*
   - (vii) *How would you prepare $Pt(PPh_3)_4$? How does it react with CH_3I?*
   - (viii) *What is fulminating gold?*
   - (ix) *Give the formula and structure of a stable complex of Ag(III).*
   - (x) *What is purple of Cassius? What is its use?*
   - (xi) *Silver iodide dissolves in excess KI solution.*
   - (xii) *The aqua nickel(II) ion is paramagnetic, but the aqua palladium(II) ion is diamagnetic.*

6. *What are the common oxidation states of copper, silver and gold? Suggest a likely explanation for the difference observed.*

7. *How are the structures of $NbCl_5$ and $NbOCl_3$ related? Why is the latter compound less volatile?*

   [**Hint :** Nb—O—Nb linkage.]

8. *What is the basis for the practical applications mentioned against each substance?*
   - (i) *MoS_2 is used as an upper cylinder lubricant in automobiles.*
   - (ii) *"Chromic acid" is used to clean laboratory glassware.*
   - (iii) *Tungsten carbide is used in the tip of rock-boring drills.*
   - (iv) *Tungsten wire is used as filaments in electric lamps.*
   - (v) *"Cisplatin" is used in cancer chemotherapy.*

9. *Identify the substances marked A, B, C, D.*

   A lemon yellow powder(A) was obtained by heating tungsten strongly in oxygen.

   *A part of (A) was fused with solid NaOH and the product was heated with sodium when a brightly coloured lustrous solid (**B**) was obtained.*

   *Another portion of (A) was dissolved in aquesous NaOH. When this solution was gradually acidified, almost colourless crystals (**C**) appeared around pH 4. (C) has Na : W about 10 : 12.*

   *(C) was redissolved in alkali and disodium hydrogen phosphate was added. The pH was now again lowered when a crystalline precipitate(**D**) was obtained.*

   [WO_3; Na_xWO_3 (x = 0.3 to 0.9; "tungsten bronze"); $Na_{10}H_{10}[W_{12}O_{46}].23H_2O$ (sodium paratungstate); $Na_3[PW_{12}O_{40}].nH_2O$ (sodium 12-tungstophosphate).]

10. (a) *What is the product of reducing $KReO_4$ with potassium metal in ethylenediamine?*

    (b) *Write the half-cell reaction for reduction of TcO_4^- and ReO_4^- ions in acidic aqueous medium. Are they stronger or milder oxidizing agents than MnO_4^-?*

11. *Write the chemical reactions associated with the following observations and comment on the nature of the products :*
    - (i) *PtF_6 reacts with oxygen to produce a compound of empirical formula PtF_6O_2. The compound has two unpaired electrons and reacts with KF to give potassium hexafluoroplatinate(V).*
    - (ii) *The end product in (i) is hydrolyzed by water vapour to hexafluoroplatinic(IV) acid, hydrated PtO_2 and O_2.*

12. (a) *Mention the important oxidation states of the nine elements in Group VIII of Mendeleev periodic table, making separate categories for simple ions and complex species.*

    (b) *Which of these elements show an oxidation state of VIII? Give examples.*

    (c) *How would you divide the elements in four categories based on chemical similarity?*

    [(c) Fe—Co—Ni; Ru—Os; Rh—Ir; Pd—Pt]

13. *$Pt(CN)_2$ reacts with aqueous ammonia producing $Pt(CN)_2(NH_3)_2$. Suggest three likely structures for this compound and mention one distinctive feature for each.*

    [**Hint :** *cis-* and *trans-* forms of $[Pt(CN)_2(NH_3)_2]$ may be differentiated by dipole moment. Both are non-electrolytes. $[Pt(NH_3)_4][Pt(CN)_4]$ would be an electrolyte.]

CHAPTER THIRTY

ELEMENTS OF GROUP 12 (IIB)

Zn, Cd, Hg

OBJECTIVES

- **30.1** Introduction
    - (i) History, abundance & occurrence [30.1.1]
    - (ii) Isolation [30.1.2]
    - (iii) Properties of the elements [30.1.3]
    - (iv) Uses [30.1.4]
- **30.2** General group trend
    - (i) Comparison with main group elements [30.2.1]
    - (ii) Aqueous solution chemistry [30.2.2]
    - (iii) The M_2^{2+} ion [30.2.3]
    - (iv) Other polymercury cations [30.2.4]
    - (v) Complex compounds [30.2.5]
- **30.3** Principal compounds
    - (i) Compounds of Hg (I) [30.3.1]
    - (ii) Compounds in II state [30.3.2]
    - (iii) Organometallic compounds [30.3.3]
- **30.4** Environmental aspects
- **30.5** Detection and Estimation

30

ZINC, CADMIUM, MERCURY

Zn : $3d^{10}4s^2$ **Atomic number** : 30 **Atomic weight** : 65.39 **M.P.** : 419.5°C
Cd : $4d^{10}5s^2$ **Atomic number** : 48 **Atomic weight** : 112.41 **M.P.** : 320.8°C
Hg : $4f^{14}5d^{10}6s^2$ **Atomic number** : 80 **Atomic weight** : 200.59 **M.P.** : −38.9°C

30.1 INTRODUCTION

The elements zinc, cadmium and mercury are last members in each *d*-series but have no characteristics of the transition metals. The reason was mentioned earlier — the rise in Z_{eff} along each series gradually makes the *d*-shell a part of the inner core, leaving only the outer *s*-pair for valence participation. The relativistic effect mentioned in the last chapter also plays a prominent role in the heavier members. The weak participation of the outer electrons in metallic bonding is also reflected in the low melting and boiling points of these elements.

Though the elements involve only the outer *s*-electrons in their chemistry, they differ appreciably from the main group IIA (2) elements (Mg, Ca, Sr, Ba) in having a filled d^{10} (with $4f^{14}$ for Hg) core in the penultimate shell.

30.1.1 History, abundance and occurrence

Making of brass from copper and zinc ores was known in ancient times in Palestine, Rome, India and China. Extraction of zinc was difficult as the metal passed to the vapour state at the high temperature required for the reduction of its ores (~1000°C). The technique of isolating zinc by condensing its vapour has been mentioned by Nagarjuna (8-9 centry A. D.); from here the know-how seems to have passed to China during the Ming dynasty (1368-1644). China became the main supplier of zinc to Europe where zinc industry started only in the eighteenth century. The name zinc may be related to the German word *Zinke* for spike or tooth; it might also originate from the Latin word denoting leucoma or white deposit.

Cadmium was discovered by F. Stromeyer (Göttingen) in 1817 following the observation that some samples of calamin, supposed to contain zinc carbonate, gave a yellow residue on calcination instead of the expected white zinc oxide. Failing to detect either iron or lead in the samples, Stromeyer ultimately established the presence of the oxide of a new metal. He separated it from zinc oxide and reduced it to the metal which he named cadmium from "cadmia", the Greek word for natural $ZnCO_3$ (calamine).

Man discovered mercury in ancient times as it is easily liberated from cinnabar, HgS at high temperature. Cinnabar was widely used as a pigment. Elemental mercury was known in ancient India, China, Egypt and Greece. Indian Ayurveda describes the method of preparation of very pure HgS in the form of *Swarna-sindura* or *Makaradhwaj*. Aristotle named mercury "liquid silver"; it was also called "silver water" from which the Latin name *hydrargyrum* was derived. Its great mobility seems to have inspired the name mercury, after the name of the Roman god who serves as the messenger of other goods.

Zinc is slightly more abundant (76 ppm) in the earth's crust than copper (68 ppm). Cadmium and mercury are still less abundant—0.16 and 0.08 ppm respectively. All the elements are chalcophiles (section 16.3) and occur mainly as sulphides.

ZnS is called zinc blende in Europe and sphalerite in USA, the latter always containing a large amount of iron and often written as (ZnFe)S. Zinc carbonate, $ZnCO_3$, is the next important ore of zinc. It is called smithsonite in the USA and calamine in Europe. The major zinc producing countries are Canada, Russian countries, Australia, China, Peru and the USA. Zinc also occurs as the silicate ore hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$ and franklinite, ZnO.FeO, Fe_2O_3, but these are not commercially important. Cadmium is mostly found in association with zinc (0.1-0.2%) but it also occurs very rarely as the sulphide mineral greenockite, CdS. Mercury occurs mainly as cinnabar, HgS. Rich deposits occur in Spain (where it is being worked since the Roman time), and also in Russia, Algeria, Mexico, Yugoslavia and Italy.

In India, remnants of centuryold zinc smelter plants have been found in the Zawar hills in Udaipur, Rajasthan. The place still contains vast deposits of good quality zinc sulphide ores, together with galena. A workable deposit of zinc blende of considerable purity has also been discovered in the Riasi district of Kashmir. Small pockets of sphalerite and limonite occur in the Buxa-Dooars area of Jalpaiguri (W.B.), Almora, Tehri Garhwal and Bhotang (Sikkim).

Zinc is biologically the second most important transition metal. The functioning of several enzymes depend on zinc, for example carboxypeptidase A and carbonic anhydrase (Chapter 33).

30.1.2 Isolation of the metals

Unlike iron, the reduction of zinc oxide by carbon is not effective below the boiling point of zinc (907°C). The zinc vapour, on the other hand, is largely reoxidized during cooling :

$$ZnO + CO \rightleftharpoons Zn + CO_2$$

Hence zinc could not be extracted in methods similar to those adopted for iron or copper. Early methods of zinc extraction involved (i) concentration of the ore by froth floatation (ii) roasting (900°-1000°C) to ZnO and (iii) reduction of ZnO by carbon in fireclay retorts. But the thermal efficiency of the process was poorer than that of a blast furnace where the ore and the fuel come in direct contact.

In the electrolytic method, the ore is roasted at a lower temperature (~650°C) to $ZnSO_4$. The roasted mass is extracted with dilute H_2SO_4 and the extract treated with milk of lime to precipitate iron, aluminium, silica etc. Copper and cadmium are next precipitated by zinc dust and the solution of zinc sulfate electrolysed using aluminium anode and zinc cathode under a high current density. The method gives very pure zinc (~99.9%) but involves high cost of electricity.

Zinc is now extracted by specially designed blast furnaces. The ore, roasted to oxide, is reduced by coke to the metal which volatilizes with the hot blast. The issuing gas is suddenly "chilled" by pouring molten lead on it so that reoxidation of zinc during cooling becomes negligible. Liquid zinc collects at the bottom of the chamber and is ~99% pure; this may be further purified by vacuum distillation. The blast furnace method can efficiently handle mixed lead-zinc ores when the lead collects at the bottom of the furnace.

Cadmium is recovered during purification of zinc by distillation or by precipitation with metallic zinc as in the electrolytic process.

The extraction of mercury is relatively simple. The crushed ore (HgS) is concentrated by floatation and heated in a current of air (~600°C) when it first gets oxidized followed by decomposition.

$$2HgS + 3O_2 = 2HgO + 2SO_2.$$

$$2HgO = 2Hg + O_2.$$

The mercury passes with the vapour which is condensed.

Specially rich ores may also be roasted with scrap iron or quicklime :

$$HgS + Fe = FeS + Hg$$

$$4HgS + 4CaO = CaSO_4 + 3CaS + 4Hg.$$

The crude mercury contains more basic metals like lead, zinc, copper and iron as impurities. These are oxidized by blowing air through the hot metal when a scum is formed on the surface of mercury. The scum may be removed by filtration through chamois leather. The metal is further purified by distillation under reduced pressure.

30.1.3 Properties of the metals

Zinc and cadmium are lustrous silvery metals with a bluish tinge, tarnishable in moist air. Mercury is a shinning grey liquid at ordinary temperature. Some properties of the elements are summarized in Table 30.1.

TABLE 30.1

Some properties of Zn, Cd and Hg

		Zn	Cd	Hg
M.P. (°C)		419.5	320.8	−38.9
B.P. (°C)		907	765	357
Density (g cm^{-3})		7.1	8.7	13.6
Metallic radius (12 coord, pm)		134	151	151
Ionization Energy, kJ mol^{-1}	I_1	906	876	1007
	I_2	1733	1631	1809
	I_3	3831	3644	3300
Electrical resistivity (μ ohm cm, 20°C)		5.8	7.5	95.8
E^0 (M^{2+} - M), V		−0.76	−0.40	+0.85

The elements are characterized by low melting and boiling points; this is consistent wih expected weak metallic bonding from strongly bound *ns*-electrons, the $(n-1)d$ electrons being buried in the core owing to high effective nuclear charge. Mercury, a liquid at ordinary temperature, has an appreciable vapour pressure at ordinary temperature (~ 0.002 mm of Hg at 25°C): it forms monatomic vapours. The vapour is highly toxic (see later).

Zinc and cadmium form distorted hexagonal close packed metallic lattice with elongated distance between close packed layers (Fig. 30.1)-their densities are slightly lower than those of copper and silver respectively.

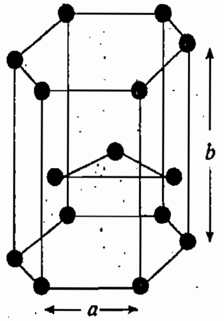


Fig. 30.1

Structure of zinc and cadmium.

Black circles represent metal atoms.

$a = 2r$ (r = metallic radius)

The ratio b/a is ~1.87 instead of the ideal value of 1.63 for this arrangement.

Zinc and cadmium react with oxygen, sulphur, phosphorus and the halogens on heating and so does mercury, excepting phosphorus. Mercury forms HgO around 300-350°C, but above 400°C, the oxide decomposes into the elements

$$HgO(s) = Hg(s) + \frac{1}{2}O_2 ; \quad \Delta H = 160 \text{ kJ mol}^{-1}$$

It may be recalled that the formation of HgO and its thermal decomposition was studied by Lavoisier and Priestley in their historical experiments.

Zinc and cadmium liberate hydrogen from nonoxidizing acids but mercury is nonreactive. Mercury dissolves in concentrated HNO_3 and hot concentrated H_2SO_4; dilute nitric acid slowly forms $Hg_2(NO_3)_2$. Only zinc dissolves in concentrated alkali solutions to form the $Zn(OH)_4^{2-}$ ion (zincates), commonly represented as ZnO_2^{2-}.

All the elements have notable tendency to form alloys with other metals. We have already mentioned a number of zinc alloys like the brasses. Mercury alloys, called *amalgams*, are sometimes formed very vigorously, as with Na or K. Some of these also have a stoichiometric compositon, for example Hg_2Na. Metals of the first transition series, except Mn and Cu, generally do not form amalgams. This is why iron-containers are often used to store mercury. Heavier transition metals readily form amalgams.

30.1.4 Uses

Zinc is largely used to provide corrosion-resistant coating on iron. A thin layer of zinc may be applied on the iron surface through electrodeposition (galvanization), or by dipping in molten zinc, when it is often called "hot-dip galvanization". Zinc coating may also be applied by spraying molten zinc or by heating the article with powdered zinc (sherardization).

The second large use of zinc is in making different alloys like brass. Such alloys are widely used in making machine parts and in diecasting.

Zinc is also consumed in making dry cells ("batteries") used in torch lights, transistors etc. Zinc oxide is a primary ingredient in paints. Granulated zinc and zinc dust are used as reducing agents in the laboratory. Zinc salts are also used in medicine.

Cadmium is also used largely in cadmium plating of steel to prevent corrosion. Cadmium rods are used in nuclear reactors as absorber of neutron. Rechargeable batteries are made of nickel-cadmium cells. Cadmium compounds are used as stabilizers in PVC against degradation by heat or uv radiation. Cadmium-amalgam is also used in the laboratory as a reducing agent.

Mercury is still largely used in electrolytic cells to produce alkali (NaOH) and chlorine though contamination of effluent water by mercury causes severe environmental pollution. Mercury is also consumed by the electrical and electronic industries in making AC rectifiers and mercury vapour lamps. In the laboratory, mercury is widely used in making thermometers, barometers and other pressure gauzes. Mercury compounds, for example phenyl mercury(II) acetate and other organo compounds have fungicidal and germicidal properties (e.g., mercurochrome lotion, Fig. 30.8). The use of mercury in the extraction of precious metals (Ag, Au) by amalgamation is now being gradually replaced by the cyanide process.

30.2 GENERAL CHEMICAL TREND

The elements Zn, Cd and Hg belong to the *d*-block but are not included among the transition series of elements as they do not form any compound in which the *d*-shell is partially occupied. The poor shielding provided by the *d*-electrons results in a steady increase in effective nuclear charge along each transition series which is further reinforced by the presence of the f^{14} core in the third transition series. This gradually

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pulls the *d*-electrons into the core so that at Zn, Cd and Hg they are no more involved in the valence of the elements. This also makes the metals softer and lower melting in comparison to other transition metals. The ionization enthalpies I_1, I_2 and I_3 (Table 30.1) also indicate the same trend. For all the three elements, I_3 is considerably higher than I_1, or I_2, indicating stronger binding for the *d*-electrons, and leading to a stable oxidation state of +II corresponding to the ionization of *s*-electrons only. For mercury, the values of I_1 and I_2 are as such much higher, owing mainly to inadequate screening of the nuclear charge by the $4f^{14}$ shell. This fact, together with a low value for the hydration enthalpy of the large Hg^{2+} ion, makes a positive $E°$-value for Hg^{2+}-Hg.

On the other hand, zinc and cadmium are considerably more electropositive than their neighbours in the periodic table; they also show closer resemblance to each other than with mercury. The chlorides of zinc and cadmium are fairly ionic, but $HgCl_2$ forms a molecular crystal. $Hg(OH)_2$ is an extremely weak base, while $Zn(OH)_2$ is amphoteric and $Cd(OH)_2$ is more basic than $Zn(OH)_2$. Mercury also forms a stable +1 state as the Hg_2^{2+} ion, while other M_2^{2+} ions are unstable. It also forms a short-lived Hg(III) complex and shows other low partial oxidation states.

Trivalent mercury is claimed to be formed in the electrochemical oxidation of the Hg(II)-cyclam complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) in acetonitrile solution at −78°C. The paramagnetic Hg(III)-cyclam complex has a half life of about ~5s and has been characterized by cyclic voltametry, epr and electronic absorption spectroscopy. The $E°$ value estimated for the Hg^{III}-Hg^{II} complex is about 1.7 V.

Zinc also shows certain similarities with the main group (*s*-block) elements beryllium and calcium. However, the elements (Zn, Cd, Hg) also resemble the transition elements in forming complex compounds with a variety of ligands like ammonia, amines, halide ions and cyanide. But complexes with other strong π-acceptor ligands, e.g., carbonyl, nitrosyl and olefin complexes, are not known. The metals are evidently reluctant to $M \rightarrow L$ π-bond formation, a consequence of their high effective nuclear charge and closed d^{10} configuration.

30.2.1 Comparison with main group elements

In spite of their ns^2 outer electron configuration, the first and second ionization energies of zinc, cadmium and mercury are considerably higher than those of the corresponding alkaline earth metal calcium, strontium and barium. The presence of a filled $4f^{14}$ shell and relativity effects make the first ionization energy of mercury still greater and even higher than the second ionization energy of barium. The radii of M^{2+} ions are also smaller for the zinc group metals (Table 30.2 and Fig. 30.2).

TABLE 30.2

Comparison of ionization energy and ionic radii : Zn, Cd, Hg vs Ca, Sr, Ba

		I_1, kJ mol^{-1}	I_2, kJ mol^{-1}	$r_{M^{2+}}$, pm
Zn	[Ar] $3d^{10}4s^2$	906	1733	88
Ca	[Ar] $4s^2$	589	1146	114
Cd	[Kr] $4d^{10}5s^2$	876	1631	109
Sr	[Kr] $5s^2$	549	1064	132
Hg	[Xe] $4f^{14}5d^{10}6s^2$	1007	1809	110
Ba	[Xe] $6s^2$	503	965	149

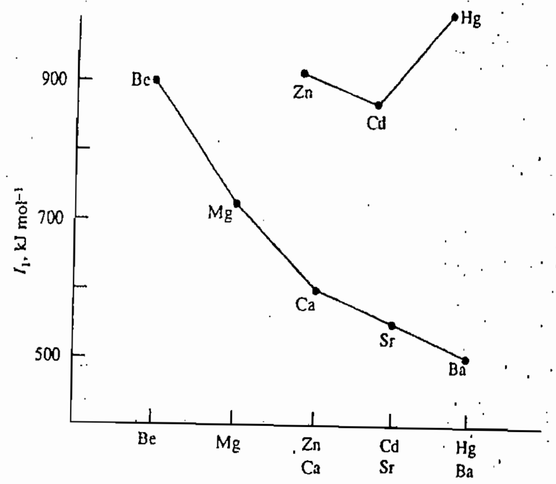


Fig. 30.2
First ionization energies of Zn, Cd, Hg with those of Ca, Sr, Ba.

The second ionization energies of the elements follow a similar trend, and on the whole we expect the zinc group elements to exhibit much lower chemical activity in comparison to the main group elements. The standard reduction potentials of the metals (Table 30.1) also support this conclusion. The smaller ionic radii for the M^{2+} ions further suggest that they will have stronger polarizing power. In view of their high first and second ionization energies, it may be more advantageous for these elements to form two collinear bonds involving $ns^2 \rightarrow ns^1np^1$ promotion. Values for this promotion energy are also quite high, as shown below :

	Zn	Cd	Hg
$ns^2 \rightarrow ns^1np^1$ promotion energy : kJ mol^{-1}	432	408	524

Two-coordination is a common feature in the case of mercury. In the main group elements, only beryllium shows any marked tendency towards linear two-coordination.

Comparison of zinc with beryllium

The first and second ionization energies of zinc are quite close to those of beryllium in Gr. IIA(2) and the two elements may be expected to have certain similarities in their chemistry. However, zinc is much larger in size in comparison to beryllium and hence should have a higher coordination number. Certain points of similarity between the two elements are noteworthy.

(i) Both the metals have a slightly distorted hexagonal close-packed structure.

(ii) The metals dissolve in strong bases forming soluble beryllates or zincates and evolve hydrogen. ZnO and BeO are thus amphoteric while CdO or MgO are not.

(iii) Both BeO and ZnO have the wurtzite structure in which the metals are 4-coordinate. MgO and CdO on the other hand, have the NaCl structure (6-coordinate). Beryllium and zinc are also 4-coordinate in their orthosilicates Be_2SiO_4 and Zn_2SiO_4 while magnesium is six-coordinate in Mg_2SiO_4.

(iv) Both Be(II) and Zn(II) form aqua ions $Be(H_2O)_4^{2+}$ and $Zn(H_2O)_6^{2+}$ in aqueous solutions. Such solutions are acidic owing to hydrolysis :

$$[M(H_2O)_n]^{2+} \longrightarrow [M(OH)(H_2O)_{n-1}]^{+} + H^{+}\,(aq)$$

The Zn^{2+} ion, though large, develops its polarizing power from the greater ease of distortion of its filled *d*-shell by the presence of ligands. In effect, the ligands experience an effective ionic charge somewhat greater than +2.

(v) Like Be(II), Zn(II) also forms a basic acetate (ethanoate) of the formula $Zn_4O(CH_3COO)_6$ (see section 19.3.5 for the structure of the beryllium compound). Magnesium and cadmium do not form such basic acetates.

(vi) Both beryllium and zinc form tetrahedral and covalent complexes of the type $MX_2.2L$. The tetrahedral BeL_4^{2+} ion is present in compounds having the stoichiometry $BeX_2.4L$. Zinc with its larger size, can form complexes containing the octahedral ZnL_6^{2+} ion, e.g., in hydrates and ammines.

Similarities with Gallium

The effect of poor shielding by the d^{10} core extends beyond the *d*-block and gives rise to certain similarities between zinc and the next *p*-block element, gallium.

(i) Both metals burn in air to give their oxides—Ga_2O_3 and ZnO respectively. The oxides are also formed by heating the respective hydroxide and nitrate.

(ii) Both gallium and zinc dissolve in acids and alkalis evolving H_2. The acid solutions contain the Ga^{3+} or Zn^{2+} ions (aquated) while the alkali solutions contain the $Ga(OH)_4^-$ or $Zn(OH)_4^{2-}$ ions.

(iii) The halides (except fluoride), sulphate, nitrate and perchlorates of both zinc and gallium are soluble in water. ZnF_2 is slightly soluble.

The oxides, hydroxides and phosphates of both the metals are insoluble in water.

(iv) Addition of aqueous ammonia to solutions containing Ga^{3+} ions gives white precipitate of GaO.OH, soluble in excess of reagent forming $Ga(OH)_4^-$. Solutions of Zn^{2+} give white precipitate of $Zn(OH)_2$, soluble in excess ammonia forming $Zn(NH_3)_4^{2+}$.

However, addition of sodium carbonate to solutions containing Zn^{2+} produces a white precipitate of basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2$ while solutions of Ga^{3+} precipitate $Ga(OH)_3$. Similarly, Zn^{2+} alone produces a white precipitate (a) of zinc oxalate with sodium oxalate solution and (b) of zinc cyanide with potassium cyanide solution which dissolves in excess of the reagent to $[Zn(CN)_4]^{2-}$.

30.2.2 Aqueous solution chemistry

The standard electrode potentials (v) for the elements in acid medium are as follows :

$$\begin{array}{ccccc}
+\text{II} & & +\text{I} & & 0 \\
Zn^{2+} & & \xrightarrow{\quad -0.76 \quad} & & Zn \\
Cd^{2+} & & \xrightarrow{\quad -0.40 \quad} & & Cd \\
Hg^{2+} & \xrightarrow{0.91} & Hg_2^{2+} & \xrightarrow{0.796} & Hg \\
 & & \underbrace{\qquad\qquad\qquad}_{0.854} & &
\end{array}$$

The large difference between cadmium and mercury may be partly ascribed to the higher hydration energy of the smaller Cd^{2+} ion. The values show that mercury is much less reactive than the other two metals.

The $E°$ values for Hg^{2+}-Hg and Hg_2^{2+}-Hg suggest that oxidizing agents with $E°$ (reduction) values higher than 0.796V but lower than 0.854 V would oxidize Hg only to Hg_2^{2+} but not to Hg^{2+}. In reality, however, no common oxidizing agent operates within such a narrow range, so that oxidation of Hg by common oxidizing agents produces Hg(II). Hg(I) may be obtained only in presence of excess Hg itself which reduces Hg (II) according to the equation

$$Hg\ (l) + Hg^{2+} = Hg_2^{2+}\ ; \qquad E = 0.115\ V$$

Reduction of Hg(II) by other reducing agents also produce Hg(I) in solution as the dimercury(I) ion, $[Hg_2(H_2O)_2]^{2+}$ which is stable in acidic solution. The ion readily undergoes disproportionation (section 30.2.3), specially in presence of reagents which complex or form insoluble precipitate with Hg(II), for example, OH^-, CN^-, NH_3, S^{2-} etc. Hence mercury(I) oxides, cyanide, sulphide etc. are not known.

Hg_2F_2 is unstable to water, giving HF and HgO, together with Hg. Other halides are insoluble. Mercurous nitrate and perchlorate are very soluble in water. Hydrates $Hg_2(NO_3)_2.2H_2O$ and $Hg_2(ClO_4)_2.4H_2O$ may be isolated from such solutions. The former contains the ion $[H_2O—Hg—Hg—OH_2]^{2+}$. Other salts are sparingly soluble, viz., the sulfate, chlorate, perchlorate, iodate and acetate. The halides of Hg(I) are insoluble. The nature of the Hg_2^{2+} ion has been discussed in section 30.2.3.

For all the members of the family the $M(H_2O)_6^{2+}$ ions are quite stable in aqueous solution and may be obtained when their perchlorates are dissolved in water (the anion being feebly coordinating). The solutions react acidic owing to extensive hydrolysis giving species like $ZnOH^+$, $CdOH^+$, Cd_2OH^{3+} and $HgOH^+$. In concentrations below $0.1M$ in perchlorate solutions, the principal species appear to be the $MOH^+\ (aq)$ ions, as examplified by the high value of equilibrium constant for the following process

$$[Cd(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Cd(OH)\ (H_2O)_5]^+ + H_3O^+;\ K \simeq 10^6.$$

In more concentrated solutions, cadmium forms the Cd_2OH^{3+} ion

$$2Cd^{2+}(aq) + H_2O \rightleftharpoons [Cd_2OH]^{3+}\ (aq) + H^+.$$

The hydrolytic behaviour of the Hg^{2+} ion may be summarily represented by the equilibria

$$Hg^{2+}\ (aq) + H_2O \rightleftharpoons Hg(OH)^+\ (aq) + H^+;\ K = 2.6 \times 10^{-4}$$

$$Hg(OH)^+\ (aq) + H_2O \rightleftharpoons Hg(OH)_2 + H^+;\ K = 2.6 \times 10^{-3}.$$

However, the hydroxide cannot be isolated, yellow to red HgO being precipitated instead.

Dilute solutions of zinc chloride also contain the $Zn(H_2O)_6^{2+}$ ion but concentrated solutions contain chlorocomplexes like $ZnCl^+\ (aq)$, $ZnCl_2\ (aq)$ and $ZnCl_4^{2-}\ (aq)$. In solutions above $2M$ concentration, electrolysis moves zinc towards the anode. Simultaneous hydrolysis also takes place, the solution attaining a pH of about 1.0 in $6M$ solution. Cadmium chloride is strongly self-complexed even in dilute solutions. Mercury(II) chloride enters solution as virtually undissociated $HgCl_2$ molecule.

Many oxo-salts may be crystallized as hydrates from aqueous solutions; some zinc salts are isostructural with corresponding magnesium salts, for example,

$ZnSO_4.7H_2O$ and $MgSO_4.7H_2O$
$Zn(BrO_3)_2.6H_2O$ and $Mg(BrO_3)_2.6H_2O$
$Zn(ClO_4)_2.6H_2O$ and $Mg(ClO_4)_2.6H_2O$

Many salts may be prepared by dissolving the oxide in appropriate acid or by metathesis.

$$ZnO + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2O$$

$$ZnO + H_2SiF_6 \longrightarrow ZnSiF_6 + H_2O$$

$$Hg(NO_3)_2 + 2NaIO_3 \longrightarrow Hg(IO_3)_2\downarrow + 2NaNO_3$$

$$ZnSO_4 + BaI_2 \longrightarrow ZnI_2 + BaSO_4\downarrow$$

$$CdSO_4 + Ba(SCN)_2 \longrightarrow Cd(SCN)_2 + BaSO_4\downarrow$$

30.2.3 The +I state : M_2^{2+} ion

The large differences between the 1st and 2nd ionization energies for the elements suggest that the formation of a M^+ derivative might be possible for them. In practice, however, the univalent state appears important only for mercury in the form of Hg_2^{2+}; Zn_2^{2+} and Cd_2^{2+} ions are known only in M-MCl_2 melts which readily disproportionate in aqueous solution, for example,

$$Cd_2^{2+} \longrightarrow Cd\downarrow + Cd^{2+}$$

While the +II state is favoured for zinc and cadmium by higher hydration energies for the +2 ion and/or bond energies for divalent compounds, it is also true that the Hg—Hg bond in Hg_2^{2+} is definitely stronger than the Zn—Zn or Cd—Cd bond in their M_2^{2+} species. In fact, force constant data suggest the order of bond strength Zn—Zn < Cd—Cd < Hg—Hg, which is against the normal trend observed in any group in the periodic table. For homonuclear bonds, bond strength is expected to decrease with the involvement of larger and more diffuse orbitals as one passes to the heavier members down any group. The anomalous behaviour of mercury has been qualitatively associated with the electron attachment enthalpy of the Hg^+ ion (equal to $-I_1$ of Hg); since the first ionization energy of Hg is considerably higher than those of Zn or Cd, the electron attachment enthalpy of Hg^+ is also considerably higher in magnitude than for Zn^+ or Cd^+. This may be supposed to promote overlap between 6s orbitals of two Hg^+ ions, forming a strong Hg—Hg bond. The high effective nuclear charge of Hg (consequent to poor shielding by the d^{10} and f^{14} core) facilitates the overlap by lowering the energy of the 6*s* orbitals (or "contracting" them). The bonding situation is similar to that occurring in gaseous alkali metal dimers and the H_2 molecule. Spectroscopically it is also indicated that the bond energy is HgH^+ is greater than that in CdH^+.

The Zn_2^{2+} ion has been characterized by Raman spectroscopy in the yellow diamagnetic glassy solid obtained by adding zinc to molten $ZnCl_2$ at 500-700°C and subsequent cooling. Similary, molten $CdCl_2$—$AlCl_3$ mixtures may be reduced by cadmium to yellow solutions containing Cd_2^{2+} from which solid $Cd_2(AlCl_4)_2$ has been isolated. The Cd—Cd bond length in the ion is 258 pm, which is slightly longer than the Hg—Hg bond length of 254 pm in $Hg_2(NO_3)_2.2H_2O$.

Evidences for the dimeric ion Hg_2^{2+}

The dimeric nature of the Hg_2^{2+} ion has been established by several independent evidences :

(i) X-ray crystal structures of mercury(I) compounds show the existence of discrete Hg—Hg units. The distance (249-254 pm) is less than twice the van der Waals radius of mercury.

(ii) All mercury(I) compounds are diamagnetic whereas the Hg^+ ion ($6s^1$) would have one unpaired electron.

(iii) The Raman spectrum of aqueous solutions of mercurous nitrate shows a strong line at 172 cm^{-1} due to the vibration of the Hg—Hg bond.

(iv) Concentration cells consisting of mercury(I) salts give e.m.f. data consistent with a +2 charge on the mercurous ion.

The mercury(I)-mercury(II) equilibrium.

In aqueous solution, the Hg_2^{2+} ion readily tends to disproportionate into Hg(II) and Hg. The equilibrium between Hg(I) and Hg(II) is very delicate, as one may readily appreciate from the following $E°$ values :

$$\tfrac{1}{2}Hg_2^{2+} + e \rightleftharpoons Hg\,(l)\,; \quad E° = 0.796\text{ V}$$

$$Hg^{2+} + e \rightleftharpoons \tfrac{1}{2}Hg_2^{2+}\,; \quad E° = 0.911\text{ V}\,.$$

Subtracting the second from the first, we get,

$$Hg_2^{2+} \rightleftharpoons Hg\,(l) + Hg^{2+} \quad E° = -0.115\text{ V}$$

From the relation $E° = (RT/nF)\ln K$, we get, at 25°C,

$$K = \frac{[Hg^{2+}]}{[Hg_2^{2+}]} = 1.124 \times 10^{-2}.$$

This shows that in any solution containing Hg(I), there will be rather more than 1% Hg(II) in equilibrium.

Q. 30.1 *Is it possible to obtain Hg(I) free from Hg(II)? Justify your answer.*
Hint : See above equilibrium.

The equilibrium between Hg(II) and Hg(I) is easily disturbed by lowering the concentration of Hg^{2+} ion either by precipitation or complexation with suitable reagents when the disproportionation would shift to right. For example, addition of cyanide ion forms soluble but unionized $Hg(CN)_2$, thus lowering the concentration of free Hg^{2+}. As a consequence, all Hg(I) disproportionates readily into $Hg(CN)_2$ and a grey precipitate of metallic Hg.

$$Hg_2^{2+} + 2CN^- \longrightarrow Hg\,(l) + Hg(CN)_2\,(aq)$$

Similarly, adition of OH^- (or S^{2-}) ions remove Hg^{2+} by precipitation of HgO (or HgS), pushing the disproportionation to completion. Such disproportionation thus implies that sulfides, oxides or cyanides of Hg (I) do not exist.

$$Hg_2^{2+} + 2OH^- \longrightarrow Hg\,(l) + HgO\downarrow + H_2O$$

$$Hg_2^{2+} + S^{2-} \longrightarrow Hg\,(l) + HgS$$

The reactions with OH^- and CN^- appear to proceed by cleavage of the Hg—Hg bond in the rate determining step, for example,

$$Hg_2^{2+} + CN^- \rightleftharpoons Hg_2CN^+ \qquad \textit{(rapid equilibrium)}$$

$$Hg_2CN^+ \longrightarrow Hg + HgCN^+ \qquad \textit{(slow)}$$

$$Hg_2CN^+ + CN^- \longrightarrow Hg + Hg(CN)_2 \qquad \textit{(fast)}$$

$$HgCN^+ + CN^- \longrightarrow Hg(CN)_2 \qquad \textit{(fast)}$$

The Hg_2^{2+} unit may be prepared in liquid SO_2 by oxidizing Hg with AsF_5 :

$$2Hg + 3AsF_5 = Hg_2(AsF_6)_2 + AsF_3$$

The presence of Hg_2^{2+} unit in the colourless solution has been characterized by ^{199}Hg nmr spectra. But the reaction also yields other subvalent polyatomic mercury cations like Hg_3^{2+} and Hg_4^{2+} (see below).

30.2.4 Oxidation states below 1 : polyatomic mercury cations

Oxidation of mercury with either AsF_5 or SbF_5 in liquid SO_2 produces successively Hg_2^{2+}, Hg_3^{2+} and Hg_4^{2+} :

$$3Hg + 3AsF_5 = Hg_3(AsF_6)_2 + AsF_3$$

$$4Hg + 3AsF_5 = Hg_4(AsF_6)_2 + AsF_3$$

The first reaction produces a yellow solution while the second one gives a red solution in which the Hg_n^{2+} species have been characterized by ^{199}Hg nmr spectra. The salts $Hg_3(AsF_6)_2$, $Hg_4(AsF_6)_2$ and $Hg_3(AlCl_4)_2$ have been isolated and studied by x-ray crystallography. The Hg_n^{2+} ions are almost linear; the Hg—Hg distance in Hg_3^{2+} is 255.2 pm while the Hg_4^{2+} is centrosymmetrio with an angle of 176° and different Hg—Hg separations.

$$Hg \overset{257\text{ pm}}{\rule[0.5ex]{3em}{0.4pt}} Hg \overset{270\text{ pm}}{\rule[0.5ex]{3em}{0.4pt}} Hg \overset{257\text{ pm}}{\rule[0.5ex]{3em}{0.4pt}} Hg$$

Very weak Hg---Hg interactions between the ions give rise to infinite zigzag chains running through the crystals.

Golden yellow metal-like solids approximating compositions $Hg_{2.82}AsF_6$ and $Hg_{2.9}SbF_6$ may be obtained using smaller amounts of oxidants or low temperatures (–20°C). They contain chains of Hg-atoms passing in two directions at right angles (non-intersecting) through a host lattice of AsF_6^- or SbF_6^- ions; the average Hg—Hg distance is 264 pm. These compounds can be transformed into silvery compounds of composition Hg_3MF_6 (M = As, Sb) which have close-packed array of Hg-atoms in hexagonal sheets; the sheets are separated by sheets of MF_6^- anions.

30.2.5 Complex compounds

Zinc, cadmium and mercury possess stronger tendency to form complex compounds than the main group elements calcium, strontium etc. Though all these elements have an outer ns^2 electron configuration, the sizes of Zn^{2+}, Cd^{2+} and Hg^{2+} ions are relatively smaller than Ca^{2+}, Sr^{2+} and Ba^{2+} owing to poor shielding provided by the filled *d*- and *f*-shells in the former group of ions. Even the Hg^{2+} ion is smaller than the Ca^{2+} ion. Now, a smaller ion will get higher ion-dipole contribution in bonding to ligands in the process of complex formation. Secondly, a filled $(n-1)$ *d*-shell is more easily polarized or deformed by ligand electrons than are filled *np* orbitals. Consequently, a ligand on Zn^{2+}, Cd^{2+} or Hg^{2+} will experience a greater nuclear charge.

The complexes of Zn, Cd and Hg will not gain any stabilization from ligand field (LFSE) as their *d*-orbitals are completely filled.

At the same time, the stability of the d^{10} core makes the M(II) ions reluctant to back-bonding and we do not find their complexes with π-acceptor ligands like CO, NO or alkenes. Their cyanides are stabilized mainly by σ-bonding alone. Similarly, the filled *d*-shell does not allow electron acceptance into these orbitals, so that even good π-donor ligands like cyclopentadienide also form σ-bonded complexes with the metals.

Since the complexes of these metals cannot gain any stabilization by virtue of their geometry (LFSE = 0 for all cases), the stereochemistry is determined by the steric requirements of the ligands and the size and polarizing power of the cation. Both Zn(II) and Cd(II) form complexes with coordination number four and six, Cd(II) more readily in C.N. six (larger size). Mercury(II) is predominantly two-coordinate : the *d*-orbitals are sufficiently lowered in energy to promote $s - d_{z^2}$ hybridization (section 26.4.1). This may be aided by greater deformability of the large d^{10} core; as two ligands approach the Hg^{2+} ion from two sides along the Z-axis, the *d*-electron population will be deformed or pushed in the *xy*-plane. This enhanced electron density will now repel other ligands approaching in this plane.

In keeping with its similarities to the main group II elements, zinc forms complexes with many *O*-and *N*-donor ligands, behaving as a class-a metal. However, it also forms complexes with many *S*-donor ligands. Cadmium, though similar to zinc, falls on the borderline of class-a and class-b. Hg(II) is definitely a class-b metal as it forms stable complexes with mainly *P*-and *S*-donor ligands.

30.2.6 Main compound types

In the following section we shall have a short account of the various compounds of the Gr 12 elements—namely, the oxides, sulfides, halides, oxoacid salts; complex compounds and organometallic compounds. The gradual change from zinc to mercury follows the trend mentioned earlier—mercury is distinctly different from zinc and cadmium, wich have many similarities among themselves. All the elements form the oxide MO of which ZnO is amphoteric and white, CdO is brown and HgO may be yellow or red. The colour change, ascribed to charge transfer with increasing polarization, is more prominently displayed in the sulfides and iodides : ZnS white; CdS orange yellow; HgS black or red; ZnI_2 and CdI_2 white; HgI_2 red (yellow). In the +I state, only mercury forms the halides Hg_2X_2.

30.3 PRINCIPAL COMPOUNDS

As already explained, only mercury forms a limited number of compounds in the +I state. The only other oxidation state for the elements is +II. The compounds of Hg(I) are discussed first.

30.3.1 Compounds of Hg(I)

The limitations of Hg(I) compounds have ben discussed in sections 30.2.2 and 30.2.3.

Mercury(I) oxide and hydroxide are not known. When alkali is added to an aqueous solution containing Hg_2^{2+}, a black solid is precipitated which is an intimate mixture of HgO and Hg.

All four halides of Hg(I) are known.

Hg_2F_2 is prepared by dissolving Hg_2CO_3 (see below) in aqueous HF. It is soluble in water but is readily hydrolyzed to HgO, Hg and HF. Other Hg(I) halides are very insoluble in water (they are more covalent) and hence escape the chance of hydrolysis. These may be precipitated by the appropriate X^- ion from aqueous solutions of Hg_2^{2+}, mostly the nitrate. They may also be prepared by reducing HgX_2 with Hg.

[Sec. 30.3.1 compound of Hg(I)]

Except fluoride, the halides are predominantly covalent which sublime on gentle heating :

Hg_2F_2	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2
Yellow	White	White	Yellow
decomp>540°C	sub 383°C	sub 345°C	sub 140°C

When Hg_2Cl_2 and Hg_2Br_2 sublime, their vapours show densities corresponding to "HgX" owing to complete disproportionation :

$$Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$$

This is supported by (i) their diamagnetism and (ii) uv absorption band at 254 nm characteristic of mercury vapour. Hg_2I_2 is more unstable than the others and disproportionates simply on warming with water.

The crystal structures of the halides show the presence of discrete Hg_2 units, as illustrated by Hg_2Cl_2 (Fig. 30.3).

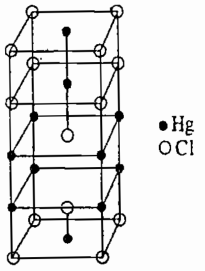


Fig. 30.3. Tetragonal unit cell of Hg_2Cl_2.

Mercurous Chloride, Calomel, Hg_2Cl_2 is prepared by heating (i) $HgCl_2$ with Hg or (ii) a mixture of $HgSO_4$, Hg and NaCl in an iron pot.

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$$

Hg_2Cl_2 collects in the sublimate which is ground and boiled with water to remove Hg(II).

Highly insoluble in water, Hg_2Cl_2 dissolves in aqua regia, hot concentrated HNO_3 and in hot concentrated HCl. In the last case, Hg is also separated.

$$Hg_2Cl_2 + 2Cl = 2HgCl_2 \text{ (}\textit{aqua regia}\text{)}$$

$$3Hg_2Cl_2 + 8HNO_3 = 3HgCl_2 + 3Hg(NO_3)_2 + 2NO + 4H_2O$$

$$Hg_2Cl_2 + HCl = Hg + H[HgCl_3]$$

$$Hg_2Cl_2 + 2HCl = Hg + H_2[HgCl_4]$$

Hg_2Cl_2 turns black with ammonia :

$$Hg_2Cl_2 + 2NH_3 = Hg(NH_2)Cl + Hg + NH_4Cl$$

Hg_2Cl_2 (white) received the name *calomel* (*beautiful black* in Greek) owing to the formation of this black mass.

Calomel is used in making calomel electrode and in medicine.

Mercurous iodide, Hg_2I_2 (yellow) is obtained as a green precipitate on adding KI to a solution of $Hg_2(NO_3)_2$. The green colour appears to be owing to partial decomposition into Hg. Hg_2I_2 dissolves in KI with the separation of finely divided Hg.

$$Hg_2I_2 + 2KI = K_2[HgI_4] + Hg$$

Mercurous nitrate, $Hg_2(NO_3)_2$, is obtained by the action of cold dilute HNO_3 upon excess of Hg. It crystallizes as the colourless dihydrate $Hg_2(NO_3)_2.2H_2O$. The aqueous solution is stable in presence of dilute HNO_3; otherwise a white basic sulfate is precipitated.

Mercurous carbonate, Hg_2CO_3 is precipitated as a yellow powder from a solution of $Hg_2(NO_3)_2$ by sodium bicarbonate. It decomposes on exposure to light, or rapidly on heating to 130°C : $Hg_2CO_3 = Hg + HgO + CO_2$

Mercurous sulfate, Hg_2SO_4 is prepared by heating excess of mercury with concentrated H_2SO_4. The sparingly soluble white powder is deposited on dilution with water. It is readily soluble in concentrated H_2SO_4. Hydrolysis occurs in aqueous solution to a basic sulfate. It is used as a depolarizer in standard Weston cell.

Mercurous thiocyanate, $Hg_2(SCN)_2$, is obtained as a white crystalline precipitate by adding ammonium thiocyanate to a solution of mercurous nitrate.

Complex Compounds

Most ligands form more stable complexes with Hg(II) than with Hg(I); in addition the Hg_2^{2+} has a low tendency to form coordinate bonds. Consequently common ligands like CN^-, OH^-, I^-, ammonia and amines prompt mercury(I) to disproportionate in favour of forming Hg(II) complex. Only *N*-bases of weak basicity like aniline and 1, 10-phenanthroline form stable complexes, e.g., $[Hg_2(C_6H_5NH_2)]^{2+}$. The 2-coordinate $[H_2O.Hg.OH_2]^{2+}$ is present in $Hg_2(NO_3)_2.2H_2O$. Complexes of the type $[Hg_2L_4]^{2+}$ and $[Hg_2L_6]^{2+}$ are formed with triphenyl phosphine oxide or pyridine-*N*-oxide. Other *O*-donor ligands like oxalate, succinate, pyrophosphate and tripolyphosphate complexes are also known to form stable complexes with Hg_2^{2+}, for example $[Hg_2(P_2O_7)_2]^{6-}$.

30.3.2 Compounds of Zn, Cd and Hg in the II state

The oxides, sulfides and halides are the most important binary compounds of these metals. The hydrides, nitrides and carbides (acetylides) are unstable.

ZnH_2 has been isolated as a colourless solid by reduction of $ZnBr_2$ (or ZnI_2) with LiH (or NaH) in tetrahydrofuran. ZnH_2 and CdH_2 are also obtained by reducing the metal dialkyls with $LiAlH_4$ in ether :

$$Zn(CH_3)_2 + 2LiAlH_4 \longrightarrow ZnH_2 + 2LiAlH_3(CH_3).$$

ZnH_2 decomposes at room temperature; CdH_2 decomposes at still lower temperature.

Oxides

The normal oxide MO is formed by each of the elements; peroxides MO_2 are known for zinc and cadmium.

The oxides MO are formed by heating the metals or their sulfides in air or by thermal decomposition of the carbonates.

In contrast to the elements of the calcium group, the stability of the oxides of zinc group decreases with increasing atomic number :

	ZnO	CdO	HgO	
ΔG^0_f	–321	–229	–59	kJ mol^{-1}
Decomposition temperature	1950	1813	400	°C

ZnO is white at ordinary temperature and has the wurtzite structure; it also occurs in the zinc blende form. At higher temperature, ZnO turns yellow owing to loss of oxygen from the lattice to a non-stoichiometric composition $Zn_{1+x}O$. The vacant lattice points may trap electrons which are excited by visible radiation to impart the yellow colour. The colour disappears on cooling. CdO, which is commonly brown, may have colours from yellow to black; it adopts the NaCl type lattice and the colour change is again due mainly to lattice defects. HgO, which adopts only the zinc blende form, may be yellow or red depending on the particle size. The red form is obtained by slow heating of mercury in O_2 at about 350°C or by heating $Hg(NO_3)_2$. The yellow form is precipitated by alkali from aqueous solutions of Hg(II).

$$Hg(NO_3)_2 + 2KOH = HgO\downarrow + 2KNO_3 + H_2O$$

Both forms have the same zig-zag chain structure with virtually linear O—Hg—O units.

ZnO is amphoteric in nature; it dissolves in acids to produce Zn^{2+} (*aq*) ions and in aqueous alkali to $[Zn(OH)_4]^{2-}$ (commonly written as ZnO_2^{2-}). Addition of alkali to Zn-salts first precipitates white gelatinous $Zn(OH)_2$ which dissolves in further alkali. Solids $NaZn(OH)_3$ and $Na_2Zn(OH)_4$ may be crystallized from the solution.

$$Zn(OH)_2 + 2NaOH = Na_2[Zn(OH)_4]$$

CdO, being more basic than ZnO, is practically insoluble in alkalis. Addition of alkali to Cd^{2+} in solution precipitates white $Cd(OH)_2$ which may be dissolved in concentrated alkali on prolonged boiling to hydroxocadmiates, e.g., $K_4[Cd(OH)_6]$. However, when such solutions are slowly cooled or diluted, only $Cd(OH)_2$ separates out. In fact, the solubility of $Cd(OH)_2$ rises only from 0.0003 g per 100 g in pure water to 0.13 g per 100 g in 5*M* NaOH solution at room temperature.

Zinc hydroxide (and also cadmium hydroxide) dissolves in aqueous ammonia forming ammines such as $[Zn(NH_3)_4(H_2O)_2]^{2+}$.

Mercury (II) hydroxide is unknown. When aqueous solutions containing Hg(II) are treated with alkali, yellow HgO is precipitated.

When zinc and cadmium hydroxides are treated with aqueous H_2O_2, the hydrated peroxides are obtained.

Zinc oxide is largely used (i) as a white pigment (ii) in the production of rubber (it reduces the time of vulcanization) (iii) in glass, enamels and glazes (iv) in making zinc salts of fatty acids e.g., zinc stearate which are useful as paint driers, stabilizers in plastics and fungicides.

CdO is used (i) in the production of decorative glasses and enamels (ii) as a catalyst in several hydrogenation and dehydrogenation processes and in Ni-Cd storage cells.

Sulfides (and other chalcogenides)

The sulfides of zinc, cadmium and mercury are very familiar to us in the routine group analysis of cations. These, as well as other chalcogenides may be made by direct union under heat, or by treating aqueous M(II) with H_2S, H_2Se or H_2Te

$$Hg + S \longrightarrow HgS$$

$$Cd(NO_3)_2 + H_2Te \longrightarrow CdTe\downarrow + 2HNO_3$$

HgS and CdS are precipitated by H_2S from dilute HCl medium, CdS requiring a faintly acid medium for complete precipitation. ZnS is precipitated from ammoniacal solution.

ZnS appears in two crystal structures known by their own names : the zinc blende form and the wurtzite form. The zinc blende form transforms into the wurtzite form at 1020°C. Both forms involve the metal in tetrahedral coordination; the zinc blende structure may be viewed as a diamond structure in which one half of the C-atoms have been replaced by Zn and the other half by S. The wurtzite structure, typical of the mineral wurtzite (ZnS), has two interpenetrating hexagonal close-packed lattices of Zn and S atoms. See Chapter 23, figure 23-VII.

The above structures are also adopted by other chalcogenides of these group e.g., ZnTe, CdS and CdSe occur in both wurtzite and zinc blende forms. ZnSe, CdTe, HgSe and HgTe are found in the zinc blende form only. HgS occurs in two forms—in the zinc blende form and in a distored NaCl lattice.

The sulfides also become gradually less stable from ZnS to HgS :

	ZnS	CdS	HgS	
ΔG^0_f	–200	–153	–51	kJ mol^{-1}

Because of the low stability of HgS, it is directly converted to Hg on heating (see extraction).

ZnS and CdS are readily soluble in dilute acids but black HgS dissolves only in aqua regia, HBr and HI (conc.).

Roasted ZnS is much less reactive which is used as a white pigment. *Lithopone* ($ZnS + BaSO_4$) is prepared by adding BaS to $ZnSO_4$ solution. ZnS is also used as a phosphor in TV screens, cathode-ray tubes, radar screens, and fluorescent paints. It gives fluorescence or luminescence when excited by X-rays, cathode rays or γ-rays.

CdS is used in pigments in admixture with ZnS, CdSe etc. A growing range of polynuclear sulphides and selenides of zinc and cadmium are being prepared e.g., the $[S_4Cd_{10}(SR)_{16}]^{4-}$ cluster which may be helpful in understanding the biological role of these metals.

Halides

All four halides of these elements are known. The fluorides MF_2 are ionic having high melting points (Table 30.3). The chlorides, bromides and iodides of zinc and cadmium are also ionic though with appreciable polarization, and they crystallize in layer lattices. In contrast, mercury(II) chlorides, bromides and iodides are covalent solids with much lower melting and boiling points.

TABLE 30.3

Halides of Zn(II), Cd(II), Hg(II) (m.p./b.p. in °C)

ZnF_2	**$ZnCl_2$**	**$ZnBr_2$**	**ZnI_2**
White	White	White	White
872°/1500°	275°/756°	394°/702°	446°/dec>700°
CdF_2	**$CdCl_2$**	**$CdBr_2$**	**CdI_2**
White	White	pale yl.	White
1049°/1748°	570°/980°	566°/865°	390°/788°
HgF_2	**$HgCl_2$**	**$HgBr_2$**	**HgI_2**
White	White	White	Red/Yellow
decomp>640°	280°/303°	238°/318°	257°/351°

ZnF_2 and CdF_2 are only slightly soluble in water, owing to their high lattice energy and weak complexing tendency of fluoride ion in solution. They may be prepared from solutions of Zn(II) or Cd(II) salts with any soluble fluoride. Mercury(II) fluoride is completely hydrolyzed in aqueous solution. ZnF_2 has the rutile sturcture, while CdF_2 and HgF_2 have the calcium fluoride structure.

The chlorides, bromides and iodides of zinc and cadmium are also ionic but the effect of polarized anions is reflected in their much lower melting points. The compounds are highly soluble in water as well as in alcohols, ethers, amines, ketones esters etc. ($BeCl_2$, $BeBr_2$ and BeI_2 behave similarly). However, the solubility in water is also associated with ready formation of complex ions : a 0.5*M* solution of $CdBr_2$ contains $Cd^{2+}(aq)$, $CdBr_2$, $CdBr_3^-$ and $CdBr_4^{2-}$. Concentrated solution of cadmium halides show "abnormal transport number" owing to migration of cadmium to the anode as the complex anion, which is formed through "autocomplex" formation :

$$2CdX_2 = Cd^{++} + CdX_4^{2-}$$

Zinc chloride, $ZnCl_2$, may be prepared readily in solution by dissolving Zn, ZnO or $ZnCO_3$ in HCl; concentration yields deliquescent crystals of $ZnCl_2.H_2O$. On heating, this forms a basic chloride

$$ZnCl_2.H_2O = Zn(OH)Cl + HCl$$

Anhydrous zinc chloride may be prepared by heating (i) Zn or ZnO in chlorine (ii) Zn or ZnO in chlorine (iii) Zn or $ZnCl_2.H_2O$ in HCl gas. It is a colourless, glassy, highly deliquescent solid.

Zinc chloride is used as a catalyst in organic reactions; as a dehydrating agent; in making soldering fluids; in preserving wood and in the preparation of vulcanized fibre and activated charcoal. In soldering, it removes the surface coating of oxide films, ensuring stronger joint. In wood preservation, zinc chloride forms covalent bonds with the oxygen atoms in cellulose fibres which are thus coated with a layer of toxic zinc chloride.

Other halides of zinc and cadmium may be prepared by dissolving the oxide or carbonate in appropriate HX.

The chloride, bromide and iodide of Hg(II) are only slightly soluble in water, $HgCl_2 > HgBr_2 > HgI_2$. There is little or no ionization to form Hg^{2+} (*aq*) ions in such solutions which mainly contain HgX^+, HgX_2 and HgX_4^{2-}. The iodide complexes being most stable, addition of I^- ions to a solution of Hg(II) initially forms the soluble HgI^+ complex ion; HgI_2 is not precipitated until about 0.2 mol of I^- ions have been added, although the solubility of HgI_2 is very small, $\approx 10^{-4}$ mol L^{-1}. The red precipitate of HgI_2 dissolves in excess iodide to the colourless HgI_4^{2-} ion.

Solid $HgCl_2$ is molecular with two Hg—Cl bonds at 225 pm; the next nearest Hg—Cl distance of ~334 pm suggests little interaction with distant chlorines. In gaseous $HgCl_2$, the Hg—Cl distance is also 228 pm, supporting the molecular nature of the solid. $HgBr_2$ also forms a distorted molecular lattice with two Hg—Br distances (248 pm) much shorter than the rest (323 pm). The Hg—Br distance in $HgBr_2$ vapour is 240 pm, less than that in the solid. Solid HgI_2 forms a layer lattice consisting of HgI_4 tetrahedra (Hg—I = 278 pm). The Hg—I distance in the vapour phase is again distinctly less at 275 pm, showing departure from a molecular solid.

Vapours of anhydrous chlorides, bromides and iodides of all three metals consist of linear X—M—X molecules. Zinc halides are more volatile in presence of metallic zinc which may be due to the formation of gaseous ZnX or $(ZnX)_2$. However, all attempts to condense the lower vapour by quenching have failed—the product is always Zn and ZnX_2.

Mercuric Chloride, $HgCl_2$, corrosive sublimate, is prepared by heating mercury in chlorine or by heating a dry mixture of mercuric sulfate and sodium chloride when the mercuric chloride is obtained as a white sublimate (hence the name). It is sparingly soluble in cold water but freely in hot water, mainly undissociated. It is more soluble in alcohol and ether.

On boiling with aqueous ammonia solution, mercuric chloride gives an "*infusible white precipitate*" of $Hg(NH_2)Cl$ which is hydrolyzed by digestion to yield "*chloride of Millon's base*", $NH_2HgO.HgCl$.

$$HgCl_2 + 2NH_3 = Hg(NH_2)Cl + NH_4Cl$$

$$2Hg(NH_2)Cl + H_2O = (NH_2)HgOHgCl + NH_4Cl$$

$HgCl_2$ reacts with gaseous ammonia to form the *"fusible white precipitate"* of $HgCl_2.2NH_3$.

The composition and structure of these compounds have been discussed separately.

Mercuric chloride oxidizes stannous chloride to stannic chloride, a reaction commonly used in traditional volumetric estimation of iron(III) after reduction with $SnCl_2$.

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

Crystalline complex salts $K[HgCl_3]$ and $Na_2[HgCl_4]$ may be obtained by reacting solutions of the alkali metal chlorides with $HgCl_2$.

Potassium iodide gives with mercuric chloride an initial yellow precipitate of HgI_2 which rapidly turns red and finally dissolves in excess KI to K_2HgI_4.

Nessler's reagent is an alkaline solution of K_2HgI_4 which gives a brown precipitate with ammonia (detection of NH_3).

$$2K_2HgI_4 + NH_3 + 3KOH = Hg_2NI.H_2O + 7KI + 2H_2O$$

$Hg_2NI.H_2O$ is called the iodide of Millon's base (see later).

Mercuric chloride is a deadly poison - its lethal dose is only 0.2-0.4 g. The antidote is the raw white of an egg followed by emetic. It is used in preserving wood, skins and furs and as an antiseptic and disinfectant.

Salts of oxo-acids

A general method of preparation of the oxoacid salts is to dissolve an excess of the metal oxide (or carbonate in case of Zn and Cd) in the relevant acid and crystallize. Some examples are

$$ZnO + H_2SeO_4 \longrightarrow Zn(SeO_4)_2 \text{ (several hydrates)}$$

$$ZnO + HCOOH \longrightarrow Zn\,(OOCH)_2.2H_2O$$

$$ZnO + H_3PO_4 \longrightarrow Zn_3(PO_4)_2$$

Zinc carbonate is precipitated by adding sodium bicarbonate to a solution of zinc salt (addition of sodium carbonate precipitates a basic salt).

Zinc sulfate, $ZnSO_4.7H_2O$, white vitreol, appears in colourless efflorescent crystals on crystallization of zinc sulfate solution (Zn or ZnO plus dilute H_2SO_4) below 30°C. It is isomorphous with $MgSO_4.7H_2O$ (Epsom salt) and $FeSO_4.7H_2O$ (green vitreol). The hydrate becomes anhydrous on heating at 450°C but decomposes to ZnO on further heating :

$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2$$

Industrially, zinc sulfate is produced by roasting the sulfide ore in air below 700°C and leaching the mass with dilute sulphuric acid. It is used in making the white pigment *lithopone* : ($BaSO_4 + ZnS$); as a mordant in calico printing and as an eye lotion (0.125 per cent). Zinc sulfate is used in medicine to supplement intake of zinc.

Zinc nitrate, $Zn(NO_3)_2.6H_2O$ may be crystallized from a solution of $ZnCO_3$ in dilute HNO_3. The deliquescent crystals cannot be made anhydrous by heating as decomposition takes place. The anhydrous nitrate is best made using liquid N_2O_4 :

$$Zn + N_2O_4\,(l) \longrightarrow NO + Zn(NO_3)_2.2N_2O_4$$

The solvent may be evaporated in vacuum at 100°C.

Zinc acetate (ethanoate), $Zn(CH_3COO)_2.2H_2O$, crystallizes from a solution of zinc oxide or carbonate in warm glacial acetic acid. The dihydrate turns anhydrous on heating to ~100°C. On further strong heating, the anhydrous salt partly decomposes to the volatile **basic zinc acetate $Zn_4O(CH_3COO)_6$**, isostructural with the beryllium analog (19-VIII). However, basic zinc acetate is readily hydrolyzed whereas the Be-salt is not. The larger size and higher permissible coordination number of the zinc ion facilitates initial attack by water molecules.

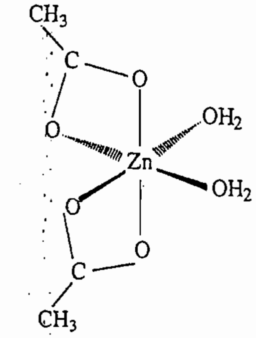


Fig. 30.4
Octahedral coordination of zinc in zinc acetate dihydrate.

Cadmium sulfate, $3CdSO_4.8H_2O$, separates in monoclinic prismatic crystals from a solution of Cd or CdO in dilute H_2SO_4. It is used in the Weston cell.

Mercuric nitrate, $Hg(NO_3)_2.H_2O$ deposits as colourless deliquescent crystals from a soluion of mercury in hot concentrated HNO_3. It is soluble in water containing nitric acid but otherwise gets extensively hydrolyzed and in dilute solution breaks up completely into HgO and HNO_3.

Mercuric sulfate, $HgSO_4$ crystallizes in silvery plates from a solution of mercury in boiling concentrated sulfuric acid. It is hydrolyzed by water to a lemon coloured basic sulfate.

Zinc ammonium phosphate is precipitated from a solution of zinc salt by disodium hydrogen phosphate in presence of ammonium chloride. Precipitation is best carried out at pH of 6.6 when it is almost quantitative. The precipitate may be dried and weighed as such or ignited to $Zn_2P_2O_7$ to estimate the zinc.

Other compounds of mercury(II)

Mercuric cyanide, $Hg(CN)_2$ is formed by the reaction between an alkali cyanide and a mercury(II) solution—the resulting solution on concentration yields colourless crystals. It is fairly soluble in water but not in ethanol. $Hg(CN)_2$ is practically undissociated in solution as it fails to give any precipitate with KOH or KI solutions. It decomposes on heating to Hg and $(CN)_2$. With excess cyanide ion, complexes of the type $[Hg(CN)_3]^-$ and $[Hg(CN)_4]^{2-}$ are formed.

The solid consists of discrete linear molecules.

Mercuric thiocyanate, $Hg(SCN)_2$ is formed as a sparingly soluble white precipitate from reaction of Hg(II) and SCN^- ions in solution. The compound is practically undissociated in solution as indicated by its vanishingly small electrical conductance. Excess thiocyanate forms soluble complexes $[Hg(SCN)_3]^-$ and $[Hg(SCN)_4]^{2-}$.

When ignited in air, pellets of $Hg(SCN)_2$ swells enormously into a curly snake-like residue of spongy ash and hence its use in fireworks (*Pharaoh's serpent*). The final product is some polymerised cyanogen compound.

Crystalline $Hg(SCN)_2$ is built up of distorted octahedral units with bridging SCN groups.

Mercuric fulminate, $Hg(ONC)_2$ is obtained as a white precipitate by warming a solution of mercuric nitrate with excess of nitric acid and alcohol. The compound explodes on gentle shock and hence is used in making detonators.

Complex compounds

Certain general features of the complex compounds formed by zinc, cadmium and mercury have been mentioned earlier in section 30.2.5. The coordination numbers adopted by the metals are commonly 2, 4, 5 or 6, though mercury rarely exhibits the coordination number 6.

HgO, $HgCl_2$, $HgBr_2$, HgI_2 and $Hg(CN)_2$ contain 2-coordinate mercury. The gaseous halides of zinc and cadmium and the alkyls and aryls of all three metals contain 2-coordination. The preference of mercury for 2-coordination has been discussed in Chapter 26.

A few planar 3-coordinate mercury complexes are known, for example $[MeHg\ dipy]^+$ and $Hg(SiMe_3)_3^-$.

4-coordinate tetrahedral complexes are numerous e.g.

neutral	**anionic**
$Znpy_2Cl_2$	ZnX_4^{2-} (Cl, Br)
$Cdpy_2Cl_2$	CdI_4^{2-}
$HgI_2\,[PPh_3]_2$	HgI_4^{2-}
$ZnPh_2\,(PPh_3)_2$	$M(CN)_4^{2-}$. (M = Zn, Cd, Hg)

Ph = C_6H_5; py = pyridine

In keeping with their class-b character, the elements do not form stable complexes with F^-. MX_4^{2-} species are formed with all other halides, those of mercury being most stable. The stability of Hg(II)—halo complexes increases in the series F^-—Cl^-—Br^-—I^-. The following stability constant data are illustrative.

	$ZnCl_4^{2-}$	$CdCl_4^{2-}$	$HgCl_4^{2-}$
log K_{st}	−1.52	1.7	15.22

	$HgCl_4^{2-}$	$HgBr_4^{2-}$	HgI_4^{2-}
log K_{st}	15.22	21.00	29.83

Tetrahedral MX_4-type complexes are also formed by NH_3, CN^-, amines etc. ligands. While the Hg(II)-complexes are many orders of magnitude more stable than the complexes of either Zn or Cd, the Zn-complexes are more stable than those of Cd(II), as shown by the stability constant data :

	$Zn(NH_3)_4^{2+}$	$Cd(NH_3)_4^{2+}$	$Hg(NH_3)_4^{2+}$
log K_{st} (approx)	9	7	19

	$ZnCl_4^{2-}$	$CdCl_4^{2-}$	$HgCl_4^{2-}$
log K_{st} (approx)	21	19	41

The reaction between Hg(II) and aqueous NH_3 forms, in addition to the ammine complex, amino and imino compounds, e.g.,

$$Hg^{2+} + 2NH_3 \rightleftharpoons [Hg\text{-}NH_2]^+ + NH_4^+$$

[Sec. 30.3.2 *Complex compounds*]

This reaction may be suppressed by using a large excess of NH_4^+. Hence $[Hg(NH_3)_4]^{2+}$ is best prepared in presence of an excess of NH_4^+ and with counterions like NO_3^- and ClO_4^- which themselves are feebly coordinating.

The relative affinities of Zn(II) and Cd(II) for *N*-and *S*-donor atoms are demonstrated by the thiocyanate complexes. $[Zn(NCS)_4]^{2-}$ contains the metal *N*-bonded while the softer Cd(II) is *S*-bonded in $[Cd(SCN)_4]^{2-}$.

Bis(glycinyl)zinc(II) is a *planar* 4-coordinate complex of zinc.

Five-coordinate complexes in the group include the $CdCl_5^{3-}$ ion (*tbp*) which has been isolated using the large cation $[Co(NH_3)_6]^{3+}$. $Zn(acac)_2.H_2O$ and $Zn(glycinate)_2.H_2O$ are distorted trigonal bipyramidal. The $ZnCl_2$(terpyridyl) and its mercury analog are also similar, the tridentate ligand occupying one equatorial and the two axial positions of the trigonal bipyramid (Fig. 30.5).

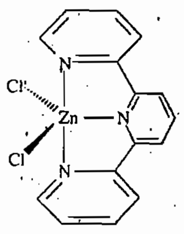


Fig. 30.5
Distorted trigonal bipyramid structure of $ZnCl_2$(terpyridyl).

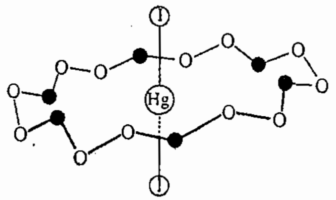
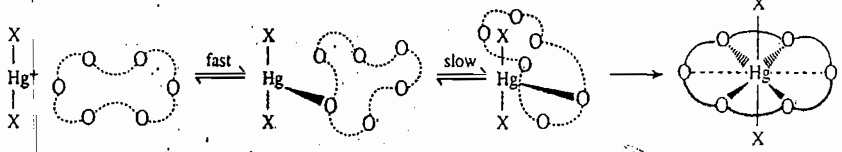


Fig. 30.6
Gross. structure of HgX_2(18-C-6).

Certain $HgX_2.L$ complexes have trigonal planar $HgX_2.L$ moiety, for example X = Cl and L = PEt_3. There appears two more relatively weaker axial halogen bridges from neighbouring molecules.

Six coordinate $Zn(H_2O)_6^{2+}$ and $Cd(H_2O)_6^{2+}$ ions are present in some hydrates of these metals, e.g., $ZnSO_4.7H_2O$ and $Zn(ClO_4)_2.6H_2O$. Hexaammines $M(NH_3)_6X_2$ (X = Cl, Br, I) are known for zinc and cadmium but they are not very stable. The complexes show considerable dissociation pressure of ammonia at room temperature and have to be stored in sealed tubes. The trimer $[Zn(acac)_2]_3$ contains zinc in both 5- and 6-coordination. The $[M(en)_3]^{2+}$ complexes also contain the metals in six-coordination. $[Hg\,(pyridine\text{-}N\text{-}oxide)_6]^{2+}$ and $[Hg\,(DMSO)_6]^{2+}$ have been isolated as their perchlorates (DMSO = dimethylsulfoxide). Cadmium and mercury dihalides form complexes with 18-crown-6 in which a linear dihalide molecule is "threaded through" the cavity of the crown ether (Fig. 30.6). The metal atom has weak bonding interactions from the six ether oxygens and is thus effectively 8-coordinated. The following mechanism has been suggested for the formation of these types of complexes :



Presumably zinc is too small to interact with the six oxygens.

Reactions of Hg(II) with ammonia

In the last section, we have mentioned the formation of Hg(II)—N covalent bonds in the reaction of Hg(II) with aqueous ammonia :

$$Hg^{2+} + 2NH_3 \rightleftharpoons [Hg—NH_2]^+ + NH_4^+$$

Actually such reactions give a variety of products depending upon the conditions. The reaction between $HgCl_2$ and aqueous NH_3 produces a number of products in which the hydrogens of NH_3 are substituted by Hg. Three main reactions may be identified :

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_3)_2Cl_2\,(s) \qquad \text{"fusible white precipitate"}$$

$$Hg(NH_3)_2Cl_2 \rightleftharpoons Hg(NH_2)Cl + NH_4Cl \qquad \text{"infusible white precipitate"}$$

$$2Hg(NH_2)Cl + H_2O \rightleftharpoons [Hg_2NCl\,(H_2O)] + NH_4Cl \qquad \text{"chloride of Millon's base"}$$

In presence of excess NH_4Cl, $HgCl_2$ reacts with boiling ammonia solution to form the white precipitate of $Hg(NH_3)_2Cl_2$—the subsequent reactions are suppressed by the presence of NH_4^+. The same compound is also formed by reaction between $HgCl_2$ and $NH_3(g)$. The precipitate melts when heated undergoing decomposition and hence was named the *fusible white precipitate*. X-ray studies reveal that the compound consists of linear $NH_3—Hg—NH_3$ units inserted in a cubic lattic of Cl^- ions, each Hg(II) attaining six-coordination from four Cl^- and two NH_3 in a distorted octahedral arrangement.

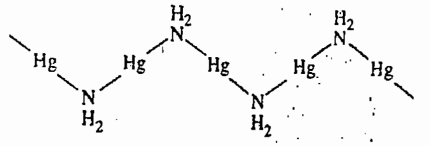
The fusible white precipitate may be hydrolyzed to get the "chloride of Millon's base" (see below) :

$$2Hg(NH_3)_2Cl_2 + H_2O = Hg_2NCl.H_2O + 3NH_4Cl$$

Addition of dilute aqueous NH_3 to a solution of $HgCl_2$ gives a white precipitate of $Hg(NH_2)Cl$ which decomposes on heating into Hg_2Cl_2, NH_3 and N_2 *without melting*. Hence it was called the *"infusible white precipitate"*. It is also formed by the action of $NaNH_2$ on $HgCl_2$:

$$HgCl_2 + NaNH_2 = Cl—Hg—NH_2 + NaCl$$

The compound consists of parallel chains of zig-zag $NH_2—Hg—NH_2$ units separated by Cl^- ions :



The infusible white precipitate is converted to the "chloride of Millon's base" (see below) on digestion with water at 60°-70°C for about 12 hours.

$$2HgNH_2Cl + H_2O = Hg_2NCl.H_2O + NH_4Cl$$

"Millon's base" is formed as a yellow powder when yellow mercuric oxide is gently warmed with aqueous ammonia (discovered by Millon in 1845). It has the composition $[Hg_2N(OH).2H_2O]$, which reacts with acids to give salts $Hg_2NX.n\,H_2O$ where $X = NO_3^-$, ClO_4^-, Cl^-, Br^- or I^-; $n = 0 - 2$. The base, as well as the salts consist of three-dimensional framework of Hg_2N^+ units in which OH^-/X^- and water molecules occupy interstitial cavities. The base thus functions as an anion exahanger.

In the network, each Hg is linearly attached to two nitrogens and each nitrogen is tetrahedrally joined to four Hg, the Hg—N distances varying between 204-209 pm depending on the size of X.

The iodide of Millon's base is formed as a brown precipitate by reaction of ammonia with Nessler's reagent (see halides of Hg).

30.3.3 Organometallic compounds

Zinc alkyls are one of the oldest known organometallics, discovered by Sir Edward Frankland in 1849 (Zeise's salt was discovered in 1827). A wide range of organometallic compounds of all three elements in the group are now well known and extensively used in organic synthesis—some of them having vital biological and environmental significance. As mentioned earlier, the compounds are mainly σ-bonded organometallics.

Zinc alkyls were originally prepared by heating zinc with boiling alkyl halides in an inert atmosphere of CO_2 or N_2, followed by distillation of the volatile dialkyl :

$$Zn + RX \longrightarrow RZnX$$
$$2RZnX \longrightarrow ZnR_2 + ZnX_2$$

Dialkyls and diaryls of zinc, cadmium and mercury are now readily prepared by the action of Grignard reagents or lithium alkyls/aryls on ether solutions of the anhydrous metal halides :

$$CdCl_2 + 2RMgX \longrightarrow CdR_2 + 2MgXCl$$
$$HgCl_2 + 2LiR \longrightarrow HgR_2 + 2LiCl$$

The MR_2 compounds may be allowed to react further with one mole MX_2 in an organic solvent to give the organometal halide RMX :

$$CdR_2 + CdX_2 \longrightarrow 2RCdX.$$

Many alkylzinc halides may be prepared directly from the appropriate alkyl halides and zinc dust. Organomercury compounds of the type RHgX may be prepared by the action of HgX_2 on a hydrocarbon (*mercuration*) :

$$HgX_2 + RH \longrightarrow RHgX + HX$$

The dialkyls and diaryls R_2M of all the elements are covalent, nonpolar, monomeric liquids or low-melting solids. The organozinc and organo-cadmium compounds are very sensitive to air and water; the lower R_2Zn compounds spontaneously catch fire in air (*pyrophoric*) producing a smoke of ZnO. The R_2Cd compounds are somewhat less sensitive in this respect and do not normally catch fire in air. However, they are also thermally less stable than their zinc analogs, owing mainly to lower Cd—C bond strength. The C—Zn bond also possesses greater carbanionic character than the C—Cd bond; this is reflected in the ability of zinc alkyls to add to C ═ O bonds in ketones :

$$(CH_3)_2Zn + (CH_3)_2C═O \longrightarrow (CH_3)_3C—O—ZnCH_3$$

Cadmium and mercury alkyls do not give this reaction with their less polar M—C bond.

The alkylzinc compounds are mild Lewis acids, forming stable complexes with amines, particularly chelating amines, e.g., 2, 2′-dipyridyl.

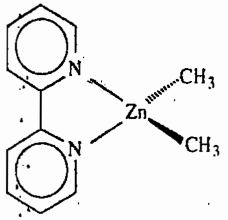


Fig. 30.7
The complex of 2, 2′-dipyridyl with $Zn(CH_3)_2$.

The organomercurials are highly stable towards air and water, not due to any extra stability of the Hg—C σ-bond, but owing to low polarity of the Hg—C bond and low affinity of mercury for oxygen. The compounds are photochemically and thermally unstable owing to low bond energy.

Although the zinc alkyls are nonpolar and nonconductors of electricity, they may dissolve alkyls of the alkali metals to give ionizing solutions containing complex anions, e.g.,

$$Na\,[Zn(C_2H_5)_3],\ Li_2\,[Zn(CH_3)_4]\ \text{and}\ K_2\,[Zn\,(C \equiv CH)_4].$$

Such complexes are also formed by the reaction of the free alkali metals with an alkylzinc :

$$2Rb + 3Zn\,(C_2H_5)_2 \longrightarrow Zn + 2Rb[Zn(C_2H_5)_3]$$

Both R_2Zn and R_2Cd compounds readily react with compounds containing active hydrogen, e.g.,

$$R_2Zn + R'OH \longrightarrow RZnOR' + RH$$

The less reactive R_2Cd compounds are often used to prepare ketones from acid chlorides :

$$2R'COCl + CdR_2 \longrightarrow 2R'COR + CdCl_2$$

The dialkyl and diaryls of mercury are valuable starting materials for preparation of a large number of organometallic compounds by interchange :

$$R_2Hg + M \longrightarrow R_nM + Hg$$

The reaction goes almost to completion when M is a metal of the alkali and alkaline earth group, Zn, Al, Ga, Sn, Pb, Sb, Bi, Se and Te.

Organomercury compounds of the type **RHgX** are crystalline solids. When the X group is able to form covalent bond to Hg, such as Cl, Br, I, CN, SCN or OH, the compounds are nonpolar, but ionic character develops when X is SO_4^{2-}, NO_3^- or F^-. The latter compounds are water-soluble. Many **RHgX** derivatives have been widely used as pesticides, but high toxicity of the compounds cause pollution hazards (sec. 30.4).

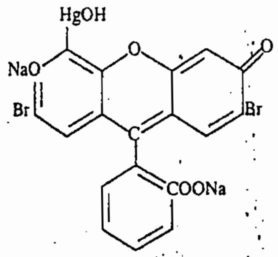


Fig. 30.8

Mercurochrome

A derivative of fluorescein, it is widely used in first aid.

Mercury(II) salts, notably the acetate, trifluoroacetate or nitrate can add to unsaturated compounds to form Hg—C bonds, often called *mercuration* reactions. When mercuric acetate in methanol reacts with aromatic hydrocarbons, mercury substitutes one or more of the hydrogen atoms in the aromatic ring. The active species in the reaction is thought to be $HgOAc^+$:

$$ArH + HgOAc^+ \longrightarrow [ArH\,HgOAc]^+ \longrightarrow ArHgOAc + H^+$$

$$(C_6H_6 + Hg(OAc)_2 \longrightarrow C_6H_5Hg(OAc) + HOAc)$$

The cyclopentadienyl compounds of these elements are structurally varied. Methyl (cyclopentadienyl)zinc is monomeric in the gas phase [Fig. 30.9(a)] but forms a zigzag chain in the solid where each C_5H_5 group is pentahapto to two zinc atoms [Fig. 30.9(b)].

[**Sec. 30.4** *Environmental aspects*]

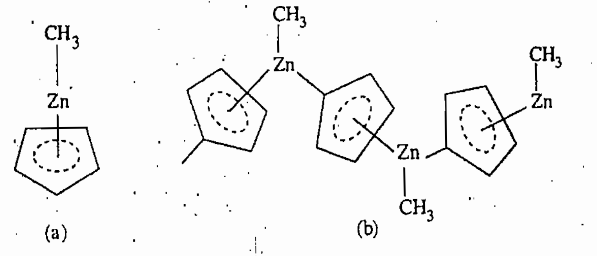


Fig. 30.9

$CH_3Zn\cdot(\eta^5\text{-}C_5H_5)$: **(a) gaseous and (b) solid.**

The mercury cyclopentadienyls are monohapto, again illustrating the notable reluctance of the metal to form π-bonds. In compounds of the type $[Hg(\eta^1 - C_5H_5)_2]$ and $[Hg(\eta^1 - C_5H_5)X]$, the point of attachment of Hg to the C_5H_5-ring changes rapidly, so that the five carbon atoms appear indistinguishable on an nmr time scale ("ring whizzing"). X-ray study on $[Hg(\eta^1 - C_5H_4PPh_3)I_2]_2$ confirms the presence of one Hg—C σ-bond for each ring in the dimer.

30.4 ENVIRONMENTAL ASPECTS

While zinc is one of the most important metals in the living world, cadmium and mercury have no known biological roles and are highly toxic.

Cadmium enters water through industrial discharges or deterioration of galvanized pipes. It is toxic to certain fish at concentrations above 200 ppb, while the normal level of Cd in potable waters is 0.4-60 ppb.

Cadmium may also concentrate in plants where they enter with zinc. Cadmium entering the human body in small amounts is mostly (~ 99%) eliminated through the kidneys but the residual fraction is bound by the body proteins metallothionein and may ultimately lead to kidney disfunction. Excessive daily dosage or inhalation may replace zinc in our body and inhibit the action of zinc enzymes, resulting in severe metabolic disorders. An outbreak of cadmium poisoning occurred in Japan in the form of *itai itai* or Ouch Ouch disease when the victims suffered from fragile bones.

Mercury itself is toxic and owing to its low vapour pressure, easily enters our body unless precaution is taken. It produces tremor, headaches, inflammation of the bladder and loss of memory and other brain disorders. Alfred Stock became a victim of such poisoning during constant handling of vacuum pumps in connection with his researches on boron and silicon hydrides.

Elemental mercury enters the sewage water mainly through effluents of alkali and chlorine industries using mercury cathodes. The mercury is eventually converted by anaerobic methane-synthesizing bacteria into species like CH_3Hg^+ and $(CH_3)_2Hg$. The conversion is probably facilitated by Co(III) in vitamin B_{12} coenzyme : a CH_3-group bound to Co(III) is transferred to Hg(II). The $(CH_3)_2Hg$ is converted to CH_3Hg^+ (specially in acid medium) which enters plankton and therefrom into our food chain via fishes. The concentration of Hg is enriched by a large factor at each step. Organomercurials also enter sewage water and our food chain through pesticides and fungicides, particularly those used in the treatment of seeds.

The methyl mercury cation may attach to cell membranes and brain tissues where they are retained for long period of time. (We have noted earlier that the Hg—C bond is rather insensitive to air and water). The mercury may inhibit normal functioning of the brain. The poisoning effect may be traced to the very high affinity of the soft Hg atom for sulfhydryl (SH) groups in enzyme (Fig. 30.10). Blood levels of 0.5 ppm of CH_3Hg^+ is considered sufficient to disrupt normal physiological functioning.

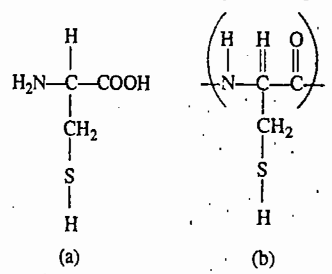


Fig. 30.10

(a) Cystein; (b) Cystein unit in a protein.

The level of mercury in natural water is about 0.001-0.0001 ppm but sewage effluents may sometimes contain 10 times as much. Such mercury, ultimately converted to CH_3Hg^+, may enter our food chain through fishes. The tragic "Minamata disaster" in the Minamata Bay in Japan (1953-60) occurred by intake of sea-fish containing 27-102 ppm of mercury in the form of CH_3Hg^+ (see box).

The Tragedy of Minamata

Minamata is a heavily industrialized town in Japan's southernmost island Kyushu. During 1953, the inhabitants observed an unusual disease among cats belonging to families of fishermen, causing paralysis and eventually death. The first human case was detected in December the same year, the number rising steeply in the three subsequent years :

1954	1955	1956	1957	1958	1959	1960
12	15	50	6	5	18	4

On the whole, about 52 humans died and more than 60 others were permanently disabled; affected mothers gave birth to 20 babies with genetic disorders.

Investigation by the Kumamoto University revealed that fishes in the sea were contaminated with mercury in the effluents of a large industrial plant producing PVC, other plastics and chemicals. The chlorine for making PVC was produced electrolytically using flowing mercury cathode. Mercury(II) sulfate was also used as a catalyst in several organic synthesis. The effluents from these plants flowed into settling ponds and then via a canal into the Minamata Bay. Fishing was banned after these findings and a new effluent system was developed. A partial return to fishing in 1958 again recorded a large number of poisoning in 1959. The situation has been under control since 1961.

A more tragic report of mercury poisoning came from Iraq in 1972 where 450 people died after consuming wheat dusted with mercury-containing pesticides.

30.5 DETECTION AND ESTIMATION

30.5.1 Zinc

Zinc salts form an incrustation of the oxide when heated on a charcoal with sodium carbonate. The oxide, which turns yellow when hot, produces a green mass ("Rinmann's green) when heated with a drop of cobalt nitrate solution.

Zinc belongs to Group IIB of the conventional group separation of cations where it is precipitated by NH_4HS. The white ZnS is insoluble in dilute acetic acid and alkalis but soluble in dilute mineral acid.

Zinc may be detected by the formation of a violet precipitate of $Zn[Hg(SCN)_4]$ and $Cu[Hg(SCN)_4]$ when a faintly acid zinc salt solution is treated with a little 0.1 per cent copper sulfate solution followed by ammonium mercuric thiocyanate solution ($HgCl_2 + NH_4SCN$). Iron salts produce a red colour with the reagent which may be prevented by adding a little alkali fluoride.

Zinc may be estimated by precipitation as zinc ammonium phosphate (pH ~ 6.5) followed by ignition (800°—900°C) to the pyrophosphote :

$$2Zn(NH_4)PO_4 = Zn_2P_2O_7 + 2NH_3 + H_2O.$$

The precipitate of $Zn(NH_4)PO_4$ may also be weighed after drying at 105°C. Zinc may also be precipitated from dilute acetic acid or slightly ammoniacal medium with quinaldinic acid (HQ) and weighed as $ZnQ_2.H_2O$ (quinaldinic acid = quinoline-α-carboxylic acid, $C_9H_6N.CO_2H$).

Zinc may be estimated volumetrically by reacting the precipitated ZnS (pH 2—3) with excess standard iodine solution (acid) and back-titrating the remaining iodine (*iodometry*). It may also be estimated by gradual addition of potassium ferricyanide solution to a solution of zinc (acid) containing excess KI and immediately titrating the liberated iodine. The reaction is quantitative in presence of zinc ions which remove $[Fe(CN)_6]^{4-}$ formed as sparingly soluble $K_2Zn_3[Fe(CN)_6]_2$ (see variation of redox potential with precipitation, Chapter 9).

30.5.2 Cadmium

Cadmium is detected in Gr. IIA of conventional group separation of cations. It forms bright yellow precipitate of CdS from faintly acid medium (< 1.5 *N*); the precipitate is insoluble in yellow ammonium sulfide and in alkali.

Cadmium is usually estimated as the sulfate or pyrophosphate. It may also be electrodeposited from cyanide solution as the metal and weighed.

30.5.3 Mercury

Mercury compounds deposit a shining mirror of metallic mercury when heated with an excess of sodium carbonate or soda-lime in a bulb-tube.

$$2HgCl_2 + 2Na_2CO_3 = 2Hg + 4NaCl + 2CO_2 + O_2$$

Mercury(I) salts precipitate white Hg_2Cl_2 with dilute HCl (Gr. I) and mercury(II) salts are precipitated in Gr. II as black HgS, soluble only in aqua regia. When bright copper turnings are added to solutions of Hg(II), they get a dull coating of mercury.

Mercury may be estimated by precipitation of HgS and weighing. Hg(II) salts may be titrated with standard ammonium thiocyanate solution using ferric alum as an indicator. Mercury is also determined conveniently by electrodeposition on a platinum cathode and weighing.

SUMMARY

Introduction. The last member in each *d*-series, namely zinc, cadmium and mercury differ from the transition elements owing to strong binding of the *d*-electrons to the inner core and their non-participation in valence. The elements are characterized by low melting and boiling points, consistent with weak metallic bonding from the *s*-electrons only.

For all the elements I_3 is considerably higher than I_1 or I_2, leading to a stable oxidation state of +II. For mercury, I_1 and I_2 are also much higher (inadequate screening by $4f^{14}$ core), the main reason for its poor electropositive character. Thus zinc and cadmium show closer resemblance to each other than with mercury. The chlorides of zinc and cadmium are fairly ionic, but mercuric chloride forms a molecular cyrstal. $Hg(OH)_2$ is an extremely weak base, while $Zn(OH)_2$ is amphoteric and $Cd(OH)_2$ is somewhat more basic. Mercury also forms a stable +I state as the Hg_2^{2+} ion, while other M_2^{2+} are unstable. It also forms a short-lived Hg(III) complex.

The elements also resemble the transition elements in forming complex compounds with a variety of ligands like ammonia, amines, halide ions and cyanide. But complexes with other strong π-acceptor ligands like CO, NO etc. are not known. The metals are evidently reluctant to M ⟶ L π-bond formation, a consequence to their high effective nuclear charge. The complexes cannot gain any stabilization from ligand field (d^{10} configuration). While zinc and cadmium commonly adopt coordination numbers 4 and 6, mercury is predominantly 2-coordinate (s-d_{z^2} hybridization). Zinc behaves mainly as a class-a metal, cadmium falls on the borderline and mercury(II) behaves as a typical class-b metal.

The elements form a large number of organometallic compounds which are mainly σ-bonded.

EXERCISE

1. *Explain your observations with balanced equations for the following :*
   - (i) *Reaction of zinc with hot aqueous alkali.*
   - (ii) *H_2S is passed into a solution of zinc sulfate.*
   - (iii) *H_2S is passed into a solution of zinc sulfate containing sodium acetate.*
   - (iv) *Aqueous ammonia is added to a precipitate of Hg_2Cl_2.*
   - (v) *Mercury(II) chloride is heated with solid sodium carbonate.*
   - (vi) *$HgCl_2$ reacts with boiling aqueous ammonia in presence of excess NH_4Cl.*
   - (vii) *Dilute aqueous ammonia is added to an aqueous solution of $HgCl_2$ and the product is digested with water.*

   What are the basic structural units in the products obtained in (vi) and (vii)?

2. (a) *Compare and contrast the chemistry of zinc and beryllium.*

   (b) *Compare the chemistry of Zn—Cd with that of Hg.*

3. (a) *Why it is not possible to isolate oxide, hydroxide or sulfide of Hg(I)?*

   (b) *State some of the factors which alter the ease of disproportionation of Hg(I) in solution.*

4. *Some E° values are given below :*

$$Hg_2^{2+} + 2e \rightleftharpoons 2Hg \qquad 0.796\ V$$
$$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+} \qquad 0.911\ V$$
$$Hg^{2+} + 2e \rightleftharpoons Hg \qquad 0.854\ V$$

   (a) *Find the value of the equilibrium constant for the disproportionation of Hg(I).*

   (b) *If E° for the Cl_2—Cl^- system is 1.36 V, what would be the result of adding one mole of chlorine to ten moles of mercury?*

   [(b) $HgCl_2$ formed will be reduced by excess of Hg; one mole mercurous chloride will be formed.]

5. *In the system mercury-mercurous nitrate, a ten-fold change in the concentration of mercurous nitrate alters the potential of the mercurous-mercury couple by 0.029V (at 25°C). Use this information to find the charge on the mercurous ion. (Assume concentration = activity).*

   [**Hint :** If the ion is written Hg_x^{x+}, the half-cell would be

$$Hg_x^{x+} + xe \rightleftharpoons xHg$$

$$E = E° + \frac{0.059}{x} \log a \text{ (where } a = \text{acitivity of the mercury(I) ion)}$$

   If the concentration (= a) is increased tenfold, log a changes by unity. Hence

$$\Delta E = 0.029\ V = \frac{0.059}{x} \quad \text{or } x = 2.]$$

6. *What are the structures of (i) mercuric chloride (ii) cadmium chloride and (iii) cadmium iodide?*

7. *The stepwise formation constants for the Hg^{2+}—Cl^- system at 25°C are as follows :*

log K_1	K_2	K_3	K_4
6.7	6.5	0.95	1.05

   Comment on the sudden drop from K_2 to K_3.

8. *What happens when mercurous nitrate solution is separately mixed with the following (i) aqueous ammonia (ii) excess KI (iii) KCN (iv) KBr.*

9. *The Hg(I)—Hg(II) equilibrium might be written in either of the two forms :*

   (i) $Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$

   (ii) $Hg^{2+} + Hg \rightleftharpoons 2Hg^{+}$

   To verify which equation is correct, mercury(II) perchlorate is shaken with liquid mercury to reach equilibrium. Analysis shows that the ratio Hg^{I}/Hg^{II} in the resulting solution is independent of the concentration of Hg(II).

   What should be the conclusion?

   [**Hint :** 1 mol Hg(II) produces 1 mol Hg(I) in equilibrium (i) but 2 mol Hg(I) in equilibrium (ii). Hence the equilibrium is represented by (i)]

CHEMISTRY OF THE ELEMENTS

SECTION—IV : THE f-BLOCK ELEMENTS

CHAPTER THIRTYONE

ELEMENTS OF THE *f*-BLOCK
LANTHANIDES AND ACTINIDES

OBJECTIVES

31

PART A : ELEMENTS OF THE 4*f*-SERIES

31.1 INTRODUCTION

The *f*-block elements appear in two series characterized by the filling of 4*f* and 5*f* orbitals in the respective third inner principal quantum level from outermost. The first series contains the fourteen elements cerium to lutetium (Z = 58 – 71) and are called ***lanthanides*** as they appear after lanthanum; the second series (thorium to lawrencium, Z = 90 – 103) appears after actinium and are called the actinides. The scandium group elements (Group IIIA or 3) Sc, Y and La are formally part of the *d*-block (outer electron configuration (n – 1) d^1ns^2 but they lack the common features of *d*-block elements in showing a single stable oxidation state III (Chapter 28-29), and closely resemble the lanthanides. Yttrium and lanthanum also occur with the lanthanides and the sixteen elements together are called the *rare earth elements* (see History). These elements resemble one another much more closely than do the elements in any *d*-series. The actinide elements, however, differ appreciably in their individual chemistry and are discussed in a separate section.

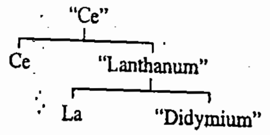
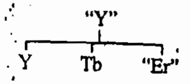
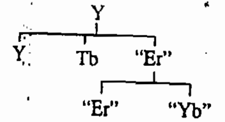
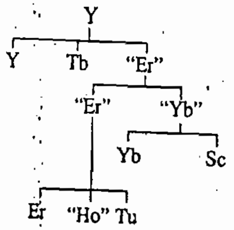
31.1.1 History, abundance and occurrence

The history of rare-earth elements (henceforth written REE) covers a long span of more than 113 years—from 1774 (discovery of "yttrium") to 1907 (discovery of lutetium) with promethium prepared artificially much later (1926). The REEs were first recognized as their oxides and hence named "earths"—chemists of the past used this term for many oxides, for example the "alkaline earths" (CaO, MgO etc.). In fact, many REEs were first discovered in the form of their oxides from which the pure metals were isolated much later. Until about 1920, the oxides of REE as well as ThO_2 and ZrO_2 were classed as "rare earths".

The isolation and chemical identification of the rare earth elements proceeded through "a sea of errors" in which "truth was almost drowning" (G. Urbain, french chemist). What was claimed to be a new element was often shown to contain a previously known element or sometimes more than one element. The REE-s are chemically very close to one another; so the classical chemists had to depend on (i) the differences in the base character of their hydroxides—the hydroxides of the heavier lanthanides were less basic in nature and precipitated first when a solution containing the REEs was gradually made alkaline; (ii) the differences in the solubilities of various salts, like the oxalates, double sulfates and double nitrates. Laborius repetitions and skilful manipulations were necessary to achieve such separations.

The discovery of the REE-s may be divided into two branches—one containing the lighter REE's of the "cerium group", consisting of La to about Eu; and the other containing the heavier REE's of the "yttrium" group, consisting of Gd to Lu plus Y as well. As explained earlier, the initial claim for a new element was often proved wrong in course of time. Such names have been put within inverted commas (" ") in the following panel.

Year	Scientists	Event	Note
1794	Gadolin (Finland)	"Yttrium" discovered	From a mineral found in Ytterby, Sweden. The mineral was named *Ytterbite* and later *Gadolinite*.
1803	Berzelius and Hisinger (Sweden); Klaproth (Germany)	"Cerium" discovered independently in *Cerite*.	Named after the asteroid *ceres* discovered in 1801.

Year	Scientists	Event	Note
1826 — 1839	Mosander (Sweden)	"Cerium" shown to be a mixture of elements.  	"Lanthanum" named from Greek for "hidden" (to escape notice). "Didymium" means *twin*.
1843	Mosander	"Yttrium" shown to consist of Yttrium, terbium and "erbium".  	All names derived from *Ytterbium*.
1878	Marignac (Switzerland)	"Erbium" shown to consist of "Ytterbium".  	
1879	Nilson (Sweden)	"Scandium" isolated from "Ytterbium".	Named after Scandinavia.
	Cleve (Sweden)	"Erbium" separated into erbium, "holmium" and thulium.  	Holmium named from old name of Stockholm. Thulium named after *Thule*, a legendery country at the world's end.
1879	L. de Boisbaudran (France)	"Didymium" shown to contain "Samarium".	Named after the mineral *samarskite* from which it was isolated.
1880	Marignac	Gadolinium isolated from "Samarium"	After Gadolin, the pioneer in REE chemistry.
1886	C. Auer von Welsbach (Austria)	Praseodymium and neodymium isolated from "didymium".	Didymos means twin. Praseos = leek green; neos = new.
	Boisbaudran	Dysprosium isolated from "Holmium".	Greek dysprosistos = hard to obtain.
1901	E. A. Demarcay	Europium was isolated.	After Europe.
1907	Urabain (France) (Also Welsbach and James, somewhat later; Welsbach named the elements as casseopium (cp) and aldebaranium)	Isolated lutetium (then written as lutecium) from "Ytterbium".	Named after Lutetia—the old name of Paris.

[**Sec. 31.1.1** *Abundance, occurrence*]

Attempts to isolate element 61 from natural sources failed over years; X-ray identification of the element was claimed in 1926 when the element was variously named illinium and florentium. Isotopes of the element were also claimed to have been produced artificially through Nd(d, n) reactions. Finally, the element was detected in 1945 in fission products of U-235 through ion-exchange chromatography (Marinsky, Glendenin and Coryell, USA). The final report, however, was published in 1947 and the element named promethium after a suggestion by Mrs Coryell. In an ancient Greek myth, Prometheus stole fire from heaven, gave it to man and was consequently put to extreme torture by Zeus. Element 61 was obtained owing to the harnessing of nuclear fission by man and it was also a warning against the impeding danger that mankind will be tortured by the hawk of war, wrote the scientists.

Traces of natural promethium (^{147}Pm, $t_{\frac{1}{2}}$ = 2.62 y) have been detected in 1968 in uranium minerals (pitch blende).

Terrestrial abundance

Except promethium, which occurs only in traces (10^{-20} ppm) in uranium minerals, other "rare earth elements" are in fact not rare in abundance. The most abundant REE cerium (66 ppm) is actually five times more abundant than lead; the next most abundant element neodymium (40 ppm) is similarly three times as abundant as Pb. The abundances of other REE's are quite small in comparison to Ce and Nd : Pr, Sm, Gd > 5 ppm; Lu (0.8 ppm) and Tm (0.5 ppm) are among the least abundant while others occur to the extent of 1—4 ppm in the earth's crust. However they are very dispersed.

Lanthanides with odd atomic numbers have only one natural isotope (except Eu and Lu, which have two). The even-number lanthanides have seven natural isotopes (except Er, 6 isotopes and Ce, 4 isotopes). Artificial radioactive isotopes have been obtained for all the REE's.

Occurrence

There are more than 200 minerals known to contain the REE-s but the two most commercially important minerals are (i) *monazite*, a mixed phosphate of La, Ce, Th and other REEs and (ii) *bastnaesite*, a fluoride carbonate of La and REEs, but the heavier REEs (Y onward) are virtually absent in it. *Xenotime* is also another rare-earth orthophosphate containing thorium (4-6% ThO_2) and a high percentage of yttrium (~ 61% as Y_2O_3).

Monazite, which is chemically quite inert and has a high density, is mostly concentrated in beach sands and river beds through weathering. It occurs in southern India (see below), South Africa, Brazil, Australia and Malaysia. Bastnesite occurs mainly in the USA and China.

In India, monazite is extensively found as beach sand in Andhra (Vishakhapatnam), Kerala (Chavara, north of Quilon) and Tamil Nadu (Cape Comorin and Tanjore). It also occurs as an alluvial deposit in Ranchi (Bihar) and Purulia (WB). The total Indian reserves of monazite are estimated at over 5 million tonnes. Besides REE-s, it is also a rich source of thorium (8-10.5% ThO_2), together with 0.3-0.4% U_3O_8. A typical composition of Kerala monazite is given below :

TABLE 31.1

Chemical composition of Kerala monazite (per cent)

Thoria, ThO_2	8.1	Y_2O_3	0.4
Ceria, Ce_2O_3	30.6	Dy, Ho, Er, Yb, Lu oxides	0.1
La_2O_3	15.7		
Nd_2O_3	10.5	U_3O_8	0.3
Pr_2O_3	2.9	P_2O_5	26.2
Eu, Gd, Tb oxides	0.7	CaO	1.0

31.1.2 Isolation of the REE-s

A. *From monazite*

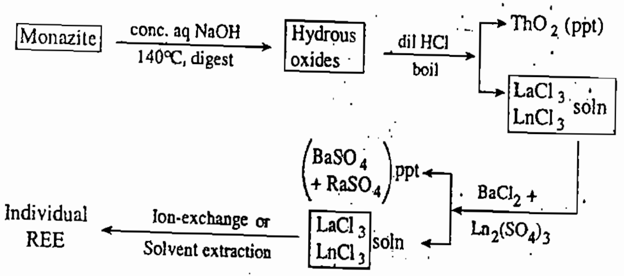
Details of the procedure vary with the composition of the ore. Typical procedures involve concentration of the ore by washing etc., breaking the ore by digestion with acid or alkali, the latter being more commonly used at present. The main steps involved in obtaining a solution containing different rare-earth elements (common symbol Ln) are as follows :

(i) Digestion of the concentrated ore by concentrated aqueous NaOH (73%) at 140°C, followed by extraction with water.

(ii) The slurry of impure hydrous oxides is boiled with HCl around pH = 3.5. ThO_2 is precipitated and filtered out.

(iii) The filtrate containing $LaCl_3$ and $LnCl_3$ is treated with a solution of $BaCl_2$ and stoichiometric amount of $Ln_2(SO_4)_3$ to precipitate the entire barium as $BaSO_4$. The precipitated $BaSO_4$ carries with it traces of $RaSO_4$ (formed by 228-Ra, daughter of Th) and is removed by filtration.

(iv) The filtrate contains $LaCl_3$ and $LnCl_3$ from which lanthanum may be separated by fractional crystallization of $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$. However, most modern methods use solvent extraction or ion-exchange processes, described below.



(v) **Solvent extraction :** Tri-*n*-butyl phosphine oxide $(n\text{-BuO})_3PO$ is the most commonly used solvent for extraction of the lanthanides from dilute nitric acid solution. The solubility of Ln(III) elements increases slightly with increasing atomic number but the efficiency of the process may be highly increased by employing continuous counter current procedure which enables large number of partitions suitable for large-scale production. Kilogram quantities of gadolinium have been prepared by this method. Bis (2-ethylhexyl)phosphinic acid (DEHPA) offers a higher separation factor (~ 2.5) between adjacent rare-earth elements and is now largely used for solvent extraction.

(vi) **Ion-exchange process :** This is the most rapid and effective general procedure for the separation of rare earth elements. As a direct consequence of poor screening by the 4*f* shell, the size of Ln^{3+} ions decreases gradually from Ce^{3+} to Lu^{3+} (*lanthanide contraction*). Accordingly, the binding of the Ln^{3+} ions to a complexing agent like EDTA gradually and regularly increases with increasing atomic number of the REE : the overall formation constant of $EDTA^{4-}$ complex of La^{3+} is $10^{15.3}$ and of Lu^{3+} is $10^{19.2}$. So, when a mixture of Ln^{3+} ions bound on an ion exchange bed (e.g., Dowex-50) is eluted with a dilute solution of EDTA under adjusted conditions, the rare-earth ions will be eluted in a sequence from higher atomic number to lower atomic number; that is, Lu^{3+} is eluted first followed by Yb^{3+} and so on.

A solution containing various Ln^{3+} ions is run down a column of cation exchange resin like Dowex-50 when the Ln^{3+} ions are absorbed on the resin bed replacing the hydrogen in $-SO_3H$ groups (resin = R) :

$$Ln^{3+}(aq) + 3H\text{—}R(s) \rightleftharpoons LnR_3(s) + 3H^+(aq)$$

Affinity of the Ln^{3+} ions for the resin increases slightly with increase in atomic number but this is not sufficient to effect a good separation. The Ln^{3+} ions are washed down or eluted from the resin bed with a complexing agent like a dilute solution of triammonium-EDTA, $(NH_4)_3HEDTA$ at pH 8 or a buffered solution of citric acid/ammonium citrate. Equilibrium of the following type is now established :

$$Ln^{3+}R_3(s) + 3NH_4^+ + HEDTA^{3-} + xH_2O \rightleftharpoons [Ln(H_2O)_xHEDTA](aq) + 3NH_4^+\text{—}R(s)$$

At any point in the column, the equilibrium is gradually pushed to right with the continuous arrival of fresh eluting agent and removal of the Ln^{3+}-EDTA complex to lower layers in the column. The process is in fact repeated automatically at various layers in the resin bed; as the heavier Ln^{3+} ions form stronger complexes with EDTA, they are gradually enriched in the solution phase and are eluted in the *reverse order of their atomic number*. The different Ln^{3+} ions concentrate in bands in different regions in the column and their downward movement may be followed by atomic fluorescence spectroscopy. Separate metal ions are collected in separate containers. A typical elution curve is shown in Fig. 31.1.

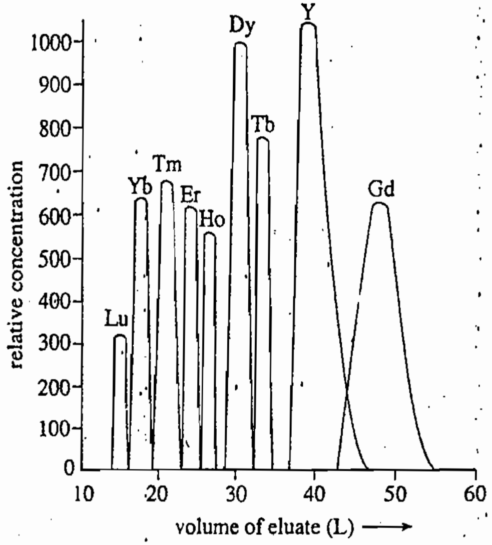


Fig. 31.1
A typical elution curve for Ln^{3+}-ions from an ion exchange resin column.

The efficiency of the ion-exchange method is further enhanced by "displacement chromatography". In this method, the eluted solution containing Ln(III)-EDTAH complex and $(NH_4)_3$-EDTAH is passed through a second column charged with Cu(II) or Zn(II) on the resin-bed. The smaller Cu^{2+} ion on the resin-bed is now displaced as the soluble $[HEDTA]^{3-}$ complex when the Ln^{3+} ions are deposited on the resin bed in a compact band. The concentration of the EDTA is kept below 0.015*M*, otherwise $Cu_2(EDTA).5H_2O$ will be precipitated.

The Ln^{3+} ions are now eluted from the resin-bed by $(NH_4)_3HEDTA$ in succession, each Ln^{3+} ion undergoing automatically multiple fractionation and concentration as it percolates down different layers in the resin-bed.

From the solutions obtained from ion-exchange columns, the lanthanides may be precipitated as fluorides or hydroxides or oxalates. The last two compounds yield the oxides on heating. The oxides may be reconverted to the chlorides by the action of ammonium chloride or carbon tetrachloride.

(vii) **Chemical methods :** Among all the Ln^{3+} ions in solution, only cerium is readily oxidized to a stable + IV oxidation state by say, hypochlorite (NaOCl or bleaching powder) in alkaline medium. The Ce^{4+} ion has a smaller size and higher charge than other Ln^{3+} ions and is readily separated from the rest as insoluble CeO_2 or $Ce(IO_3)_4$. The Ce^{4+} may also be separated by solvent extraction using tributyl phophate in nitric acid solution.

Europium(III) is readily reduced to Eu(II) using zinc amalgam or on a mercury cathode. The Eu^{2+}, radius 110 pm (compare Sr^{2+}, 116 pm), shows many similarities with the alkaline earth metal ions and is readily separated from other Ln^{3+} ions as insoluble $EuSO_4$. Sm^{2+} and Yb^{2+} are also formed by similar reduction of their +III ions, but these are slowly oxidized by water.

Other lanthanide elements may be separated only through repeated fractional crystallizations. Pure thulium bromide was prepared after about 15,000 recrystallizations (C. James, 1911).

B. *From Bastnaesite*

Treatment of Bastnaesite is easier in the sense that the mineral does not contain any thorium or its radioactive product. The calcium carbonate is decomposed by HCl and the lanthanum metals are converted to their chlorides by heating with carbon in a stream of chlorine at 1200°C. The residue on leaching with water gives a solution containing various $LnCl_3$.

Alternatively, the bastnaesite, after decomposing $CaCO_3$, may be subjected to oxidizing roast in air; the resulting mixture of Ln_2O_3 and CeO_2 is leached with 0.5 *M* HCl when CeO_2 is left insoluble. The resulting solution contains the REEs as chlorides ($LnCl_3$).

The individual REE-s may now be separated by solvent extraction or ion-exchange methods.

C. *Preparation of the metals*

A major quantity of the lanthanides are used directly without separation of individual metals, for example, the *mischmetal*, (Ce 50; La 40; Fe 7; others 3) used in lighter flints and as an additive to steel. It is usually prepared by electrolytic reduction of a mixture of fused $LnCl_3$ with NaCl or $CaCl_2$ in a refractory lined steel cell which acts as the cathode; a graphite rod is used as the anode. The method is also useful for the production of elemental Ce, Sm, Eu and Yb.

The REEs may also be prepared by reduction of the anhydrous halides with calcium in a tantalum crucible under argon atmosphere. The fluorides are preferred over other halides since these are nonhygroscopic in nature and the side product CaF_2 has a high melting point. The lanthanide trifluoride LnF_3 is heated with calcium under argon atmosphere—the unchanged calcium is removed by melting under vacuum. The method is not suitable for Sm, Eu and Yb which are reduced to the II state.

31.1.3 Uses of the REE-s

1. The largest use of the lanthanides is in the form of an additive to steels ($<$ 1% La or Ln) to improve strength and workablity. Separation is often unnecessary for the purpose and the mixture of $LaCl_3/LnCl_3$ is reduced electrolytically to *mischmetal* (see before) which is added to steel and used in lighter flints.

2. Mixed lanthanides are also added to zeolites to enhance their catalytic activity, specially in the cracking of petroleum.

3. Ln-Co alloys are used in making permanent magnets. Neodymium is particularly used in making magnetic alloys.

[Sec.31.2.1 *Physical properties*]

4. "Didymium", the natural mixture of Pr and Nd (see history) is used in protective glasses to cut uv radiation. Neodymium lasers, particularly a liquid laser using Nd_2O_3 dissolved in selenium oxychloride, are very powerful and offer many technical advantages.

5. Oxides of some lanthanide elements are used as activators in phosphors, e.g., Eu^{3+} for the red colour in TV and Tb^{3+} in fluorescent tubes. The latter, together with Eu^{2+} and Tm^{3+} are also used as activators in X-ray intensifiers where Gd and La-oxides are used as support media.

6. Gd, Sm, Eu and Dy have large cross-sections for neutron capture and are used in control rods in atomic piles.

7. The lanthanide elements have the potentiality of finding use in solid oxide fuel cells.

8. Rare earth oxides have been used as high temperature superconductors, for example 93K YBCO superconductor $YBa_2Cu_3O_{7-x}$ ($x \simeq 0.1$) and the 35K superconductor $La_{5-x}Ba_xCu_5O_{5(3-y)}$, discovered first (1986) in the series for which Bednorz and Mueller (Switzerland) were awarded the 1987 Noble Prize in Physics (see high temperature superconductors, Section 31.3.6).

31.2 GENERAL CHARACTERISTICS

31.2.1 Electron configuration and some physical properties

The ground state electron configurations, melting and boiling points, densities etc. of the lanthanides are given in Table 31.2.

TABLE 31.2

Electron configuration and some physical properties of lanthanum and the lanthanides

Element	Outer electron configuration (a) Ground state atom (b) M^{3+} ion			M.P. °C	B.P. °C	Density g cm^{-3}	Electrical resistivity µ ohm cm at 25°C
		(a)	(b)				
La	[Xe]	$5d^16s^2$	$4f^0$	920	3420	6.2	57-80
Ce	[Xe]	$4f^15d^16s^2$	$4f^1$	798	3433	6.77	73
Pr	[Xe]	$4f^36s^2$	$4f^2$	931	3520	6.77	68
Nd	[Xe]	$4f^46s^2$	$4f^3$	1021	3074	7.01	64
Pm	[Xe]	$4f^56s^2$	$4f^4$	1042	—	—	—
Sm	[Xe]	$4f^66s^2$	$4f^5$	1074	1794	7.52	88
Eu	[Xe]	$4f^76s^2$	$4f^6$	822	1429	5.23	90
Gd	[Xe]	$4f^75d^16s^2$	$4f^7$	1313	3273	7.90	134
Tb	[Xe]	$4f^96s^2$	$4f^8$	1365	3230	8.23	114
Dy	[Xe]	$4f^{10}6s^2$	$4f^9$	1412	2567	8.55	57
Ho	[Xe]	$4f^{11}6s^2$	$4f^{10}$	1474	2700	8.8	87
Er	[Xe]	$4f^{12}6s^2$	$4f^{11}$	1529	2868	9.1	87
Tm	[Xe]	$4f^{13}6s^2$	$4f^{12}$	1545	1950	9.3	79
Yb	[Xe]	$4f^{14}6s^2$	$4f^{13}$	819	1196	6.97	29
Lu	[Xe]	$4f^{14}5d^16s^2$	$4f^{14}$	1663	3402	9.84	79

The ground-state electron configurations of the lanthanide elements are generally of the type [Xe]$4f^n6s^2$. Lanthanum is outside this generalization, but as explained earlier, is included in the table for its uniform trivalence and other similarities. Among the lanthanides, exceptions to the $4f^n5d^06s^2$ pattern are found in three cases : (a) at Ce, where the increase in effective nuclear charge after La is not sufficient to stabilize the $4f^25d^0$ electron configuration compared to $4f^15d^1$. A popular version of this says that the nuclear charge is insufficient to contract the 4*f* orbitals and lower their energy well below the 5*d*.

(b) Gadolinium has the f^7d^1 configuration, consistent with our expectation for a exchange-energy stabilized half-filled *f*-shell.

(c) Lutetium also has the $f^{14}d^1$ configuration where the last electron is added beyond the capacity of the 4*f*-shell.

The electron configuration of the Ln^{3+} ions vary regularly from $4f^1$ for Ce^{3+} to $4f^{14}$ for Lu^{3+}.

The densities and melting and boiling points of the elements show a periodic variation, reaching minima at Eu and Yb. A similar trend is observed for the enthalpy of atomization (Fig. 31.2). The low values for europium and ytterbium are probably due to stability and consequent reluctance of the $4f^7$ and $4f^{14}$ inner core to participate in metallic bonding. This leaves only the two outer 6*s* electrons to enter the conduction bands, thus leaving larger cores and weaker binding forces. We shall later find that these elements also show the greatest tendencies to exist in the divalent state.

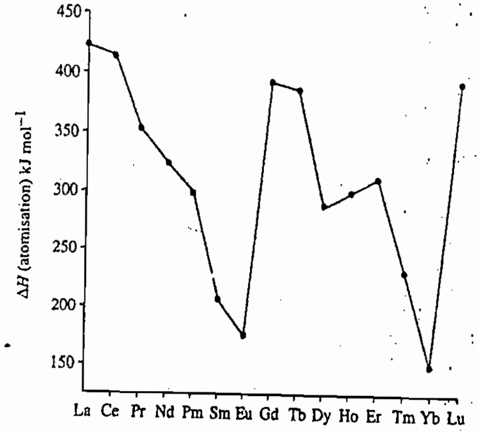


Fig. 31.2 Variation of enthalpy of atomization for the lanthanides.

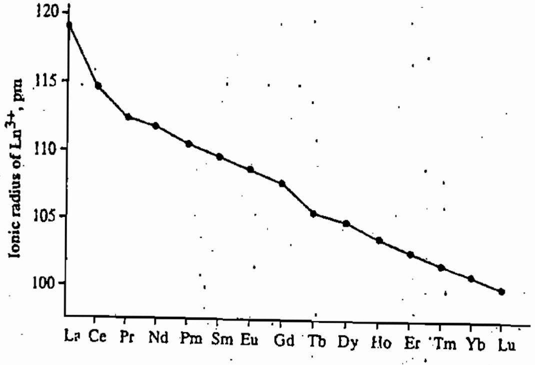


Fig. 31.3 Ionic radii of Ln^{3+} ions.

[**Sec. 31.2.1** *Lanthanide contraction*]

The atomic and ionic radii (Table 31.3 and Fig. 31.3) of lanthanum and the lanthanides show a steady decrease along the series; this is commonly known as *lanthanide contraction*. The underlying reason for this has been mentioned earlier (Chapter 4)—poor shielding by the 4*f* electrons causes the effective nuclear charge to rise steadily across the series. The relativistic effect also contributes to the lanthanide contraction. We have already come across some of the far reaching consequences of lanthanide contraction, for example, the close similarity in properties between the elements of 4*d* and 5*d* transition series. The close similarity in properties of Y(III) with heavier lanthanides may also be traced to the similarity in size of Y^{3+} (104 pm) to Ho^{3+}. Ionization energies of the lanthanides vary rather irregularly within the series (Fig. 31.4 and 31.5). Several factors are involved in the process of ionization, for example, the changing effective nuclear charge with varying shielding effect, the nature of the orbital involved, exchange energy, relativistic effect and so on. The variation of I_3 shows two sharp peaks at Eu and Yb, corresponding to removal of an electron from the half-filled $4f^7$ and $4f^{14}$-shell respectively. The plot of $(I_1 + I_2 + I_3)$ also shows an almost parallel trend, suggesting the dominant role of I_3 in determining the variation of $(I_1 + I_2 + I_3)$. The stable oxidation states shown by the elements is largely determined by their ionization energies. We shall shortly explore this aspect.

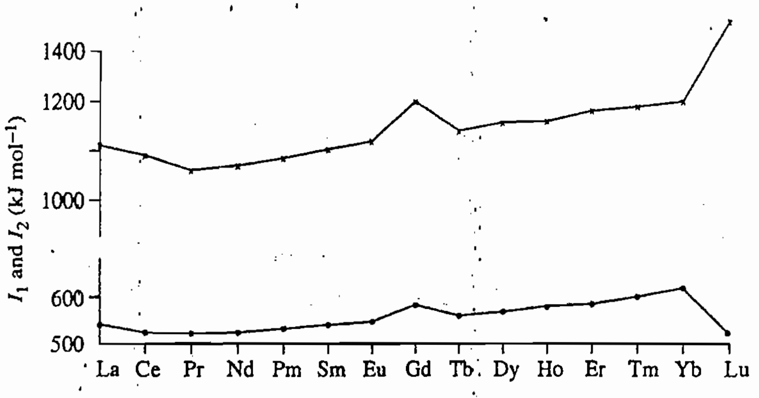


Fig. 31.4

Plot of I_1 and I_2 for lanthanide elements.

Fig. 31.5

Plot of I_3 and $(I_1 + I_2 + I_3)$ for lanthanides (kJ mol⁻¹).

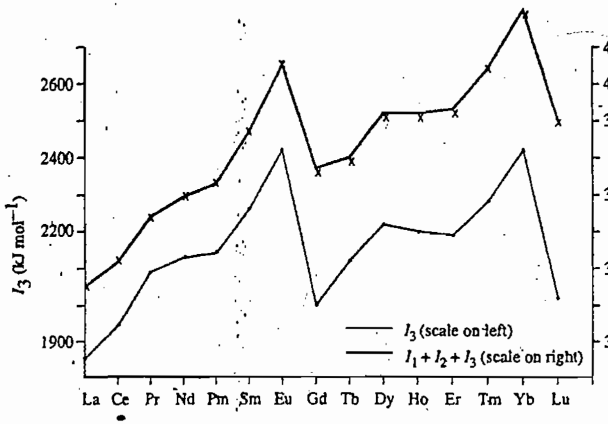


TABLE 31.3

Atomic and ionic radii, ionization energies, E^0 for the lanthanides

Element	Metal radius (C.N. = 6; pm)	Ionic radius (M^{3+}, C.N. = 6; pm)	I_1	I_2	I_3	$E°$ (V) M^{3+}—M
			kJ mol^{-1}			
La	187 (12-coord)	117	538	1067	1850	−2.37
Ce	181.8	115	528	1047	1949	−2.34
Pr	182.4	113	523	1018	2090	−2.35
Nd	181.4	112	530	1034	2128	−2.32
Pm	181	111	536	1052	2140	−2.3
Sm	180	110	543	1068	2260	−2.30
Eu	208	109	547	1085	2425	−1.99
Gd	180	108	592	1172	1999	−2.3
Tb	177	106	564	1112	2122	−2.3
Dy	178	105	572	1126	2220	−2.3
Ho	176	104	581	1139	2200	−2.33
Er	176	103	589	1151	2190	−2.31
Tm	175	102	597	1163	2284	−2.3
Yb	193	101	603	1175	2415	−2.2
Lu	174	100	524	1341	2022	−2.3

31.2.2 Chemical reactivity

The lanthanide elements (as well as La and Y) are all silvery white, soft and malleable with high electrical conductivity. Eu and Yb are pale yellow. They are highly electropositive and reactive, the heavier elements being comparable to calcium and scandium to aluminium. The compact metals are quite stable to dry air at ordinary temperature but rapidly become dull in humid atmosphere. All of them burn in air to form oxides Ln_2O_3 and nitrides LnN (cerium gives CeO_2). Powdered cerium is even pyrophoric. Yttrium usually forms a protective oxide coating on it and remains unattacked by air even at 1000°C.

On heating, lanthanides react with a number of non-metals like nitrogen, sulphur, carbon, silicon, phosphorus, hydrogen etc. The hydrides, formed in stable MH_2 and MH_3 phases, usually have a defect lattice and are non-stoichiometric (Chapter 17); the composition MH_3 is not fully attained even for the most hydrogenated species. The hydrides appear to contain the H^- ion with some salt-like character, but also contain extra delocalized electrons which impart some metallic properties. As a result, these hydrides are intermediate in character between the saline hydrides of *s*-block and the metallic hydrides of the *d*-block elements. Hydrides formed by the lanthanide elements in conjunction with some transition element may act as promising hydrogen storage material. Thus, an alloy like $LnNi_5$ may take up hydrogen reversibly to form $LnNi_5H_6$ where Ln may be suitably varied between La, Ce, Pr, Nd or a mixture of them.

On heating with carbon, the lanthanides form carbides Ln_3C, Ln_2C_3 and LnC_2, nearly all of which show metallic conductivity. The C—C distance in the anion of CeC_2 is 128 pm compared to 119 pm in CaC_2; the anion is therefore supposed to be C_2^{3-} and the carbide $Ce^{3+}C_2^{3-}$, having some overlap between the occupied antibonding orbital of the C_2^{3-} ion and the conduction band of the solid.

[Sec. 31.2.3 *Oxidation states*]

The elements normally form trihalides with the halogens but Ce and Tb give CeF_4 and TbF_4 respectively. Complex fluorides of Pr(IV), Nd(IV) and Dy(IV) are also formed.

Non-availability of *d*-electrons for π-bonding does not favour the formation of carbonyls by most lanthanides. However, an unstable $Nd(CO)_6$ has been prepared by matrix isolation. Similarly, the compound $[(C_5Me_5)_2Sm]_2N_2$ has been reported to contain a dinitrogen unit bonded sidewise to two Sm atoms.

Because the lanthanides stand far above hydrogen in the electrochemical series, they react directly with water, rapidly on heating, to liberate hydrogen. Reactions with acids are more vigorous, but the metals do not dissolve in alkalis. They are also stable in HF and H_3PO_4 owing to the formation of a protective film of insoluble salts.

Europium and ytterbium dissolve in liquid ammonia at −78°C forming blue solutions which give spectra characteristic of M^{2+} and ammoniated electrons. The solutions decolorize slowly but the concentrated solutions appear golden.

Some reactions of the lanthanide elements are shown in Figure 31.6.

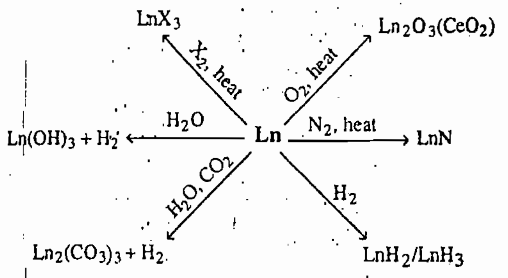


Fig. 31.6 Some reactions of lanthanides (X = halogen).

31.2.3 Oxidation states

The principal oxidation state of all the elements is +III. The elements adjacent to lanthanum ($4f^0$), gadolinium ($4f^7$) and lutetium ($4f^{14}$) also exhibit other oxidation states;

Ce ($4f^15d^16s^2$) : IV; Pr ($4f^36s^2$) : IV, but much less important than with Ce;

Eu ($4f^76s^2$) : II; Tb ($4f^96s^2$) : IV; Dy ($4f^{10}6s^2$) : IV; Yb ($4f^{14}6s^2$) : II; Tm ($4f^{13}6s^2$) : II. The oxidation states commonly encountered for the elements are shown below :

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
III	III, IV	III, (IV)	III	III	III (II)	III (II)	III
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
III (IV)	III (IV)	III	III	III (II)	III, II	III	

The common occurrence of the +3 oxidation state for all lanthanides appears to be a consequence of greater stabilization of 4*f* orbitals in comparison to 5*d* or 6*s* with increasing ionic charge. We recall (Chapter 3) that the order of penetration of orbitals into the inner electron core decreases as 4*f* > 5*d* > 6*s*. As successive ionization increases the net charge on the lanthanide cation, the 4*f* electrons are affected most, that is their energy is lowered to the greatest extent. In the Ln^{3+} ion, the 4*f* electrons are thus stabilized to a greater extent than the 5*d* or 6*s* electrons; so these latter electrons usually ionize in most cases. Ce and Pr appear exception to this generalization since in these elements, the 4*f* electrons are not sufficiently stabilized. The occurrence of Tb(IV), Eu(II) and Yb(II) may be similarly related to the stability of half-filled $4f^7$ or filled $4f^{14}$ configurations. However, this cannot be the sole criterion for the occurrence of these oxidation states in view of many known exceptions, for example :

$$Sm^{2+}\ (f^6) \text{ but no } Sm^{+}\ (f^7);\ Tm^{2+}\ (f^{13}) \text{ but no } Tm^{+}\ (f^{14}).$$

$$Pr^{4+}\ (f^1) \text{ but no } Pr^{V}\ (f^0);\ Nd^{4+}\ (f^2) \text{ but no } Nd^{VI}\ (f^0)$$

As we have noted earlier, the formation and stabilization of any ion in a particular oxidation state may be depicted in a relevant Born-Haber cycle in terms of several enthalpy terms like sublimation/ionization of the metal, hydration of the ion etc. The oxidation states of the lanthanides are thus collective effects of several related factors.

31.2.4 Complex compounds

In general, the lanthanide elements show much less tendency toward complex formation when compared to the *d*-block elements. Presumably their larger size and lower electronegativity do not promote covalent contribution to bond formation with the ligands. The deeply buried *f*-orbitals with their diffuse nature seem to be reluctant in bonding. Complexes of the heavier REE-s in high coordination numbers are likely to involve the *f*-orbitals, since the use of *s*, *p* and *d*-orbitals in the valence shell of an atom permits a maximum coordination number of nine in a covalent species having all bonds with bond order one. Higher coordination number implies a bond order less than one or the involvement of *f*-orbitals. In low coordination number also, certain shapes, for example a regular cube, will require participation of *f*-orbitals from symmetry considerations. The involvement of the *f*-orbitals are apparent in the electronic effects which are revealed in the spectral and magnetic properties mentioned later. Absence of electrons suitable for π-backdonation also disfavours complex formation with π-acid ligands.

Certain general features of the coordination compounds of lanthanide elements are noteworthy :

(i) The lanthanides generally exhibit high coordination numbers—C.N. 6 and less are found only with very bulky ligands. The commom coordination numbers are 7, 8 or 9 while still higher coordination numbers are also observed frequently. The larger, lighter lanthanides show C.N. 10 and higher with chelating ligands having small bites, e.g., $[Ce(NO_3)_6]^{3-}$ has a C.N. 12.

(ii) The Ln^{3+} cations are typical class-a acceptors and show preference for *O*-donor ligands. Their coordination chemistry is however, much less extensive than that of *d*-elements. Crystal field stabilization effects are also small.

(iii) Since the lanthanides have several energetically accessible orbitals, they can easily change their coordination number and stereochemistry. As such, the complexes are very labile and stereoisomerism is not commonly observed among them.

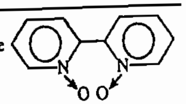
(iv) Since the Ln^{3+} ions are strongly hydrated in aqueous solution, only complexes formed by strong complexing agents can be isolated from such solutions and these too may contain unspecified number of coordinated water molecules.

Some typical examples of coordination compounds formed by the lanthanide ions are given in Table 31.4. The table is not exhaustive and many other geometries are known.

TABLE 31.4

Some coordination compounds of the lanthanide metals

Oxidation State	Coordination Number	Geometry	Example
+3	3	Pyramidal	$[Ln\{N(SiMe_3)_2\}_3]$ Ln = Nd, Eu, Yb
	4	Tetrahedral	$[Ln(mesityl)_4]^-$
		Tetrahedral (dist)	$[Ln\{N(SiMe_3)_2\}_3\ OPPh_3]$ Ln = Eu, Lu
	6	Octahedral	$[Ln\ X_6]^{3-}$ X = Cl, Br; Ln = Dy – Lu $[Er(NCS)_6]^{3-}$
	8	Dodecahedral	$[Ho\ (tropolonate)_4]^-$
		Cubic	$[La(bipyO_2^*)_4]^+$
		Square antiprism	$[Eu(acac)_3(phen)]$
		Square antiprism (dist)	$[La(acac)_3(H_2O)_2]$
	9	Tricapped trigonal prism	$[Ln(H_2O)_9]^{3+}$, $[Eu(terpy)_3]^{3+}$
		Bicapped dodecahedral	$[Ln(NO_3)_5]^{2-}$ (Ln = Ce, Eu)
	10	Bicapped dodecahedron	$[Ce(NO_3)_5]^{2-}$ (also Eu)
	12	Icosahedral (dist)	$[Ce(NO_3)_6]^{3-}$
+4	6	Octahedral	$[CeCl_6]^{2-}$
	8	Square antiprism	$[Ce(acac)_4]$
	12	Icosahedral (dist)	$[Ce(NO_3)_6]^{2-}$

* $bipyO_2$ = 2,2′-bipyridine dioxide 

31.2.5 Spectral and magnetic properties

Aqueous solutions of most lanthanide ions are coloured, except when the ions have f^0, f^1, f^7, f^{13} or f^{14} configurations :

Colourless :	$La^{3+}\ (f^0)$	*Coloured* :	$Pr^{3+}, Tm^{3+}\ (f^2, f^{12})$	green
	$Ce^{3+}\ (f^1)$		$Nd^{3+}, Er^{3+}\ (f^3, f^{11})$	lilac
	$Gd^{3+}\ (f^7)$		$Pm^{3+}, Ho^{3+}\ (f^4, f^{10})$	pink, yellow
	$Yb^{3+}\ (f^{13})$		$Sm^{3+}, Dy^{3+}\ (f^5, f^9)$	yellow
	$Lu^{3+}\ (f^{14})$		$Eu^{3+}, Tb^{3+}\ (f^6, f^8)$	pale pink

It may be noted that ions with f^n and f^{14-n} configurations have similar colours. We remember that such colours are produced by absorption of electromagnetic radiation in the visible region corresponding to transition of the ions from their ground states to excited states. For the Ln^{3+} ions, such excited states arise from the same $4f^n$

configuration as the ground term. The transitions involved are thus mainly *f-f* transitions, which are forbidden like *d-d* transitions. However, the relaxation available in *d-d* transitions owing to distortion from crystal field effects is much less pronounced for the deep-seated 4*f* orbitals. Hence the colours of the Ln^{3+}-aqua ions are less intense.

Though the basic principles underlying the spectral and magnetic behaviour are essentially the same as those outlined earlier in connection with the *d*-metal ions (Chapter 27), there are certain important differences.

(i) The *f*-orbitals lie deep in the atom and are shielded from interference by the nature of the ligands or by thermal vibrations. The bands arising from *f-f* transitions are thus sharp in contrast to *d-d* transitions which give broad bands due mainly to environmental effects (Chapter 27).

(ii) At the same time, spin-orbit coupling for the lanthanides becomes more important than crystal field effects and states with different *J* values are sufficiently apart in energy; electronic transition between them gives rise to sharp bands.

(iii) The number of theoretically possible transitions are large, giving several peaks in the electronic spectrum. For an *f*-electron, $l = 3$ and m_l may have values 3, 2, 1, 0, −1, −2. This gives rise to a high value of *L* for several f^n configurations (see Table 31.5).

Let us take the case of an f^2 configuration for which $L = 5$, $S = 1$ gives the ground state ${}^3H_4$. The possible states *S*, *P*, *D*, *F* and *G*, many of them with different possible values of *J*, ultimately suggest a large number of transitions even after applying the selection rules.

Thus, the electronic spectrum of a lanthanide ion consists typically of a large number of sharp bands, as shown in Fig. 31.7. $4f \rightarrow 5d$ transitions give rise to broader bands which are more intense since they are not orbitally forbidden. Ce^{3+} (f^1) and Tb^{3+} (f^8) show such bands in the ultraviolet.

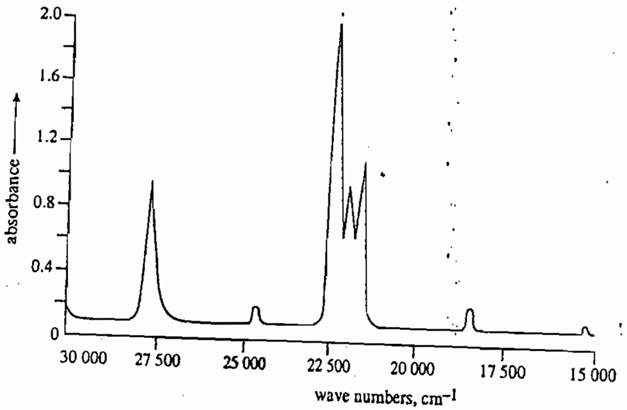


Fig. 31.7
Nature of visible and near uv spectrum of an Ln^{3+} ion.

(iv) Though crystal field effects are small, fine structure is observed in some bands owing to lifting of the degeneracy of some states by such effects. Intensities of some bands may also be affected by the nature of the coordinated ligands.

(v) We have mentioned the use of Eu(III) and Tb(III) oxides as phosphors in TV screen. In these, and also in Sm(III) and Dy(III), the ligands have excited states which are only slightly above those of the metal. During deexcitation, electrons of the ligand (excited by the electric discharge on the screen) have a fair chance to return to the excited states of the metal and then to the ground state (also of the metal). Such transitions give rise to the observed fluorescence.

[Sec. 31.2.5 *Magnetic properties*]

The bulk magnetic properties of the lanthanide ions also follow from the general principles laid down in Chapter 27, but here also, a difference is observed from the *d*-block transition metal ions : the observed magnetic moments do not follow the simple spin-only formula. In connection with the transition metal ions, we noted that the orbital contributions to magnetic moments get practically quenched through mutual interaction. In case of the lanthanide ions, this does not appear to take place—the *f*-orbitals lie too deep inside the atom for such quenching to occur. The observed magnetic moments of lanthanide ions are found to be in good agreement with values calculated from Russel-Saunders, *LS* coupling (Chapter 27) : $\mu = g\sqrt{J\,(J+1)}$. The spin-orbit coupling constants are also quite large, of the order of 1000 cm⁻¹. This makes the usual separation between states with different *J* values much larger compared to kT (~ 200 cm⁻¹ at ordinary temperature). So, states with *J* values higher than the ground state are usually unoccupied. This is reflected in the observed magnetic moments (Table 31.5 and Fig. 31.8) which are in good agreement with those calculated from *J*-values but differ widely from the spin-only values.

(Remember *J* can take values $|L+S|, |L+S-1|, \ldots\ldots |L-S|$; the ground state is that with *J* equal to $|L-S|$ if the *f*-shell is less than half-filled, and equal to $|L+S|$ when more than half-filled.)

TABLE 31.5

Magnetic moments (B.M.) of Ln^{3+} ions

Ion	Electron Configuration (outer)	Ground state	g	Magnetic Moment (μ_B)		
				Spin-only	$g\sqrt{J\,(J+1)}$	Observed
La^{3+}	$4f^0$	${}^1S_0$	0	0.0	0.0	0.0
Ce^{3+}	$4f^1$	${}^2F_{\frac{5}{2}}$	$^6/_7$	1.7	2.54	2.3-2.5
Pr^{3+}	$4f^2$	${}^3H_4$	$^4/_5$	2.8	3.58	3.4-3.6
Nd^{3+}	$4f^3$	${}^4I_{\frac{9}{2}}$	$^8/_{11}$	3.9	3.62	3.5-3.6
Pm^{3+}	$4f^4$	${}^5I_4$	$^3/_5$	4.9	2.68	2.7
Sm^{3+}	$4f^5$	${}^6H_{\frac{5}{2}}$	$^2/_7$	5.9	0.84	1.5-1.6
Eu^{3+}	$4f^6$	${}^7F_0$	1	6.9	0.0	3.4-3.6
Gd^{3+}	$4f^7$	${}^8S_{\frac{7}{2}}$	2	7.9	7.94	7.8-8.0
Tb^{3+}	$4f^8$	${}^7F_6$	$^3/_2$	6.9	9.72	9.4-9.6
Dy^{3+}	$4f^9$	${}^6H_{\frac{15}{2}}$	$^4/_3$	5.9	10.63	10.4-10.5
Ho^{3+}	$4f^{10}$	${}^5I_8$	$^5/_4$	4.9	10.60	10.3-10.5
Er^{3+}	$4f^{11}$	${}^4I_{\frac{15}{2}}$	$^6/_5$	3.9	9.57	9.4-9.6
Tm^{3+}	$4f^{12}$	${}^3H_6$	$^7/_6$	2.9	7.63	7.1-7.4
Yb^{3+}	$4f^{13}$	${}^2F_{\frac{7}{2}}$	$^8/_7$	1.7	4.50	4.4-4.9
Lu^{3+}	$4f^{14}$	${}^1S_0$	1	0.0	0.0	0.0

Sm(III) and Eu(III) stand notable exceptions from the general agreement found in other lanthanides. We may look at the values of the spin-orbit coupling constants (λ) and the separation between the ground state and first excited states (ΔE) for these ions :

	λ	ΔE
Sm^{3+}	240 cm^{-1}	$\frac{7}{2}\lambda$ (= 840 cm^{-1})
Eu^{3+}	230 cm^{-1}	λ (= 230 cm^{-1})

Comparison with the value of ~200 cm^{-1} for kT at ordinary temperature leads us to conclude that the first excited state of Sm^{3+} and the first two or three excited states of Eu^{3+} will be populated. Mixing of these states with higher J values causes the observed magnetic moment to be higher.

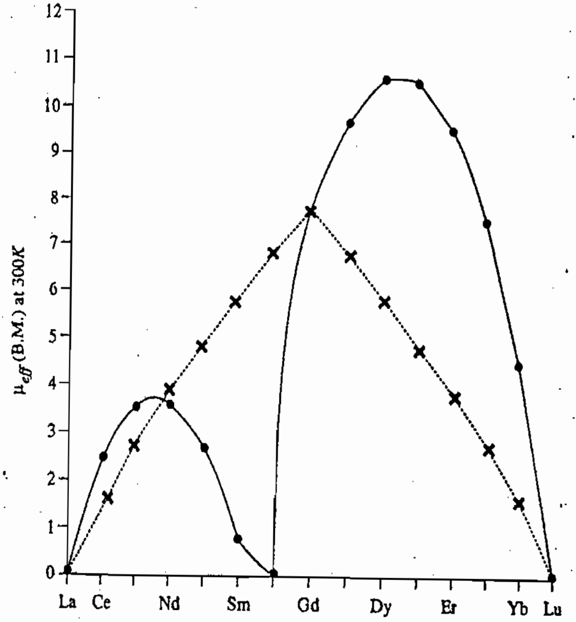


Fig. 31.8
Magnetic moments of Ln^{3+} ions.
—— : values calculated from $g\sqrt{J(J+1)}$.
……… : spin-only values

31.3 CHEMISTRY OF PRINCIPAL OXIDATION STATES

Unlike other sections, we discuss here the lanthanide elements together according to their principal oxidation states. Quite understandably, this is mainly due to close similarity between the elements.

31.3.1 Oxidation state III

General characteristics

(i) Compounds in this oxidation state are predominantly ionic owing to large sizes of the Ln^{3+} ions. As expected, ionic character decreases with decrease in size of the cation and there is an increase in the tendency of $[Ln(H_2O)_n]^{3+}$ ions to undergo hydrolysis.

(ii) For the hydroxides $Ln(OH)_3$, decreasing ionic character implies lowering of basic character. In fact, the last few hydroxides, for example $Yb(OH)_3$ and $Lu(OH)_3$, will even dissolve in hot concentrated NaOH, with difficulty though.

(iii) Solubilities of the salts in water are determined in a complicated way by factors like lattice energy of the solid, hydration enthalpies of the ions and entropy factors. Hence it is difficult to draw any clear cut generalization from size factor alone. Both lattice energy and hydration enthalpies increase with decrease in ionic radii; while the first disfavours solubility, the second factor favours solubility (Chapter 6) and it is not always possible to find a consistent trend. Generally it is found that oxalates, double sulfates and double nitrates of the lighter cerium group lanthanides are somewhat less soluble than the salts of heavier yttrium group lanthanides; for basic nitrates, the trend is reversed. Classical separations of the lanthanides were based on these differences in solubility.

(iv) As a consequence of lanthanide contraction, the Ln^{3+} ions show changes in coordination through the series La^{3+} to Lu^{3+} and pronounced changes in structural types are observed at several points. In many cases, more than one structure is adopted.

The spectral and magnetic properties of the ions have been discussed earlier.

Oxides and hydroxides

The oxides Ln_2O_3 have high enthalpies and Gibbs energies of formation (ΔG_f^0 of the order of -1600 kJ mol^{-1}). These are readily formed by heating the metals or their suitable compounds (e.g. the oxalates) in air. The oxides are refractory in nature, having melting points of the order of 2000°C. Their colours vary according to the colour of Ln^{3+} ions noted before.

The oxides are readily soluble in acids but like Al_2O_3, lose their chemical activity after calcining. They normally do not react with alkali solutions. The oxides resemble the alkaline earth metal oxides (CaO—BaO) : they absorb CO_2 to form carbonates and moisture to form hydroxides.

The hydroxides $Ln(OH)_3$ are definite hydroxides and not simply hydrated oxides. They form gelatinous precipitates on adding ammonia or dilute alkali to solutions of Ln^{3+}. Basic character, thermal stability and solubility of the hydroxides decrease with decrease in ionic radii from La^{3+} to Lu^{3+}. K_{sp} of $La(OH)_3$: 1.0×10^{-19}, $Pr(OH)_3$: 10^{-20}, $Lu(OH)_3$: 2.5×10^{-24}.

The crystalline hydroxides may be obtained by aging the oxides Ln_2O_3 in strong alkali at high temperature and pressure. Their structures are hexagonal with tricapped trigonal prismatic coordination (C.N. = 9).

Scandium does not appear to form a definite hydroxide, although ScO(OH) is well established [compare AlO(OH)]. Sc_2O_3, with water, forms $Sc_2O_3 . nH_2O$ which dissolves in excess alkali to $Sc(OH)_6^{3-}$.

Halides

All four trihalides are known for the lanthanide elements. These have high negative enthalpy and Gibbs energies of formation (see later). The trifluorides, highly insoluble even in strongly acidic media (3*M* HNO_3), are readily obtained by direct precipitation from solutions containing Ln^{3+}; this also constitutes a test for the ions. ScF_3 and fluorides of the heavier lanthanides are soluble in excess of HF owing to complex formation. The fluorides may also be dissolved in 3*M* HNO_3 saturated with boric acid which forms stable BF_4^- with the fluoride ion.

The chlorides as well as other halides are soluble in water and deliquescent hydrated crystals may be obtained from such solutions. Chlorides of the elements La-Nd generally form hydrates $LnCl_3.7H_2O$; the remaining lanthanides, including Y, form hydrates with six molecules of water.

On heating, the hydrated chlorides give the oxochloride LnOCl except $ScCl_3$ and $CeCl_3$ which give Sc_2O_3 and CeO_2 respectively. Other halides behave similarly. Hence the anhydrous halides are prepared by reacting the metals with HCl (*g*), Br_2 or I_2. The chlorides may also be made by heating the oxide with excess of ammonium chloride at about 300°C.

$$Ln_2O_3 + 6NH_4Cl = 2LnCl_3 + 6NH_3 + 3H_2O$$

The halides react with glass at high temperatures forming oxohalides (and SiX_4).

ΔG_f^0 for some crystalline trichlorides are as follows (kJ mol^{-1}) :

$CeCl_3$	$PrCl_3$	$NdCl_3$	$PmCl_3$	$SmCl_3$	$EuCl_3$	$GdCl_3$	$TbCl_3$
−983	−1020	−963	−882	−863	−803	−928	−803

The enthalpy of atomization of the trihalides also show similar periodic variations (Fig. 31.9). The trihalides of europium ($4f^7\,6s^2$) and ytterbium ($4f^{14}6s^2$) are marked by low values. This may be related to the stability of $4f^7$ and $4f^{14}$ configuration.

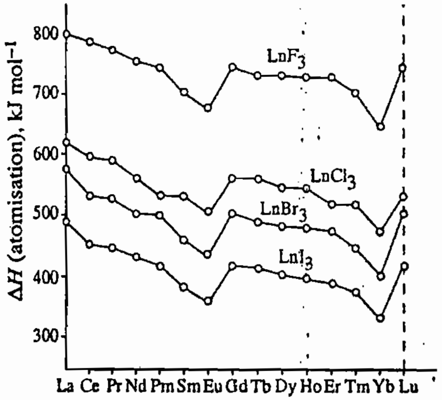


Fig. 31.9. Variation of the enthalpy of atomisation of lanthanide trihalides along the series.

Salts of oxoacids

The lanthanide elements form salts with most oxoacid anions including the strongly stabilizing ones. The hydrated salts of common acids can be readily obtained by dissolving the oxide in acid and crystallizing. They contain the $[Ln(H_2O)_n]^{3+}$ ion and their colour varies accordingly.

The salts mostly resemble those of the alkaline earth metals; for example, the carbonates, sulfates, nitrates and perchlorates, all resemble the calcium salts. The carbonates, phosphates and oxalates of REE are practically insoluble in water; most of the others are rather more soluble than the calcium salts. Only scandium carbonate dissolves in hot ammonium carbonate with double salt formation; this provides a method for the separation of scandium from yttrium and lanthanum.

Lanthanides may be estimated gravimetrically by precipitation of the "oxalate" from dilute nitric acid solution followed by ignition to the oxide. From such acid medium, ammonium oxalate usually precipitates $NH_4LnOx_2.1\text{—}3\ H_2O$. The normal oxalate of lighter REE-s are obtained by ammonium oxalate from neutral solutions; heavier lanthanides give a mixed oxalate. The carbonates obtained from aqueous solutions by adding say Na_2CO_3 are mostly basic carbonates. Normal carbonates are best made by hydrolysis of chloroacetates, e.g.,

[Sec. 31.3.1
Ox. state III—
complexes]

$$2\ La(Cl_3C.COO)_3 + 11H_2O \longrightarrow La_2(CO_3)_3.8H_2O + 3CO_2 + 6CHCl_3$$

$La_2(CO_3)_3.8H_2O$ involves both unidentate and bidentate carbonate ligand around 10-coordinate La.

The Ln(III)-salts readily form a number of double salts, most common being the nitrates and sulfates such as.

$$2Ln(NO_3)_3.3Mg(NO_3)_2.24H_2O$$
$$Ln(NO_3)_3.2NH_4NO_3.4H_2O$$
$$Ln_2(SO_4)_3.3Na_2SO_4.12H_2O$$

The double sulfates of the lighter cerium group REE-s (La-Eu) are only sparingly soluble in sodium sulfate while those of the yttrium group (Gd-Lu and Y) are appreciably soluble. This fact may be used to separate the REE-s into two broad groups, from which further separations may be achieved by fractional crystallizations.

Other binary compounds

The sulfides Ln_2S_3 may be obtained by direct reaction at high temperature or by reacting $LnCl_3$ with H_2S at 1100°C. The compounds are semiconducting in nature and stable in dry air but undergo hydrolysis in presence of moisture. All of them liberate H_2S by the action of acids. When heated with excess of sulfur in a sealed tube at 600°C, Ln_2S_3 are converted to products with compositions upto about LnS_2. These appear to be polysulfides of Ln(III).

Besides the hydrides and carbides mentioned before, the lanthanide elements also form a variety of borides and also nitrides, phosphides etc (LnX, X = N, P, As, Sb, Bi). The latter compounds have the NaCl structure.

Complex compounds

The general characteristics of complex compounds of lanthanides discussed in section 31.2.4 refer mostly to the +3 oxidation state, the most common one for these elements. As already mentioned, the most common aqua ion is the nine-coordinate $[Ln(H_2O)_9]^{3+}$. Stable complexes are formed by chelating oxygen ligands like the anions of citric, tartaric, oxalic etc. acids. The NO_3^- ion is also known to form many stable complexes in high coordination numbers. β-diketonates and EDTA complexes are also well-known.

β-diketones such as acetylacetone form insoluble octahedral complexes which are often hydrated or solvated, e.g., $[Ln(acac)_3].C_2H_5OH.3H_2O$. The anhydrous species obtained by vacuum dehydration of such products appear to be polymeric. Scandium, because of its small size, forms a more stable complex compared to the lanthanides; this may be sublimed at ~200°C while others decompose on heating. Fluorinated β-diketonates form more stable and volatile complexes which are suitable for gas chromatographic separation. Some lanthanide β-diketonate complexes possess anti-knock properties. Solutions of β-diketonate complexes, of particularly Eu^{3+} and Pr^{3+} in organic solvents often give much better resolution of nmr spectra of an organic molecule in contact with the complex and hence their use as nmr shift reagents.

Chelating ligands like EDTA and citric acid form soluble complexes with lanthanides which are useful in their separation by ion-exchange (see isolation).

Though the coordination number of the metal in these complexes is usually six, higher coordination numbers are frequently attained as for example in $La(acac)_3\,(H_2O)_2$ and $Y(CF_3COCHCOCF_3)_4$ (both C.N. 8). Nine-coordinate $Nd(H_2O)_9^{3+}$ ion is present in $Nd(BrO_3)_3.9H_2O$—the $Ln(H_2O)_9^{3+}$ ions occurring in many crystalline hydrates which may be obtained with common anions. 10-coordination is found in La(EDTA)$(H_2O)_4.3H_2O$ and $La_2(CO_3)_3.8H_2O$.

The complex nitrate $[Ce(NO_3)_5]^{2-}$ also contains ten-coordinate cerium with five bidentate NO_3 groups at the apieces of a trigonal bipyramid, forming a bicapped dodecahedron. Similar ten-coordinate complex nitrates are also formed by other lanthanides but Sc in $Sc(NO_3)_5^{2-}$ is nine-coordinate, one nitrate group bonding through only one oxygen atom. $[Ce(NO_3)_6]^{2-}$ has a distorted icosahedral structure in which the cerium is 12-coordinate.

Lanthanides also form numerous complexes with N-donor ligands like en, dien, dipy and N-bonded thiocyanate. The $Ln(NCS)_6^{3-}$ ions are octahedral, but complexes with higher coordination number are more frequent, for example $Ln(en)_3Cl_3$. $Ln[N(SiMe_3)_2]_3$ complexes are pyramidal with Ln = Sc, Nd, Eu and Gd.

Crown ethers form various complexes with the lanthanides depending on the size of the cavity and the radii of Ln^{3+} ions. 18-crown-6 (C) forms most stable complexes with the larger lanthanides (La-Gd) of the type $[Ln(NO_3)_2C]_3$ $[Ln(NO_3)_6]$ where the Ln in the cationic part is 10-coordinate. La, Ce, Pr and Nd also form a 12-coordinate complex of the type $[Ln(NO_3)_3C]$. Smaller lanthanides (Tb-Lu) which do not fit the large ether-cavity form complexes of the type $[Ln(NO_3)_3(H_2O)_3]C$.

31.3.2 Oxidation state II

This oxidation state is most important for europium, though other lanthanides also may be obtained in this state under appropriate conditions. After Eu^{2+} $(4f^7)$, Yb^{2+} $(4f^{14})$ comes next in stability, followed by Sm^{II}, Tm^{II}, Gd^{II} and so on.

$$Eu(II) > Yb(II) > Sm(II) > Tm(II) \geq Gd(II) \doteq Nb(II)$$

For aqueous solution, some relevant standard redox potentials are

$$Eu^{3+} + e \rightleftharpoons Eu^{2+} \qquad E^\circ = -0.35\ V$$
$$Sm^{3+} + e \rightleftharpoons Sm^{2+} \qquad E^\circ = -1.5\ V$$
$$Yb^{3+} + e \rightleftharpoons Yb^{2+} \qquad E^\circ = -1.1\ V$$

We observe that E° for Eu(III)-Eu(II) is comparable to that for Cr(III)-Cr(II), and colourless to pale greenish yellow solutions of Eu(II), which are relatively stable in dark, may be used in analysis in absence of air. In contrast, aqueous Yb(II) (yellow) and Sm(II) (blood-red) are highly unstable with respect to oxidation by water.

Lanthanides in oxidation state II may be obtained from the trihalides by **thermal** decomposition or reduction by hydrogen or metals. The decomposition

$$LnX_3 \longrightarrow LnX_2 + \tfrac{1}{2}X_2$$

is most likely to occur when the loss in lattice energy between LnX_3 and LnX_2 is minimum, that is when X = I. In fact, it is observed that for Ln = Sm or Yb, only the triiodide decomposes readily to the diiodide; the chloride and bromide require reduction by hydrogen (heat). But when Ln = Eu, all the chloride, bromide and iodide may be decomposed thermally to the dihalide. Trifluorides of Sm, Eu and Yb may be reduced to the difluoride by calcium metal at high temperature.

The lanthanide trihalides may also be reduced by comproportionation reaction at 500°C-600°C.

$$2LnX_3 + Ln \longrightarrow 3LnX_2$$

Diiodides of La, Ce, Pr, Nd, Pm, Gd and Tm have been obtained in this manner.

Solid $EuCl_2$ is readily prepared by reducing $EuCl_3$ with hydrogen

$$EuCl_3 + H_2 = EuCl_2 + HCl$$

$EuCl_2$ forms a dihydrate which is very insoluble in concentrated HCl. In solution, Eu(II) is readily reduced by magnesium, zinc or alkali metal amalgams. Eu(II) has many similarities with Ca^{2+}. For example, both $EuSO_4$ and $EuCO_3$ may be precipitated from solution; EuH_2 is ionic in nature and isomorphous with CaH_2. However, the oxide EuO does not seem to exist, though EuS, EuSe or EuTe may be prepared.

As shown by the E_0 value for Eu(III)-Eu(II), Eu(II) solutions are strongly reducing in nature and gets readily oxidized by air. The solids are comparatively more stable.

$EuCl_2$, $EuBr_2$ and EuI_2 show magnetic moments of ~7.9 B.M. corresponding to seven unpaired electrons. The magnetic properties of Eu^{2+} are in many ways identical with those of Gd^{3+} over a wide range of temperature and both ions conform to $4f^7$ configuration.

The hydrides and dihalides of other lanthanides often have structures similar to those of calcium salts. YbH_2, like EuH_2, is ionic and isomorphous with CaH_2; SmF_2 and EuF_2 are isomorphous with CaF_2. The diiodides of Sm, Eu, Tm and Yb are also saline, but those of La, Ce, Pr and Gd are metallic. NdI_2 may exist in both forms—the ionic form may be converted to the metallic form by applying pressure.

Sulfides LnS may be obtained by direct synthesis; those of Sm. Eu and Yb are ionic with NaCl structure.

Samarium(II) forms a number of compounds, for example, the halides, sulfate, carbonate, phosphate and hydroxide. Sm(II) and Eu(II) may be separated from other lanthanides by reduction of the trichlorides by sodium amalgam and alcohol. Controlled oxidation now produces only Sm(III) which is thus separated from Eu(II).

Ytterbium(II) also forms compounds similar to Sm(II); and probably the monoxide YbO.

31.3.3 Oxidation state IV

Only cerium exists in oxidation state IV which is stable in solution as well as in the solid. Ce(IV) corresponds to an $f^0d^0s^0$ noble gas configuration. Other elements forming only unstable solid compounds in this oxidation state are Pr, Nb, Tb and Dy. Tb(IV) has the f^7 configuration.

The only binary compounds known for Ce(IV) are the oxide CeO_2 and fluoride CeF_4.CeO_2 is produced by heating $Ce(OH)_3$ or other decomposable oxysalt (e.g., the oxalate) in air or oxygen or in solution by oxidation of Ce^{III} by OCl^-. The oxide, colourless when pure, is insoluble in strong acids or alkalis but dissolves in acids in presence of reducing agents to produce Ce(III) in solution. From this solution Ce(IV) may be obtained by oxidation wih strong oxidizing agents like peroxodisulfate. Hydrated yellow $CeO_2.nH_2O$ appears as a gelatinous precipitate by bases from solutions of Ce(IV). CeF_4 may be prepared by reacting CeF_3 (or $CeCl_3$) in fluorine at room temperature. It is stable upto 800°C.

For the half-reaction

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$

$E^\circ = 1.70$ V in molar $HClO_4$ where complexation is expected to be small; Ce(IV) is thus unstable with respect to reduction by water but the process is very slow at oridinary temperatures so that cerium(IV)-sulfate may be used as an oxidant in titrations in place of permanganate or dichromate. As Ce(IV) is an one electron oxidant, its reaction paths are less complex than those of the other two oxidants. In acetic acid solution, it oxidizes aldehydes and ketones at the α-carbon atom. A solution of $(NH_4)_2[Ce(NO_3)_6]$ oxidizes toluene to benzaldehyde.

Q. 31.1 $E°$ for Ce(IV)-Ce(III) in different acid medium (1*M* in each case) are

$HClO_4$	HNO_3	H_2SO_4	HCl
1.70 V	1.61 V	1.44 V	1.44

Comment.

Hint : Ce(IV) is more strongly complexed than Ce(III) by the anions of the acid whose complexing ability decreases from Cl^- to ClO_4^-.

Owing to its higher charge-density, the Ce^{4+} ion forms stronger complexes compared to the Ln^{3+} ions. The $[Ce(NO_3)_6]^{2-}$ ion contains 12-coordinate cerium(IV) with six bidentate NO_3 groups. From this, Ph_3PO replaces two trans-nitrates to form the neutral 10-coordinate complex $[Ce(NO_3)_4(OPPh_3)_2]$. The fluorocomplexes $(NH_4)_4[CeF_8]$ and $(NH_4)_3[CeF_7].H_2O$ may be prepared from aqueous solution; the former gives $(NH_4)_2[CeF_6]$ on heating. The anion is again eight-coordinate through fluoride bridges (square antiprismatic). The $CeCl_6^{2-}$ ion has been isolated as the pyridinium salt (octahedral). Complexes with chelating *O*-donor ligands like β-diketonates have also been obtained from aqueous solution.

The aqeous chemistry of Ce^{4+} has many similarities with Zr^{IV}, Hf^{IV} and the tetravalent actinides. Like ZrF_4, CeF_4 has a nearly square antiprismatic coordination around the cerium; Ce^{IV} forms an insoluble oxalate and a phosphate insoluble in 4*M* HNO_3. $Ce(IO_3)_4$ is also insoluble in 6*M* HNO_3. These facts may be used to separate Ce^{IV} from other Ln(III). Ce(IV) is also much more readily extracted into organic solvents by tributyl phosphate than other Ln(III) ions.

Praseodymium forms black PrO_2 (non-stoichiometric) when Pr_2O_3 is heated in air (500°C. 100 atm) It is often formulated as Pr_6O_{11} but is much more complicated in nature. It dissolves in acids forming Pr(III) and liberating oxygen. A yellow Pr(IV) oxide is also obtained by oxidation of Pr(III) in concentrated aqueous KOH by ozone or electrolytically, PrF_4 may be obtained by the action of KrF_2 on PrO_2; $NaPrF_5$ and Na_2PrF_6 are obtained when Pr(III) salts are heated in F_2 (300°-500°C) with stoichiometric quantities of alkali fluorides. PrF_4 has a structure similar to that of CeF_4 (and ZrF_4). Pr(IV) does not exist in aqueous solution; the estimated $E°$ value for Pr(IV)-Pr(III) is ~2.9 V, sufficient to oxidize water.

Terbium(IV) oxide may be obtained by oxidation of Tb_2O_3 by atomic oxygen at 450°C. Other oxides obtained by heating oxo-salts are actually non-stoichiometric with the limiting composition $TbO_{1.75}$ and may contain both Tb(IV) and Tb(III). Oxidation of TbF_3 with F_2 at 300-400°C gives colourless TbF_4 which is isostructural with CeF_4.

Fluorination of NdF_3 in presence of CsF gives a double salt containing 10-20 per cent Nd(IV). Similar fluorination of DyF_3 gives products containing up to 50 per cent Dy(IV).

31.3.4 Low formal oxidation states

A number of subhalides are known for the lanthanides. The monochloride LnCl formed by all the lanthanides (and also by Sc and Y) has a layer structure of Cl-Ln-Ln-Cl units in cubic close packing. The compounds show metallic conductivity owing to delocalization of two electrons per metal atom. Other cations may be interspaced between two 4-layer units while C, O or H may be held between the metal layers. Similar LnBr phases are also known with Ln = Y, La and Pr.

Ln_2Cl_3 (Ln = Gd, Tb) compounds have infinite chains of octahedral metal units sharing opposite edges. These may be reduced to LnCl at 800°C.

31.3.5 Organometallic compounds

The organometallic compounds of lanthanides are mostly formed by cyclopentadienyl (Cp) and its derivatives. The compounds $LnCp_3$ may be prepared by the general reaction

$$LnCl_3 + 3NaCp \longrightarrow LnCp_3 + 3NaCl$$

where Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb.

$EuCp_3$ has to be prepared indirectly to avoid reduction to $EuCp_2$. σ-bonded alkyls and aryls are also known for the lanthanides.

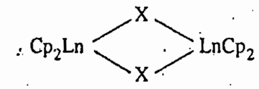
The compounds are very sensitive to air and moisture and basically ionic in nature. They are associated in the solid state but form discrete adducts $LnCp_3D$ with neutral donor ligands (D) like R_3P, RNC and THF.

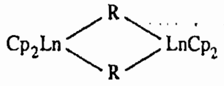
In these adducts, the three η^5-Cp units and the donor D are arranged in a nearly tetrahedral arrangement around the Ln atom.

Organocompounds of the type Cp_2LnX may be obtained through reactions of the type

$$LnX_3 + 2NaCp \longrightarrow Cp_2LnX + 2NaX \quad \text{or,} \quad LnX_3 + 2Cp_3Ln \longrightarrow 3Cp_2LnX$$

The compounds are dimeric with halogen bridges (31-I) which can be converted to other compounds like $[Cp_2LnR]_x$ where R = H or an organic group. These compounds are also dimeric with bridging R or H (31-II). Compounds of the type $CpLnX_2$ have also been prepared.


31-I


31-II

The organolanthanide compounds offer a unique scope to study the effects of regular variation in size of the Ln^{3+} ions (from Ln = La to Ln = Lu) on the steric requirements of the cyclopentadienyl group. As the $C_5H_5^-$ ring is gradually substituted to, say, $C_5Me_5^-$, the increased bulk of the ligand shows marked changes in structure and chemical properties of the organolanthanides formed. Thus, the $C_5Me_5^-$ ring is so bulky that it does not lead to $Ln(C_5Me_5)_3$ but forms $(C_5Me_5)_2LnR$ species (R = H, CH_3 etc.). A small lanthanide like Lu attached to the bulky C_5Me_5 group undergoes many interesting reactions, e.g.,

$$(C_5Me_5)_2LuR + C_6H_6 \longrightarrow (C_5Me_5)_2LuC_6H_5 + RH$$

$$(C_5Me_5)_2LuH + D_2 \longrightarrow (C_5Me_5)_2LuD + HD$$

$$(C_5Me_5)_2LuR + CH_4 \longrightarrow (C_5Me_5)_2LuCH_3 + RH.$$

The last reaction provides an example of forming an M—C bond in a homogeneous reaction taking place under mild conditions.

Cyclooctatetraene, $C_8H_8^{2-}$, forms sandwich complexes with the lanthanides and actinides, for example $[K(diglyme)]^+[Ln(C_8H_8)_2]^-$. The cerium compound contains the Ce^{III} symmetrically sandwiched between two parallel C_8H_8 rings. A similar sandwich compound is formed by Ce^{IV} in $Ce(C_8H_8)_2$. Divalent lanthanide species $Ln(C_8H_8)$ and $Ln(C_8H_8)^{2-}$ are known for Ln = Yb, Eu and Sm.

A benzene π-complex comparable to $(C_6H_6)_2Cr$ is formed in $Me_6C_6Sm(AlCl_4)_3$.

σ-bonded alkyls and aryls of lanthanides may be prepared by metathesis in tetrahydrofuran or ether solution :

$$LnCl_3 + 3LiR \longrightarrow LnR_3 + 3LiCl$$

The octahedral methyl derivatives $[LnMe_6]^{3-}$ are known for most lanthanides. These, like other organo-lanthanides, are mostly thermally stable but unstable with respect to air and water. Mixed alkylcyclopentadienyls have also been studied in recent times.

31.3.6 High temperature superconductors

Superconductivity is characterized mainly by zero resistivity below a certain critical temperature (T_c) and perfect diamagnetism or exclusion of a magnetic field, called the *Meissner effect*. The phenomenon was first detected by K. Onnes in 1911 in mercury below 4.2 K (Fig. 31.10). Subsequently many other elements as well as compounds were found to exhibit this behaviour below their respective critical temperatures : Zn and Cd <1K; Pb 7.19K; Nb 9.5K; La 6.0 K etc. The alkali metals, coinage metals or the ferromagnetic metals Fe, Co and Ni do not display super conductivity. Solid compounds showed this property with a somewhat higher T_c and search was on for superconductors with high T_c. NbN and Nb_3S_n were found to have T_c between 15-20K; Nb_3Ge was the material with highest known T_c (~23K) until 1986.

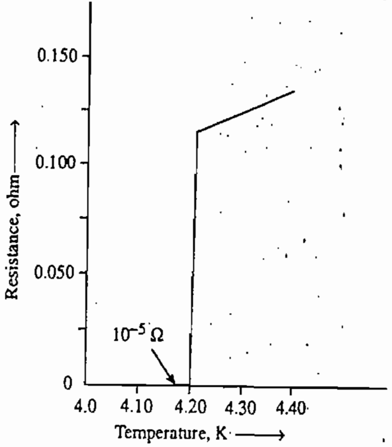


Fig. 31.10 : Resistance of a sample of mercury at low temperature.

Like other conducting materials, superconducting materials show a finite resistance above T_c. As the conduction electrons move through the body of the conductor, their interaction with lattice vibrations give rise to this resistance. As temperature of the conductor increases, the amplitude of atomic vibrations increases causing more scattering of the conduction electrons. This is why we find the resistance of metals to increase with temperature. In superconducting substances, the electrons are believed to move through the lattice in a concerted manner with lattice vibrations. Hence no electrons are scattered, recording zero resistance.

By 1985, zero resistance was observed in some mixed oxide and mixed sulfide systems like Li_2TiO_4 (T_c = 13.7 K) and $PbMo_6S_8$ (T_c = 15.2K). Other systems studied had still lower T_c. In 1986, Bednorz and Müller observed very low resistance in a mixed oxide system like $La_{2-x}Ba_xCuO_4$ which showed a rather high T_c, 35K (awarded 1987 Nobel Prize in Physics). Since then there has been a extensive search for new superconducting materials having high values of T_c. A series of mixed copper oxides have been developed with highest recorded T_c of 134 K. Some representative oxide systems are :

Composition	T_c
$La_{1.8}Ba_{0.2}CuO_4$	35K
$La_{1.85}Sr_{0.15}CuO_4$	40K
$YBa_2Cu_3O_7$	93K
$Tl_2Ba_2CuO_6$	80K
$Tl_2Ba_2CaCu_2O_8$	105K
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125K
$Tl_2Ba_2Ca_3Cu_4O_{12}$	115K
$HgBa_2Ca_2Cu_3O_{10}$	134K

[Sec.31.3.6
High temperatur
superconductors

The superconducting materials represented by the idealized formula $YBa_2Cu_3O_7$ have been widely studied. The compounds are actually non-stoichiometric, $YBa_2Cu_3O_{7-\delta}$, $0<\delta<1$. When $\delta \approx 0$, T_c has the highest value of 93K; it falls rapidly as δ increases. The oxygen stoichiometry is carefully maintained in two stages : (i) a mixture of $BaCO_3$, Y_2O_3 at CuO is heated for some days at 940°C and quenched to room temperature (ii) the oxygen-deficient material so obtained (δ = 0.3 approx) is annealed in oxygen (400-450°C) and slowly cooled to room temperature.

The structure of $YBa_2Cu_3O_7$ may be derived from the structure of perovskite shown before (Fig. 28.12). This is illustrated in Fig. 31.11.

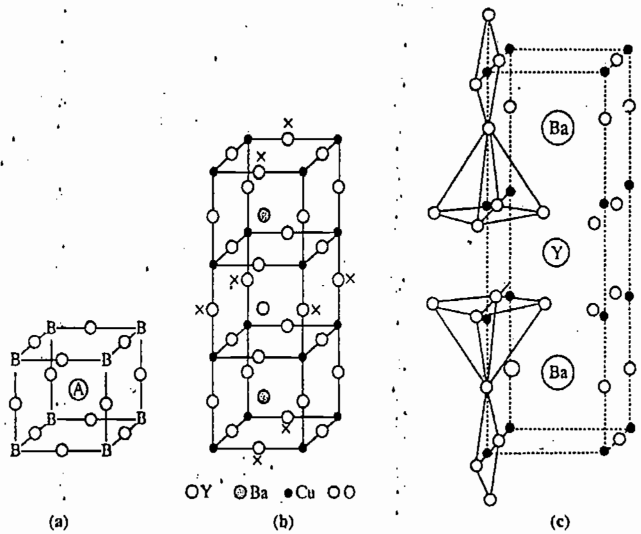


Fig. 31.11

Structure of $YBa_2Cu_3O_7$ superconductor.

(a) The unit cell of perovskite, a mixed oxide mineral with the general formula ABO_3. The large A ion (center) is surrounded by 8 B ions and 12 oxide ions. (Each B is surrounded octahedrally by 6 oxygen).

(b) Stacking of three perovskite unit cells. The A cations are replaced by Ba and Y in the sequence Ba—Y—Ba—Ba—Y—Ba—Ba—Y. The B cations are Cu. The composition at (b) corresponds to $YBa_2Cu_3O_9$. Removal of some O atoms around Y and Ba (shown by ×) now gives the $YBa_2Cu_3O_7$ structure shown in C.

(c) The $YBa_2Cu_3O_7$ structure. Unlike the B-sites in Perovskites, the Cu atoms have 5-coordination (square pyramid) and 4-coordination (square planar) as shown. The 5-coordinate copper is displaced about 30 pm from the plane of the oxide ions. Sheets and chains of CuO_4 and CuO_5 units are also present in many other high temperature superconductors.

The average oxidation number of Cu comes out as +2.33 (Y = +3, Ba = +2, O = −2). This may arise due to presence of Cu(II) and Cu(III).

A major problem in the practical application of superconductors is their low critical current density in the form of wires — that is the maximum current the superconductor can carry without loss of its property is very low. This may be somewhat improved in thin films — of the order of several million amperes per square centimeter; and this may introduce their use in microelectronic applications.

PART B : THE ACTINIDE ELEMENTS (ACTINONS)

31.4 Introduction

The second series of *f*-block elements results from the filling of 5*f* orbitals and consists of the elements thorium (Z = 90) to lawrencium (Z = 103). Actinium, like lanthanum, is often included with these elements for comparison. All of them are radioactive, but the most abundant isotopes of thorium and uranium have very long half-lives—^{232}Th : 1.4×10^{10} y and ^{238}U : 4.5×10^9 y and for many practical purposes their activity may be considered negligible. Except actinium, thorium, protactinium and uranium, all elements in this series are synthetic.

The names, symbols, most likely electron configurations and half-lives of main isotopes of the elements are given in Table 31.6 (most abundant/common isotope shown in bold).

TABLE 31.6

Actinium and the actinide elements

Atomic Number	Name	Symbol	Electron Configuration (after Rn-core)	Half-lives	
89	Actinium	Ac	$6d^17s^2$	**227** (98.6% β, 1.4% α)	21.8 y
90	Thorium	Th	$6d^27s^2$	**232** (α)	1.4×10^{10} y
91	Protactinium	Pa	$5f^26d^17s^2$ $(5f^16d^27s^2)$	**231** (α)	3.3×10^4 y
92	Uranium	U	$5f^36d^17s^2$	235 (α)	7×10^8 y
				238 (α)	4.5×10^9 y
93	Neptunium	Np	$5f^46d^17s^2$ $(5f^57s^2)$	**237** (α)	2.14×10^6 y
94	Plutonium	Pu	$5f^67s^2$	**239** (α)	2.44×10^4 y
				242 ( )	3.79×10^5 y
				244 ( )	8.3×10^7 y
95	Americium	Am	$5f^77s^2$	**241** (α)	433 y
				243 ( )	7380 y
96	Curium	Cm	$5f^76d^17s^2$	242 (α)	163 d
				244 (α)	18.1 y
				247 ( )	8×10^7 y
				248 ( )	3.4×10^5 y
97	Berkelium	Bk	$5f^97s^2$ $(5f^86d^17s^2)$	247	1400 y
				249 (β)	320 d
98	Californium	Cf	$5f^{10}7s^2$	249	351 y
				252 (α)	2.64 y
99	Einsteinium	Es	$5f^{11}7s^2$	253	20.5 d
				254	1.5 y
100	Fermium	Fm	$5f^{12}7s^2$	**257** (α)	100.5 d
101	Mendelevium	Md	$5f^{13}7s^2$	256 (β⁺ and E.C.)	78 min
102	Nobelium	No	$5f^{14}7s^2$	259 (α, E.C.)	58 min
103	Lawrencium	Lr	$5f^{14}6d^17s^2$	262 (α)	3.6 h

31.4.1 History, abundance and occurrence

History

Uranium was "discovered" in 1789 by M. Klaproth in a specimen of pitchblende—it was named uranium after the recently discovered planet uranus (1781). However, doubts remained about the actual nature of the product isolated by Klaproth (it was actually an oxide of uranium). Elemental uranium was obtained sixty years later by E. Peligot (France) in 1841. Moissan first prepared an ingot of the metal by fusing it in his newly devised electric furnace (1896) and presented it to Henri Becquerel. Soon followed the discovery of radioactivity.

Thorium was named by Berzelius in 1815 in honour of Thor, the ancient Scandinavian god of thunder. But the name was given to a new element which was *supposed* to be present in a rare mineral analysed by him. Actually, the "oxide" of the new element claimed by Berzelius was yttrium phosphate. However, the name was reassigned to a new element discovered by him in 1828 in an ore from Norweigh; the ore was subsequently known as *thorite*. For long the element thorium remained known in the form of its oxide—the metallic form was prepared only in 1870's.

After successful discovery of radium and polonium in uranium minerals, the Curies suggested that urdnium ores could contain more unknown radioactive elements. Following this, Debierne discovered (1899) a new element from uranium ores and called it actinium (from the Greek for radiation). However, he actually isolated a complex mixture of radioactive substances including actinium—about 100000 times more active than uranium; he thought it to be an α-emitter. In fact, actinium is a mild β-emitter whose activity was difficult to detect at that time. The identity of actinium was confirmed during the next few years. In 1909, Cameron placed the symbol Ac into the third group of the periodic system, though the position of actinium in the periodic table was reliably established in 1913. However, the radiation emitted by actinium seemed to be so weak that some scientists even doubted if it emits at all. Only in 1935 were the β-rays emitted by actinium reliably detected.

A short-lived isotope of protactinium, $^{234}_{91}Pa$, was identified by Fajans and Göhring (1913) in the uranium-238 decay series. They named it brevium for its short life. The isotope ^{231}Pa, with a half-life of 32760 y, was later (1917) identified by Hahn and Meitner and independently by Soddy and Cranston in the U-235 series. Fajans showed noble gesture by giving up his claim for the discovery of the element but since the latter isotope had a long life, he suggested to change the name brevium to *proto*actinium (from the Greek for "preceding uranium") which was shortened to protactinium in 1949.

The elements neptunium to lawrencium were obtained by bombardment of uranium and other heavy nuclides with neutron and other accelerated ions (see section 14.4).

Abundance and occurrence

Only thorium and uranium occur naturally to any useful extent, the half lives of ^{232}Th, ^{235}U and ^{238}U being long enough for this purpose. Traces of other elements like ^{244}Pu, ^{231}Pa and ^{227}Ac also occur in traces as members of the decay series of uranium and thorium (section 13.1.5).

Thorium (8.1 ppm in the earth's crust) has an abundance comparable to that of boron. Uranium is somewhat less abundant—2.3 ppm but it is more abundant than many familiar metals like tin.

Thorium occurs in monazite sand (Chapter 30) which may contain up to 20 per cent ThO_2, the average being less than 10 per cent. Monazite occurs in India, South Africa, Brazil, Australia and Malaysia. A second important mineral is uranothorite, a mixed uranium-thorium silicate which accompanies pitchblende. It is found in Canada and though the thorium content is low (0.4% ThO_2), it is obtained as a co-product in the isolation of uranium.

The occurrence of monazite in India has been mentioned in connection with the rare earth elements. The known Indian reserves of ThO_2 are estimated to be around 5 million tonnes.

Naturally occurring uranium consists mainly of ^{238}U (99.3%) and ^{235}U (0.7%). The most important source of uranium is *pitchblende*, U_3O_8, found mainly in the Great Bear lake in Canada (30-62% U_3O_8), Katanga in East Africa (5-50% U_3O_8). *Carnotite*, $K(UO_2)\,VO_4\cdot\frac{3}{2}H_2O$ occurs in Siberia (Russia) and the USA.

India has some deposits of uranium containing rocks in Bihar (Jadugoda) and Rajasthan. The uranium content varies from 0.02-0.1 per cent. The proved uranium reserve of India is calculated around 30,000 tonnes and another 30,000 tonnes of "inferred resources" are available. Uranium-bearing sedimentary rocks found in Saharanpur, U.P. (6 km from Tibli) is rich in uranium content (0.6-0.7 per cent).

The monazite sand found in India also contains a small fraction, 0.2-0.4 percent, of uranium oxide. The uranium is obtained as a by-product in thorium extraction.

31.4.2 Isolation of the elements

Thorium

Thorium is extracted mainly from monazite sand which is attacked by digestion with concentrated alkali (section 31.1.2) followed by baking with dilute hydrochloric acid. The residue of thorium dioxide is dissolved in nitric acid and the thorium is extracted by tributyl phosphate, $(n\text{-BuO})_3PO$, diluted with kerosene.

Thorium metal is made by reduction of ThO_2/ThF_4 with calcium under argon atmosphere. Pure thorium may be prepared by decomposing ThI_4 on a hot filament (Van Arkel process).

Uranium

The extraction of uranium from pitchblende consists of the following main steps:

(i) Pitchblende, which has a high density, is concentrated through gravity separation by suspension in water. The concentrated ore is roasted to eliminate moisture, As, Sb etc. and decompose carbonates.

(ii) The roasted ore is digested with 1 : 1 H_2SO_4 in presence of MnO_2 (or $NaClO_3$) to ensure oxidation of all uranium to U(VI).

$$U_3O_8 + 6H_2SO_4 + \tfrac{1}{2}O_2 = 3H_2[UO_2(SO_4)_2] + 3H_2O$$

$PbSO_4$, $RaSO_4$ and silica are left insoluble; addition of a small amount of $BaCl_2$ aids precipitation of $RaSO_4$ with the $BaSO_4$. The solution contains U(VI) as the sulfato complex $[UO_2(SO_4)_2]^{2-}$, together with Cu(II), Mn(II) etc.

(iii) *Classically*, the solution containing U(VI) was boiled with excess sodium carbonate when sodium diuranate first precipitated dissolved to a carbonato complex :

$$2H_2[UO_2(SO_4)_2] + 5Na_2CO_3 = Na_2U_2O_7 + 4Na_2SO_4 + 5CO_2 + 2H_2O$$

$$Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O = 2Na_4[UO_2(CO_3)_3] + 6NaOH$$

Iron, aluminium, manganese etc. passed into the insoluble precipitate and were removed by filtration.

The filtrate was treated with HCl/H_2S to precipitate lead and copper. The filtrate, freed from H_2S, was treated by ammonia to precipitate ammonium diuranate (*"yellow cake"*)

$$2UO_2Cl_2 + 6NH_3 + 3H_2O = (NH_4)_2U_2O_7 + 4NH_4Cl$$

The conversion of yellow cake to fuel grade uranium is described at (v).

(iv) At present, the disulfatouranylate complex anion is concentrated on an anion exchange resin from which it is extracted with concentrated HNO_3. The uranyl nitrate so obtained is further purified by solvent extraction with tributyl phosphate (TBP) in kerosene (or hexane). Diethyl ether or methyl isobutyl ketone are also used for the solvent extraction.

The uranium is next stripped out of the organic phase by sulfuric acid and precipitated as "yellow cake" (mainly ammonium diuranate) by adding ammonia.

The yellow cake or ammonium diuranate obtained in the classical chemical procedure (step iii) is decomposed by heat to the oxide which is converted to uranium metal as outlined below.

(v) The "yellow cake", approximating $(NH_4)_2U_2O_7$, is heated at 300°C to yellow UO_3. This is reduced with hydrogen at 700°C to UO_2 (black). The dioxide is converted to UF_4 by heating with HF at 550°C.

$$(NH_4)_2U_2O_7 = 2UO_3 + 2NH_3 + H_2O\ ;\ UO_3 + H_2 = UO_2 + H_2O$$

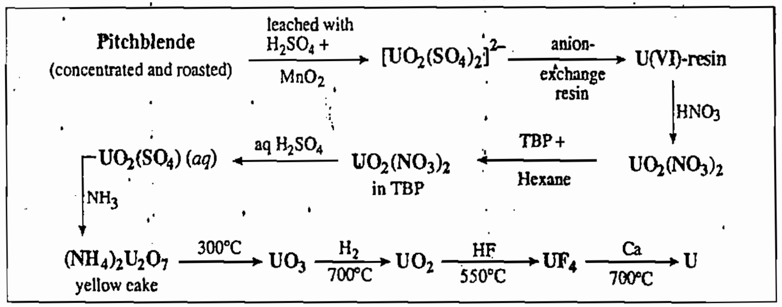
$$UO_2 + 4HF = UF_4 + 2H_2O\ ;\ UF_4 + 2Ca = U + 2CaF_2$$

Uranium metal is finally obtained by reducing UF_4 with calcium (or Mg), at about 700°C. The metal is separated from slag (CaF_2), allowed to solidify and remelted in vacuum to obtain pure uranium.

(vi) Alternatively, the uranyl nitrate enriched by solvent extraction is re-extracted with water and finally converted to UO_3 by heat :

$$2UO_2(NO_3)_2 = 2UO_3 + 4NO_2 + O_2$$

The remaining steps via UO_2 and UF_4 are same as above.



Enrichment of uranium for nuclear fuel

Thermonuclear reactors are based on U-235 (Chapter 14). So ordinary uranium, which contains mostly U-238, has to be enriched in U-235 for use as a nuclear fuel. This is achieved by multi-stage gas diffusion process of UF_6. Gas centrifuge process, also in multistage cascade system, is being used as an alternative in many plants. Another promising alternative depends on the appreciable difference in ionization energies of U-235 and U-238. A mixture containing both kinds of atoms in the vapour state are subjected to a tuned laser beam when only the U-235 atoms are ionized; the ions are subsequently collected on a negative electrode (*"Laser isotope separation"*).

Recovery of uranium from fission products

Nearly fifty per cent of the total reactor requirement of uranium comes from reprocessing of nuclear fuels. Since many of the fission products in a nuclear reactor strongly absorb neutrons, they have to be cleared from time to time for smooth running of the reactor. These fission products are next separated from the unchanged uranium in a number of stages.

The exact composition of the irradiated fuel mixture depends on the reactor details. In general, it consists mainly of high concentration of elements in the 2nd transition series together with Xe, Cs, Ba and the lanthanides (mass numbers 90-100 and 130-145); these are associated with the unchanged uranium and strongly radioactive products like Pu, Np, Am and Cm. All these are present in a very high-temperature system—some as alloys and some in their oxide phase. The main steps involved in the recovery of uranium from the mixture are as follows :

(i) Cooling by immersion in ponds for about 100 days.

(ii) Dissolution in 7*M* HNO_3.

(iii) Solvent extraction of UO_2^{2+} and Pu(IV) in TBP-hexane mixture; other fission products and Np, Am etc. are left in the aqueous phase.

(iv) Reduction of Pu(IV) with aqueous iron (II) sulfamate when the Pu(III) passes into the aqueous phase.

(v) The UO_2^{2+} is extracted into aqueous phase with 0.2 *M* HNO_3 and the solution evaporated to $UO_2(NO_3)_2.6H_2O$.

(vi) The nitrate is decomposed by heat to UO_3, followed by reduction to UO_2 and so on.

Isolation of other actinide elements

^{227}Ac and ^{231}Pa are both formed in the decay of ^{235}U and are isolated from Pitchblende (less than a milligram per ton). ^{227}Ac is now also made by (n, γ) reaction on ^{226}Ra when the resulting ^{227}Ra undergoes β-decay to ^{227}Ac.

Neptunium-239 and Plutonium-239 are both formed in nuclear reactors by (n, γ) reactions on U-238 (section 14.3.4). From the irradiated fuel elements, Pu(IV) and UO_2^{2+} are extracted into TBP-hexane layer (see above for recovery of U). The plutonium is reduced by iron (II) sulfamate to Pu(III) which passes into the aqueous phase. This is reoxidized to Pu(IV) and precipitated as the oxalate. This is decomposed thermally at 300°C to PuO_2 from which plutonium metal may be prepared by usual procedure.

Prolonged irradiation of ^{239}Pu in a pile successively forms small quantities of other isotopes of mass number 240, 241, 242 and 243. Of these, Pu-243 ($t_{\frac{1}{2}}$ = 5h) decays by β emission to Am-243 ($t_{\frac{1}{2}}$= 7650 y). ^{244}Am, obtained by further irradiation of ^{243}Am, decays to ^{244}Cm. Multiple neutron capture and beta-decay now produces milligram quantities of ^{249}Bk, ^{252}Cf, ^{253}Es and ^{254}Es and traces of ^{257}Fm. Later actinide elements are prepared by heavy ion bombardment reactions like

$$^{253}_{99}Es + {}^{4}_{2}He \longrightarrow {}^{256}_{101}Md + {}^{1}_{0}n$$

$$^{241}_{94}Pu + {}^{16}_{8}O \longrightarrow {}^{253}_{102}No + 4{}^{1}_{0}n$$

$$^{252}_{98}Cf + {}^{11}_{5}B \longrightarrow {}^{257}_{103}Lr + 6{}^{1}_{0}n$$

Since the probability of the desired nuclear reaction is low and only small quantities of the target material are available, the methods yield only trace amounts of the isotopes—sometimes a few atoms. Hence special detection techniques are necessary for these isotopes (see below). Last, but not the least, intense activity of the sample requires special handling procedures through remote control.

Identification of the heavier actinides is based on their decay properties which are compared to those predicted for the desired isotope. The irradiated target is dissolved in acid and the solution is passed through an ion-exchange column which is in fact only a few beads of the resin in view of the minute quantities involved. The actinides retained on the resin bed are now eluted with ammonium 2-hydroxybutyrate. The effect of actinide contraction (compare lanthanide contraction) causes the heavier actinide ions (An^{3+}) to be eluted first—the order of elution being exactly similar to that observed with the Ln^{3+} ions. The individual An^{3+} ions show distinct peaks of activity against the number of drops of eluants (Fig. 31.12).

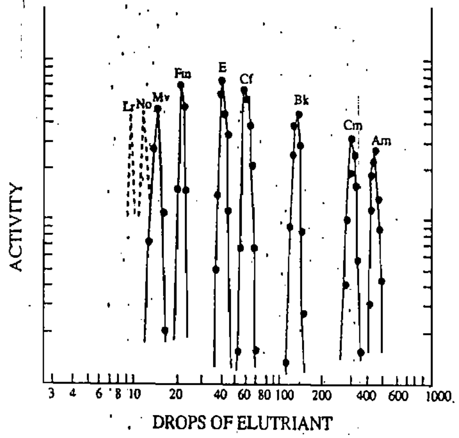


Fig. 31.12
Type of elution curve for the actinide ions (An^{3+}).

31.4.3 Uses

Non-fission applications of the actinide elements are few. Thorium dioxide is used in gas mantles together with CeO_2 and other lanthanum oxides; uranium compounds are used in colouring glass and ceramics. The main use of uranium, thorium and plutonium is as nuclear fuel. UO_2 now largely replaces uranium metal in reactors owing to its higher melting point and low chemical reactivity. Thorium-232 and uranium-238 may also be used in breeder reactors to produce U-233 and Pu-239 respectively (Chapter 14).

The inherent radioactivity of some actinides has been utilized in making light-weight power-source. Isotopes which emit only α-particles require relatively little shielding since the α-particles are easily stopped by surrounding atoms and their kinetic energies are converted to heat energies. Using suitable thermopiles, this heat energy can be converted to an uninterrupted power supply for a long time. Pu-238 is most useful for the purpose, produced as

$$^{237}_{93}Np\,(n, \gamma)\;{}^{238}_{93}Np \xrightarrow{\beta^-} {}^{238}_{94}Pu\ (t_{\frac{1}{2}} = 86y)$$

The energy output from Pu-238 is about 0.56 Wg^{-1} which can be converted to electricity with a Pb-Te thermocouple. Kilogrammes of PuO_2 have been used in Apollo and Galileo spacecrafts for this purpose. A small but significant use is in making heart "pace makers" which require only ~160 mg of Pu and lasts five times longer than conventional batteries. These are physiologically harmless as no γ-radiations are emitted. ^{241}Am ($t_{\frac{1}{2}}$ = 458 y) and ^{242}Cm ($t_{\frac{1}{2}}$ = 162 days) have also been used as power source and as a source of ionization in smoke detectors.

31.4.4 Properties of the elements

As simple substances, the elements are silvery-white metals of high density and relatively high melting and boiling points. Some properties of the elements are given in Table 31.7. (An = General symbol of an actinide).

TABLE 31.7

Some properties of the actinide elements

Element	Density g cm^{-3}	M.P. °C	B.P. °C	Radius of An^{3+} (C.N. = 6) pm	$E°$ An^{3+} – An
Ac	—	817	2470	111	–2.13
Th	11.7	1750	4780	—	–1.17
Pa	15.4	1572	4720	104	–1.49
U	19.1	1135	3820	103	–1.66
Np	20.5	644	3900	101	–1.79
Pu	19.9	640	3228	100	–2.00
Am	13.7	1176	2610	98	–2.07
Cm	13.5	1345	—	97	–2.06
Bk	14.8	1050	—	96	–1.97
Cf	—	900	—	95	–2.01
Es	—	860	—	—	–1.98
Fm	—	1530	—	—	–1.95
Md	—	828	—	—	–1.66
No	—	827	—	—	–1.78
Lr	—	1630	—	—	–2.06

The actinide elements are highly electropositive and very reactive, specially in the finely divided state. The first members crystallize in a variety of structures; from americium, the structures are based on hexagonal close packing. The metals burn in oxygen to form oxides corresponding to their stablest oxidation state, e.g.,

$$Th + O_2 = ThO_2 \qquad 4Pa + 5O_2 = 2Pa_2O_5$$

$$3U + 4O_2 = U_3O_8\,(UO_2.2UO_3) \qquad Pu + O_2 = PuO_2$$

The actinides react with most of the other non-metals on heating, including hydrogen. The hydrides are often non-stoichiometric, e.g., Th_4H_{15}; phases with idealized compositions MH_2 and between MH_3 to MH_4 are most common. The hydrides are very reactive and decompose on heating to yield the metal in a pure and finely divided state. The metals also form alloys with other metals.

Since the actinides stand much above hydrogen in the electrochemical series, they are oxidized by water and even more so by acids. With boiling water, they form a mixture of oxide and hydride. Most metals are only slightly attacked by concentrated nitric acid, probably owing to the formation of a protective oxide layer. Under normal conditions, the metals do not react with alkalis.

31.4.5 Chemical reactivity & trend

Though the general chemical behaviour of the actinides follows the trend set by the lanthanides, there are certain differences which may be assigned to the 5*f*-orbitals involved, or more precisely, to the smaller difference in energy between the 5*f* and 6*d*- orbitals than between the 4*f* and 5*d*. This is particularly true at the beginning of the series; later, however, the 5*f*-orbitals become more stable as shown by the ground state electron configuration of the elements. The An^{3+} and An^{4+} cations have the general 5f^n configuration. Poor shielding by the 5*f*-orbitals and consequent rise in effective nuclear charge along the series give rise to a decrease in ionic radii (*the actinide contraction*).

Oxidation States

Unlike the lanthanides, actinides offer a number of characteristic oxidation states, at least two oxidation states being found for most actinides. This may arise due to proximity in successive ionization energies, but for higher oxidation states, where covalent bonding is more likely, other factors need consideration. The 5*f*-orbitals have a longer spatial extension than the 4*f*-orbitals and can participate better in covalent bonding; at the same time, the energy differences between the 5*f*, 6*d* as well as 7*s* and 7*p*-orbitals may often be overcome by chemical binding energies, justifying their involvement in higher oxidation states. In fact, the electron spin resonance spectrum of UF_3 in a CaF_2 lattice shows fine structures corresponding to spin-interactions of U^{3+} and the F$^-$ ions, supporting longer spatial extension of the 5*f*-orbitals. The corresponding ion in the 4*f* series, Nd^{3+}, does not show such effect in NdF_3. The common oxidation states of actinium and the actinide ions are shown below (most stable states in bold).

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3			3	3	3	3	3	3	3	2	2	2	2	
	4	4	4	4	4	4	4	4	4	3	3	3		3
		5	5	5	5	5								
			6	6	6	6								
				7	7									

Several features of the distribution of oxidation states are noteworthy.

(i) For elements upto uranium, the most stable oxidation state involves all the valence electrons,

(ii) Neptunium also shows an oxidation state of +VII involving all the valence electrons, but the most stable state is Np(V). Np(VIII) is strongly oxidizing.

(iii) Plutonium and americium show their highest oxidation states +VII and +VI, but the most stable states are Pu(IV) and Am(III). The following elements have their stable oxidation state +III.

The overall pattern thus resembles the *d*-block elements where the valence electrons are fully utilized in the most stable oxidation state until the middle of the series after which it becomes oxidizing in nature [e.g., Mn(VII) and Os(VIII)]. The III-state becomes stabilized only in the later actinides.

(iv) The importance of the f^7 configuration is shown in Bk(IV) (compare Tb(IV)) which has some stability in spite of its oxidizing nature. However, Am(II), also f^7, has been reported only in a chloride melt, in contrast to Eu(II) which has a stable aqueous chemistry.

(v) The oxidation state II appears important for the later actinide elements and is more stable than for the corresponding lanthanides. Md(II) is moderately stable while No(II) requires strong oxidizing agents (e.g., MnO_4^- or Ce^{IV}) to be oxidized to No(III) and is relatively much more stable than the corresponding 4f^{14} ion Yb^{2+}.

The oxidation-state vs free-energy diagram of Th, U, Pu and Am are given in Figure 31.13.

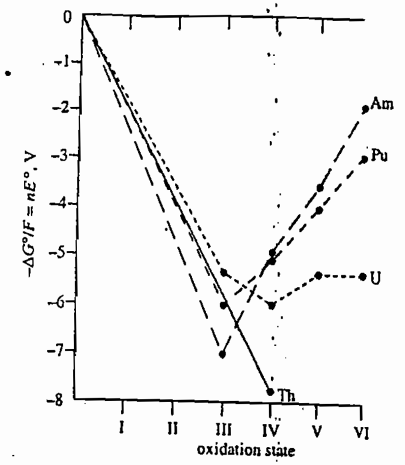


Fig. 31.13
Oxidation state vs free energy diagram of Th, U, Pu, Am.

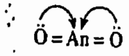
The dioxo ions, AnO_2^+ and AnO_2^{2+}

Many of the compounds of uranium and other actinides in the highest An(V) and An(VI) oxidation states involve AnO_2^+ and AnO_2^{2+} species known as *actinyls* that remain unchanged in various chemical reactions : UO_2^{2+} *uranyl*, NpO_2^{2+} *neptunyl* etc.

The AnO_2^+ and AnO_2^{2+} ions are all linear and their stability follows the order

$$UO_2^{2+} \sim NpO_2^{2+} > PuO_2^{2+} > NpO_2^+ > PuO_2^+ > AmO_2^+$$

The An—O bond essentially consits of one σ plus two π bonds formed by suitable combinations of *d*- and *f*-orbitals on the metal. Broadly speaking, two of the bonds are formed by two unpaired electrons each of the actinide and oxygen atoms, while the third is formed by an unshared pair of electron of the oxygen atom and a free orbital of the actinide atom :



$$\ddot{O}=An=\ddot{O}$$

Consideration of m.o.-s reveal that these are filled at UO_2^{2+}; in later actinyl ions successive electrons enter nonbonding orbitals. In lighter actinides, e.g., protactinium, the 5*f*-orbitals are not sufficiently lowered in energy to provide good σ-overlap with the oxygen 2*p*-orbital; the PaO_2^{2+} ion is thus nonexistent. The instability of UO_2^+ may be similarly related to the lower charge on uranium, which reduces the uranium oxygen overlap.

Compounds of the uranyl ion have been discussed later.

Magnetic and Spectral behaviour

The magnetic and spectral behaviours of the actinide elements are complicated. The 5*f*-5*f* transitions are weaker than 4*f*-4*f* transitions and the 5*f*-orbitals show significant crystal field stabilization effects. The bands observed are broader, more intense and more dependent on ligands than in the case of the lanthanide elements. The *LS* coupling scheme partially breaks owing to high spin-orbit coupling constants which are approximately twice those for the lanthanides. The magnetic properties of the actinide ions show an overall similarity to those of corresponding lanthanide ions but are somewhat lower due to quenching of orbital contribution by crystal field effects.

The actinide elements also form stable complexes with common ligands like the halide, nitrate, carbonate and oxalate ions as well as multidentate chelating agents. Cyano and carbonyl complexes are not formed. Many organometallic compounds are known, specially those formed by $C_5H_5^-$ and its derivatives (also $C_8H_8^{2-}$). $(C_5Me_5)_2UCl_2$ catalyzes the polymerization of ethylene.

31.5 SOME INDIVIDUAL ACTINIDES

31.5.1 Thorium

Thorium resembles hafnium in its stable IV oxidation state. ThO_2 is obtained by igniting the precipitate of $Th(OH)_4$ obtained from solutions of Th^{4+} at a pH of about 6. Basic in nature, $Th(OH)_4$ is insoluble in alkali solution; however, it dissolves in alkali carbonates owing to the formation of carbonato complex, e.g., $M_2^I[Th(CO_3)_3]$. It also absorbs CO_2 from air. The Th^{4+} (*aq*) ion is present in dilute aqueous solutions in acid medium—the large size of the ion (94 pm) provides a low enough charge density to allow its existence without causing appreciable polarization. Hydrolysis occurs in concentrated solutions and at higher pH. ThO_2 has the CaF_2 structure and is also obtained by heating either the metal in oxygen or its oxysalts. The oxide is highly stable and refractory in nature (m.p. 3050°C)—it is soluble only in HF-HNO_3 mixtures.

E° for Th^{4+}-Th is −1.9V, consistent with the high stability of IV state. In fact, there is no evidence for any other oxidation state in aqueous media.

The tetrahalides ThX_4 may be prepared by heating ThO_2 in HX at 600°C, by direct synthesis, or by the action of halogen on ThO_2 and carbon. All the tetrahalides are colourless crystalline solids. ThF_4 (m.p. 1110°C) is ionic, involatile and insoluble in water. Other tetrahalides sublime in vacuum above 500°C and form oxohalides $ThOX_2$ with water vapour. $ThCl_4$ is soluble in water. It conducts electricity in the fused state.

The most common oxo-acid salt is the nitrate which crystallizes as $Th(NO_3)_4.5H_2O$. It is soluble in water as well as alcohol. Like the fluoride, the oxalate and phosphate salts are insoluble and may be precipitated from strongly acidic solution.

Thorium(IV) tends to form complexes with high coordination numbers. $Th(acac)_4$, readily formed in aqueous solution, is a non-electrolyte volatile complex soluble in organic solvents; it has a square antiprismatic structure. In $Th(NO_3)_4.5H_2O$, three water molecules are coordinated to thorium; with four didentate nitrate groups, this makes a coordination number of 11. $[Th(NO_3)_6]^{2-}$ is icosahedral in the magnesium salt. Octahedral $ThCl_6^{2-}$ is readily formed by $ThCl_4$ from aqueous solution but ThF_4 does not dissolve in alkali metal fluoride solutions. Complex fluorides may, however, be made by heating the appropriate fluorides. $(NH_4)_5ThF_9$ has the dodecahedral ThF_8^{4-} ion together with extra F^- ions; $(NH_4)_3ThF_7$ and $(NH_4)_4ThF_8$ both contain ThF_9 units joined into infinite chains of $[ThF_7]_n^{3n-}$ anions. Eight-coordination through sulfur is found in the complex $Th(S_2CNEt_2)_4$.

ThI_2 and ThI_3 may be prepared by heating ThI_4 with thorium metal. ThI_3 is also formed by heating stoichiometric amounts of iodine and thorium in a vacuum at 550°C. ThI_2 may be obtained by electrochemical oxidation of thorium in a solution of iodine in acetonitrile. Both of these compounds react with water evolving H_2 and forming Th(IV) in solution. The compounds are metallic in character.

Thorium is precipitated as $Th(OH)_4$ in group IIIA of conventional group separation. The precipitate, insoluble in excess alkali, dissolves in dilute HCl. From this solution, thorium may be precipitated as the oxalate, together with cerium(III) oxalate. Only thorium oxalate dissolves in (i) a large excess of hot concentrated ammonium oxalate or (ii) ammonium acetate and acetic acid.

Thorium may also be estimated by precipitation of thorium oxalate (~ 3.5% HCl) followed by ignition to ThO_2. Sebacic acid precipitates thorium quantitatively from a faintly acid medum; the precipitate is also ignited to ThO_2 and weighed.

31.5.2 Protactinium

Pa-231 may be isolated from the decay products of U-235 in pitchblende through a lengthy process, ultimately in the form of Pa_2O_5. The oxide readily dissolves in acids only in presence of complexing anions like fluoride, oxalate, citrate etc.

PaF_5 may be prepared by reacting Pa_2O_5 with BrF_3. With HF, Pa_2O_5 gives a hydrated fluoride which cannot be dehydrated without decomposition. The anhydrous fluoride may be prepared by reacting fluorine with PaF_4 which, in turn, is obtained by heating Pa_2O_5 with HF and H_2 at 400°C.

$PaCl_5$ may be prepared by reacting Pa_2O_5 with $SOCl_2$. Reduction of $PaCl_5$ with H_2 at 400°C gives $PaCl_4$. PaI_5, prepared by heating Pa_2O_5 with AlI_3 at 350°C, may be reduced by Al at 400°C to PaI_4. This decomposes to PaI_3 on heating.

$E°$ for Pa(V)-Pa(IV) is about –0.1V and the reduction may be carried out by zinc, but the solution is rapidly oxidized by air. The absorption spectrum of an aqueous solution of $PaCl_4$ is similar to that of Ce^{3+}, suggesting the presence of a single *f*-electron.

31.5.3 Uranium

The isolation of uranium has been discussed before.

Uranium shows mainly four oxidation states — III, IV, V and VI. The VI state is most stable.

Oxides

Uranium forms three main oxides—UO_3, UO_2 and U_3O_8. The yellow trioxide may be obtained by heating uranyl nitrate, hydroxide or peroxide to ~350°C. "Ammonium diuranate" also produces UO_3 when heated below 580°C.

Green-black U_3O_8 is formed on heating UO_3 to 700°C. UO_2 (black) is formed by the reduction of UO_3 with H_2 (<600°C) or CO (350°C). It is often non-stoichiometric :

$$3UO_3 = U_3O_8 + \tfrac{1}{2}O_2; \quad UO_3 + CO = UO_2 + CO_2$$

Two other less familiar oxides are U_3O_7 and U_4O_9.

All the oxides dissolve in nitric acid to form solutions containing the uranyl ion, UO_2^{2+}.

Fusion of uranium oxides with alkali and alkaline earth metal carbonates produces uranates and diuranates :

$$Na_2CO_3 + UO_3 = Na_2UO_4 + CO_2$$

$$Na_2CO_3 + 2UO_3 = Na_2U_2O_7 + CO_2$$

However, the discrete UO_4^{2-} ion does not exist as such—the compounds contain distorted octahedral UO_6 units linked to one another.

Sodium diuranate, $Na_2U_2O_7.6H_2O$ is obtained as a yellow precipitate by adding sodium hydroxide solution to a solution of uranyl salt. It is soluble in ammonium carbonate :

$$2UO_2(NO_3)_2 + 6NaOH = Na_2U_2O_7 + 4NaNO_3 + 3H_2O$$

It is used for painting procelain (*uranium yellow*) and in making fluorescent glass.

Ammonium diurante, obtained by addition of aqueous ammonia to a solution of uranyl nitrate, is actually a hydrated uranyl hydroxide containing NH_4^+. It is soluble in ammonium carbonate solution forming a carbonate complex. On heating below 580°C, $(NH_4)_2U_2O_7$ decomposes to UO_3; U_3O_8 is formed above this temperature.

Halides

Uranium forms a number of stable halides in different oxidation states (Table 31.8).

TABLE 31.8
Halides of uranium

UF_6	UF_5	UF_4	UF_3
colorless	pale blue-white	green	green
UCl_6	U_2Cl_{10}	UCl_4	UCl_3
green	red	green	red
		UBr_4	UBr_3
		brown	red
		UI_4	UI_3
		black	black

Uranium hexafluoride, UF_6, is a volatile solid that sublimes at 56°C and has been used in the separation of U-isotopes by gaseous diffusion. It may be prepared by heating UO_3 or UO_2 or UF_4 with F_2 or ClF_3.

$$UO_2 + 4HF = UF_4 + 2H_2O; \; 3UF_4 + 2ClF_3 = 3UF_6 + Cl_2$$

It is a strong fluorinating agent, converting, for example, CS_2 to SF_4. UF_6 gets immediately hydrolyzed by water and combines with alkali metal fluorides to give complex species like UF_7^- and UF_8^{2-}. The UF_6 molecules (and other hexahalides) are octahedral.

Uranium pentafluoride, UF_5, is a pale blue-white solid formed by the action of F_2 on UF_4 (100°C) or anhydrous HF on UCl_5. Reduction of UF_6 may also be achieved by PF_3 or Me_3SiX (X = Cl, Br) :

$$UF_6 + Me_3SiX = Me_3SiF + \tfrac{1}{2}X_2 + UF_5$$

On heating, it decomposes to UF_4 and UF_6. It has two crystalline forms (α and β) both of which involve polymeric structure. The molten halide conducts electricity. Alkali metal fluorides (MF) combine with UF_5 to form MUF_6. UF_5 also dissolves in donor solvents (L) like DMF, DMSO and CH_3CN to form salt-like adducts $[UF_4L_n][UF_6]$, $n = 3, 4$.

Uranium tetrafluoride, UF_4, forms green crystals which may be obtained by heating UO_2 in HF (or $C_2Cl_4F_2$) at 550°C or by reducing UF_6 with H_2 at ordinary temperature. It is also obtained by heating NH_4UF_5 at 500°C. UF_4 is sparingly soluble in water and has an essentially ionic structure with a high melting point, 1036°C. Double fluorides like $NaUF_5$, Na_3UF_7 and KU_2F_9 are known.

Uranium trifluoride, UF_3 is a high melting nonvolatile solid obtained by reduction of UF_4 with H_2. It is insoluble in water or dilute acids, comparable to the lanthanide trifluorides.

Uranium hexachloride, UCl_6, forms as dark green-black crystals by chlorination of UO_3 or U_3O_8 by C_2Cl_6 below 200°C. Thermal decomposition of UCl_5 also produces UCl_5. The solid sublimes in vacuum and melts at 177°C with decompostion. It is vigorously hydrolyzed by water to UO_2Cl_2.

Uranium pentachloride, U_2Cl_{10}, is obtained by the action of Cl_2 on UCl_4 at 500°C. The deep red deliquescent crystals readily lose chlorine even at room temperature and decompose to UCl_4 and UCl_6 on heating. It is dimeric with two UCl_6 octahedra sharing an edge with two Cl bridges. Polymeric forms are also known. With Al_2Cl_6 it forms a volatile complex $UAlCl_8$.

Uranium tetrachloride, UCl_4, is obtained by chlorinating UO_3 with CCl_4 at 115°C or by heating UO_2 with CCl_4 at 500°C. UO_3 (or, U_3O_8) may also be chlorinated by C_2Cl_6 at 210°C to UCl_4. The dark green deliquescent crystals (mp 590°C) dissolve in water with extensive hydrolysis. These also dissolve in alcohol and benzene and form various adducts with *O*- and *N*- donor ligands, for example $UCl_4(MeCN)_4$ and $[UCl_2(DMSO)_6][UCl_6]$. On heating in oxygen at 350°C, UCl_4 forms UO_2Cl_2.

Uranium trichloride, UCl_3, may be obtained by heating UH_3 in HCl at 250°C or by reduction of UCl_4 with hydrogen. It forms purple solution in water from which dark red hygroscopic needles may be crystallized. The solution evolves hydrogen and quickly turns to the green colour characteristic of U(IV). UCl_3 crystallizes with nine-coordinated U(III)—three chloride ions are in the same plane as the U, while three are above it and three below. The UCl_4^- ion is also known, but it is readily oxidized.

Halogeno complexes, particularly with fluoride and chloride, are known for all uranium halides. These are usually made by reacting the uranium halides with alkali metal halides in the molten state or in solvent such as $SOCl_2$.

The oxohalides UO_2X_2 are stable, water-soluble compounds. These may be prepared from the halides or oxides :

$$UCl_4 + O_2 \longrightarrow UO_2Cl_2 + Cl_2 \quad (350°C)$$
$$UO_3 + 2HF \longrightarrow UO_2F_2 + H_2O \quad (400°C)$$

Aqueous solution chemistry

The main chemistry of uranium in aqueous solution concerns the UO_2^{2+} ion, though other ions in lower oxidation states are also known. The major species in aqueous solution are summarized below.

Ion	Preparation	Characteristic
U^{3+}	UO_2^{2+} + Zn/Hg	Oxidized by H_2O (slow) and air (rapid) to U^{4+}.
U^{4+} (green)	U^{3+} + air/O_2	Stable; slowly oxidized by air to UO_2^{2+}.
UO_2^+ (transient)	—	Disproportionates to U^{4+} and UO_2^{2+}.
UO_2^{2+} (yellow-green)	U^{4+} + HNO_3	Very stable.

Formal reduction potentials at 25°C in 1*M* acid solution are shown below.

$$\underbrace{UO_2^{2+} \xrightarrow{0.17V} UO_2^{+} \xrightarrow{0.38V} U^{4+}}_{0.27V} \xrightarrow{-0.52V} U^{3+} \xrightarrow{-1.66V} U$$

[Sec.31.5.3
Aqueous solution chemistry]

The diagram clearly indicates the stability of the uranyl ion and disproportionation of UO_2^+ to UO_2^{2+} and U^{4+} :

$$2UO_2^+ + 2H^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 2H_2O$$

The changes UO_2^{2+} to UO_2^+ and U^{4+} to U^{3+} (and the reverse processes) involve only the transfer of an electron and takes place readily; but the change UO_2^+ to U^{4+} (and its reverse) involves a structural reorganization and is slow and often irreversible.

The uranyl ion also undergoes hydrolysis in solution forming species like $U_2O_5^{2+}$ and $U_3O_8^{2+}$:

$$2UO_2^{2+} + H_2O \rightleftharpoons U_2O_5^{2+} + 2H^+$$
$$3UO_2^{2+} + 2H_2O \rightleftharpoons U_3O_8^{2+} + 4H^+$$

These exist as hydroxy-bridged polymers like $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$. The uranyl ion forms several salts, the most common being the nitrate $UO_2(NO_3)_2$, nH_2O (n = 2, 3 or 6). It also forms a series of stable complexes in which the affinity for fluoride is appreciably higher than with other halides, showing class-a character of the cation. Complexes are also known with many *O*-donor ligands like SO_4^{2-}, CO_3^{2-}, NO_3^- and carboxylates.

Uranyl Nitrate, $UO_2(NO_3)_2$ is formed when UO_3 or any other oxide of U is dissolved in nitric acid. The solution deposits lemon-yellow crystals of the hexahydrate—the deliquescent crystals have a yellow green fluorescene. It is freely soluble in water, alcohol and ether. Crystals with three and two molecules of water may be obtained from concentrated solution and fuming nitric acid respectively.

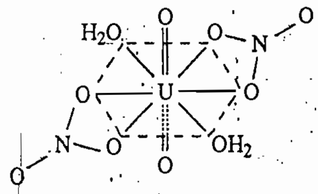


Fig. 31.14
The structure of $[UO_2(NO_3)_2, 2H_2O].4H_2O$.
The bidentate nitrate groups and the water molecules occur at a plane perpendicular to the linear O—U—O axis (C.N. of U = 8)

U = O : 176 pm   U—OH$_2$: 240 pm

U—ONO$_2$: 252 pm

The anhydrous nitrate may be prepared using N_2O_4 (*l*) in CH_3CN :

$$U + N_2O_4\,(l) \longrightarrow UO_2(NO_3)_2.N_2O_4.2CH_3CN.$$

On heating to 163°C, the anhydrous nitrate is left.

Uranyl sulfate, $UO_2SO_4.3H_2O$ may be prepared by evaporating uranyl nitrate to white fumes with concentrated H_2SO_4 followed by leaching with water. Yellowish green crystals may be isolated from the concentrated solution. Conductivity measurements suggest that the concentrated solution contains the complex ion $[UO_2(SO_4)_2]^{2-}$ ion.

Uranyl chloride, UO_2Cl_2 may be prepared anhydrous by the action of Cl_2 on UO_2 (500°C) or of O_2 on UCl_4 (300°C).

$$UO_2 + Cl_2 = UO_2Cl_2 \qquad UCl_4 + O_2 = UO_2Cl_2 + Cl_2$$

A solution of UO_3 in HCl yields yellow green crystals of $UO_2Cl_2.3H_2O$.

Uranyl carbonate, UO_2CO_3 is present in the mineral *rutherfordite* (East Africa). It may be precipitated from solutions containing the uranyl ion with ammonium (or sodium) carbonate. The precipitate dissolves in excess of the reagent forming a yellow solution containing $(NH_4)_4[UO_2(CO_3)_3]$ which may be crystallized as the dihydrate. Prolonged boiling with water decomposes it to ammonium diuranate, $(NH_4)_2U_2O_7$.

Uranyl sulfide, UO_2S may be obtained as a brown precipitate by adding ammonium sulfide to uranyl salt solution. The precipitate is soluble in dilute acids, including acetic acid.

Uranyl ferrocyanide, $[UO_2)_2[Fe(CN)_6]$ is formed as a brown precipitate by potassium ferrocyanide on uranyl nitrate solution. The precipitate turns yellow on adding caustic soda solution owing to the formation of sodium diuranate.

Uranyl acetate, $UO_2(CH_3COO)_2.2H_2O$ may be prepared by dissolving UO_3 in acetic acid and crystallizing. It has a strong tendency to form the anionic complex $[UO_2(CH_3COO)_3]^-$ by combining with other acetates. Zinc uranyl acetate, prepared by dissolving zinc acetate and uranyl acetate in acetic acid, forms faint yellow crystalline precipitate of sodium zinc uranyl acetate $NaZn[UO_2(OAc)_3]_3.9H_2O$. Magnesium uranyl acetate gives a similar precipitate. Both are used in the detection of sodium.

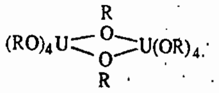
Addition of H_2O_2 to a solution of uranyl ion gives a light yellow precipitate which may be formulated as uranyl peroxide dihydrate, UO_2^{2+} (O_2^{2-}) $(H_2O)_2$. In presence of NaOH, H_2O_2 forms the stable salt $Na_4[UO_2(O_2)_3]$.

Uranium(V) may be stabilized in solution against disproportionation through complex formation with the fluoride ion, e.g., UF_6^- can be precipitated from aqueous HF solutions. UF_7^{2-} and UF_8^{3-} ions are formed in non-aqueous medium. In Na_3UF_8 the F^- ions occur at the corners of nearly perfect cube. The alkoxides $U(OR)_5$ are also stable thermally and towards disproportionation.

$$UCl_4 + 4NaOR \longrightarrow U(OR)_4 \xrightarrow{O_2/NaOR} U(OR)_5$$

$$UCl_5 + 5ROH + 5NH_3 \longrightarrow U(OR)_5 + 5NH_4Cl$$

The alkoxides have a dimeric structure with bridging OR groups (31-III)



$$(RO)_4U\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\lesssim_{O}^{O}\gtrsim}}U(OR)_4.$$

31-III

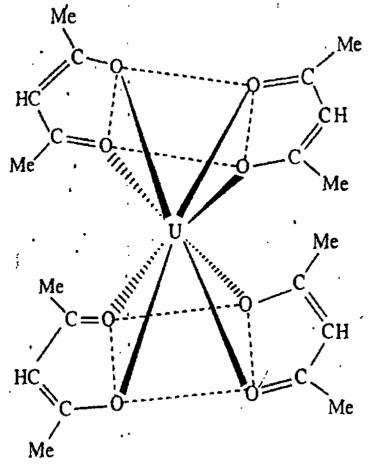
Uranium(IV) is rapidly oxidized in solution to UO_2^{2+} by Cr(VI), Ce(IV) or Mn(VII) but oxidation by air is slow. Salts of U(IV) with fluoride, phosphate and iodate may be precipitated from acidic medium. $U(SO_4)_2$ is formed when a solution of UO_3 (or U_3O_8) in concentrated H_2SO_4 is mixed with alcohol and then exposed to sunlight; dark green crystals of $U(SO_4)_2.4H_2O$ separate slowly which are soluble in water. Other hydrates are also known. $U(C_2O_4)_2$ is also obtained in dark green crystals from a solution obtained by reduction of U(VI) by oxalic acid. It is insoluble in water and dilute acids but dissolves in solutions of alkali metal salts forming the complex anion $[U(C_2O_4]^{4-}$. Other complex species like $[U(CO_3)_5]^{6-}$, $[U(NO_3)_6]^{2-}$ and a series of fluoro complexes UF_5^-, UF_6^{2-}, UF_7^{3-}, UF_8^{4-} and $U_6F_{31}^{7-}$ are also known.

$U(BH_4)_4$ is prepared by the reaction

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2AlF_2.BH_4$$

It is a thermally stable polymeric solid which decomposes on heating in solution to $U(BH_4)_3$. Several ether adducts are known, e.g., $U(BH_4)_4$ $(THF)_2$ (monomeric) and $[U(BH_4)_4(Et_2O)]_\infty$. $U(BH_4)_3$ also forms numerous adducts like $U(BH_4)_3(THF)_3$.

The $U(BH_4)_4$ unit is tetrahedral having all BH_4^- as η^3. In the helical polymer, each U is surrounded by six BH_4^- ions, two cis terminal groups attached by three H and four bridging groups attached by two H.



31-IV

Like Th(IV), U(IV) forms the acetylacetone (acac) complex $U(acac)_4$ which is precipitated by the ligand from aqueous solution by adding alkali. In this the uranium is eight-coordinate in a square antiprism environment (31-IV).

The square antiprism structure may be visualized by imagining the top face of a cube twisted through 45° relative to the bottom face.

The U^{3+} (*aq*) ion is prepared by reduction of UO_2^{2+} (zinc amalgam or electrolytically). A solution containing the ion in 1 *M* HCl is stable but in stronger acid medium it gets readily oxidized. As expected, U^{3+} is a strong reducing agent. Crystal hydrates $UF_3.H_2O$ and $U_2(SO_4)_3.5H_2O$ have been isolated. The hydrate $(NH_4)U(SO_4)_2.(H_2O)_4$ contains nine-coordinate U (III) and can be handled in air.

Uranium is also included in group IIIA of qualitative analysis where it is precipitated as ammonium diuranate. The precipitate is soluble in ammonium carbonate solution (aluminium hydroxide is insoluble). The solution is acidified and treated with potassium ferrocyanide solution. A brown precipitate of $(UO_2)_2[Fe(CN)_6]$ is formed which turns yellow on the addition of aqueous NaOH.

Uranium(VI) salts may be reduced to green U(IV) by zinc and hydrochloric acid; the U(IV) may be titrated with permanganate

$$2MnO_4^- + 5U^{4+} + 2H_2O \longrightarrow 2Mn^{2+} + 5UO_2^{2+} + 4H^+$$

Uranyl salts may be precipitated as $(NH_4)_2U_2O_7$ or oxinate and subsequently weighed as U_3O_8.

31.5.4 Neptunium, plutonium, americium

The elements closely resemble uranium in their reactivity and combine with most elements. Their hydrides, stoichiometric AnH_2 and non-stoichiometric up to $AnH_{2.7}$, however, resemble the lanthanum hydrides more than uranium hydrides.

Like uranium, these elements also show the four main oxidation states III, IV, V and VI but a VII state exists in strongly alkaline medium which has been isolated as Li_5AnO_6 for Np and Pu. This state may be obtained by strong oxidizing agents like ozone, XeO_3 or periodate in strongly alkaline medium.

The most stable oxides of the elements are the dioxides AnO_2 which are formed on heating the hydroxides or nitrates of the metals in any oxidation state. No anhydrous trioxides AnO_3 are known, but hydrated PuO_3 and NpO_3 may be obtained by the action of ozone on respective $An(OH)_4$. Li_5AnO_6 (An = Np, Pu) is obtained by heating the AnO_2 with Li_2O in oxygen at 400°C.

Volatile hexafluorides are formed only by Np and Pu but these compounds decompose readily into fluorine and NpF_5/PuF_4. Thus, there is a steady decrease in the stability of the higher oxidation state—americium forming only AmF_3 and AmF_4. All the tri- and tetrafluorides may be precipitated from aqueous solutions. The highest chlorides are $NpCl_4$, $PuCl_3$ and $AmCl_3$. Only americium forms dihalides AmX_2 (X = Cl, Br, I). These ionic halides may be prepared by heating americium with appropriate HgX_2. Plutonium forms $Cs_2[PuCl_6]$ when $PuCl_3$ is warmed with chlorine (50°C) in presence of CsCl.

Like uranium, the III, IV, V and VI oxidation states of the metals in solution are present as An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+} ions and their hydrolytic tendencies are also similar. The VII state of Np and Pu are unstable in aqueous acids—they decompose with liberation of O_2. The oxidation state VI also becomes increasingly unstable and oxidizing from UO_2^{2+} to AmO_2^{2+}; AmO_2^{2+} is a strong oxidizing agent comparable to MnO_4^-. The oxidation state V, present as AnO_2^+, is most stable for neptunium. NpO_2^+, unlike UO_2^+, is stable with respect to disproportionation. PuO_2^+ is just unstable with respect to such disproportionation into PuO_2^{2+} and Pu^{4+}. Both PuO_2^+ and AmO_2^+ are more stable than UO_2^+. However, in hydrogen fluoride medium instead of water, $CsUF_6$ dissolves unchanged while $CsNpF_6$ disproportionates to NpF_4 and NpF_6. For americium, all oxidation states above III are oxidizing. AmO_2^+ and Am^{4+} are also thermodynamically unstable. Am(IV) may exist in aqueous solution only as AmF_6^{2-} (AmO_2 + HF).

31.5.5 Curium to lawrencium

Except curium, which is available in gram quantities, the other elements are available only in traces. These are usually studied by carrier methods, that is, following the radiation characteristic of the element in the course of a chemical reaction. For example, when a solution of An^{3+} and Ln^{3+} is reduced with sodium amalgam and extracted, mendelevium is found to accompany Eu and not La. Since we know that Eu^{3+} is reduced to Eu^{2+}, we conclude that Md^{3+} is also reduced to Md^{2+}. The chemistry of lawrencium is based on the study of experiments involving only a few atoms.

For the elements curium to einsteinium, several compounds have been characterized in different oxidation states :

Halides	CmF_4	CmX_3	
	BkF_4	BkX_3	$CfBr_2$
	CfF_4	CfX_3	CfI_2
		EsX_3 (F, Cl, Br, I)	EsX_2 (Cl, Br, I)
Oxides and Hydroxides	CmO_2	Cm_2O_3	$Cm(OH)_3$
	BkO_2	Bk_2O_3	$Bk(OH)_3$
	CfO_2	Cf_2O_3	$Cf(OH)_3$
		Es_2O_3	
Oxohalides	CmOX (F, Cl, Br, I)		
	BkOX (Cl, Br, I)		
	CfOX (F, Cl, Br, I)		
	EsOX (Cl, Br, I)		

The III state is the most stable state for these actinides, Cm(III) showing magnetic properties corresponding to f^7 configuration. It resembles gadolinium in its behaviour, showing strong resistance toward oxidation to Cm(IV). However, solid Cm(IV) oxides and fluorides are known, as shown above. Bk(III) may be oxidized by bromate to Bk(IV) in solution which is strongly oxidizing. Cf(IV) is unstable and there appears to be no evidence of an An(IV) species in solution for later actinides.

The dipositive state becomes important for the later actinides. Their stabilities towards oxidation is $Cf^{2+} < Es^{2+} < Fm^{2+} < Md^{2+} << No^{2+}$. The II state appears to be the most stable state of nobelium in solution. Lawrencium appears to exist only in the tripositive state corresponding to the f^{14} configuration.

SUMMARY

Introduction. The *f*-block elements form two distinct series characterized by the filling of 4*f* and 5*f* orbitals. The first series of elements, together with yttrium and lanthanum are commonly referred to as the rare earth elements; the elements La—Lu are called lanthanides. They resemble one another closely in their chemistry. The 5*f*-series of elements (Th—Lr) are known as actinides as they appear after actinium. They differ appreciably in their individual chemistry.

Lanthanides : Most lanthanides occur in Monazite sand which is a mixed phosphate of La (~15%), Ce (~30%), Th (~8%), U (~0.3%) and other rare earth elements (values in parenthesis refer to respective common oxides). The mineral is usually digested by concentrated NaOH. The hydrous oxides except ThO_2 dissolve in dilute HCl. The solution is subjected to ion-exchange or solvent extraction. In the ion exchange method the lanthanide ions (Ln^{3+} in general) are first arrested on a resin bed and then eluted with a complexing agent like triammonium EDTA or citric acid-ammonium citrate. The heavier lanthanide ions form stronger complex with the eluting agent (smaller size) and are eluted first.

The lanthanide elements (Ln) are all silvery white soft metals. They are highly electropositive and reactive, burning in air to Ln_2O_3 and LnN (cerium gives CeO_2). The elements normally form trihalides with the halogens but Ce and Tb give CeF_4/TbF_4 respectively.

The common principal oxidation state of all the lanthanides is III. This appears to be a consequence of greater stabilization of 4*f*-orbitals in comparison to 5*d* or 6*s*, so that these later electrons hardly take part in valence. Ce and Pr (and Tb, Dy) show in addition oxidation state IV. Eu, Sm, Yb and Tm show the additional oxidation state II.

The Ln^{3+} ions show much less tendency toward complex formation compared to the *d*-block elements. Presumably their larger size and lower electronegativity do not promote covalent bond formation. The deeply buried *f*-orbitals with their diffuse nature also seem to be reluctant to complex formation. In heavier REE-s, participation by *f*-orbitals give rise to high coordination numbers. Non-availability of electrons for π-bonding does not favour the formation of complexes with π-acid ligands like CO.

The Ln^{3+} ions are coloured in aqueous solution except for f^0, f^1, f^7 and f^{14} configurations. The colours are less intense since relaxation of selection rule for *f*-*f* transitions is less compared to relaxation for *d*-*d* transitions; in case of Ln^{3+}, crystal field effects are much less pronounced with the deep-seated 4*f* orbitals. Due to this deep-seated nature, the 4*f*-orbitals are also better shielded from environmental perturbation and hence the bands arising from *f*-*f* transitions are very sharp. Spin-orbit coupling for the lanthanides also becomes more important than crystal field effects. The spectra consist of larger number of peaks compared to *d*-series elements.

The deep seated nature of the *f*-orbitals also gives rise to less quenching of orbital contributions to magnetic moments; the values are mostly in good agreement with *L*-*S* coupling scheme rather than the spin-only values.

Actinides : All the actinide elements are radioactive but the most abundant isotopes of thorium, ^{232}Th, and uranium, ^{238}U, have half-lives of the order of 10^{10} years. Except actinium, thorium, protactinium and uranium, all elements in the series are synthetic.

Only thorium and uranium occur naturally to any useful extent. Thorium occurs in monazite sand while the principal ore of uranium is pitchblende. The metals are extracted in large quantities through a series of complicated steps, U-235 for nuclear fuel is enriched by gas diffusion of UF_6 or by selective laser ionization of U-235.

Many of the lighter actinides are obtained as decay products of U-235 or by (*n*, γ) reaction on U-238. The later actinides are prepared in extremely small quantities by heavy ion bombardment on lighter actinides. These are arrested on an ion exchange resin, and selectively eluted. The heavier (and smaller due to actinide contraction) actinides are eluted first.

The actinide elements are highly electropositive and chemically very reactive. Though the general chemical behaviour follows the trend set by the lanthanides, certain differences arise due to smaller energy difference between *5f* and *6d* than between *4f* and *5d*. Thus, the actinides offer a number of characteristic oxidation states, at least two for most actinides. The *5f* orbitals have a longer spatial extension than the *4f* orbitals and can participate better in covalent bonding. The higher oxidation states may also involve *6d*, *7s* and *7p* orbitals due to proximity in energy. The most stable oxidation states for uranium are VI, followed by IV. Thorium is most stable as Th(IV).

The actinides form AnO_2^+ and AnO_2^{2+} ions, the uranyl ion UO_2^{2+} being most stable (O = U = O).

The spectra arising from *5f*-*5f* transitions are weaker than *4f*-*4f* transitions and the *5f*-orbitals show significant crystal field stabilization effects. The bands observed are broader, more intense and more dependent on ligands than with the lanthanides. The magnetic properties of the actinide ions show an overall similarity to those of the corresponding lanthanide ions but are somewhat lower due to quenching of orbital contribution by crystal field effects.

EXERCISE

1. *What is "lanthanide contraction"?*
2. *"The rare earth elements are not all really as rare as they are thought to be"— justify with suitable examples.*

   Mention a few important applications of rare earth elements.
3. *(a) Justify the position of the lanthanides in the periodic table.*
   - *(b) Discuss their relationship to the Group 13(III) elements B-Tl.*
   - *(c) Why are scandium and yttrium usually considered along with the lanthanide elements?*
4. *(a) "The lanthanide elements show the common stable oxidation state of +3"—comment.*
   - *(b) Which lanthanide elements show departure from the usual +3 oxidation state? Give electron configurations of these ions.*
5. *What are the main differences in the spectral and magnetic behaviours among (i) the elements of 4f and 5f series; (ii) the elements of f-block and d-block?*
6. *Comment on the following :*
   - *(a) EDTA forms a stronger complex with Lu(III) than with La(III).*
   - *(b) cation exchange resins in the acid form absorb La^{3+} ions more strongly than Lu^{3+} ions from aqueous solution.*

     [**Hint :** The smaller ion is more strongly hydrated and the water molecules are displaced by edta with difficulty; both basically *O*-donors.]
   - *(c) $\Delta H°$ for $[Ln(EDTA)]^-$ complexes are almost all nearly equal to zero.*

     [**Hint :** See hint to (b).]
   - *(d) The electronic spectrum of Ln^{3+} ions gives rise to multiple sharp peaks.*
   - *(e) $E°$ for the Ce^{IV}—Ce^{III} couple in 1M acid solution decreases as $HClO_4 > HNO_3 > H_2SO_4 > HCl$.*
7. *How would you prepare (a) Uranium hydride; (b) U(IV) borohydride; (c) UCl_4; (d) $U(OC_2H_5)_5$; (e) UF_6; (f) zinc uranyl acetate?*

CHAPTER THIRTYTWO

ORGANOMETALLIC COMPOUNDS

OBJECTIVES

32.1 Organometallics—I
- Introduction [32.1.1]
- Main group organometallics—a review [32.1.2]
- σ-bonded organometallics of transition metals [32.1.3]
- Complexes formed by carbon monoxide [32.1.4]
- Complexes formed by nitric oxide [32.1.5]
- Cyano complexes [32.1.6]
- Isocyanide complex [32.1.7]
- Complexes of dihapto dihydrogen [32.1.8]

32.2 Organometallics—II
- Alkene complexes [32.2.1]
- Alkyne complexes [32.2.2]
- Allyl complexes [32.2.3]

32.3 Organometallic compounds in homogeneous catalysis
- Hydrogenation [32.3.1]
- Hydroformylation [32.3.2]
- Methanol, acetic acid and synthetic gasoline [32.3.3]

32.4 Metal atom clusters
- Metal carbonyl clusters [32.4.1]
- Halide clusters [32.4.2]

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ORGANOMETALLIC COMPOUNDS

32.1 ORGANOMETALLICS—I

32.1.1 Introduction

The vast domain of organometallic compounds includes compounds containing at least one metal-carbon (M—C) bond*, where M may also represent non-metals like B, Si, P or As. Accordingly, the metal carbonyls belong to the category of organometallics but species like $[Co(en)_3]^{3+}$ and $B(OCH_3)_3$ do not : these do not have any M—C bond.

Broadly, we may classify the organometallic compounds into two general categories : (i) compounds dominated by M—C bonds and (ii) compounds dominated by M—M bonds, i.e., metal clusters. Each category of compounds will be discussed separately. Coordination compounds of dihydrogen will also be included in this chapter. As we shall soon realize, all these compounds may be covered by a common bonding description.

Returning to the main stream of organometallics (i.e., those dominated by the nature of the M—C bond), we can again classify them into three categories depending upon the nature of M—C bond.

(a) The M—C bond is a conventional σ-bond. We have come across a large number of such σ-bonded organometallics in our discussion of the main group chemistry. As we shall presently see, σ-bonded organometallics of transition metals are comparatively less stable.

(b). Compounds formed by σ-donor and π-acceptor ligands like carbon monoxide.

(c) Organometallics formed by π-electron donors like the olefins and other π-systems.

(d) Organometallic compounds of highly electropositive metals are mostly ionic and may be kept in a separate class. They are insoluble in hydrocarbon solvents and highly reactive in nature, particularly when they contain an unstable carbanion. If the electron density of the carbanion is delocalized, stable salt-like compounds are obtained. Such compounds are also highly reactive, for example $Ph_3C^-Na^+$ and $(C_5H_5^-)_2Ca$.

σ-bonded organometallics are formed by most of the non-metals and also by metals of low electropositive character. The transition metals form fewer σ-bonded compounds and those too are highly reactive (Ch. 28, 29). The M—C bond in these compounds may be regarded as a normal 2-center 2-electron bond and partial substitution of halogen or similar groups by organic groups may take place, as in Me_3SnCl, $MeSnCl_3$ etc. However, the M—C bond in these compounds also may have appreciable ionic character, though covalence predominates.

Certain differences between the organometallic compounds and organic chemistry are noteworthy :

(i) The M—C bonds are mostly more polar than the C—C bond.

(ii) The octet limitation of carbon is lifted with other elements having possibility of using higher *d*-orbitals e.g., SiR_4 versus CR_4.

(iii) Presence of lone pairs of electrons on M may impart donor ability in alkyls or aryls, as in PEt_3, SMe_2 etc.

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* or interaction from a delocalized π-system as in C_2H_4, C_6H_6 or even acetylacetone.

[Sec. 32.1.2 *Organometallics — main groups*]

(iv) When M is electron deficient or coordinatively unsaturated, the organometallic compounds may develop Lewis acid character as in BR_3 or ZnR_2. As we shall soon appreciate, the σ-bonded alkyls or aryls of transition metals are particularly unstable owing to their high reactivity arising from coordinative unsaturation.

There are also a large number of *non-classically bonded organometallics* in which the bonding cannot be described by conventional 2*c*—2*e* bond or ionic description. We have already encountered such examples in the alkyls of Li, Be and Al with multicenter bonding type. Further examples of such non-classically bonded compounds will be found in the transition metal compounds of alkenes, alkynes and other ring systems.

32.1.2 Organometallics of main groups (and group 12) : a review

Organometallic compounds of the main group elements and the zinc group may be prepared by four main types of reactions :

(i) Reaction of the metal with haloalkanes/haloarenes. Active metals like Mg or Al produce organometallic halides :

$$2Li + CH_3Br \longrightarrow LiCH_3 + LiBr$$

$$Mg + CH_3Br \longrightarrow CH_3MgBr \text{ (in ether)}$$

(ii) Replacement of a metal from its organocompound by a more electropositive metal (*transmetallation*) :

$$Mg + Hg(CH_3)_2 \longrightarrow Mg(CH_3)_2 + Hg$$

(iii) Double decomposition between an organometallic compound and a halide

$$3GeCl_4 + 2Al_2(CH_3)_6 \longrightarrow 3Ge(CH_3)_4 + 4AlCl_3$$

(iv) Addition of an M—H bond to a carbon-carbon multiple bond :

$$SiH_4 + H_2C = CH_2 \xrightarrow[i\text{-}PrOH]{H_2PtCl_6} CH_3CH_2SiH_3 \text{ (hydrosilylation)}$$

The formula of simple alkyls and aryls of main group and zinc group elements follow from the normal hydride for each group. Taking the methyl compounds as example, the simple formula are $LiCH_3$ for group 1, $Be(CH_3)_2$ for group 2 and so on (Table 32.1). Like the ionic hydrides of groups 1 and 2, the alkyls and aryls also possess appreciable ionic character. The compounds are electron deficient and polymeric in nature involving methyl bridges—a 4*c*—2*e* bonding description fits $(LiCH_3)_4$ and a 3*c*—2*e* bonding is adequate for the beryllium and magnesium alkyls. Compounds of more electropositive alkali and alkaline earth metals (Na—Cs; Ca—Ba) are predominantly ionic.

The dialkyls of the zinc group (Gr 12) are monomeric linear molecules in solid, liquid or gas phase inspite of having four valence electrons. The relatively high effective nuclear charge and consequent large separation between *s* and *p*-orbitals, together with diminished M—C bond strength may stand against sp^3 hybridization in these elements. The bonding may involve *sp* hybrid orbitals but other possibilities also exist. A 3*c*—2*e* bond description has also been suggested.

The simple organometallics of Group 13(III) are also electron deficient and tend to polymerize, particularly the alkylaluminiums. $B(CH_3)_3$ is monomeric, which may be due to likely steric repulsion in a bridged structure. However, $Ga(CH_3)_3$ and $In(CH_3)_3$ are also monomeric, though they do not have the steric problem. It may be possible that the larger size of the atoms and their diminished bond energy do not favour a stable bridged structure. The likelihood of internuclear repulsion in the proximity of the bridged structure cannot be ruled out too.

The tetraalkyls of group 14(IV) are electron precise, the central atom having an octet with no lone pairs of electrons. Thus, $Si(CH_3)_4$ does not exhibit Lewis basicity. Also, it does not have a low-lying vacant orbital (or cannot dissociate into a fragment that does); so it does not exhibit Lewis acidity either. Low electropositive character of silicon also renders weak carbanionic character on the alkyl.

The organometallics of Group 15(V) elements are electron rich in having a central atom with a lone pair of electrons. Thus, $As(CH_3)_3$ is a mild Lewis base. High electronegativity of arsenic leaves only weak carbanionic character on it and the compound is not a strong reducing agent nor a Lewis acid.

Properties of the organometallic compounds have been discussed groupwise in relevant chapters. In general, stability of the alkyls decrease downward along any periodic group, a reflection of the decreasing M—C bond strength (Table 32.1).

TABLE 32.1

Standard enthalpy of formation of $M(CH_3)_n$ (g) in groups 12—15 and M—C bond enthalpy (in parentheses);

(all values in kJ mol^{-1})

GROUPS			
12(IIB)	**13(III)**	**14(IV)**	**15(V)**
	$B(CH_3)_3$	$C(CH_3)_4$	$N(CH_3)_3$
	−124 (365)	−167 (358)	−24 (314)
	$Al(CH_3)_3$	$Si(CH_3)_4$	$P(CH_3)_3$
	−74 (274)	−239 (311)	−101 (276)
$Zn(CH_3)_2$	$Ga(CH_3)_3$	$Ge(CH_3)_4$	$As(CH_3)_3$
+53 (177)	−45 (247)	−71 (249)	+13 (229)
$Cd(CH_3)_2$	$In(CH_3)_3$	$Sn(CH_3)_4$	$Sb(CH_3)_3$
+101 (139)	? (160)	+21 (217)	+32 (214)
$Hg(CH_3)_2$	$Tl(CH_3)_3$	$Pb(CH_3)_4$	$Bi(CH_3)_3$
+94 (121)	—	+136 (152)	+194 (141)

It appears that the methyl compounds of lighter elements in Groups 13(III) to 15(V) are exothermic and likely to be stable with respect to the elements. However, they will be unstable with respect to reactions like

$$M(CH_3)_2\,(g) \longrightarrow M\,(s) + C_2H_6$$

The organometallics of more electropositive elements are spontaneously flammable in air, e.g., $(LiCH_3)_4$, $Zn(CH_3)_2$, $B(CH_3)_3$ and $Al_2(CH_3)_6$ while compounds such as $Si(CH_3)_4$ and $Sn(CH_3)_4$ burn in air on heating. The former compounds are formed by elements with unfilled valence orbitals or they can dissociate to fragments with unfilled orbitals. The latter compounds, in contrast, do not have low-lying empty orbitals.

The organometallic compounds are potential reducing agents. The organic group attached to an electropositive metal also acquires appreciable carbanionic character and functions as a strong nucleophile and Lewis base. This behaviour is largely diminished for less metallic elements like boron and silicon, $B(CH_3)_3$ and $Si(CH_3)_4$ are not readily hydrolyzed and oxidized in air; the aluminium alkyls, on the other hand, are very sensitive to hydrolysis and oxidation.

$$Al(C_2H_5)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3C_2H_6$$

$$2Ga(CH_3)_3 + 2ROH \longrightarrow [(CH_3)_2GaOR]_2 + 2CH_4.$$

The $Ga(CH_3)_2$ group is quite resistant to protolysis and $[Ga(CH_3)_2en]^+$ can be handled in aqueous solution.

Thus, hydrolytic tendency decreases down a group. This may be ascribed to decreasing electropositive character of the metal and consequent weaker carbanion character of the compounds. The organometallics of the elements of group 14 and 15 do not undergo hydrolysis.

Q. 32.1 *Suggest a probable explanation for the observations :*

$$Ph_3SiH + LiCH_3 \longrightarrow Ph_3SiCH_3 + LiH$$

but, $$Ph_3GeH + LiCH_3 \longrightarrow LiGePh_3 + CH_4$$

Hint : In Ph_3GeH the hydrogen is "protonic". This reaction shows that Ge is more electronegative than Si.

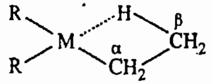
Electron-deficient organometallics may use their vacant orbital to function as a Lewis acid :

$$BPh_3 + LiPh \longrightarrow Li[BPh_4]$$

$$Al_2Me_6 + 2NEt_3 \longrightarrow 2Me_3AlNEt_3.$$

In compounds containing the metal in low coordination number, the metal may form a bridged intermediate with a hydrogen in the β-position (next nearest) and lead to *β-hydrogen elimination* :

$$R_2MCH_2CH_3 \longrightarrow R_2MH + H_2C = CH_2$$



32-1

Q. 32.2 *Arrange the compounds as stated :*

(a) *$B(CH_3)_3$, $Al(CH_3)_3$, $Ga(CH_3)_3$: tendency to form dimer by methyl bridge*

(b) *$Si(CH_3)_4$, $As(CH_3)_3$: relative Lewis basicity*

(c) *$(LiCH_3)_4$, $B(CH_3)_3$, $Si(CH_3)_4$: relative Lewis acidity*

(d) *$B(CH_3)_3$, $Al_2(CH_3)_6$: relative reducing power.*

Ans. :

(a) B < Al < Ga

(b) As > Si. $Si(CH_3)_4$ has no lone pair of electrons nor any loosely held bond pair. It is not basic at all.

(c) B > Li > Si. $Si(CH_3)_4$ exhibits no Lewis acidity.

(d) Al > B.

32.1.3 σ-Bonded organometallics of transition metals

In contrast to the main group elements, transition elements form fewer simple alkyls or aryls. Such compounds are also mostly unstable under ordinary conditions and cannot be obtained by common methods. Thus, reaction of $FeBr_2$ with C_2H_5MgBr does not lead to the isolation of $(C_2H_5)_2Fe$. However, the compound $(Me_3PtI)_4$ was prepared as early as 1909 (Pope and Peachy). Stable alkyl and aryl compounds are also known when other π-acceptor ligands are present (CO, PR_3, alkenes, alkynes, η^5-Cp etc.) or with groups like $—CH_2Ph$, $—CH_2SiMe_3$, $—CH_2CMe_3$, 1-norbornyl etc. Stable Co—C bond is present in nature in vitamin B_{12} related compounds (Ch. 26, 28).

Such M—C σ-bonds are also present in many model compounds, for example, in the cobaloximes, sec. 28.8.7.

It is now established that the transition metal-carbon σ-bond is *not* inherently weak. Thus, the Pb—C bond energy in $PbEt_4$ is 130 kJ mol^{-1} while the Ti—C bond energy is around 200 kJ mol^{-1}; yet $TiMe_4$ is unstable above −20°C. The main reason for the instability of such compounds lie in the easy reactivity of such bonds. The metal centres are usually coordinately unsaturated, providing an easy path for decomposition. Typical values of some M—C bond dissociation enthalpies in some σ-bonded organometallics of transition metals are given in Table 32.2.

TABLE 32.2

Some M—C σ-bond dissociation enthalpies (kJ mol^{-1})

$Ti(CH_2CMe_3)_4$ 198			$Mn(CO)_5Me$ 187
$Zr(CH_2CMe_3)_4$ 249			
$Hf(CH_2CMe_3)_4$ 266	$TaMe_5$ 261	WMe_6 160	$Re(CO)_5Me$ 220

The data reflect one major contrast from the main group compounds : as one moves to heavier transition metals, the M—C bond strength increases.

Preparation

Several methods have been developed to make compounds with M—C bonds, some of which are specific. A few examples are given.

(i) *Use of Grignard reagents* :

$$CuX + RMgX \longrightarrow CuR + MgX_2$$

$$AuBr_3 + 2RMgBr \longrightarrow AuR_2Br + 2MgBr_2$$

$$PtCl_4 + CH_3MgX \longrightarrow [Pt(CH_3)_4X]_4$$

(ii) *By alkyls and aryls of other metals* :

Dialkylmagnesium is often a better reagent than Grignard reagents. Alkyls and aryls of other metals like Li, Zn, Al, Sn and Hg are also used :

$$CuX + LiR \longrightarrow CuR + LiX$$

$$WCl_6 + 6AlMe_3 \longrightarrow WMe_6 + 6Me_2AlCl$$

Aluminium alkyls usually transfer only one alkyl group.

Instead of the metal halides, acetates and alkoxides are often more convenient.

(iii) *Nucleophilic attack by a carbohylate anion* :

$$Na^+ [Mn(CO)_5]^- + CH_3I \longrightarrow CH_3Mn(CO)_5 + NaI.$$

(iv) *Oxidative addition* :

$$IrCl(CO)(PPh_3)_2 + CH_3I \longrightarrow Ir(CH_3)(Cl)(I)(CO)(PPh_3)_2.$$

(v) *Cocondensation of metal vapour with alkyl/aryl halides*

$$Pd + CF_3I \longrightarrow (PdICF_3)_n.$$

(vi) *Insertion* :

$$CpFe(CO)_3CH_3 + CO \longrightarrow Cp(CO)_2FeC(O)CH_3.$$

(vii) *Elimination* :

$$Ni(bipy)(CO_2Ph)_2 \longrightarrow Ni(bipy)Ph_2 + 2CO_2.$$

[Sec. 32.1.3 *Organometallics (σ)—transition metals*]

Properties and reactions

The binary alkyls and aryls of the transition metals are thermally unstable compounds known only at low temperatures. Thus, $TiMe_4$ (yellow) decomposes above −20°C while $TiEt_4$ is still less stable (see reactions); $TaMe_5$ and WMe_6 explode in air at room temperature; CuMe forms a yellow polymeric solid which explodes in dry air; AuR_3 is stable in ether below −35°C.

It has been mentioned earlier that stability of a compound is greatly enhanced when π-acid ligands such as CO, η^5-C_5H_5 or PR_3 are present. In contrast to $TiMe_4$, $Ti(bipy)Me_4$ is sufficiently thermally stable. However, their presence is not a must. Stable compounds are also formed when β-hydrogen elimination is excluded, for example, by using groups like $—CH_2Ph$, $—CH_2SiMe_3$, $—CH_2CMe_3$, $—CH_2P^+Me_3$ and 1-norbornyl. Some stable compounds of this kind are listed below :

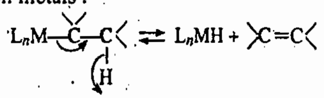
TABLE 32.3

Some binary alkyls of transition metals

$Ti(CH_2Ph)_4$	red crystals, m.p. 70°C. Tetrahedral
$VO(CH_2SiMe_3)_3$	yellow needles, m.p. 75°C
$Cr(CH_2SiMe_3)_4$	red needles, m.p. 40°C
$Cr(1\text{-norbornyl})_4$	red-brown crystals; d^2 (paramagnetic)
$Mo_2(CH_2SiMe_3)_6$	yellow plates, decomp. 135°C; (Mo≡Mo)
$Re(CH_3)_6$	green crystals, octahedral; d^1 (paramagnetic)

Thermal decomposition of these compounds may proceed mainly along two paths : (i) homolytic dissociation to radicals, (ii) hydrogen transfer reactions. The latter path mostly involves transfer of a β-hydrogen but transfer of α–, γ–, δ– and ε-hydride are also known.

β-hydride transfer is the most important mode of reaction of the σ-bonded organometallics of transition metals :



$$L_nM—\overset{\diagdown\diagup}{C}—\underset{H}{\overset{|}{C}}\langle \rightleftharpoons L_nMH + \rangle C=C\langle$$

$$\underset{=Bu}{(Ph_3P)_2Pt(CH_2CH_2CH_2CH_3)_2} \longrightarrow (Ph_3P)_2Pt(H)(Bu) + H_2C=CH.CH_2CH_3$$

$$\downarrow$$

$$Pt(PPh_3)_2 + CH_3CH_2CH_2CH_3$$

The reverse process of β-elimination (*hydrometalation*), that is addition of alkenes to M—H bond, plays an important role in catalysis.

β-hydride transfer is also known for acyls and alkoxides.

Other important types of reactions are exemplified by

α-H transfer : WMe_6 (or, $TaMe_6$) $\longrightarrow \underset{\text{polymeric}}{W(CH_2)_3} + 3CH_4$

reductive elimination : $Ph_3P\,Au^{III}Me_3 \longrightarrow Ph_3PAu^IMe + C_2H_6$

binuclear elimination : $2[Bu_3PCuBu] \longrightarrow 2PBu_3 + 2Cu + n\text{-}C_4H_{10}$ + 1-butene

Thermal stability of these compounds is greatly increased by the presence of ligands which firmly block the coordination sites of the metal. π-bonding ligands are very effective in this respect but M—C σ-bonds are also known with NH_3 or H_2O as other ligands in substitution-inert complexes of Cr^{III}, Co^{III} and Rh^{III}. The observed trend in stability of η^1-compounds also follow this interpretation :

$$\text{alkyl} < \text{aryl} < o\text{-substituted aryl} < —C{\equiv}CH.$$

32.1.4 Complexes formed by carbon monoxide

We have noted earlier (Ch. 27) how some ligands like carbon monoxide stabilize low oxidation states of metals through metal-ligand π-back bonding. The ligands effectively act as π-acceptors or π-acids by receiving electron density into their π*-m.o.-s. The carbon monoxide complexes may be considered representative of such complexes.

The complexes discussed in this section are different from the so-called *π-complexes* where the ligands use π-orbitals for both donation and back-acceptance of electrons (section 32.2). The ligands included here use σ-orbitals to transfer electron density to the metal and establish π-back bonding through π-orbitals whose nodal planes include the σ-bond axis. Thus the metal and the ligands lie in the same plane (containing the L → M σ-bond axis). For π-complexes, the metal will be necessarily out of the molecular plane of the ligand.

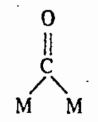
The first metal carbonyls $Ni(CO)_4$ and $Fe(CO)_5$ were discovered more than a century ago by A. Mond (1890 and 1891 respectively). Since then a large number of carbon monoxide complexes have been prepared. With the exception of borane carbonyl, H_3BCO, the known carbonyls are always formed by transition metals. The role of back-bonding from the metals in stabilizing the compounds is evident. This is further supported by the low stability or even absence of carbonyls of heavier transition metals including the end members in each series — Cu, Ag and Au. A compound of the composition $K_6(CO)_6$ has been prepared from potassium and carbon monoxide but this has been shown to be a derivative of $C_6(OH)_6$ (hexahydroxybenzene).

The carbon monoxide metal complexes may be of a diverse type. Some of these are as follows :

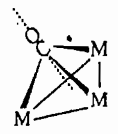
Type	Example
Mononuclear carbonyls	$Fe(CO)_5$, $Ni(CO)_4$
Binuclear carbonyls	$Fe_2(CO)_9$
Polynuclear carbonyls	$Fe_3(CO)_{12}$
Metal carbonyl clusters	$Co_6(CO)_{16}$, $[Rh_{12}(CO)_{30}]^{2-}$
Carbonylate anions	$[HFe(CO)_4]^-$
Carbonyl hydrides	$HCo(CO)_4$
Carbonyl halides	$[Mn(CO)_4Br]_2$

Almost all carbonyls and related complexes follow the 18-electron rule. A rationale for this was given in Chapter 27 in terms of filling of the nine low lying bonding and non-bonding molecular orbitals. $V(CO)_6$ (17-electrons) stands an exception to the 18-electron rule-presumably due to steric problems of 7-coordination in a dimer. We shall again refer to the 18-electron rule in connection with the structure of carbonyls.

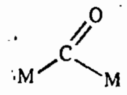
Besides forming the terminal $M \leftarrow C \equiv O$ bond, carbon monoxide can also function as a bridging ligand with its carbon end. The symmetrical doubly bridging mode (32-IIa) is very common in several transition metal carbonyls. The triply bridging mode (32-IIb) is relatively less common, a few examples being $Rh_6(CO)_{16}$, $Fe_4(CO)_4(\eta^5\text{-}Cp)_4$ (32-XXIIb) and $Ni_3(CO)_2(\eta^5\text{-}Cp)_3$ (Fig. 32.1). In $Rh_6(CO)_{16}$, the Rh atoms form an octahedron of which four faces contain each a triply bridging CO, that is, the compound is $[Rh_6(\mu_3\text{-}CO)_4(CO)_{12}]$.



32-II(a)



32-II(b)



32-II(c)

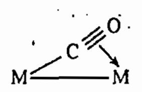
Bridge CO groups may be distinguished from terminal CO groups by ir spectrum (see later).

Though the doubly bridging CO groups are mostly symmetrically placed between the two metal atoms as shown in 32-II(a), a few cases of unsymmetrical bridging are known with unequal M—C distances (32-IIc). Such coordination modes, which are intermediate between terminal and bridge coordinations, have been termed semibridging. This type of bonding may arise due to structural, electronic or steric factors. $Os_4(CO)_{14}$ contains four semibridging CO groups (Fig. 32.1).

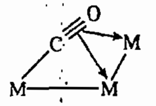
A triply bridging carbon monoxide molecule can also coordinate unsymmetrically.

In the $[HFe_4(CO)_{13}]^-$ ion, a single CO molecule is joined to four Fe atoms. Three Fe atoms are bridged by the C-end of the CO ligand while the fourth Fe interacts with the π-cloud of the CO. The CO molecule in this case functions as a four-electron donor.

Side-on bonding from CO as shown in 32-III(a) and (b) are also known. In 32-III(a), the CO group is a 4-electron donor (2σ + 2π); an example of this type of coordination is $Mn_2(CO)_5(dppm)_2$ (dppm ≡ bis(diphenylphosphino) methane). In 32-III(b), CO serves as a 6-electron donor (2σ + 4π), an example being $(\eta^5\text{-}Cp)_3Nb_3(CO)_7$. Both these types of coordination by CO have CNR analogues.



32-III(a)



32-III(b)

Though carbon monoxide always coordinates through the carbon end in stable metal carbonyls, formation of an isocarbonyl (carbonyl) gold, COAuCO, has been suggested from spectroscopic data on the product of cocondensation of gold atoms with excess CO at very low temperature (6-10K). Condensation of CO and Au in rare gas matrix produces OCAuCO.

Preparation

A. *Direct synthesis*

Many finely divided metals react with carbon monoxide directly; except nickel, high temperature and pressure are required to attain appreciable rate of reaction.

$Ni\,(s) + 4CO\,(g) \longrightarrow Ni(CO)_4\,(l)$ 30°C; 1 atm

$Fe\,(s) + 5CO\,(g) \longrightarrow Fe(CO)_5$ (*l* at room temp.) 200°C; 200 atm

$2Co\,(s) + 8CO\,(g) \longrightarrow Co_2(CO)_8$ (*s* at room temp.) 150°C; 35 atm

$Cr(CO)_6$ and $Mo(CO)_6$ are formed similarly.

The first carbonyl compound $Ni(CO)_4$ was prepared in this method. The process is still used in the extraction of nickel (Ch. 28).

Many unstable carbonyls have been prepared by the action of CO on metal atoms in a noble gas matrix at very low temperature (*matrix isolation*), e.g., $Ti(CO)_6$, $Pd(CO)_4$, $Ag_2(CO)_6$ etc.

B. *Reductive carbonylation*

This method involves reduction of a metal compound in presence of carbon monoxide, usually at high pressures (200-300 atm). CO may itself act as the reducing agent in some cases, e.g.,

$$OsO_4 + 9CO \longrightarrow Os(CO)_5 + 4CO_2; \qquad 250°C, 350 \text{ atm}$$

Usually an additional reducing agent is needed, for example, H_2, metals (e.g., Na, Al, Mg, Cu) or alkylaluminium compounds :

$$2CoCO_3 + 2H_2 + 8CO \longrightarrow Co_2(CO)_8 + 2CO_2 + 2H_2O \qquad 150°C, 250\text{-}300 \text{ atm}$$

$$CrCl_3 + Al + 6CO \xrightarrow[\text{benzene}]{AlCl_3} Cr(CO)_6\ (soln) + AlCl_3\ (soln)$$

$$CrCl_3 + LiAlH_4 + 6CO \xrightarrow{\text{ether}} Cr(CO)_6\ (soln) + LiCl + AlCl_3 \qquad 115°C, 70 \text{ atm}$$

$$VCl_3 + Na + CO \xrightarrow{\text{diglyme}} [Na\ (\text{diglyme})_2]\ [V(CO)_6] \qquad 150°C, 150 \text{ atm.}$$

$$\Big\downarrow HCl$$

$$V(CO)_6\ (soln)$$

C. *Thermolysis and photolysis*

Carbonyls containing more metals (per CO) are formed by photolysis and thermolysis of lower carbonyls. Fragments produced by M—CO bond cleavage combine to form the higher carbonyls :

$$3Os(CO)_5 \xrightarrow{\Delta} Os_3(CO)_{12} + 3CO$$

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO.$$

Carbonyl compounds containing *two different metals* may be prepared by reactions like

$$3Fe(CO)_5 + Ru_3(CO)_{12} \xrightarrow{110°C} FeRu_2(CO)_{12} + Fe_2Ru(CO)_{12} + 3CO$$

$$Na[Co(CO)_4] + Mn(CO)_5Br \xrightarrow{THF} (OC)_4CoMn(CO)_5 + NaBr.$$

Properties and reactions

Physical properties of some stable binary carbonyls are shown in Table 32.4. $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$ and $Ni(CO)_4$ are liquids at ordinary temperature; most other carbonyls are volatile solids. Their vapours are toxic. Non-polar, most of them are soluble in hydrocarbon and other organic solvents, but in water they are either insoluble [e.g., $Ni(CO)_4$] or undergo decomposition [e.g., $Fe(CO)_5$]. Only $Fe_2(CO)_9$ is insoluble in inert solvents. Though thermodynamically unstable with respect to oxidation by air, some carbonyls are quite stable in air at ordinary temperatures e.g., $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$; $Fe(CO)_5$ and $Ni(CO)_4$ are oxidized comparatively easily and their vapours form explosive mixtures with air. $Co_2(CO)_8$ reacts with air at ordinary temperature.

TABLE 32.4

Some representative binary carbonyls

$V(CO)_6$ (*s*) dark green dec. 70°C, sublimes paramagnetic (1*e*)	$Cr(CO)_6$ (*s*) colourless dec. 180°C, sublimes	$Mn_2(CO)_{10}$ (*s*) yellow m.p. 154°C, sublimes	$Fe(CO)_5$ (*l*) yellow m.p. –20°/b.p. 103°C	$Co_2(CO)_8$ (*s*) orange m.p. 51°C, sublimes	$Ni(CO)_4$ (*l*) colourless m.p. –25°C, b.p. 42° Toxic, flammable
			$Fe_2(CO)_9$ (*s*) orange dec. 100°C, insoluble, non-volatile	$Co_4(CO)_{12}$ black dec. 60°C	
			$Fe_3(CO)_{12}$ (*s*) green dec. 140°C, mod. soluble		
	$Mo(CO)_6$ (*s*) colourless dec. 180°, sublimes	$Tc_2(CO)_{10}$ (*s*) colourless m.p. 160°, sublimes	$Ru(CO)_5$ (*l*) colourless m.p. –16°	$Rh_4(CO)_{12}$ (*s*) red dec. 150°	
			$Ru_3(CO)_{12}$ (*s*) orange m.p. 150°		
	$W(CO)_6$ (*s*) colourless dec. 180°, sublimes	$Re_2(CO)_{10}$ (*s*) colourless m.p. 177°, sublimes.	$Os(CO)_5$ (*l*) colourless m.p. 2°	$Ir(CO)_{12}$ (*s*) yellow dec. 210°	$Pt(CO)_4$ transient existence

We also observe that most of the mononuclear carbonyls are nearly colourless while the polynuclear carbonyls are coloured. The intensity of colour increases with increasing number of metal atoms. Such colours of polynuclear carbonyls arise from electronic transitions between orbitals largely localized on the metal framework.

The main reactions of simple metal carbonyls at the metal center involve substitution, reduction, oxidation and condensation into clusters. The CO ligand may also be attacked by nucleophiles and electrophiles.

(i) *Substitution*

The CO groups in carbonyls may be displaced by a variety of ligands such as PX_3, PR_3, NR_3, SR_2, OR_2, RNC or unsaturated organic molecules like C_6H_6 or cycloheptatriene.

$$Fe(CO)_5 + PPh_3 \longrightarrow Ph_3PFe(CO)_4 + (Ph_3P)_2Fe(CO)_3 \ldots\ldots \text{so on}$$

$$Cr(CO)_6 + C_6H_6 \longrightarrow (C_6H_6)Cr(CO)_3 + 3CO$$

The substitutions usually follow a dissociatively activated path. We recall that most simple carbonyls conform to the 18-electron rule and expect that an associatively activated path involving a 20-electron activated complex would be energetically unfavourable.

In certain carbonyls, as in $Ni(CO)_4$, dissociation of the first CO appears quite fast at ordinary temperature but in most cases substitution is favoured by thermal or photochemical excitation or by the intermediacy of the solvent :

$$Ni(CO)_4 \xrightarrow{PF_3/30°C} Ni(CO)_2(PF_3)_2$$

$$Cr(CO)_6 \xrightarrow[+\text{ diglyme}]{\text{heat or uv ray}} Cr(CO)_5\ \text{diglyme} \xrightarrow{L} Cr(CO)_5L.$$

Substitution reactions by bulky ligands are naturally hindered by steric repulsion. The extent of crowding caused by a ligand has been compared in terms of the angle of the cone containing the ligands at the estimated metal-ligand distance in a to-the-scale space-filling model (Tolman's *cone angle*). Hence substitution at $Mo(CO)_6$ is expected to take place more readily with PMe_3 (cone angle 118°) than with PPh_3 (cone angle 145°). The CO ligand is comparatively "slim" in having a cone angle of only 95°.

(ii) *Carbonylate anions*

Most metal carbonyls may be reduced to metal carbonylate anions by the action of alkali or other reducing agents :

$$Fe(CO)_5 + 3NaOH \xrightarrow{H_2O} Na[HFe(CO)_4] + Na_2CO_3 + H_2O$$

$$Fe(CO)_5 + 2Na \longrightarrow Na_2[Fe(CO)_4] + CO \quad \text{(in liq. } NH_3\text{)}$$

$$Cr(CO)_6 + Na/Hg \longrightarrow Na_2[Cr(CO)_5] + CO \quad \text{(THF, 65°C)}$$

$$Co_2(CO)_8 + 2Li[HBEt_3] \longrightarrow 2Li[Co(CO)_4] + 2BEt_3 + H_2 \quad \text{(THF, 25°)}$$

$$Mn_2(CO)_{10} + 2KH \longrightarrow 2K[Mn(CO)_5] + H_2 \quad \text{(THF)}$$

$$Hg + Co_2(CO)_8 \longrightarrow Hg[Co(CO)_4]_2 \quad (150°C)$$

A strongly basic ligand may also cause disproportionation in some cases :

$$\overset{0}{Co_2}(CO)_8 + 6py \longrightarrow [\overset{+1}{Co}(py)_6][\overset{-1}{Co}(CO)_4] + 4CO$$

(iii) *Oxidation to metal carbonyl halides*

The metal carbonyls will be oxidized in air above room temperature to produce the metal oxide (and CO or CO_2) as the ultimate product. Here we are interested in their oxidation by halogens to metal carbonyl halides :

$$Mn_2(CO)_{10} + Cl_2 \xrightarrow{40°C} 2Mn(CO)_5Cl$$

$$Fe(CO)_5 + Br_2 \longrightarrow Fe(CO)_4Br_2 + CO.$$

(iv) *Reactions of the CO ligand*

Strong nucleophiles may attack the CO in many neutral or cationic metal carbonyls where the metal *d*-electrons are not extensively delocalized on the ligand. Lithium alkyls attack the carbon atom in $W(CO)_6$ or $Mo(CO)_6$:

$$LiCH_3 + W(CO)_6 \longrightarrow Li^+[(CO)_5W\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_3]^-$$

Attack of OH^- on a coordinated CO ligand with subsequent loss of CO_2 is thought to be a critical step in the water gas shift reaction ($H_2O + CO \rightleftharpoons CO_2 + H_2$, Section 32.3) which is homogeneously catalyzed by alkaline solutions of various metal carbonyls :

$$L_5M-CO+OH^- \longrightarrow \left[L_5M\text{—}\overset{\overset{O}{\|}}{C}\text{—}OH\right]^- \longrightarrow [L_5M\text{—}H]^- + CO_2.$$

Structure

The simple monomeric carbonyls have symmetrical structures with linear M—C—O links. $Ni(CO)_4$ is tetrahedral, $Fe(CO)_5$ is trigonal bipyramidal and the Group 16 hexacarbonyls are octahedral. In all these structures the CO ligands occupy most distant positions like the electron-pairs in the VSEPR theory. The structures may be confirmed by ^{13}C—NMR and IR spectroscopy (see bonding).

Structures of several polynuclear carbonyls have been discussed under individual metals in chapters 28 and 29. We observed that the dicarbonyls $M_2(CO)_{10}$ (M = Mn, Tc, Re) are $(CO)_5M—M(CO)_5$, the octahedron around each metal being completed by the other metal atom. $Co_2(CO)_8$ (solid) and $Fe_2(CO)_9$ contain two and three bridge >C=O groups respectively in addition to terminal CO groups and M—M bonds. The bridging CO groups may be distinguished by their lower IR stretching frequencies : 1750 – 1850 cm^{-1} vs 1850 – 2125 cm^{-1} for terminal CO groups. Thus the terminal CO groups in $Co_2(CO)_8$ show strong absorption bands at 2028 and 2104 cm^{-1} while the bridge CO groups appear at 1898 and 1867 cm^{-1} (see bonding). In hexane solution, $Co_2(CO)_8$ does not show the latter bands; the staggered structure (Fig. 32.1) is mainly present in such solution. The bridge and terminal C—O distances in $Co_2(CO)_8$ (solid) are 121 and 117 pm respectively. The Co—C (terminal) distance is 179 pm while the Co—C (bridge) distance is 192 pm.

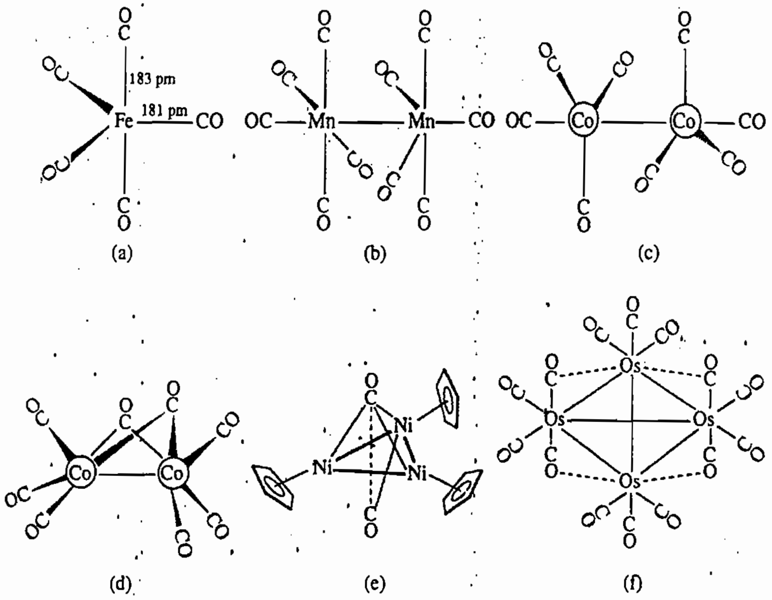


Fig. 32.1

Structure of some carbonyls : (a) ***mononuclear,*** **$Fe(CO)_5$ (b), (c),**
(d) : ***dinuclear,*** **$Mn_2(CO)_{10}$; $CO_2(CO)_8$ (*s*) and $Co_2(CO)_8$ (soln.)**
(e) triply bridging CO; (f) ***semi bridging,*** **$Os_4(CO)_{14}$.**

Since most carbonyl complexes (LNCC or low nuclearity carbonyl clusters, which contain not more than four metal atoms) follow the 18-electron rule we give here some more illustrations of the applicability of the rule (in addition to those given in chapter 27).

Q. 32.3 *Show that each Fe atom in $Fe_3(CO)_{12}$ conforms to the 18-electron rule (see Fig. 28-XIX).*

Hints : See Chapter 27 (Sec. 27.1.4) for electron counting procedure.

For *each* of the two Fe atoms bridged by CO groups, we have

3CO (terminal)	:	3 × 2*e*	= 6*e*
2 bridge CO	:	2 × 1*e*	= 2*e*
2 Fe—Fe bonds	:	2 × 1*e*	= 2*e*
Fe^0	:		= 8*e*
Total	:		18*e*

For the third Fe-atom, we have

4CO (terminal)	:	4 × 2*e*	= 8*e*
2 Fe—Fe bonds	:	2 × 1*e*	= 2*e*
Fe^0	:		= 8*e*
Total	:		18*e*

Without referring to the structure, we can also calculate the total cluster valence electron as shown below.

Q. 32.4 *Since most known carbonyls follow the 18-electron rule, we can turn the argument round and use this rule as a guideline to understand the structure of polynuclear carbonyls. Illustrate this with reference to $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.*

Hints : We look for completion of 18 electrons per atom of iron.

$Fe_2(CO)_9$	**$Fe_3(CO)_{12}$**
2Fe : 16e	3Fe : 24e
9CO : 18e	12 CO : 24e
34e	48e
We need 2 electrons to make a total of 36 (2 × 18 per Fe). This corresponds to one Fe—Fe bond.	We need 6 electrons to make the total equal to 54 (3 × 18). This requires 3 Fe—Fe bonds (2 per atom of Fe).

Q. 32.5 *Assuming the 18-electron rule to be valid, find the number of Os—Os bonds in $Os_4(CO)_{14}$, $Os_4(CO)_{15}$ and $Os_4(CO)_{16}$.*

Hints :

$$\begin{array}{lrcl} Os_4(CO)_{14} : & 4\,Os & = & 32e \\ & 14\,CO & = & \underline{28e} \\ & & & \underline{60e} \end{array}$$

12 electrons are needed to make the total equal to 72 (4 × 18 per Os). This suggests 6 Os—Os bonds (tetrahedral Os_4 cluster).

$Os_4(CO)_{15}$: Similar counting requires 5 Os—Os bonds

$Os_4(CO)_{16}$: This suggests a butterfly structure (see section 32.4.1).

Note 1 : The 18-electron rule breaks down in case of complicated polynuclear carbonyl complexes (more than 4 C-atom). Such high nuclearity carbonyl clusters have been discussed under metal cluster compounds (section 32.4).

Note 2 : Different structures consistent with the 18-e rule may be present in different environments. We have seen this in case of $Co_2(CO)_8$.

Note 3 : The number of doubly bridging CO groups cannot be predicted by the 18-e rule. Again $Co_2(CO)_8$ provides a ready example which may or may not have the bridge CO groups.

Q. 32.6 *Use the 18-e rule to predict the likely value of n in*

(i) $Ru_3(CO)_n$ (ii) $(\eta^5-Cp)Co(CO)_n$

Hint : (i) For a linear Ru-Ru-Ru arrangement, the terminal Ru atoms can never satisfy the 18e rule :

$$\begin{array}{lcl} 1Ru & : & 8e \\ 1Ru\text{–}Ru & : & 1e \\ nCO & : & \underline{2n\,e} \\ \text{Total} & & \underline{(9+2n)e} \end{array}$$

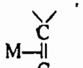
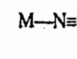
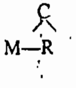
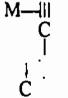
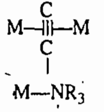
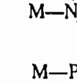
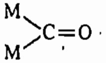
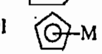
clearly, (9 + 2n) cannot equal 18 for any integral value of n.

For a triangular arrangement, each Ru has 2 Ru—Ru bonds and we have the count for each : 8 + 2 (for Ru—Ru) + 4 × 2 = 18. Hence for three Ru, n = 4 × 3 = 12.

In counting electrons for mixed carbonyl complexes, it is necessary to know the contribution from other ligands. While this can be arrived at from a judicious consideration of the bonding situation, a resume of such contributions is given in Table 32.5. The contributions correspond to the so-called "neutral atom procedure" without necessitating assignment of the oxidation state of the metal, which in fact, is often ambiguous for organometallic compounds.

TABLE 32.5

Contributions to electron counting by some common ligands

1.	Acyl		1	9.	Dihydrogen		2
2.	Alkene		2	10.	Dinitrogen	M—N≡N	2
3.	Alkyl	M—R	1	11.	Halogen	M—X:	1
					Halogen (bridge)	M—X—M	3
4.	Alkyne		2	12.	Hydrogen	M—H	1
	Alkyne (bridge)		4	13.	Isocyanide	M—CNR	2
5.	Amine	M—NR_3	2	14.	Nitrosyl (linear)	M—N≡O	2
					Nitrosyl (bent)		1
6.	Aryl	M—Ph	2	15.	Phosphines	M—PR_3	2
7.	Carbonyl (terminal)	M—CO	2	16.	η⁶-Benzene		6
	Carbonyl (bridge)						
8.	Cyanide	M—CN	2	17.	η¹-Cyclopentadienyl		1
				18.	η⁵-Cyclopentadienyl		5

Q. 32.7 *Find the values of x and y assuming validity of the 18e rule.*

(a) $Fe(\eta^5-Cp)(CO)_x(NO)_y$ (b) $Fe(\eta^5-Cp)(\eta^1-Cp)(CO)_x$

(c) $Mn(CO)_x(NO)_y$ (d) $Co_2(CO)_x(C_2H_2)$.

Hints : (a) Fe = 8 and Cp = 5 make a total of 8 + 5 = 13 electrons.

∴ CO = 2 and NO = 3 i.e., $x = y = 1$.

(b) 8 + 5 + 1 = 14; ∴ xCO = 4. (c) Mn = 7; x = 1 and y = 3 makes total = 18.

(d) 2Co = 18, C_2H_2 = 2, Co—Co = 2; x = 7 makes the total 36, i.e., 18 e per Co.

Q. 32.8 *Find the value of n assuming validity of the 18e rule.*

(a) $RuH(CO_2Me)(PPh_3)_n$ (b) $Co_3(CO)_nCH$

(c) $Fe_4(\eta^5-Cp)_2(CO)_n$

Hints : (a) $RuH(CO_2Me)(PPh_3)_n$ 8 + 1 + 3 + 2n = 18.

(b) $Co_3(CO)_nCH$ 3 × 9 + 2n + 3* + 3 × 2 (bridge†) = 3 × 18.

*1 electron of carbon is engaged in the C—H bond; 3 electrons contribute to the cluster assuming —CH to be simply C-bonded). † There will be 3 Co—Co bonds.

(c) $Fe_4(\eta^5-Cp)_2(CO)_n$ 4 × 8 + 2 × 5 + 2n + 6 × 2 (bridge†) = 4 × 18.

† 4 tetrahedral Fe atoms require 6 Fe—Fe bonds.

Bonding

We observed that many metals having high heats of atomization (~400 kJ mol^{-1}) form stable molecular carbonyls with carbon monoxide, which itself is a weak Lewis base. We have also discussed (Ch. 27) the role of carbon monoxide as a π-acceptor ligand in the light of the molecular orbital theory. The stability of metal carbonyls is better understood through the molecular orbital approach which also justifies their conformity with the 18-electron rule (Ch. 27). In valence bond description the bonding in metal carbonyls may be summarily represented by resonance hybrids of the type :

$$M{-}C{\equiv}O{:} \longleftrightarrow M{=}C{=}\ddot{O}{:}$$

To begin with a qualitative description of the bonding in metal carbonyls, let us recall the m.o. diagram for the carbon monoxide molecule (reproduced in Fig. 32.2).

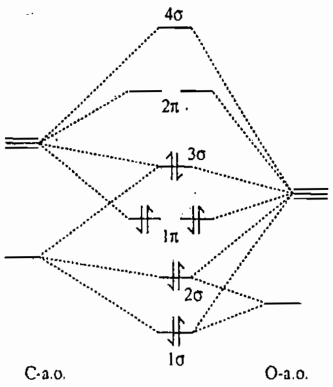


Fig. 32.2
Qualitative energy level diagram for the molecular orbitals of CO.

The HOMO is the 3σ, which has a largely non-bonding lone pair localized near the carbon p-orbital.

The LUMOs are the antibonding 2π orbitals also close to the carbon 2p atomic orbitals. These play a vital role as they can undergo π-overlap with metal d-orbitals, e.g., the t_{2g} orbitals in an octahedral field. This allows delocalization of electrons from filled d-orbitals of metals.

The first step in the formation of a terminal M—CO bond is σ-donation from the 3σ m.o. on CO (directed outward on C) to an empty metal orbital of matching symmetry (Fig. 32.3). As the metal receives electrons through σ interactions with a number of CO molecules, electron density on the metal builds up to facilitate π-back bonding to the ligand.

The second step in the bonding of metal carbonyls thus consists of π-overlap from a filled metal orbital (e.g., the t_{2g} in an octahedral field) to the LUMOs on CO (the antibonding π m.o.s).

The σ- and π-bonding interactions in metal carbonyls are said to be *synergic* as they mutually reinforce one another. The dative σ-overlap from C → M increases electron density on the metal, which now becomes a better donor via M $\nrightarrow$ C π-interaction. The π-interaction on the other hand, reduces electron density on the metal, thereby making it a good acceptor in σ-interaction. Similar arguments apply for the CO ligand. The M → C π-interaction weakens the π-bonds in CO since this increases electron density on the antibonding π^* m.o. However, this is more than compensated by the enhanced M—C bonding, making the overall process energetically favourable.

However, a series of cationic carbonyl species cannot be covered by this bonding description. These "non-classical carbonyls" show C—O stretchings higher than that in CO itself (see p 1144).

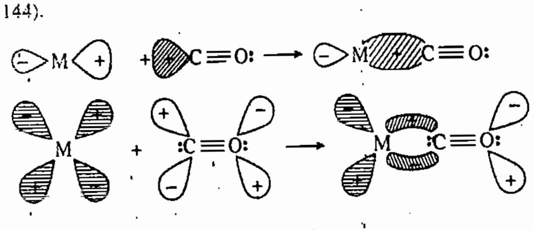


Fig. 32.3
Schematic representation of synergic σ- and π-bonds in terminal M—CO bonds in metal carbonyls.

Infrared spectra of the carbonyls show notable variation in C—O stretching frequency consistent with this bonding scheme. The stretching wave number of the CO molecule is 2143 cm^{-1}. In a transition metal carbonyl, the metal-ligand π-delocalization transfers electron density into the antibonding π-m.o.s of CO; the accompanying decrease in C—O bond order lowers the C—O stretching wave number in the range 2125-1850 cm^{-1} for terminal CO groups (Table 32.6). The value is further lowered in situations favouring M → C back donation such as enhanced negative charge on the metal (e.g., $V(CO)_6^-$). Partial substitution of CO by ligands having low or negligible π-acceptor ability also pushes more electron density on the remaining CO ligands, thereby lowering the CO stretching frequency [e.g., $Cr(CO)_3(dien)$; dien = $HN(CH_2CH_2NH_2)_2$]. Conversely, situations disfavouring back donation from the metal such as placing a positive charge on it, would raise the CO stretching frequency.

TABLE 32.6

C—O stretching wave numbers (cm^{-1}) in some carbonyl complexes

Species	$\bar{\nu}$	Species	$\bar{\nu}$
CO (g)	2143	$Mn(CO)_6^+$	2090
$Ni(CO)_4$	2060	$[Ti(CO)_6]^{2-}$	1750
$Cr(CO)_6$	2000	$[Mn(dien)(CO)_3]^+$	2020, 1900
$[V(CO)_6]^-$	1860	$[Cr(dien)(CO)_3]^+$	1900, 1760

The progressive increase in the C—O stretching frequency among the isoelectronic species $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ is accompanied by a parallel decrease in M—C stretching frequency : 460, 441 and 416 cm^{-1} respectively. A higher negative charge on the metal again results in greater π-delocalization over the M—C bond.

Double bond character of the metal-carbon bonds in carbonyl complexes implies that these bonds should be shorter than metal-carbon single bond distances. This is supported experimentally. The M—C distance is also sensitive to substitution of CO by other π-acid ligands. In $Ph_3PCr(CO)_5$, for example, the phosphorus and its *trans* CO group (Fig. 32.4) will compete for the same π-orbitals on the metal. Since CO is a stronger π-acceptor, the Cr—CO bond trans to the Cr—P bond will be stronger and shorter compared to other Cr—CO distances in this complex or in $Cr(CO)_6$. The effect is also relayed to the adjacent C—O bond; the antibonding π-orbital of CO gets more highly populated, resulting in a slight increase in the C—O bond length (Fig. 32.4). $P(OPh)_3$, a better π-acid than PPh_3, results in a stronger pm) at the cost of the Cr—CO (trans) bond (186 pm); the C—O bond trans to this ligand is also shorter (113.7 pm) as expected.

The observed C—O distances in metal carbonyls fall within the narrow range of 114-115 pm, the distance in the CO molecule being 112.8 pm. Hence we cannot put much emphasis on the variation of C—O distances unless they are not known with high precision.

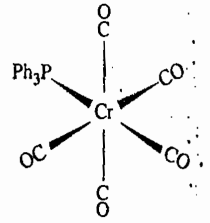


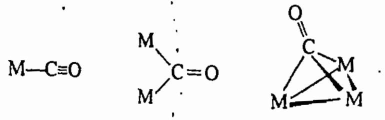
Fig. 32.4

Effect of substitution in $Cr(CO)_6$.

Cr—C in $Cr(CO)_6$	~	191.5 pm
Cr—C (*trans to* Ph_3P)	~	184.4 pm
Cr—P	~	242.2 pm
C—O in $Cr(CO)_6$	~	114.0 pm
C—O (*trans* to Ph_3P)	~	115.4 pm

The C—O stretching wave numbers of bridging carbonyls are lower than those for terminal CO groups :

terminal > doubly bridging > triply bridging



$> 1900\ cm^{-1}$ $\quad$ $1900\text{-}1850\ cm^{-1}$ $\quad$ $1620\text{-}1730\ cm^{-1}$

Though the C—O stretching frequencies of bridging carbonyl groups are comparable to those for saturated ketones (~ 1700 cm^{-1}), bridge carbonyl groups are basically different from ketonic groups. The C—C—C bond angles in ketones are typically 120° whereas the M—C—M bond angles in bridged carbonyls are often 90° or less. Metal-metal bonds are usually common for these carbonyls which imply extensive delocalization of electrons over metal orbitals and both σ and π orbitals of CO.

Q. 32.9 *Comment on the following observed values of* ν_{C-O} (cm^{-1}) :

$Cr(CO)_6$	$[Mn(CO)_6]^+$	CO	$[Ag(CO)][B(OTeF_5)_4]$	ClAuCO
1984	2094	2143	2204	2152

Hint : M—C backdonation increases electron population of antibonding π-m.o.-s of CO, lowering ν. '+' charge on metal reduces backdonation.

The HOMO in CO is slightly antibonding between C and O; donation of electron from this orbital increases C—O bond strength and raises ν_{C-O}. The C—O bond length also decreases at the same time — 107.7 pm in $[Ag(CO)]^+$ versus 112.8 pm in free CO.

Carbonylate anions and carbonyl hydrides

We have already mentioned the formation of carbonylate anions from carbonyls by the action of alkali or other methods (see properties). Some of these may also be obtained from other compounds of the metals :

$$TaCl_5 + CO + Na \xrightarrow{\text{diglyme}} [Na(diglyme)_2][Ta(CO)_6] \;\ldots\ldots\ldots (100°C,\ 200\ atm)$$

$$2Co^{2+}(aq) + 11CO + 12OH^- \xrightarrow{KCN\ (aq)} 2[Co(CO)_4]^- + 3CO_3^{2-} + 6H_2O.$$

[Sec.32.1.4 *Carbonylate anions*]

The simple carbonylate anions obey the 18-electron rule. The alkali metal salts of these anions are water soluble. They may be precipitated from such solutions by large cations like Ph_4As^+. However, in presence of water and other weak acids many carbonylate anions form hydrides.

$$Na[HFe(CO)_4] + H^+ \longrightarrow H_2Fe(CO)_4 + Na^+.$$

The carbonylate anions react with alkyl and acyl halides to give metal alkyls and metal acyls respectively.

$$[Fe(CO)_4]^{2-} + RX \longrightarrow [RFe(CO)_4]^- + X^-$$

$$[Fe(CO)_4]^{2-} + RCOCl \longrightarrow [RCOFe(CO)_4]^- + X^-.$$

Metal-metal bonds and metal-carbon (silicon) bonds are formed in the following reactions :

$$[Mn(CO)_5]^- + ClCH_2CH=CH_2 \longrightarrow (CO)_5MnCH_2CH=CH_2 + Cl^-$$

$$[Mn(CO)_5]Br + Co(CO)_4^- \longrightarrow (CO)_4CoMn(CO)_5 + Br^-$$

$$[Mn(CO)_5]^- + Ph_3PAuCl \longrightarrow Ph_3PAuMn(CO)_5 + Cl^-$$

$$SiH_3I + [Co(CO)_4]^- \longrightarrow H_3SiCo(CO)_4 + I^-.$$

Carbonyl hydrides may be obtained by acidifying aqueous solutions of alkali metal carbonylates as also by other reactions like the following :

$$Fe(CO)_4I_2 \xrightarrow{NaBH_4} H_2Fe(CO)_4 \quad (\text{in THF})$$

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4 \quad (200\ atm,\ 200°C)$$

$$Co + 4CO + \tfrac{1}{2}H_2 \longrightarrow HCo(CO)_4 \quad (50\ atm,\ 150°C)$$

$$Mo(CO)_3(P-iPr_3)_2 + H_2 \longrightarrow Mo(CO)_3(P-iPr_3)_2H_2$$

[The last compound is a dihapto dihydrogen complex (η^2-H_2).]

The carbonyl hydrides are mostly unstable compounds. $H_2Fe(CO)_4$, a yellow liquid (m.p. −70°C), decomposes above −10°C; $HCo(CO)_4$, also a yellow liquid (m.p. −20°C), decomposes above its melting point. $HMn(CO)_5$, a colourless liquid (m.p. −25°C), is stable at 25°C. The presence of M—H bonds in these compounds is confirmed by proton magnetic resonance studies. $HMn(CO)_5$ has an octahedral structure (X-ray and neutron diffraction) with Mn—H = 160 pm.

The carbonyl hydrides behave acidic in aqueous solution. $HCo(CO)_4$ (almost insoluble in water) is a quite strong acid. pK_a values for $HMn(CO)_5$ and $H_2Fe(CO)_4$ in aqueous solutions are approximately 7 and 4 respectively (pK_2 for the latter is 14).

The anionic hydridocarbonyls are hydride ion donors and may be used to reduce acid chlorides and alkyl halides.

$$RCOCl + [HCr(CO)_5]^- \longrightarrow RCHO + [ClCr(CO)_5]^-$$

In presence of acetic acid, they also reduce aldehydes and ketones to alcohols in nonpolar solvents :

$$RCHO + [HCr(CO)_5]^- + HOAc \longrightarrow RCH_2OH + [OAcCr(CO)_5]^-.$$

The carbonyl hydride $HCo(CO)_3$ is believed to be the active species formed when $Co_2(CO)_8$ acts as a catalyst in many organic reactions, for example, the conversion of alkenes to aldehydes by CO and H_2 (the 'oxo' reaction).

Cationic carbonyl complexes

A few cationic carbonyl complexes have also been characterized. Thus, the action of carbon monoxide and aluminium chloride on manganese carbonyl chloride forms a salt of the cation $[Mn(CO)_6]^+$.

$$Mn(CO)_5Cl + AlCl_3 + CO \longrightarrow [Mn(CO)_6]\,[AlCl_4]$$

Some protonated carbonyl complexes may be obtained by dissolving metal carbonyls in sulfuric acid or a mixture of HF and BF_3 :

$$Fe(CO)_5 + H^+ \longrightarrow [HFe(CO)_5]^+$$

[non-classical carbonyls]

Several cationic species, namely, $[Pd(CO)_4]^{2+}$, $[Pt(CO)_4]^{2+}$, $[AgCO]^+$, $[Ag(CO)_2]^{2+}$, $[Au(CO)_2]^{2+}$, $[Hg(CO)_2]^{2+}$, $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$ have been isolated using $[Sb_2F_{11}]^-$ as the counter-anion. All of them show C—O stretching frequencies higher than that in CO itself; for example, $[Ir(CO)_6]^{3+}$, shows three stretching modes at 2295, 2276 and 2254 cm^{-1}. They have been called "non-classical carbonyls" and probably involve σ-only M—CO bond (see in chapter Q. 32.9 for $[Ag(CO)]^+$).

Carbonyl halides

Carbonyl halides, $M_x(CO)_yX_z$, are known for several elements forming stable carbonyls and also for Pd, Pt, Au, Cu^I and Ag^I. They may be prepared by reacting the metal carbonyls with halogens or the metal halides with CO under pressure.

$$Fe(CO)_5 + I_2 \longrightarrow Fe(CO)_4I_2$$

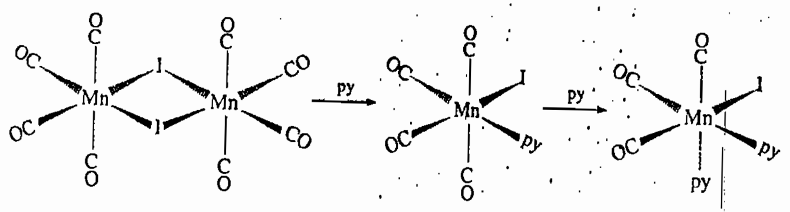
$$PtCl_2 + CO \longrightarrow [Pt(CO)Cl_2]_2 \quad (200°C)$$

$$Mn_2(CO)_{10} + Br_2 \longrightarrow 2Mn(CO)_5Br \quad 40°C$$

$$2Mn(CO)_5Br + CO \longrightarrow [Mn(CO)_4Br]_2 \quad 120°C,\ 150\ atm.$$

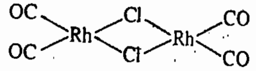
The carbonyl halides usually form pale yellow or white crystals soluble in organic solvents. $Mn(CO)_5Cl$ is a pale yellow sublimable solid that loses CO at 120° in organic solvents. Yellow $[Pt(CO)Cl_2]_2$ also sublimes near its melting point 195°C. The halides are decomposed by water.

The dimeric carbonyl halides are always bridged through the halogen and may be cleaved by other donor ligands like pyridine, isocyanides and substituted phosphine, for example,



Q. 32.10 *Though most carbonyl complexes conform to the 18-electron rule,* (a) $[Rh(CO)_2Cl]_2$ and (b) *Vaska's compound, trans*-$[(Ph_3P)_2Ir(CO)Cl]$ appear exception. Show.

Hints : Both are 16-electron species. (a) 2Rh + 4CO + 2Cl (bridge); 2 × 9 + 4 × 2 + 2 × 3



(b) $(Ph_3P)_2Ir(CO)Cl$; 2 × 2 + 9 + 2 + 1.

32.1.5 Complexes formed by nitric oxide (nitrosyls)

The nitric oxide molecule has eleven valence electrons—one more than the CO molecule, occupying the antibonding π molecular orbital (refer Fig. 32.2). As such, NO readily forms NO^+ having the same number of valence electrons as CO with identical m.o. description. Accordingly, nitric oxide can replace CO in many carbonyl complexes where it acts as an effective three electron donor, though other less common modes of coordination are also known. Example of a pure nitrosyl complex is rare, perhaps represented by $Cr(NO)_4$ alone. On the other hand there are a large number of complexes with other ligands. Linear, bent, doubly, triply and even quadruply bridged modes of coordination are known.

Unlike the carbonyls, nitric oxide complexes cannot be prepared directly using excess NO at high temperature and pressure since the oxide tends to disproportionate at high temperatures and chances of oxidation of the metal by it cannot be ruled out. Several methods of preparation of nitric oxide complexes are available :

(i) *Addition of or substitution by NO*

$$[Co(OPPh_3)_2X_2] + 2NO \longrightarrow [Co(NO)_2(OPPh_3)_2X_2]$$

$$[Cr(CO)_6] + 4NO \longrightarrow [Cr(NO)_4] + 6CO$$

$$[Fe(CO)_5] + 2NO \longrightarrow [Fe(CO)_2(NO)_2] + 3CO$$

$$[Mn(CO)_5I] + 3NO \longrightarrow [Mn(CO)(NO)_3] + 4CO + I.$$

In substitution reactions, three CO ligands are replaced by *two* NO ligands (NO is effectively a three electron donor) or one NO can replace one CO plus one halogen atom.

(ii) *Methods involving NO⁺*

$NOBF_4$, $NOPF_6$ or $NO[HSO_4]$ may be used to add to or substitute in other complexes in methanol (or CH_3CN) :

$$[Rh(CNR)_4]^+ + NO^+ \longrightarrow [Rh(CNR)_4(NO)]^{2+}$$

$$[RhCl(CO)(PPr_3)_2] + NO^+ \longrightarrow [RhCl(NO)(CO)(PPr_3)_2]^+.$$

(iii) *Oxidative addition of XNO*

$$[Ni(PPh_3)_4] + ClNO \longrightarrow [Ni(Cl)(NO)(PPh_3)_2] + 2PPh_3.$$

(iv) *Use of NH_2OH*

$$OsO_4 + NH_2OH.HCl + NCS^- \longrightarrow [Os(NO)(NCS)_5]^{2-}.$$

Basic solutions are suitable for cyano complexes :

$$[Ni(CN)_4]^{2-} + 2NH_2OH + NaOH \longrightarrow [Ni(CN)_3(NO)]^{2-} + NH_3 + NaCN + 2H_2O$$

$NaNO_2$, KNO_2, RONO and concentrated nitric acid may also be used to introduce NO in the coordination sphere of metals. Ruthenium solutions in particular form nitrosyl complexes readily with concentrated nitric acid. Other examples are also known.

$$[Fe(CN)_6]^{4-} \xrightarrow{HNO_3} [Fe(CN)_5(NO)]^{2-}$$

N-methyl-*N*-nitrosourea may also be used to prepare nitrosyl complexes from metal carbonyl hydrides :

$$[Mn(CO)_5H] + MeN(NO)CONH_2 \longrightarrow [Mn(CO)_4(NO)] + CO + MeNHCONH_2.$$

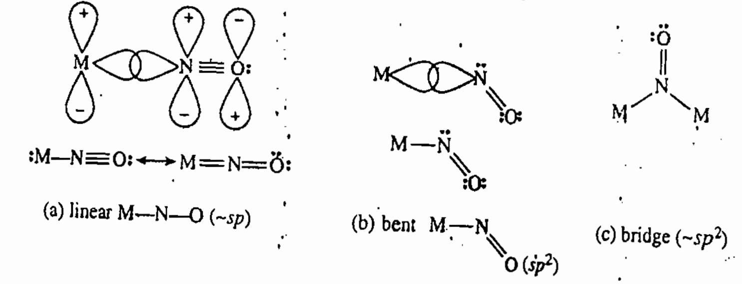
The properties of important nitrosyl complexes have been discussed in connection with individual metals. Here we discuss the general structure and bonding mode of such complexes.

Three principal modes of bonding by nitric oxide are commonly found :

(i) *terminal, linear M—N—O group.* Here NO may be regarded formally as a three electron donor : first transferring an electron to the metal followed by coordination from NO⁺. However, the M—N—O group in many such complexes have bond angles in the range 165-180°. The N—O infrared stretching modes in these cases usually fall in the range 1650-1900 cm^{-1} (in carbonyl nitrosyls; the value is very sensitive to the nature of other ligands).

(ii) *bent MNO groups* with bond angles between 120°-140°. Here the NO molecule may be considered as an 1-electron donor. Bent M—NO groups mostly show N—O stretchings at a lower range (1525-1690 cm^{-1}).

The two bonding modes are schematically shown in Fig. 32.5.



(a) linear M—N—O (~*sp*)

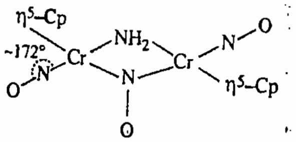
(b) bent M—N—O (sp^2)

(c) bridge (~sp^2)

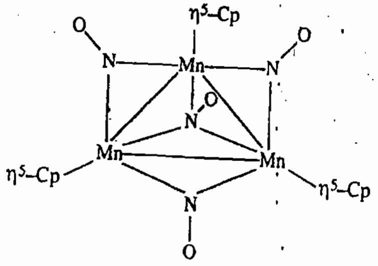
Fig. 32.5
Bonding modes of NO : (a) linear; (b) bent; (c) bridge.

Examples of some linear and bent nitrosyl complexes are given in Table 32.7.

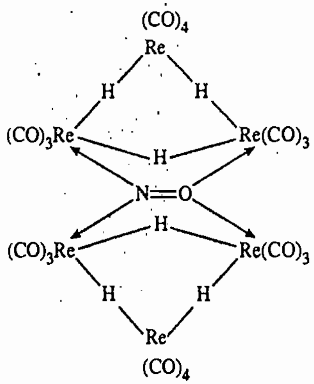
(iii) *Bridging NO groups.* Doubly, triply and even quadruply bridged nitric oxide complexes are known (32-IVa—c). ν (N—O) in bridged species occur in the range 1480-1510 cm^{-1} for μ_2 bridge and ~1320 cm^{-1} for μ_3 bridge. Both symmetric and asymmetric bridges are known.



32-IV (a)



32-IV (b)



32-IV (c)

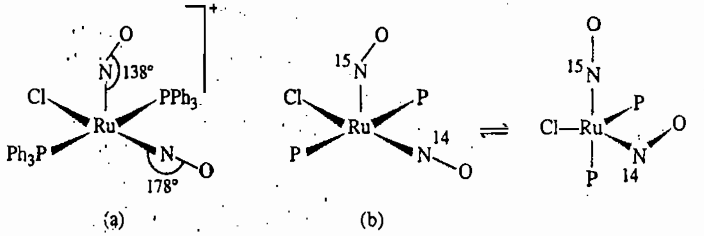
TABLE 32.7

Some examples of linear and bent coordination by NO

Compound	∠MNO	ν_{N-O} (cm^{-1})
$[Fe(NO)(mnt)_2]^-$	180°	1867
$[Co(diars)(NO)]^{2+}$	179°	1852
$Na_2[Fe(CN)_5(NO)].2H_2O$	178°	1935
$[RuH(NO)(PPh_3)_3]$	176°	1645
$K_3[Mn(CN)_5(NO)].2H_2O$	174°	1700
$[Ir(CH_3)I(NO)(PPh_3)_2]$	120°	1525
$[Ir(CO)Cl(NO)(PPh_3)_2]BF_4$	124°	1680
$[Rh(Cl)_2(NO)(PPh_3)_2]$	125°	1620
$[Co(NH_3)_5NO]^{2+}$	119°	1610
$[CoCl(en)_2(NO)]^+$	124°	1611
$[RuCl(NO)_2(PPh_3)_2]^+$	178°, 138°	1845, 1687
$[Os(NO)_2(OH)(PPh_3)_2]^+$	180°, 127°	1842, 1632

mnt = maleonitriledithiolato; diars = 1,2-bis (dimethylarsino)benzene.

The compounds at the end of Table 32.7 contain both linear and bent MNO groups (Fig. 32.6a). The ion $[RuCl(NO)_2(PPh_3)_2]^+$ is fluxional; it undergoes linear-bent exchange in solutions (Fig. 32.6b) which can be followed by ^{15}N nmr spectroscopy.



(a)

(b)

Fig. 32.6 : Structure of $[RuCl(NO)_2(PPh_3)_2]^+$.

Referring to Fig. 32.5, the N atom in a bent nitrosyl group may be approximately described by sp^2•hybridization, with a pair of electrons in an essentially non-bonding orbital. In the linear coordination mode, this electron pair is co-ordinated to the metal, making NO an effective 3-electron donor. Hence, earlier transition metals with low-lying vacant orbitals suitable for accepting more electrons supplied by the ligand are likely to form linear nitrosyls. Later transition elements having filled low-lying orbitals are thus expected to form bent nitrosyls. However, energy balance between the two forms is delicate and an equilibrium between both forms may be observed in certain cases. From CH_2Cl_2 or CH_3CN solutions, the complex ion $[Ir(\eta^3{-}C_3H_5)(NO)(PPh_3)_2]^+$ can be crystallized with appropriate counter ions either in the linear coordination or in the bent coordination.

The brown ring test for nitrates is based on the formation of the complex $[Fe(NO)(H_2O)_5]^{2+}$. The nature of the complex has been discussed earlier (p. 936, section 28.7.6).

The Roussin's red and black salts (Ch. 28) are also nitrosyl complexes with Fe—Fe interaction. These and other iron nitrosyl compounds are at present being investigated for their reported biological activity. Nitroprussides have been used to control blood pressure as they act as muscle relaxants. Roussin's black salt may have antibacterial properties while some of the red esters may enhance the activity of certain carcinogens.

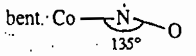
Q. 32.11 *Both $[Mn(CO)_4NO]$ and $[Fe(CO)_4CN]^-$ have tbp structure. In the former, NO occupies an equatorial position while in the latter, the CN^- occupies an axial position. Comment.*

Hint : Metal-ligand π-back bonding is favoured at an equatorial position relative to an axial position. Between NO and CN^-, NO is a stronger π-acceptor (since CN^- has a negative charge).

The complex $[Co(diars)_2NO]^{2+}$ conforms to the 18-electron rule if NO is taken as a three electron donor, that is, a linear Co—N—O arrangement is expected to confer a stable electron count for cobalt (7 + 4 × 2 + 3). Indeed, the complex is trigonal bipyramid with a linear Co—N—O in the equatorial plane for efficient π-back bonding. When treated with thiocyanate, the complex changes to one with a bent Co—N—O:

$$[Co(diars)_2NO]^{2+} + SCN^- \longrightarrow trans\text{-}Co(diars)_2(NCS)(NO)^+$$

linear Co—N—O



This is consistent with the generalizations made above — in order to accomodate the electron pair coordinated by the thiocyanate ion, an electron pair has to be transferred from the metal to the nitrogen, thereby forcing the latter to adopt a bent M—N—O arrangement. This has been called *stereochemical control of valence.*

The overall pattern of bonding in nitric oxide complexes is comparable to that in carbon monoxide complexes : first a dative σ-overlap from N to M followed by π-back bonding from metal to the antibonding π-orbital of NO. As already mentioned, the bonding is often described as a preliminary transfer of one electron from NO to M, followed by coordination from NO^+ to the reduced metal center. Such artificial description is good at the first sight as it readily explains the stronger π-acceptor behaviour of NO^+ compared to CO. However, the concept implies a very large charge separation in these otherwise covalent complexes and assigns unusually low oxidation states for the metals. The bonding in linear nitrosyls is best described in terms of molecular orbitals where the neutral NO contributes three electrons altogether.

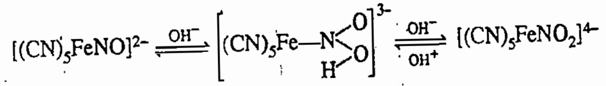
Removal of an antibonding electron from NO decreases the N—O distance in NO^+ to about 106 pm from 115 pm; the N—O stretching frequency shows a corresponding increase from 1876 cm^{-1} to 2300 cm^{-1}. In sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, the N—O distance is 113 pm and ν_{NO} is around 1939 cm^{-1}. This is consistent with the formulation of the complex as that of NO^+ with strong back-bonding to the π^*-m.o. of NO.

Under comparable conditions, M—CO and linear M—NO bonds are about equally strong. This is supported by the fact that the M—C and M—N bond lengths differ almost by a constant amount of about 7 pm, which may be associated with the difference in size of the two elements. However, substitution reactions on mixed carbonyl nitrosyls usually result in displacement of bound CO rather than NO :

$$Co(CO)_3NO \xrightarrow{L} Co(CO)_2(NO)L \quad (L = R_3P, X_3P, RNC \text{ etc.})$$

This suggests that the M—N bond is stronger than the M—C bond.

The basic difference in the electronic structure of linear and bent nitrosyl groups also causes different chemical reactivity of the two types of coordinated NO. In general, linear M—N—O groups are attacked by nucleophiles while the bent groups are susceptible to electrophilic attack in view of the lone pair of electrons on N. Thus, OH^- ion attacks NO to give the following reaction



$$[(CN)_5FeNO]^{2-} \xrightleftharpoons{OH^-} \left[(CN)_5Fe{-}N{<}^{O}_{O-H}\right]^{3-} \underset{OH^+}{\overset{OH^-}{\rightleftharpoons}} [(CN)_5FeNO_2]^{4-}$$

The detection of sulfide ion by sodium intropusside solution is based on a similar reaction.

$$[(CN)_5FeNO]^{2-} + S^{2-} \longrightarrow [(CN)_5FeNOS]^{4-}$$

Electrophilic attack at either N or O is also possible. The coordinated NO group may also be reduced by boro- or aluminohydrides or other reducing agents, for example,

$$[RuClpy_4NO]^{2+} \xrightarrow{Zn/H^+} [RuClpy_4NH_3]^+$$

Intermolecular transfer of NO between complexes suggests the formation of bridged intermediates, as in the reaction

$$CoCl(PPh_3)_3 + Rh(NO)(PPh_3)_3 \rightleftharpoons Co(NO)(PPh_3)_3 + RhCl(PPh_3)_3.$$

32.1.6 Cyano complexes

The cyanide ion, CN^-, is isoelectronic with CO and NO^+. It forms a large number of complexes with similar bonding principles in both high and low oxidation states of metals. Like CO, the CN^- ion also occupies a high position in the spectrochemical series as well as the nephelauxetic series; it is also a strong trans-directing group. However, due to its negative charge, the cyanide ion is a better σ-donor and a poorer π-acceptor compared to CO; the lower electronegativity of the N-atom is also responsible for its weak π-acidity. The σ-donor and π-acceptor properties of CN^- and other isoelectronic ions show the following order :

σ-donor : $CN^- > RNC > NO^+ \sim CO$

π-acceptor : $CN^- < RNC << CO < NO^+$.

Owing to its prominent σ-donor property, the cyanide ion forms many Werner type complexes; many such complexes have been known since Werner's time.

The cyanide ion mostly acts as a unidentate ligand coordinating always through the C-end (established by neutron diffraction), but bidentate and bridging modes are also known. We have encountered many such compounds containing chains of bridging CN groups, for example, in connection with linkage isomerism, AgCN, AuCN and the "prussian blue" compounds. The coordinated M—CN group may also establish further donor-acceptor interactions with the lone pair of electrons on the N-atom as in the complexes $K_2[Ni(CN.BF_3)_4]$, $K_4[Fe(CN.BF_3)_6]$, or $[Fe(CN.BF_3)_2(o\text{-phen})_2]$. The compounds are readily formed by the action of BF_3 on the respective cyanocomplex. A tridentate CN group is found in $CuCN.NH_3$ (Fig. 32.7).

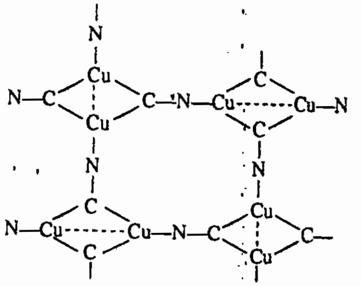
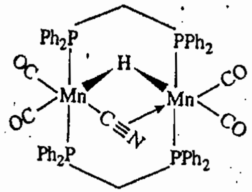


Fig. 32.7

Skeleton showing tridentate CN groups.

In the skeleton of the plane net shown for $CuCN.NH_3$, each Cu is actually 5-coordinate, being bonded to one NH_3 (not shown), two C, one N and one Cu. The Cu......Cu distance is closer than that in the metal (242 pm vs 255 pm).

The CN^- ion can also bridge with one of its π-bonds as in 32-V. The nitrogen end can be protonated to $M—C{\equiv}NH^+$.



32-V

The cyano complexes of individual elements have been discussed in relevant chapters. It may be observed that the CN group can form complexes in a variety of coordination number and structure (recall the complexes of Ag(I), Au(I), Cu(I) and Fe(II) for example). Stabilization of both low and high oxidation states of a metal is observed, for example in $K_4[Ni(CN)_4]$ and in $K_3[Mn^{III}(CN)_6]$. Some common cyano complexes of *d*-block elements are summarized in Table 32.8.

TABLE 32.8

Some cyano complexes of *d*-block elements

Gr 5	Gr 6	Gr 7	Gr 8	Gr 9	Gr 10	Gr 11	Gr 12
$[V(CN)_6]^{3-}$	$[Cr(CN)_6]^{3-}$		$[Fe(CN)_6]^{3-}$	$[Co(CN)_6]^{3-}$			
$[V(CN)_6]^{4-}$	$[Cr(CN)_6]^{4-}$	$[Mn(CN)_6]^{4-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{4-}$	$[Ni(CN)_4]^{2-}$	$[Cu(CN)_4]^{2-}$	$[Zn(CN)_4]^{2-}$
		$[Mn(CN)_6]^{5-}$				$[Cu(CN)_3]^{-}$	
					$[Ni(CN)_4]^{4-}$		
	$[Mo(CN)_8]^{3-}$						
	$[Mo(CN)_8]^{4-}$						
	$[Mo(CN)_8]^{5-}$		$[Ru(CN)_6]^{3-}$	$[Rh(CN)_6]^{3-}$			
			$[Ru(CN)_6]^{4-}$		$[Pd(CN)_4]^{2-}$		$[Cd(CN)_4]^{2-}$
					$[Pd(CN)_4]^{4-}$		
	$[W(CN)_8]^{3-}$						
	$[W(CN)_8]^{4-}$	$[Re(CN)_8]^{4-}$					
			$[Os(CN)_6]^{3-}$	$[Ir(CN)_6]^{3-}$			
			$[Os(CN)_6]^{4-}$		$[Pt(CN)_4]^{2-}$		$[Hg(CN)_4]^{2-}$

Most cyano complexes are formed rather easily by the action of aqueous KCN on aqueous solutions of the metal ion. Cyano complexes of low-valent metals cannot be prepared in this manner. These are usually prepared in liquid ammonia involving reduction with potassium metal or electrolytically :

$$[Ni(CN)_4]^{2-} + 2e \xrightarrow{\text{liq. } NH_3} [Ni(CN)_4]^{4-}$$

These are extremely unstable in air and often also in water.

The π-donor property of the metal appears to be a major factor in determining the stability of its cyano complex in a given oxidation state (Ch. 28, in-chapter Q. 28, regarding $Cu^{I}—Cu^{II}$). Large crystal field splitting and effect of spin-pairing may also become important as explained earlier (e.g., $Co^{II}—Co^{III}$, Section 28.8.4). π-donation by the metal appears most significant at about the d^6 cation in Fig. 32.8 in which the heats of formation of the cyano-complexes of some M^{2+} ions are plotted. The minima at Mn^{2+} may be associated with the high promotion energy for the d^5 system in going from high-spin to low-spin state.

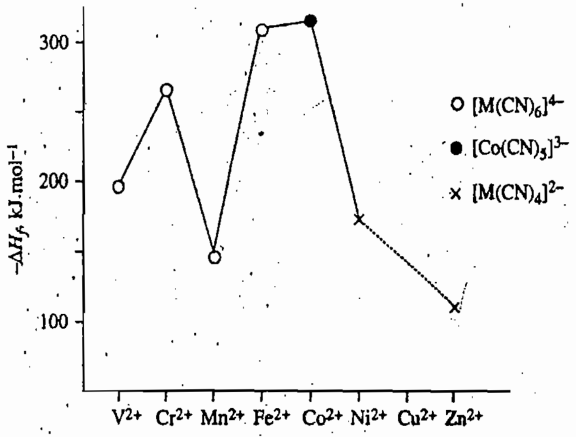


Fig. 32.8

Enthalpy of formation of some cyano complexes of M(II).

Q. 32.12 *While the Co^{3+}/Co^{2+} couple normally liberates oxygen from water, hydrogen is liberated in presence of CN^- ions. Explain.*

The bonding in the transition metal cyano complexes may be described in the same approach as applied to the transition metal carbonyls and nitrosyls. The molecular orbital description is again based on a dative carbon to metal σ-overlap followed by back bonding from filled π-symmetry orbitals of the metal to the π* m.o. of the ligand. Though the bonding description is synergic, that is σ- and π-bondings mutually reinforcing one another, the extent of π-bonding is comparatively less than in carbonyls and nitrosyls. In fact, there are enough reasons to consider the cyanide as a pseudohalide rather than a π-acid ligand. π-bonding may be appreciable only in complexes of metals in very low oxidation states, for example in $K_4[Ni(CN)_4]$. Since the CN^- ion is a strong nucleophile, it is expected to form stable complexes with metals in high oxidation states even without the involvement of π-bonding.

The valence bond description is again based on the resonance hybrids

$$M—C{\equiv}N \longleftrightarrow M{=}C{=}N$$

Since CN^- is a strong field ligand, its complexes are all low spin.

$(CN)_2$, the dicyanogen molecule itself can also function as a ligand :

$$(AgAsF_6)_n + Zn(CN)_2 \longrightarrow \{Ag[(CN)_2]_2\}_n\ (AgF_6)_n$$

The coordination involves AgNC—CNAg groups.

32.1.7 Complexes formed by isocyanides (isonitriles)

Like the cyanide group, isocyanides (RNC) also form a large number of complexes in both high and low oxidation states of a metal. Isocyanides are stronger σ donors compared to CO as the donor carbon atom is linked to the less electronegative nitrogen. For the same reason one expects it to be a weaker π-acceptor than CO.

The main difference between carbon monoxide and an isocyanide ligand is that unlike carbonyls, isocyanide complexes do not have to derive their stability from synergic π-bonding. The M—C σ-bond may be self-sufficient without support from metal-carbon π-bond. Since the RNC group is a good σ-donor, it can form complexes with metals in high oxidation states where back donation is less likely and essentially σ-only bonding is involved.

The isocyanide complexes may be prepared by substitution reactions in carbonyls or other complexes :

$$Ni(CO)_4 + 4CNAr \longrightarrow [Ni(CNAr)_4] + 4CO$$

$$2Ni(DMG)_2 + 8CNR + N_2H_4 \longrightarrow 2[Ni(CNR)_4] + 4DMGH + N_2.$$

The nickel compounds form air stable yellow crystals soluble in organic solvents. They are diamagnetic ($3d^{10}$).

Electrophilic attack on cyano complexes or metal cyanides is also a common route to isocyanide complexes :

$$CoX_2 + RNC \longrightarrow CoX_2\ (CNR)_2 \qquad X = Cl, Br, SCN; R = CH_3.$$

The green crystalline product corresponds to the formulation $[Co(CNR)_4][CoX_4]$ from conductance studies. Blue-violet square planar $[Co(CNR)_4]X_2$ compounds are also known with $R = CH_3$ and X = Cl or Br. They are reduced by hydrazine to yellow brown diamagnetic Co(I) :

$$5[Co(CNR)_4]I_2 + N_2H_4 = 4[Co(CNR)_5]I + CoI_2 + 4HI + N_2.$$

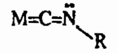
Being a better σ-donor than CO, the RNC group forms complexes with Co(II), Cr(III), Mn(II), Fe(II) etc. which have no carbonyl analogues. The weaker π-acidity of RNC compared to CO is illustrated by the following reaction in which the RNC group preferably combines to Co(I) and CO combines with Co(–I) :

$$Co_2(CO)_8 + 5RNC \longrightarrow [Co(CNR)_5][Co(CO)_4] + 4CO.$$

The cationic species may also be obtained through the metathesis :

$$[Co(CNR)_5]ClO_4 + Na[Co(CO)_4] \longrightarrow [Co(CNR)_5][Co(CO)_4] + NaClO_4.$$

The terminal MCNR groups in most isocyanide compounds are close to linear with CNC angles lying between 165-179°. However, bent isocyanide groups with CNC angles around 130-135° are also known. The i.r. band for the linear RNC group lies around 1960 cm^{-1} while the bent groups show somewhat lower bands at 1830-1870 cm^{-1}. $Ru(CNBu^t)_4PPh_3$ has almost linear t-BuNC groups at axial positions and bent t-BuNC groups at equatorial positions (with PPh_3). By analogy with nitrosyls, we may write the following valence bond structures :



$$M—C{\equiv}N—R$$

The bonding in the isocyanides is essentially similar to those in carbonyls and cyanides. The occurrence of metal-carbon π-back bonding is illustrated by the Co—C distance (187 pm) in $[Co(CNMe)_5]^+$ which is substantially shorter than a Co—C single bond (207 pm).

32.1.8 Complexes of dihapto dihydrogen

In chapter 17, we mentioned the formation of dihapto dihydrogen complexes. The field has rapidly developed in the last twenty years and more than one hundred η^2-H_2 complexes have been prepared, some of them quite stable. The bonding in these compounds is comparable to those in the carbonyls etc. complexes. The H_2 molecule acts as a σ-donor through its bonding σ-m.o. and as a π-acceptor via the vacant σ* (antibonding) m.o.

The formation of η^2-H_2 complexes was first indicated (G. J. Kubas, 1980) in the reaction of H_2 at 1 atm pressure with the coordinatively unsaturated complexes $[M(CO)_3(PCy_3)_2]$, (M = Mo, W; Cy = cyclohexyl) in toluene solution at low temperatures. The yellow crystalline products showed the composition $[M(CO)_3(H_2)(PCy_3)_2]$ and found to release the hydrogen quantitatively at room temperature on evacuation. The corresponding tri i-propylphosphine compound was studied by X-ray and neutron diffraction at –100°C which confirmed the sidewise coordination from the H_2 molecule (Fig. 32.9). The M—H_2 mode of bonding can be distinguished from M—H by solution nmr spectra.

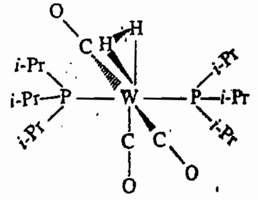


Fig. 32.9

Skeleton of *mer-trans*-$[W(CO)_3(\eta^2-H_2)(PPr^i_3)_2]$.

d_{H-H} = 84 pm (vs 74.14 pm in free H_2)

d_{W-H} = 175 pm

ν_{H-H} = 2690 cm^{-1} (vs 4159 cm^{-1} for free H_2).

η^2-H_2 complexes may be neutral or cationic but are invariably octahedral. They may also be dinuclear with the same or different metals.

Besides addition of H_2 to a coordinatively unsaturated metal center, η^2-H_2 complexes have been prepared by other methods also, for example,

(i) *displacement of other ligands*, often aided by uv irradiation :

$$Cr(CO)_6 + H_2 \xrightarrow{h\nu,\ \text{liq Xe}} [Cr(CO)_5(H_2)] + CO$$

$$[Co(CO)_3(NO)] + H_2 \xrightarrow{\text{do}} [Co(CO)_2(NO)(H_2)] + CO.$$

(ii) *protonation of a polyhydrido complex*, a strong acid like $HBF_4.Et_2O$ being used.

$$[IrH_5(PCy_3)_2] \underset{NEt_3}{\overset{H^+}{\rightleftharpoons}} [IrH_2(H_2)_2(PCy_3)_2]^+.$$

Use of deuterated acid produces η^2 – HD complexes — a fact that establishes that the H—H bond remains intact in the complex. The HD complex may be distinguished from its different proton nmr spectrum since the proton signal is split by coupling with deuterium (nuclear spin $J = 1$).

η^2-H_2 complexes are mostly formed by transition metals in groups 6—8, none being known for metals in group 3. Vanadium and niobium (Gr 5) form species like $[M(\eta^5\text{-}Cp)(CO)_3(H_2)]$. Within a given group, the first and second members form $\eta^2 - H_2$ complex but the third member tends to form polyhydrido species.

The η^2-H_2 complexes vary widely in their stability : some are quite stable at room temperature while some are stable only at very low temperature depending upon various factors like electron configuration of the metal, nature of other ligands, charge on the complex and so on. Cationic species are generally found to be more stable, specially in presence of a non-coordinating anion like BF_4^-.

As mentioned in the beginning of this section, the bonding in η^2-H_2 complexes may be rationalized by (i) σ-overlap from a filled bonding m.o. of H_2 ($1\sigma_g$) to a vacant hybrid orbital on the metal, followed by (ii) synergic π-back bonding from a filled metal orbital to the vacant antibonding m.o. of H_2 ($2\sigma_u$; Fig. 32.10). $H_2 \longrightarrow ML_n$ σ-bonding will be favoured by strong σ acidity of the ML_n system, that is when the metal is not electron rich. The bonding scheme has an overall similarity to that in complexes of other π-acid ligands, particularly the alkenes (next section) except that the orbitals involved here have σ/σ* symmetry (π/π* in case of alkenes). Back-donation of electrons to the antibonding m.o. in H_2 is expected to cause a lowering in bond order, which is supported by the lowering of $\nu_{H\text{-}H}$ to 2650-3250 cm^{-1} from 4159 cm^{-1} in free H_2. Simultaneous lengthening of H—H bond is also observed by neutron diffraction, 84 pm vs 74 pm in molecular H_2.

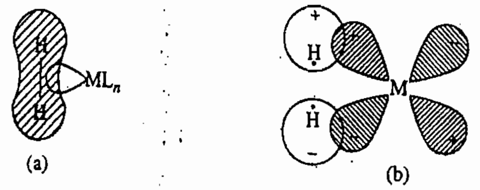


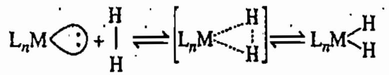
Fig. 32.10

Bonding in η^2-H_2-metal complex (schematic).

(a) $H_2(1\sigma_g) \longrightarrow$ M donation (b) M $\longrightarrow H_2(2\sigma_u)$ back-donation.

Such $\eta^2 - H_2$ complexes are likely intermediates in oxidative addition reactions of H_2 which occur with great facility in spite of the high H—H bond energy (450 kJ mol^{-1}). As back donation pushes electrons in the antibonding m.o. of H_2, the H—H bond may be easily split with the formation of two M—H bonds ;

[Sec.32.2.1
Alkene complexes]



$$L_nM + \overset{H}{\underset{H}{|}} \rightleftharpoons \left[L_nM\begin{smallmatrix}H\\ \vdots\\ H\end{smallmatrix}\right] \rightleftharpoons L_nM\begin{smallmatrix}H\\ H\end{smallmatrix}$$

An overall positive charge on the metal center diminishes back donation while an overall negative charge will favour back donation and hence rupture of the H—H bond. We recall that anionic complexes of η^2-H_2 are not known. The observed lengthening of the H—H bond is also consistent with electron population in the σ* m.o. of H_2. Intermediate cases between $M(\eta^2\text{-}H_2)$ and $M(\sigma\text{-}H)_2$ coordination are also known. A fine energy balance may even keep the two forms in equilibrium, as for example, in

$$[Nb(\eta^5\text{-}Cp)(CO)_3(\eta^2\text{-}H_2)] \xrightleftharpoons{-78° \text{ to } +25°C} [Nb(\eta^5\text{-}Cp)(CO)_3(H)_2]$$

Both M—H and M—(η^2-H_2) bonding may be present together in some compounds, for example, $[Ru^{II}(H)_2(H_2)(PPh_3)_3]$ and $[Ir^{III}(H)_2(H_2)_2(PCy_3)_2]^+$.

An asymmetric end-on η^1-H_2 coordination is also supposed to exist in $[ReCl(H_2)(PMePh_2)_4]$ and a few low temperature matrix products.

32.2 ORGANOMETALLICS-II

This section is meant to give a brief exposure to the complexes formed by alkenes, alkynes and delocalized hydrocarbon systems. Examples of application of organometallic compounds in homogeneous catalysis are given in the next section.

32.2.1 Alkene complexes

Zeise's salt, $[K\{PtCl_3(\eta^2 - C_2H_4)\}]H_2O$; (Ch. 21 and 29) is the earliest example of an organometallic compound formed by a transition metal (1827). It contains a molecule of ethylene bound to platinum as shown in 21-IX (p. 266). Zeise obtained it by refluxing $PtCl_2$ and $PtCl_4$ in ethanolic solution followed by addition of aqueous KCl and HCl. The cream yellow compound is now prepared by reacting ethylene with $K_2[PtCl_4]$ in aqueous HCl.

$$K_2[PtCl_4] + H_2C{=}CH_2 \longrightarrow K[Pt(C_2H_4)Cl_3] + KCl$$

The reaction is catalyzed by $SnCl_2$ through the intermediate formation of $[PtCl_3(SnCl_3)]^{2-}$. The original preparation of Zeise probably involved unknowing reduction of $PtCl_4$ by ethanol :

$$PtCl_4 + 2C_2H_5OH \longrightarrow PtCl_2.C_2H_4 + CH_3CHO + H_2O + 2HCl$$

$$PtCl_2.C_2H_4 + KCl \longrightarrow K[PtCl_3.C_2H_4]$$

Preparation of other alkene complexes is given later. Starting with K_2PtCl_6, Zeise's salt may be prepard by prior reduction (with say, N_2H_4) to K_2PtCl_4.

The bonding in this and related compounds was interpreted only in 1951. The structural aspects of the anion (neutron diffraction) are noteworthy :

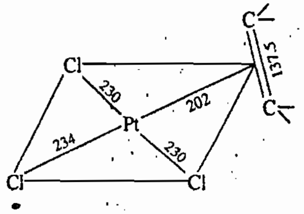


Fig. 32.11

Structure of the anion of Zeise's salt.

Figures refer to bond distances in pm (± 0.2).
Pt—C ≈ 213 pm.

(i) The C=C bond is perpendicular to the plane of the Pt and the 3 Cl^- ions with nearly equal Pt—C distances.

(ii) The Pt—Cl distance *trans* to the ethylene is longer than the other Pt—Cl distances.

(iii) The C—C distance in ethylene is 3.8 pm longer than that in free C_2H_4; there is a parallel decrease in the C=C stretching frequency from 1623 cm^{-1} in the Raman spectrum of ethylene to 1526 cm^{-1} in the i.r. spectrum of Zeise's salt.

(iv) The ethylene molecule departs from planarity : the four H-atoms are tilted back to a plane nearly 16.4 pm below the plane of the C-atoms.

The bonding was described from an MO point of view by Dewar, Chatt and Duncanson (DCD model). Though the ethylene molecule does not possess a lone pair of electrons, it can establish donor acceptor interaction with the metal by suitable orientation of the filled π and unfilled π* molecular orbitals. There is first a dative overlap of a filled π m.o. of the ethylene to a vacant $5d6s6p^2$ hybrid orbital of platinum forming a C → M σ-bond. Next, there may be metal to ligand π back bonding by overlap of a filled hybrid $5d6p$ orbital on the metal with the π* orbitals on ethylene (Fig. 32.12). As expected, the σ and π components of the metal-ligand bond mutually reinforces each other synergistically. Since the π* orbital is antibonding, population of this orbital weakens the C—C bond (compare bond lengths) but the M—C bond is strengthened at the same time. Both experimental and theoretical considerations indicate that the metal-alkene bond is essentially electroneutral — a consequence of fine balance between the two components in the bond.

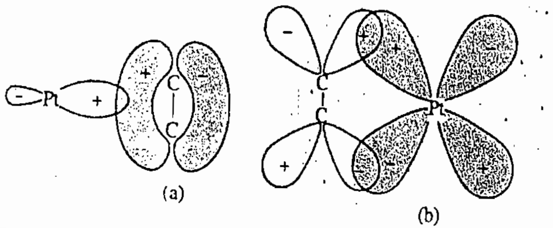


Fig. 32.12 : Bonding in $PtCl_3(C_2H_4)$ (schematic).
(a) C_2H_4 (π) ⟶ Pt (dsp^2) σ bond; (b) Pt (d_{xz} or dp hybrid) ⟶ C_2H_4 (π*) π bond.

Since the d_{xz} and d_{yz} orbitals are degenerate in the complex, the π-back bonding from metal to olefin will not be hampered if the C—C bond in ethylene remains in the plane of the $PtCl_3$ portion. In other words, the orientation of the ethylene molecule perpendicular to the $PtCl_3$ plane is not essential for the stability of the molecule — the M—C_2H_4 σ-bond (along the z-axis, say) offers no resistance to rotation of the alkene about the metal-olefin bond axis [Fig. 32.12(c)]. The rotational barrier in related complexes is only 40-70 kJ mol^{-1}. Moreover, the ^1H nmr spectrum of (η^5-Cp)$Rh(C_2H_4)$ shows two types of alkene protons at low temperatures (~0°C). As the temperature is raised to about 60°C, the protons appear equivalent, suggesting rotation of the alkene about the metal-alkene axis. Steric reasons may be supposed to operate behind the perpendicular orientation of the ethylene molecule since this arrangement provides less congestion compared to the in-plane orientation.

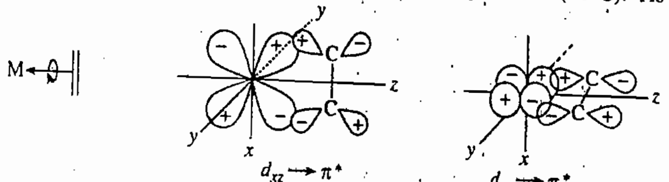
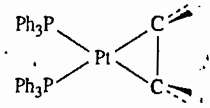


Fig. 32.12 (c) : Rotation of the ethylene molecule around Pt – C_2H_4 σ-bond axis.

Substitution of the hydrogens in ethylene by strongly electronegative atoms or groups naturally lowers the extent of ligand ⟶ M σ-bond but should favour M ⟶ ligand π back bonding. In complexes of tetracyanoethene or tetrafluoroethene, $(CN)_2C=C(CN)_2$ or C_2F_4, the bond angles within the ligands suggest tetrahedral hybridization of the carbon atoms. In $Pt(C_2H_4)_2(C_2F_4)$, all six carbon atoms are coplanar with the platinum but the Pt-ligand distances are 203 pm in case of C_2F_4 and 222 pm for C_2H_4. The C—C distances in metal-bound C_2H_4 and C_2F_4 are 138 pm and 143 pm respectively. Similarly in free $(CN)_2C=C(CN)_2$ (tetracyanoethylene), the C—C distance is 134 pm but in the planar complex $(Ph_3P)_2Pt[C_2(CN)_4]$, the C—C distance is 152 pm, nearly the same as that in ethane. Thus, it is suggestive to consider two usual 2c—2e Pt—C bonds in the metallacycle arrangement (32-VI); the carbon atoms are nearly sp^3 hybridized.



32-VI

Polyolefins with isolated double bonds may form complexes by donating two electrons per double bond to one or several metals. 1, 5- cyclooctadiene (1, 5-cod) acts as a 2 × 2 or 4 electron donor; 1, 3, 5, 7-cyclooctatetraene (cot) can function as a 4 electron donor to one or two different metals or as a 3 × 2 electron donor to a single metal.

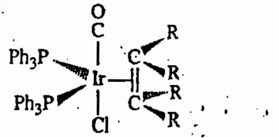
Many alkene complexes may be prepared by direct substitution of CO or other weak ligands by the alkene, e.g.,

$$Fe_2(CO)_9 + C_2H_4 \longrightarrow [Fe(CO)_4(C_2H_4)] + Fe(CO)_5 \quad (25°C, 50\ atm)$$

$$CpMn(CO)_3 + C_2H_4 \xrightarrow{h\nu\ (uv)} [MnCp(CO)_2(C_2H_4)] + CO$$

Some co-ordinatively unsaturated metal complexes react directly with olefins. Aqueous silver(I) and copper(I) combine directly with many alkenes — a reaction used for separating the alkenes from alkanes. Vaska's compound adds alkenes as follows :

$[IrCl(CO)(PPh_3)_2] + R_2C=CR_2 \rightleftharpoons$



Q. 32.13 *Addition of alkenes to Vaska's compound (see above) is strongest with tetracyanoethylene. Relative equilibrium constants for various alkenes are*

$H_2C=CH_2$	*(CN)HC=CH(CN)*	*$(CN)_2C=C(CN)_2$*
1	1500	1,40,000

Comment.

Hint : π-acid character is maximum in tetracyanoethylene. The Ir—alkene electron flow appears vital in determining the stability of the complexes.

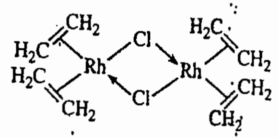
Reaction of alkenes with metal halides (or other compounds) in presence of a reducing agent also provides a convenient route to many alkene complexes. Hydrazine, $NaBH_4$, Al-(t-Bu)$_3$, zinc-ethanol etc. reducing agents have been used

$$\mathrm{Ni(acac)_2 + COD \longrightarrow (COD)_2Ni} \qquad (\mathrm{Al}\text{-}t\text{-}\mathrm{Bu_3})$$

$$\mathrm{(Ph_3P)_2PtCl_2 + C_2H_4 \longrightarrow (Ph_3P)_2Pt(C_2H_4)} \quad (\mathrm{NaBH_4 \ or \ N_2H_4})$$

Ethylene itself may also act as the reductant, as in the following reaction :

$RhCl_3 + C_2H_4$ (*excess*) ⟶



The chlorine bridges may be ruptured by suitable ligands. Thus, in presence of a base acetylacetone gives [Rh(acac)$(C_2H_4)_2$], while sodium cyclopentadienide forms [Rh(Cp)$(C_2H_4)_2$].

Cocondensation of alkenes with metal vapours at very low temperatures has been utilized for preparing many complexes :

$$\mathrm{Fe + 2COD \longrightarrow Fe(COD)_2}$$

Free alkenes are susceptible to attack by electrophiles on account of the rich π-electron cloud. On coordination to a metal, the electron population is largely diminished and the reactivity is reversed : the alkene becomes susceptible to nucleophilic attack. The nucleophilic attack of H_2O on C_2H_4 coordinated to palladium (section 29.6.5) forms the basis of the Wacker process for manufacture of acetaldehyde.

Silenes, $R_2Si{=}SiR_2$, are also known to form complexes with transition metals, for example, [{(i-Pr)$_2$Si=Si(i-Pr)$_2$}Pt($Ph_2PCH_2CH_2PPh_2$)] in which the platinum-silene bonding is comparable to that in alkene-metal complexes.

32.2.2 Alkyne complexes

Since alkynes possess two mutually perpendicular π-bonds, its ligand behaviour is expected to be more complicated than shown by the alkenes. Using one or both sets of π bonds, alkynes may function as formally 2, 3 or 4 electron donors and bridges. In the simplest case, an alkyne may use one bonding π m.o. and its corresponding π* m.o. as in the case of olefin complexes (Fig. 32.13). The other pair of π electrons may also be partly donated to a dπ-orbital of the metal suitably aligned, that is perpendicular to the $\mathrm{M}{<}^{\mathrm{C}}_{\mathrm{C}}$ plane. Synergic back-bonding is possible if the metal has a filled *d* orbital perpendicular to both of these engaged ones (Fig. 32.14).

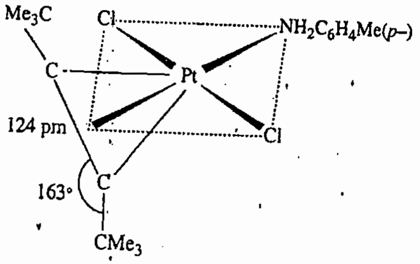


Fig. 32.13
A platinum-alkyne in which the alkyne coordinates similar to an alkene.

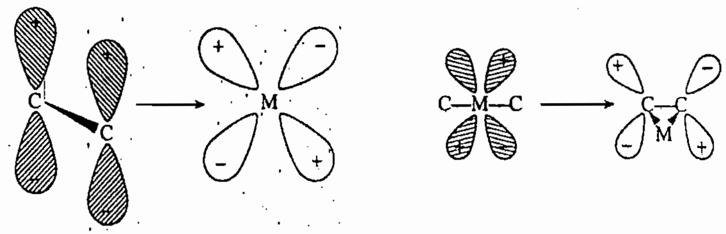
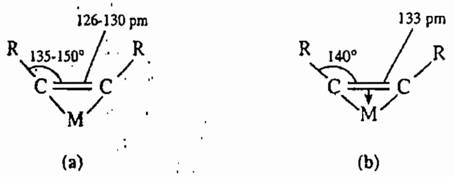


Fig. 32.14
Schematic representation of the second synergic alkyne-metal bond.

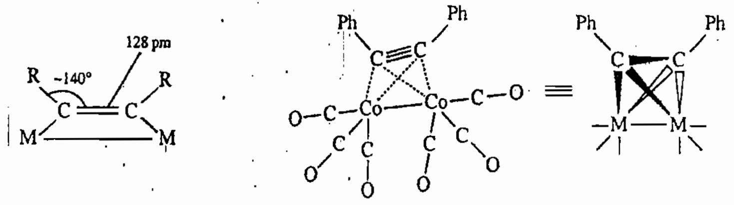
Coordination from one or both π-bonds in the alkynes is expected to lengthen the C—C distance and result in deviation from linearity, as shown in 32-VII (a) and (b). The bond length and bond angles are approximate.



(a) (b)

32-VII

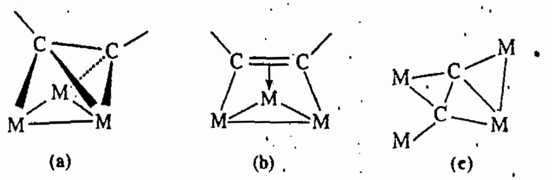
The alkynes may bridge several metal centers in a variety of roles. The common bridging mode as η^2, μ_2 ligand is shown in the planar structure of 32-VIII (a), where the alkyne acts as a two-electron donor. It may also behave in the η^2, μ_2-capacity in a distorted tetrahedral geometry [32-VIII (b)], where the alkyne is formally a four-electron donor. The bonding can be visualized as (i) the formation of two single bonds to each metal atom by donation from two sets of π bonds at 90° or, as (ii) forming two single bonds to each metal atom. The longer C—C distances (130-135 pm) in these complexes is not in good agreement with the second view.



(a) (b)

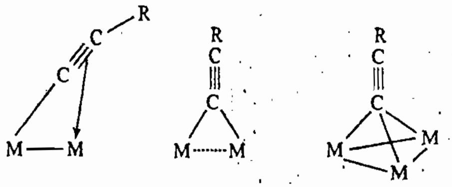
32-VIII

Alkynes are also known to form complexes with three or four metal atom clusters as a formal four-electron donor (32-IX a,b,c).



32-IX

Other bridging modes are also known, for example,



32-X

The alkyne complexes may be synthesized using the alkyne directly, often aided by uv radiation :

$$[Mn(C_5H_5)(CO)_3] + RC{\equiv}CR \xrightarrow{h\nu} [Mn(C_5H_5)(CO)_2(R_2C_2)] + CO.$$

Replacement of one CO group shows that the alkyne behaves as a monodentate ligand.

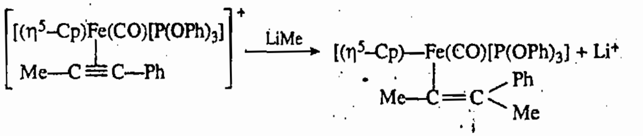
$$V(C_5H_5)(CO)_4 + RC{\equiv}CR \xrightarrow{h\nu} [V(C_5H_5)(CO)_2(R_2C_2)] + 2CO.$$

One alkyne group replaces two CO groups, acting as a didentate ligand.

The bridged cobalt compound shown in Fig. 32-VIII is obtained readily from dicobalt octacarbonyl

$$Co_2(CO)_8 + RC{\equiv}CR \xrightarrow{25°C} (CO)_3Co\ldots(\mu\text{-}RC{\equiv}CR)\ldots Co(CO)_3 + 2CO.$$

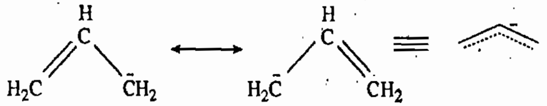
Like coordinated alkenes, coordinated alkynes are also attacked by nucleophiles, most prominently in cationic complexes.



$$\left[\begin{array}{l}[(\eta^5\text{-}Cp)Fe(CO)[P(OPh)_3]\\ \text{Me—C}{\equiv}\text{C—Ph}\end{array}\right]^+ \xrightarrow{LiMe} [(\eta^5\text{-}Cp)\text{—}Fe(CO)[P(OPh)_3] + Li^+ \quad \text{Me—C}{=}\text{C}\langle^{Ph}_{Me}$$

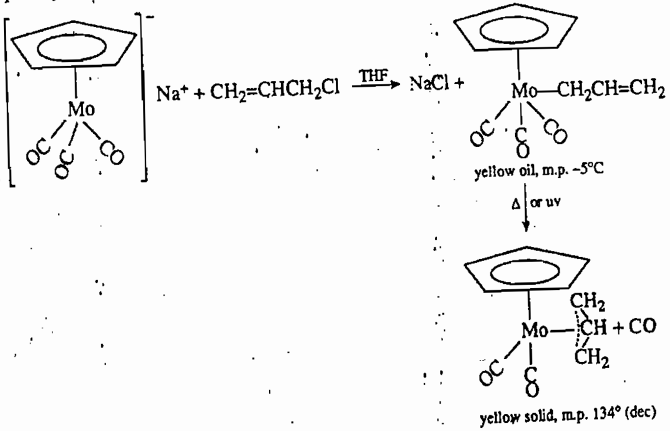
32.2.3 Allyl complexes

The allyl group $CH_2{=}CH{-}\bar{C}H_2$ may be represented by a delocalized π system :

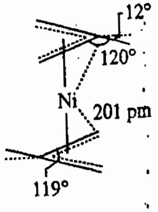


The system may be described by three π molecular orbitals, four electrons occupying the lower two m.o.-s. This leaves the third (antibonding) m.o. vacant making it a π-acid ligand. The most important allyl complexes are formed by Ni, Pd and Pt which are extensively used in catalysis. The preparation and use of bis-(π-allyl)nickel has been mentioned in section 28.9.7. This compound contains a nickel atom sandwiched between the allyl groups which act as 4-e π donor with η^3 coordination. η^1-allyl complexes are also known.

The nickel complex mentioned above is prepared from allyl Grignard reagents. Allyl halides also react with carbonylate anions to form η^1-allyl compounds which subsequently lose CO and are converted to η^3-allyl compounds. For example,



The bonding in allyl complexes may be described similar to the DCD model for alkene complexes involving donor-acceptor behaviour of the allyl group. Consistent with this description, the nickel atom in bis (η^3-2-methylallyl)nickel is equidistant from the three carbon atoms (32-XI).



32-XI

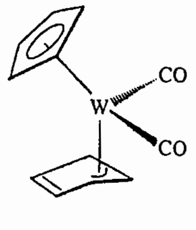
Allyl complexes are involved as intermediates in many catalytic processes as illustrated before for the nickel compound.

32.2.4 Complexes of carbocyclic π-donors

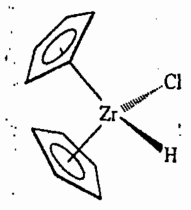
Introduction

Ferrocene (section 28.7.7) was the first example in which the delocalized π-electron cloud in an aromatic system (in this case $C_5H_5^-$) coordinates to a metal. A large number of compounds containing cyclopentadiene have since been discovered. Compounds containing other aromatic systems like C_6H_6, $C_7H_7^+$ (tropylium cation) and $C_8H_8^{2-}$ [cyclooctatetraenide anion, (cot)$^{2-}$] etc are also established. Our discussion will center largely on the compounds formed by cyclopentadiene and benzene. The C_5H_5 group is commonly represented as Cp; Me_5C_5 is usually represented by Cp*.

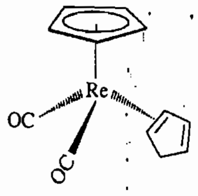
In ferrocene, as we shall presently find, the ring system and the metal atom can be considered neutral for the purpose of electron counting that is 5 per C_5H_5 ring and 8 per Fe (2 × 5 + 8 = 18). The hapticity of cyclopentadiene in the compound is 5 (η^5-). Cyclopentadiene may also form compounds as a monohapto (η^1-) one electron donor or trihapto (η^3-) three electron donor ligand. It may also act as a dihapto ligand (η^2–) in certain cases e.g., [Re(η^5–Cp)(CO)$_2$(η^2–C_5H_6)]. η^1- and η^5- coordinations exist together in Ti(C_5H_5)$_4$ (Ch. 28, Fig. 28.21). A few other modes are shown below.



32-XII (η^5–, η^3–)



32-XIII(a) (η^5–, η^5–)



32-XIII(b) (η^5–, η^2–)

There are basically three types of compounds formed by η^5-$C_5H_5^-$ and η^6-C_6H_6 :

(i) Symmetrical sandwich type complexes like (η^5-Cp)$_2$Fe, (η^6-C_6H_6)$_2$Cr and (η^5–Cp) (η^6-C_6H_6) Mn.

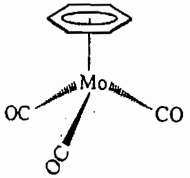
(ii) (η^5-Cp)$_2$ML$_x$ where L is some other ligand like H$^-$, R$^-$, halide, olefin or NO. The molecules are bent (32-XIIIa).

(iii) Complexes formed by one cyclic π-donor ligand (Cp or C_6H_6) with other ligands such as halogens, CO, RNC and R_3P, for example, Mo(η^6-C_6H_6)(CO)$_3$ (32-XIV).

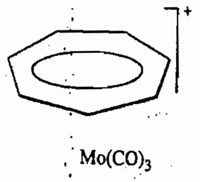
Cyclopentadiene also forms ionic compounds containing simple Cp$^-$ anions and compounds containing simple σ bonds. Ionic compounds are formed by the strongly electropositive metals like the alkali and alkaline earth group, Y, Tl(I) and the lanthanides. Compounds of divalent metals like magnesium have the formula Cp$_2$Mg and a ferrocene-like structure. But they are not sandwich compounds described below. These compounds are very reactive toward air, water and other chemicals. σ-bonded cyclopentadienyls are formed by mercury (Ch. 30) and also by metals such as iron when all but one coordination position is blocked, e.g., Fe(π-Cp)(CO)$_2$(σ-Cp).

Following ferrocene, bis(η^5-cyclopentadienyl) metal compounds are called metallocenes. However, the term may be applied to all organometallic compounds of polyhapto cyclopentadienyl ligand, while a metallocene consisting of two planar η^5-cyclopentadiene rings is called a sandwich complex for obvious reasons.

Other carbocyclic π-donor ligands are also known to form a large number of complexes. Cyclobutadiene, unstable free, also forms stable complexes like Fe(C_4H_4)(CO)$_3$ (sec. 28.7.7) and Ru(C_4H_4)(CO)$_3$. The tropylium cation, η^7-$C_7H_7^+$ is also an aromatic π-donor ligand (32-XV), formally contributing six electrons.

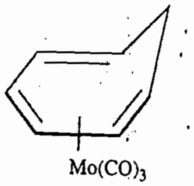


32-XIV



tricarbonyl (η^7-tropilium)-molybdenum (1+)

32-XV

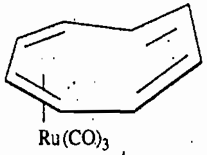


tricarbonyl (η^6-cyclo-heptatriene)-molybdenum

32-XVI

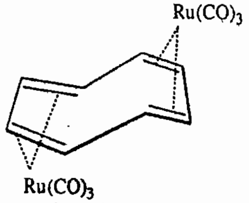
[**Sec. 32.2.4** *Ferrocene etc.*]

Cyclooctatetraene (COT) may partially use its π-electrons in bonding to metals and show η^2, η^4 or η^6 behaviour through a puckered ring (32-XVII a—c). It may also act as a bridge between two metals in the nonplanar form. The planar aromatic $C_8H_8^{2-}$ group acts as an η^8-ligand as in U(η^8–C_8H_8)$_2$ (uranocene, 32-XVII).



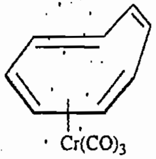
(η^4–C_8H_8)

32-XVII(a)



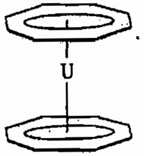
(bridge C_8H_8)

32-XVII(b)



(η^6–C_8H_8)

32-XVII(c)

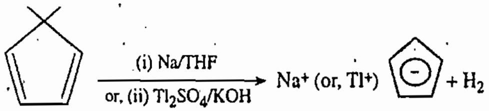


(η^8–C_8H_8)

32-XVIII

Synthesis

The history of preparation of ferrocene has been mentioned earlier (section 28.7.7). The synthesis of cyclopentadienyl compounds usually begins with the $C_5H_5^-$ ion formed by release of a proton from the weakly acidic cyclopentadiene molecule (pK_a~20).



The thallium salt is useful when the reducing power of the sodium salt is very high. However, organothallium compounds are toxic and less soluble in organic solvents. The $C_5H_5^-$ salts are hydrolytically unstable and are usually made to react directly with an anhydrous salt of the metal, e.g., FeCl$_2$ (see ferrocene). A hydrated metal salt may be used if the $C_5H_5^-$ ion is generated *in situ* :

$$2C_5H_6 + 8KOH + FeCl_2.4H_2O \longrightarrow Cp_2Fe + 2KCl + 6KOH + 6H_2O.$$

Direct reaction with cyclopentadiene is also possible in presence of a strong organic base. Amines are very useful, abstracting the proton from cyclopentadiene and allowing the reaction at a lower temperature :

$$2C_5H_6 + CoCl_2 + 2Et_2NH \xrightarrow{THF} Cp_2Co + 2Et_2NH_2Cl$$

$$Fe + 2R_3NHCl \longrightarrow FeCl_2 + 2R_3N + H_2$$

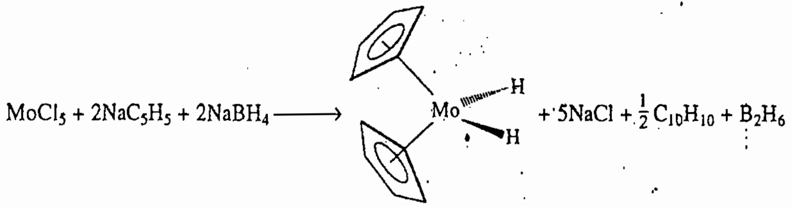
$$FeCl_2 + 2C_5H_6 + 2R_3N \longrightarrow Cp_2Fe + 2R_3NHCl.$$

Cyclopentadiene or even dicyclopentadiene may react with some finely divided metal or metal carbonyls to give complexes :

$$2C_5H_6(g) + Mg(s) \longrightarrow (C_5H_5)_2Mg + H_2$$

$$Fe(CO)_5 + C_{10}H_{12} \xrightarrow{200°C} [CpFe(CO)]_2(\mu\text{-}CO)_2.$$

In presence of $NaBH_4$, $MoCl_5$ reacts with sodium cyclopentadienide to form molybdenocene, a bent metallocene



$$MoCl_5 + 2NaC_5H_5 + 2NaBH_4 \longrightarrow Cp_2MoH_2 + 5NaCl + \tfrac{1}{2}C_{10}H_{10} + B_2H_6$$

The preparation of diarene complexes may be carried out by the aluminium reduction method as described earlier for dibenzene chromium (section 28.5.9). A still more general method involves cocondensation of the metal vapour and the ligand.

Properties

The di-η⁵-cyclopentadienyls of divalent metals are neutral molecules like Cp_2Fe and Cp_2Cr. However, they may have more complex structure than the simple sandwich type, as shown by "titanocene", Cp_2Ti (structure 28-V). The neutral Cp_2M compounds are sublimable and soluble in organic solvents. Metals in higher oxidation states III, IV and V form compounds like Cp_2Co^+, Cp_2TiCl_2 and Cp_2NbBr_3 according to the oxidation state of the metal. Some representative compounds are shown in Table 32.9.

TABLE 32.9

Some bis(η⁵-cyclopentadienyl) complexes of transition metals

Compound	Nature	Remark
$(\eta^5\text{-}Cp)_2V$	Purple, m.p. 167°C; very air-sensitive.	3 unpaired e; μ = 3.84 B.M.
$(\eta^5\text{-}Cp)_2Cr$	Scarlet crystals, m.p. 172°C; very air-sensitive.	2 unpaired e; μ = 3.20 B.M.
$(\eta^5\text{-}Cp)_2Mn$	Dark brown, m.p. 173°C; air-sensitive; hydrolyzed.	5 unpaired e; μ = 5.86 B.M.; behaves ionic
$(\eta^5\text{-}Cp)_2Fe$	Orange crystals, m.p. 174°C; air-stable; thermally stable to >500°C.	diamagnetic; can be oxidized by $Ag^+(aq)$, dil HNO_3 to Cp_2Fe^+
$(\eta^5\text{-}Cp)_2Co$	Purple-black, m.p. 174°C; readily oxidized by air to Cp_2Co^+ (stable yellow salts)	1 unpaired e; μ = 1.73 B.M.
$(\eta^5\text{-}Cp)_2Ni$	Bright green, m.p. 173°C (dec.). Oxidized slowly in air to rather unstable orange $[Cp_2Ni]^+$;	2 unpaired e; μ = 2.86 B.M. Toxic.

Metallocenes of the elements of the first transition series are isomorphous with each other and have nearly the same melting point. The elements V, Cr, Mn, Fe, Co and Ni form neutral compounds $(\eta^5\text{-}Cp)_2M$ which are mainly covalent, but the manganese compound behaves more like an ionic compound (e.g., Cp_2Mg). Thus, Cp_2Mn (i) undergoes rapid hydrolysis with water (ii) reacts immediately with $FeCl_2$ in THF to give ferrocene (iii) has a low M—C dissociation energy (212 kJ mol⁻¹ vs 302 kJ mol⁻¹ for Cp_2Fe) and (iv) has 5 unpaired electrons (μ = 5.86 B.M.). Only ferrocene, an 18 e species, is most stable among these compounds. Only Ru and Os among second and third row transition metals form stable isolable Cp_2M compounds. Cp_2Ru (light yellow, m.p. 199-201°C) is the most thermally stable metallocene (>600°C). The diamagnetic solid has an eclipsed configuration (compare ferrocene). "Cp_2Re" has a dimeric structure with Re—Re bond.

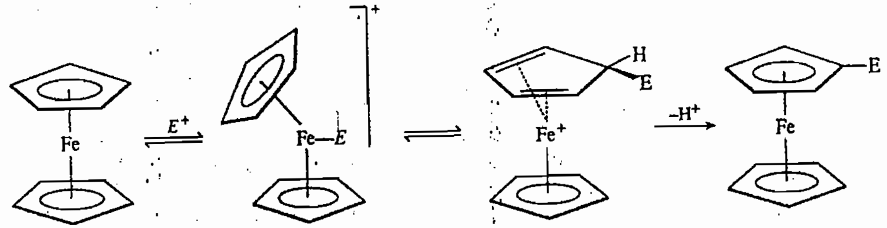
The pentamethyl cyclopentadienyls (C_5Me_5, Cp*) are often more stable as there are no replaceable H-atoms on the ring. Electron donor properties of the methyl groups make these Cp^*_2M compounds easily oxidizable. Some of the Cp^*_2M compounds are quite different from the Cp_2M compounds. Cp^*_2Ti is a yellow-orange monomer (dec. 60°C) with tilted ring. Cp^*_2Mn (orange) is low-spin (one unpaired e) whereas Cp_2Mn has five unpaired electrons.

The neutral cyclopentadienyl compounds can undergo redox reactions.

$$Cp_2Fe^+ + e \rightleftharpoons Cp_2Fe \qquad E° = -0.34V \text{ (vs SCE)}$$
$$Cp_2Cr + e \rightleftharpoons Cp_2Cr^- \qquad = -2.30V$$
$$Cp_2Cr^+ + e \rightleftharpoons Cp_2Cr \qquad = -0.67V$$
$$Cp_2Ni^+ + e \rightleftharpoons Cp_2Ni \qquad = -0.09V$$
$$Cp_2Ni^{2+} + e \rightleftharpoons Cp_2Ni^+ \qquad = +0.74V$$

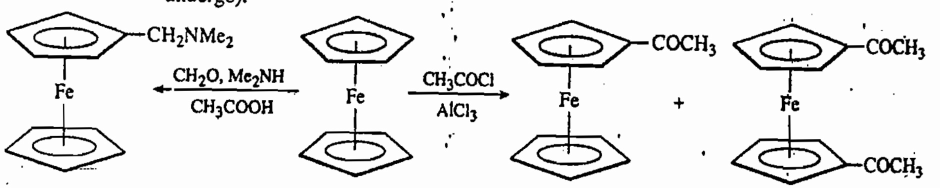
Ferrocene is readily oxidized by aqueous Ag^+ and dilute HNO_3 to stable blue-green paramagnetic ferricinium ion, $[Fe^{III}(\eta^5\text{-}Cp)_2]^+$. Very strong acids protonate ferrocene to Cp_2FeH^+ with bent rings. Cobaltocene (19e species) is readily oxidized in air to $[(\eta^5\text{-}Cp)_2Co]^+$. Nickelocene reacts with a Lewis base like BF_3 to form the triple-decker sandwich cation $[Ni_2(\eta^5\text{-}Cp)_3]^+$ (section 28.9.7, Fig. 28.47).

The general chemistry of ferrocene has been mentioned in chapter 28 (section 28.7.7). The chemistry of other metallocenes follow the same general trend. The coordinated cyclopentadienyl group resists nucleophilic attack but undergoes electrophilic substitution at a much faster rate compared to benzene (3 × 10⁶ times). It has been suggested that the electrophile (E⁺) first attacks the metal and is then transferred to the Cp ring :



Reactivity decreases with increasing size of the metal, being largely diminished in ruthenocene and osmocene.

As mentioned before, ferrocene readily undergoes Friedel-Crafts acylation and the Mannich condensation with formaldehyde and dimethylamine (benzene does not undergo).

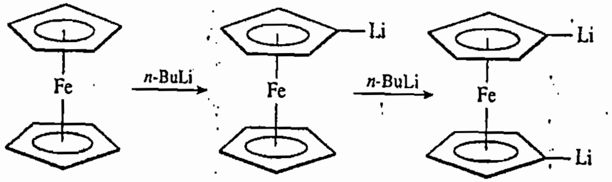


The acylation is initiated by the formation of the electrophile $CH_3\overset{+}{C}O$:

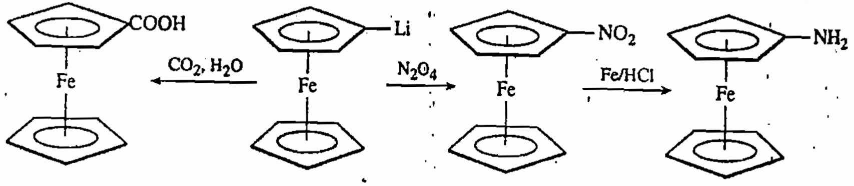
$$CH_3COCl + AlCl_3 \longrightarrow CH_3\overset{+}{C}OAlCl_4^-.$$

The same electrophile is generated by acetic anhydride and phosphoric acid but at a lower concentration. In this case only the monoacyl product is obtained since the lower concentration of CH_3CO^+ fails to attack the second Cp-ring, now deactivated by acylation of the first ring. Interestingly, the existence of only one form of the disubstituted 1,1′-derivative indicates *free rotation of the cyclopentadiene rings with respect to one another.*

Metallation proceeds readily in ferrocene :



The lithium derivatives may be utilized in making many ferrocene derivatives :



It may be recalled that direct nitration of ferrocene is not possible owing to oxidation.

Besides dibenzenechromium (section 28.5.9) several other bis-aryl complexes have been prepared, some of which are shown in Table 32.10.

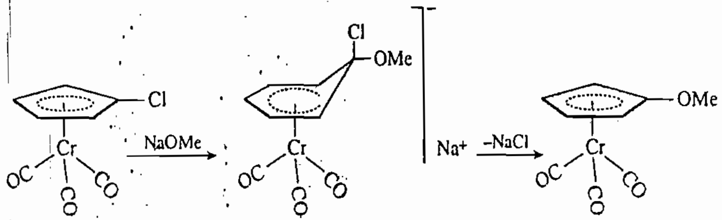
TABLE 32.10

Some bis-(π-aryl) metal complexes

$(\eta^6\text{–}C_6H_6)_2V$	Black, m.p. 227°C. Oxidized rapidly in air to red-brown $[(C_6H_6)_2V]^+$.
$(\eta^6\text{–}C_6H_6)_2Cr$	Brown-black, m.p. 284°C. Oxidized readily to yellow $[(C_6H_6)_2Cr]^+$.
$(\eta^6\text{–}C_6H_6)_2Mo$	Green, m.p. 115°C. Very air-sensitive.
$(\eta^6\text{–}C_6H_6)_2W$	Yellow-green, m.p. 160°C (dec). Less air-sensitive than the Mo-compound.
$(\eta^6\text{–}C_6H_5Cl)_2Cr$	Olive-green, m.p. 89°C; can be sublimed; air stable.
$(\eta^6\text{–}C_6H_5F)_2Cr$	Yellow, m.p. 96°C; can be sublimed; air stable.

Most neutral compounds are soluble in organic solvents and can be sublimed. They are less stable than the corresponding cyclopentadiene complexes and are easily oxidized by air. Thus dibenzene chromium, though an 18*e* species like ferrocene, is readily oxidized to the 17*e* system $[(C_6H_6)_2Cr]^+$. Coordination to the metal withdraws eletron density from the arene ring to such an extent that the ring does not respond to electrophilic attack. In fact, the compounds do not survive the conditions required for electrophilic substitution.

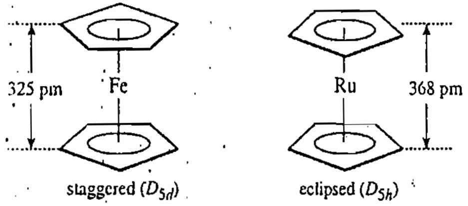
Carbon monoxide readily displaces one benzene ring from $(C_6H_6)_2Cr$ to give $(C_6H_6)Cr(CO)_3$ which is much more stable. The benzene ring in such compounds is activated toward attack by nucleophiles, for example,



There are some complexes with non-planar arenes. The η^6-arenes may have slight deformation to a boat form whereas marked deviation from planarity occurs in η^2- and η^4-modes of coordination. Thus, $(C_6Me_6)_2Ru$ would be a 20*e* system assuming both arene rings to be planar and η^6. Actually the complex is diamagnetic with one non-planar C_6Me_6 group contributing four electrons in η^4 capacity. η^2-arene complexes of Ni, Cu, Ag, Re and Os are known. Bridging arenes are also known.

Structure

Ferrocene has a sandwich structure with the iron atom held between two planar cyclopentadiene rings. The C—C distances in the rings are all equal, about 139±6 pm.



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This sandwich structure is common for all $(\eta^5\text{-Cp})_2M$ compounds but the relative orientations of the two rings may differ from one compound to another or even in two different physical states of the same compound. As mentioned earlier, in the solid state ferrocene has two C_5H_5 rings in a staggered configuration while in ruthenocene the two rings are eclipsed. The energy barrier to rotation of the rings in ferrocene are only of the order of 8-20 kJ mol^{-1} which is comparable in magnitude to intermolecular forces in the condensed phase. Hence the staggered orientation of the rings in ferrocene may well be the result of crystal packing forces. In fact, in crystalline ferrocene, there may be molecules of different orientations randomly distributed throughout the crystal. The hydrogen atoms of the rings are also slightly bent toward the metal atom. In the gas phase, the eclipsed form is about 4 kJ mol^{-1} more stable than the staggered conformation.

Bonding

The bonding in ferrocene (and similar $(\eta^5\text{-Cp})_2M$ complexes) is best described by consideration of overlap of the π-molecular orbitals of the cyclopentadiene rings with symmetry-matched orbitals of the metal. To begin with a short qualitative m.o. approach to the bonding, we first consider the π molecular orbitals of a C_5H_5 ring (Fig. 32.15).

In this connection, it may be worthwhile to recall the main points in constructing the π m.o.-s of a planar cyclic system. (i) quite similar to atomic orbitals, each m.o. will have its characteristic nodes which must be symmetrically disposed in the ring skeleton. (ii) As the extent of bonding interaction with neighbouring atoms decreases, the m.o.-s are raised in energy and the number of nodes increase successively. In Fig. 32.15 the lowest energy bonding m.o. (*a*) has no node; the next two m.o.-s of higher energy (e_1, weakly bonding) have one node each. The highest energy (e_2) orbitals have two nodes each. (iii) when a node passes through a nucleus, the a.o. of that atom does not participate in that particular m.o. (iv) The nodes must pass through the center of the structure.

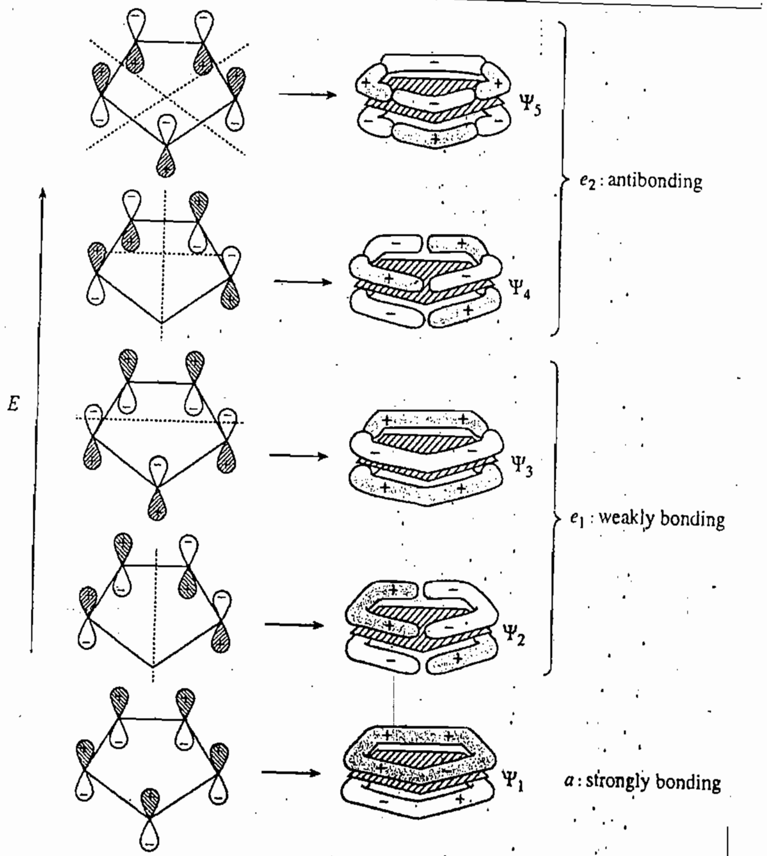
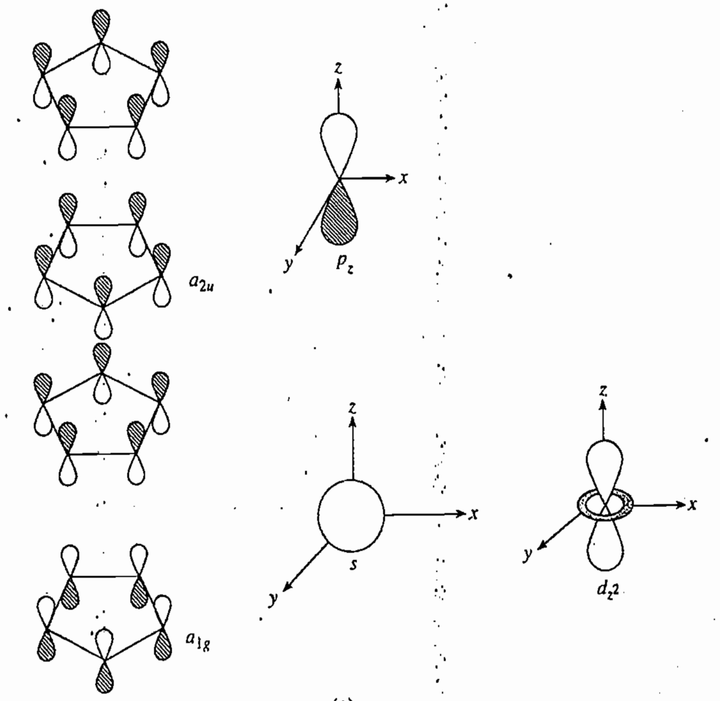


Fig. 32.15
The π molecular orbitals of the C_5H_5 ring.
(formed from various combinations of $p\pi$ atomic orbitals).
Nodes shown with broken lines.

[Sec. 32.2.4 *Ferrocene—bonding*]

Now we can combine the five m.o.-s of one C_5H_5 ring with a similar set from a second C_5H_5 ring (Fig. 32.16 shown for staggered position; similar considerations apply for the eclipsed conformation). One of these combinations will be centrosymmetric or *g*-type and the other non-centrosymmetric or *u*-type. For each set of these ligand m.o.-s the appropriate metal orbitals for symmetry allowed combinations are also shown in the figure. Except for the e_{2u} ligand group orbitals which are non bonding, each metal-ligand combination should give rise to equal number of bonding and antibonding m.o.-s for the Cp_2M molecule.



(a)

Combinations of *a*-type π m.o.-s of the C_5H_5 rings.
(metal orbitals of matching symmetry shown on right)

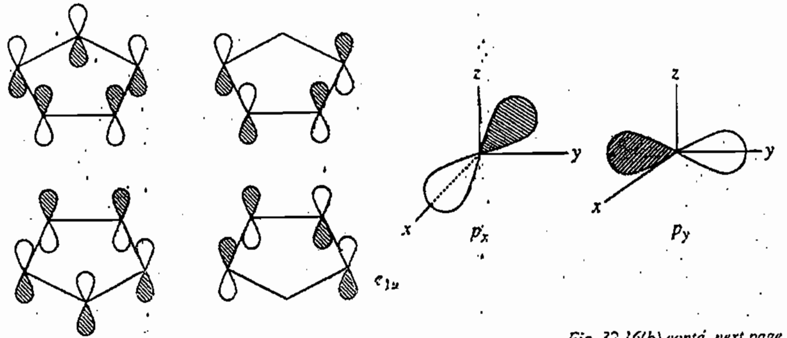
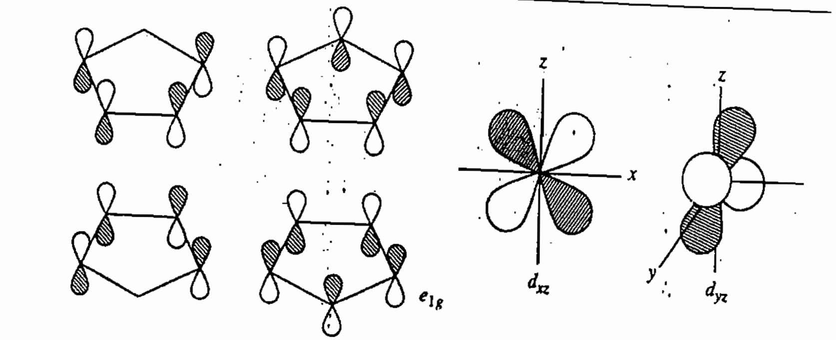
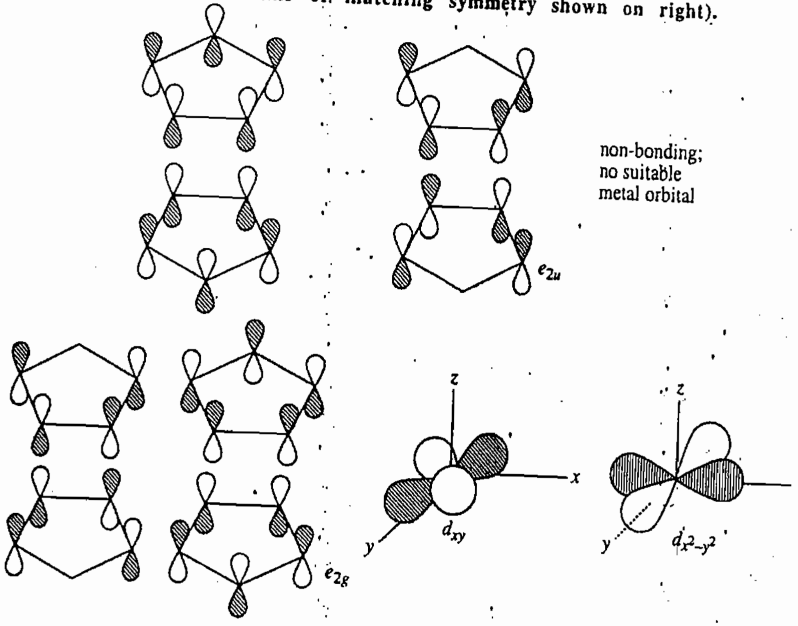


Fig. 32.16(b) contd. next page



(b)

Combinations of e_1-type π m.o.-s of the C_5H_5 rings. (metal orbitals of matching symmetry shown on right).



(c)

Combinations of e_2-type π m.o.-s of the C_5H_5 rings.

Fig. 32.16

Combination of two Cp-orbitals (staggered; D_{5d} symmetry) and metal orbitals suitable for overlap with them.

('+' and '–' signs have been dropped from the lobes for clarity.)

The approximate qualitative m.o. energy level diagram for the Cp_2M molecule is shown in Fig. 32.17. The following gross features may be noted :

(i) The lowest energy bonding m.o.-s are derived mainly from the a_{1g} and a_{2u} m.o.-s of the C_5H_5 rings. The metal *s* and d_{z^2} orbitals make only slight contribution to these m.o.-s. The *s*-a.o. of the metal lies much higher in energy while the d_{z^2} orbital has its conical nodal surface around the same region of space as the ring *p*π orbitals. The a_{2u} ligand m.o.-s are suitable for combination of metal $4p_z$ atomic orbitals which are even higher-lying than the 4*s*. The a_{1g} and a_{2u} m.o.-s are therefore mainly ligand-based.

(ii) The e_{1g} ligand orbitals combine with metal d_{xz} and d_{yz} atomic orbitals to form the next set of bonding m.o.-s. The corresponding antibonding m.o.-s ($\overset{*}{e}_{1g}$) are unoccupied in the ground state of the molecule.

The e_{1u} ligand m.o.-s are again poorly contributed to by the metal p_x and p_y a.o.-s which are higher in energy. The corresponding $\overset{*}{e}_{1u}$ antibonding m.o. lies highest in the diagram.

(iii) The m.o.-s arising from the e_{2g} ligand orbitals lie close to the metal *d*-orbitals. The $\overset{*}{a}_{1g}$ (d_{z^2}) is essentially non-bonding. The $\overset{*}{e}_{1g}$ antibonding m.o.-s mentioned before appear next higher in energy.

As mentioned earlier, the e_{2u} ligand orbitals remain non-bonding for want of metal orbitals of suitable symmetry.

The principal bonding interaction comes from overlap of the strongly bonding e_1-type ring π-orbitals and the matching *d*-orbitals (d_{xz}, d_{yz}).

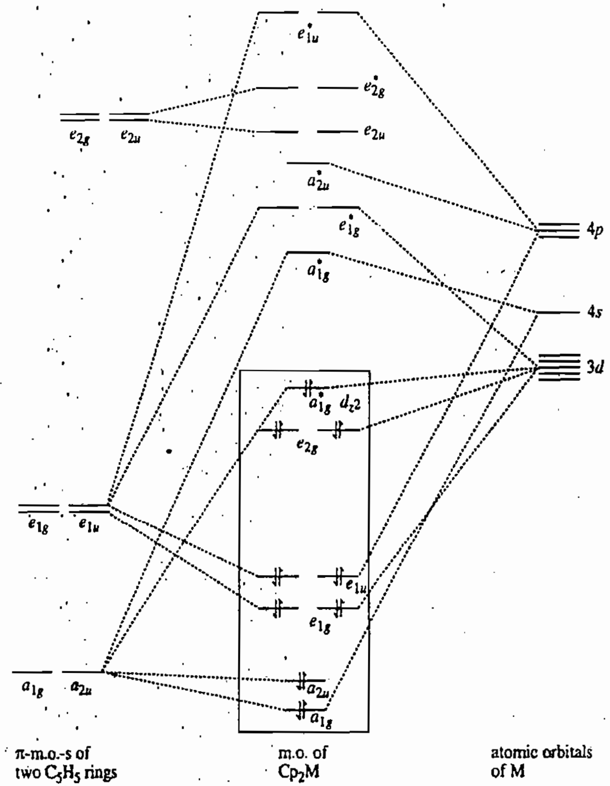


Fig. 32.17 : An approximate MO diagram for $(\eta^5\text{-}C_5H_5)_2M$ molecules.

The diagram is based on ferrocene but may be qualitatively applied to other $(\eta^5\text{–}C_5H_5)_2M$ molecules since relative energies of the orbitals vary with the nature of M. The exact order of different m.o.-s may also vary.

The overall pattern of molecular orbitals suggests that there are exactly nine bonding/non-bonding m.o.-s (boxed) which may be filled by 18 electrons to give a stable system. The upper ten m.o.-s are antibonding and any electron in them will actually destabilize the system. This explains the stability of the 18-electron ferrocene molecule (Cp_2Fe : 2Cp rings $5 \times 2 = 10e$; Fe = $8e$). The 19-electron Cp_2Co or 20-electron Cp_2Ni molecules would place 1 or 2 electrons respectively in the higher antibonding m.o. The reactivity of the 15-electron species Cp_2V or 16-electron species Cp_2Cr is similarly understood since they have unfilled bonding m.o.-s.

The occupied orbitals are either (i) *a*-type—symmetric about the 5-fold molecular axis or (ii) e_1 or e_2 type — which are also symmetric about the axis in pairs. Consequently there is no intrinsic barrier to rotation of the rings about the molecular axis; only van der Waals forces between the rings may give rise to low energy barrier to rotation.

32.3 ORGANOMETALLIC COMPOUNDS IN CATALYSIS

The last lap of the twentieth century has been marked by a rapid development of petrochemicals. Ethylene obtained by cracking and synthesis gas derived from methanol have become the starting materials for the bulk manufacture of various organic chemicals required in the production of numerous consumer goods. Most of these conversions have been found to be catalyzed by metal compounds—organometallics and complexes — either in the same phase as the reactants (*homogeneous catalysis*) or in a different phase (*heterogeneous catalysis*), such as a solid material on carbon or other supports for liquid or gaseous reactants. We have already discussed the Ziegler-Natta catalysts in polymerization of alkenes (Ch. 20). Some examples of homogeneous catalysis by transition metal organometallics are mentioned in this section.

In homogeneous reactions catalyzed by organometallic compounds, the catalyst gets intimately involved with the reactants to form various distinct intermediates during the course of the reaction. Subsequently the catalyst is regenerated in a cyclic chain. The catalytic role of the metal compound can be largely understood in terms of reactions at the metal or coordinated ligand in the light of our discussion in chapter 27 (section 27.4). Such reactions are often very selective in nature, allowing firm control on the nature of the product obtained and operate under milder temperature and pressures. However, such processes may also present the difficulty of separating the product from the excess of reactants and the catalyst (all in the same phase). This may be partly overcome by phase transfer reactions where the reactants and products are in an organic phase but the catalyst is in an aqueous phase (or vice versa).

Heterogeneous catalysts obviously offer the advantage of easy separation from the reactant and products but they often lack the delicate selectivity of homogeneously catalyzed reactions. The intermediates in such processes are less distinctly characterized but may be rationalized in terms of the same principles as applicable for the homogeneous catalysts.

32.3.1 Hydrogenation of olefins

Alkenes add hydrogen only slowly at ordinary temperature and pressure in absence of catalysts. $RhCl(PPh_3)_3$, known as *Wilkinson's catalyst*, was the first catalyst to ensure hydrogenation of olefins at ordinary temperature and pressure. It may be prepared by refluxing $RhCl_3$ with an alcoholic solution of PPh_3 in excess (sec. 29.6.4). The red compound undergoes very little dissociation in solution in benzene

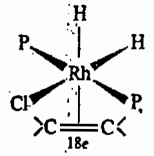
$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad K \approx 10^{-7}\ (25°C)$$

The mode of operation by the catalyst in hydrogenation lies in the ability of $RhCl(PPh_3)_2$ to react with hydrogen (oxidative addition) to form a five-coordinate dihydrido complex of Rh(III); this latter species (16*e* system) coordinates to an olefin to give a six-coordinate 18*e* complex :

(i) $\underset{16e}{RhCl(PPh_3)_3} \rightleftharpoons \underset{14e}{RhCl(PPh_3)_2}$

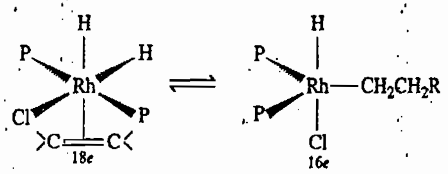
(ii) $\underset{14e}{RhCl(PPh_3)_2} + H_2 \rightleftharpoons \underset{16e}{RhCl(H)_2(PPh_3)_2}$

(iii) $RhCl(H)_2(PPh_3)_2 + CH_2 = CHR \rightleftharpoons$



The 18*e* complex now transfers a hydrogen atom to the β-carbon atom forming a 5-coordinate 16*e* intermediate. This migratory insertion makes the rate determining step :

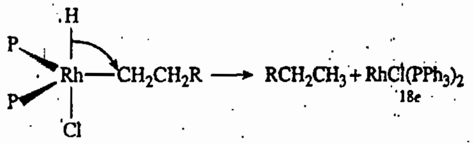
(iv)



Kinetic studies show that H_2 reacts faster than D_2, which is consistent with the assignment of rate determining step to the hydrogen insertion reaction.

Reductive elimination now gives back $RhCl(PPh_3)_2$ with the liberation of the alkane :

(v)



The actual process is more complicated since the equilibria depend on the nature and concentrations of the alkene, phosphine and the Rh-complex as well as temperature, pressure and interference by the solvent. The simplified steps are often shown in cycles like one in Fig. 32.18. Aryl phosphine complexes, more sterically hindered than alkyl phosphine analogs and hence more susceptible to dissociation, are more active than complexes with alkyl phosphines. Similarly, the alkene also must have the proper size and no steric hindrance. Ethylene is also very slow to react since it forms a strong complex with rhodium which does not dissociate further in course of the cycle. The method offers highly selective hydrogenation; chiral catalysts made from optically active chelating phosphine ligands may be used to obtain optically active saturated compounds at the end. The alkene taken must be *prochiral*, that is, its structure must lead to *R* or *S* chirality on complexation with the ligand. Depending on the mode of coordination of the alkene, the complex will be formed in two diastereoisomeric forms having different stabilities and reactivities. This fact may be utilized to obtain one or the other product in an enantioselective path. L-DOPA, a medicine used in the treatment of Parkinson's disease, is prepared in this manner.

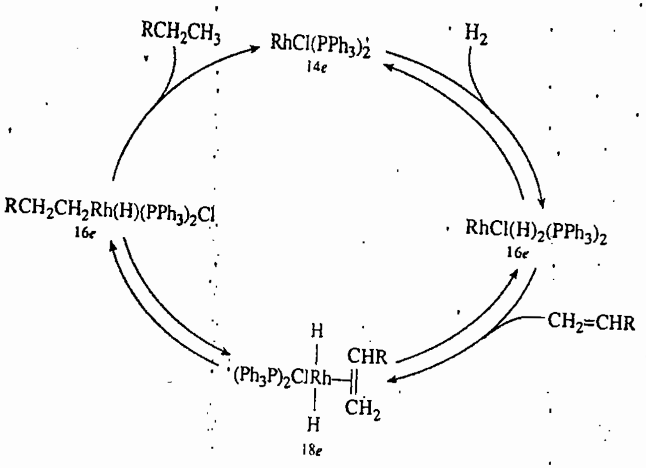
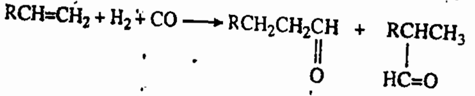


Fig. 32.18

An idealized catalytic cycle for hydrogenation of alkenes using Wilkinson's catalyst.

32.3.2 Hydroformylation (The oxo process)

The process involves addition of H_2 and CO to an olefin in presence of a cobalt or rhodium catalyst (sections 28.8.6 and 29.6.4); the product is an aldehyde :



$$RCH{=}CH_2 + H_2 + CO \longrightarrow RCH_2CH_2\underset{\underset{O}{\parallel}}{C}H + R\underset{\underset{HC=O}{|}}{C}HCH_3$$

With cobalt catalyst the process is carried out at high temperatures (150-180°C) and pressures (~200 atm). Finely divided cobalt metal or a cobalt salt may be taken, which is converted to $Co_2(CO)_8$ at the reaction condition. The active catalyst appears to be $HCo(CO)_4$:

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

High pressure prevents decomposition of the carbonyl hydride. The formation of aldehyde may be summarized by the idealized cycle in Fig. 32.19 involving (i) coordination of the alkene (ii) migratory insertion of the coordinated alkene into the Co—H bond (iii) coordination by CO to 18*e* species (iv) insertion of the CO between Co—C (alkyl) (v) oxidative addition of H_2 and (vi) reductive elimination.

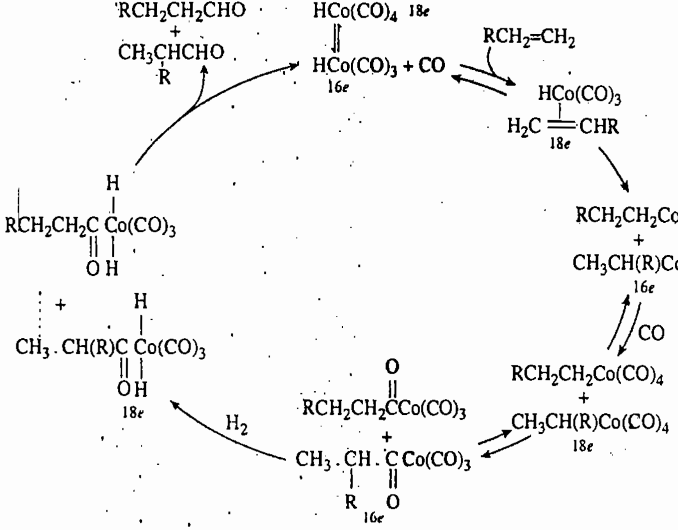


Fig. 32.19 : Catalytic cycle for hydroformylation.

The relative amounts of straight and branched chain aldehydes in the product depend on the nature of R and other constituents of the system. Straight-chain aldehydes are more desirable for certain purposes, for example in the manufacture of biodegradable detergents. The yield of straight chain product may be enhanced by a modified cobalt catalyst like $HCo(CO)_3PBu_3$.

The cobalt catalyst does not afford a high yield of the aldehyde since some alkene is hydrogenated to the saturated hydrocarbon; some ketones are also formed. Trans-$HRh(CO)(PPh_3)_3$ (Ch. 29) is a superior catalyst in this respect which works at ~ 100°C and close to one atmosphere pressure. This catalyst also functions by losing one phosphine ligand when the 16*e* species $HRh(CO)(PPh_3)_2$ is formed, the gross mechanism remaining essentially the same. The rhodium catalyst also promotes linear aldehydes.

32.3.3 Reactions of carbon monoxide and hydrogen

The use of 'synthesis gas' (H_2 + CO) was mentioned in connection with carbon monoxide (sec. 21.3.5). With increasing price of petroleum all over the world and the threat of the petroleum reserve getting fast exhausted, scientists are looking for coal as the starting material for organic chemicals as well as petroleum. Water gas, produced by passing steam over red hot coke, has been widely used as a fuel since the nineteenth century. Production of organic molecules from the carbon monoxide-hydrogen mixture requires a higher percentage of hydrogen. This is brought about by the *water gas shift reaction* (section 21.3.5) :

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H^0_{298°C} = -41.2 \text{ kJ mol}^{-1}; \quad \Delta G^0_{298°C} = -28.5 \text{ kJ mol}^{-1}.$$

The reaction is usually carried out with heterogeneous catalysts like oxides of iron-chromium or zinc-copper. At present, various homogeneous catalysts are being tried for this conversion. These include metal carbonyls and carbonyl complexes like $[HFe(CO)_4]^-$, $[Rh(CO)_2I_2]^-$ and similar complexes of Mo, W, Ir and so on. However, a commercially viable process is yet to be developed.

We have already seen how the synthesis gas is used in hydroformylation reaction to convert alkenes to aldehydes. We shall mention a few more applications of the synthesis gas in making essential organic chemicals like (i) methanol (ii) acetic acid and (iii) gasoline.

Methanol and acetic acid

Methanol is manufactured by passing synthesis gas at a pressure of 200 atmospheres over a catalyst bed consisting of oxides of copper, zinc and chromium at 300°C

$$CO + 2H_2 \longrightarrow CH_3OH.$$

The yield may be quite high (~ 90% or even more) under appropriate conditions.

Methanol is also produced by catalytic oxidation of methane, a chief component of natural gas. A mixture of methane and oxygen (9 : 1 volume ratio) is passed at ~ 100 atmosphere through a heated copper tube at 200°C :

$$CH_4 + \tfrac{1}{2} O_2 \longrightarrow CH_3OH.$$

Acetic acid may be made by carbonylation of methanol using a rhodium carbonyl iodide as homogeneous catalyst (*Monosanto acetic acid process*) :

$$CH_3OH + CO \longrightarrow CH_3COOH.$$

The overall reaction may be split into three step :

$$\begin{array}{lcll} CH_3OH + HI & \longrightarrow & CH_3I + H_2O & \text{(i)} \\ CH_3I + CO & \longrightarrow & CH_3COI & \text{(ii)} \\ CH_3COI + H_2O & \longrightarrow & CH_3COOH + HI & \text{(iii)} \\ \hline CH_3OH + CO & \longrightarrow & CH_3COOH & \end{array}$$

Reaction (ii), that is carbonylation of methyl iodide, is actually catalyzed by the rhodium catalyst according to the cycle shown in Fig. 32.20 : (i) oxidative addition of CH_3I (from CH_3OH + HI) to $[Rh(CO)_2I_2]^-$ forming a six-coordinate Rh(III) complex (ii) rearrangement to a five-coordinate acetyl complex (iii) addition of CO (iv) reductive elimination of CH_3COI and regeneration of $[Rh(CO)_2I_2]^-$. The CH_3COI gives acetic acid with water, regenerating HI.

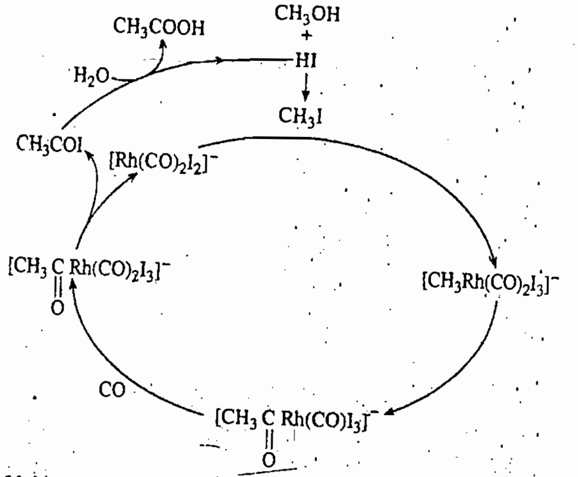


Fig. 32.20 : Catalytic cycle for Monsanto acetic acid process.

[Sec. 32.3.3 *Synthetic gasoline*]

Synthetic gasoline

Methanol may be converted to gasoline (motor fuel) over the zeolite catalyst ZSM-5 (section 21.3.6) :

$$nCH_3OH \xrightarrow{\text{ZSM-5}} -(CH_2)_n- + nH_2O$$

The interconnecting channels and the pore size in ZSM-5 are just right for condensation of the methylene groups to hydrocarbon molecules containing carbon-chains up to C_{10}. The resulting gasoline has a high octane rating ranging from 90-100. The conversion efficiency is also quite high, over 99% of the methanol being converted in a single pass.

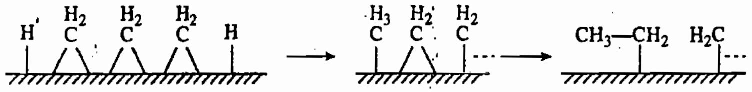
The Fischer-Tropsch process

This the oldest method for converting synthesis gas to gasoline (1923). The process involves reaction of H_2 and CO over transition metal catalysts to produce linear hydrocarbons covering a wide range (section 21.3.5).

$$nCO + (2n + 1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O.$$

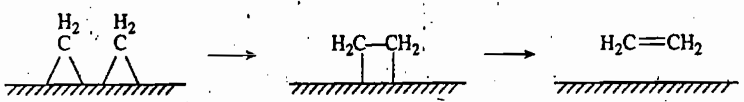
The method is still uneconomic except in countries like South Africa and New Zealand where coal is very cheap. The method will be able to compete with petroleum when (i) crude oil becomes even costlier (ii) the world reserve of petroleum appears exhausted (iii) coal becomes relatively inexpensive and (iv) suitable catalysts are found which would give hydrocarbons within a specified range.

It has been proposed that carbon monoxide dissociates on the metal surface to form metal carbides; these are subsequently hydrogenated to CH_2 groups. Both X-ray and uv photoelectron spectroscopy support such decomposition of the adsorbed CO which is related to the stability of different metal carbides. Thus platinum metals, most of which do not form carbides, adsorb CO without much dissociation; iron and nickel, which form unstable carbides, dissociate CO between 300-420K whereas molybdenum and tungsten dissociate CO below 170K, (both metals form stable carbides). The adsorbed hydrogen atoms will now convert the carbon atoms to CH or CH_2 groups which will polymerize to give the hydrocarbons :



The concentration of CH_2 groups is expected to be high on surfaces like iron where the CO is almost completely dissociated at the reaction temperature. So this is expected to produce higher hydrocarbons. On a nickel surface, CO dissociates less, producing a lower concentration of surface CH_2 and hence methane is the main product. Tungsten and molybdenum are poor Fischer-Tropsch catalysts since they form stable carbides which are not readily hydrogenated.

Diazomethane decomposes on metal surfaces to ethylene and nitrogen. This may be assumed to take place via CH_2 groups readily available from diazomethane :



When a mixture of hydrogen and diazomethane is passed over metal surfaces like Fe, Ru, Co, Ni and Pd, a wide range of alkanes C_2—C_{18} are obtained together with ethylene. This strongly supports the role of CH_2 groups in the Fischer-Tropsch process.

Studies have also been made with several bridged alkylidene complexes. However, a suitable catalyst yielding selective hydrocarbons is yet to be developed.

32.4 METAL CLUSTERS

We have already come across many examples of metal atom clusters in the previous chapters. A metal atom cluster should contain two or more metals having direct metal-metal bonding. The clusters display a structure consisting of polyhedral frameworks of metal atoms held by M—M bonds. Hg_2Cl_2, Cu(II)-acetate dihydrate and its Cr(II) and Rh(II) analogues do contain M—M bonds but the structural criterion of metal atom clusters begin with three metal atoms. Though some of these clusters (e.g., $Mo_6Cl_8^{4+}$, sec. 29.4.6) were recognized in the 1940s, the general chemistry of metal clusters has developed tremendously since 1960s. The compounds are mainly of two types — the "lower halide" type (sec. 29.3.5) and the metal carbonyl clusters.

Increasing M—M force constants and higher stability of compounds suggest that the M—M bond strength increases down any group among the *d*-block elements. As such, metal cluster compounds are more common for the *4d*- and *5d*- transition series metals, specially in the second half in each series.

32.4.1 *Metal carbonyl clusters*

The metal carbonyl clusters usually contain the metal atoms in low formal oxidation states like –1 to +1. They are formed mainly by later transition elements Fe, Co, Ni and their heavier congeners. Carbonyl clusters containing up to four metal atoms are called *low-nuclearity carbonyl clusters* (LNCC) while those with five or more metal atoms, each forming at least one M—M bond, are known as *high nuclearity carbonyl clusters* (HNCC). Mixed metal clusters, nitrosyl analogues and clusters extended by hetero-atoms (e.g., C, N, S etc.) are also known.

The synthesis of carbonyl clusters involves formation of metal-metal bonds in place of metal-CO bonds. Since the metal-metal bonds are weaker, the synthesis is usually carried out in absence of CO, so that rupture of the cluster may be avoided. Thermal condensation of simpler carbonyls with expulsion of CO is endothermic but is aided by a large increase in entropy due to liberation of CO :

$$2Co_2(CO)_8 \xrightarrow{80°C} Co_4(CO)_{12} + 4CO \quad \Delta H = 138\ \text{kJ mol}^{-1}$$

A major drawback of the method is lack of specificity, for example,

$$Os_3(CO)_{12} \xrightarrow{300°C} Os_6(CO)_{16} + Os_5(CO)_{16} + Os_7(CO)_{21} + Os_8(CO)_{23}$$

Many large clusters of the cobalt and nickel subgroups may be prepared by reducing smaller carbonyls to reactive anionic intermediates which condense to larger clusters. Thus $Ni(CO)_4$ may be reduced by Na or $NaBH_4$ in THF mainly to $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$ and other aggregates. The anions may condense with neutral carbonyls of the same metal or a different metal :

$$[Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \longrightarrow [Ni_6(CO)_{12}]^{2-} + 4CO$$

$$[Pt_3(CO)_6]^{2-} + 3Fe(CO)_5 \longrightarrow [Fe_3Pt_3(CO)_{15}]^{2-} + 6CO$$

The reactions may be termed *redox condensation* : the formal oxidation number of the metal in the product is intermediate between those on the left (comproportionation). Thus in the reaction of $Ni(CO)_4$, the product cluster has nickel in an O.N. $-\frac{1}{3}$ formed from O.N. 0 and $-\frac{2}{5}$ on the left hand side. The net effect of the condensation is distribution of the negative charge over a larger cluster, reducing electrostatic repulsion.

The carbonylate anions may react even with simple metal halides, for example,

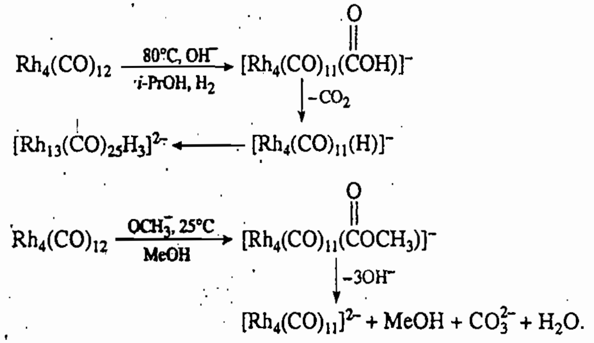
$$[Ni_6(CO)_{12}]^{2-} + PtCl_2 \longrightarrow [Ni_{38}Pt_6(CO)_{48}H_2]^{4-}.$$

The redox condensation method may be used to prepare clusters containing an encapsulted hetero atom like C, S, As etc. The condensation is carried out in presence of a suitable source for such atoms, for example, CCl_4 for C, C_2Cl_6 for C_2, H_2S for S or Ph_3As for As.

Q. 32.14 *Both nickel and platinum form large number of stable carbonyl clusters but palladium does not readily form such clusters unless stabilized by σ-donor ligands like phosphines.—Comment.*

Hint : Pd—Pd bond energy is expected to be much less compared to Ni—Ni and Pt—Pt bond energy. Sublimation energies of the three metals (kJ mol^{-1}) may be taken as a rough guide to the M—M bond energies : Ni 427; Pd 354; Pt 565.

Loss of CO from the polynuclear clusters is promoted by alcoholic base solutions, presumably through attack by OH^- on CO followed by elimination of CO_2. The resulting anionic cluster may condense to higher clusters :



$$\begin{tikzcd} Rh_4(CO)_{12} \arrow[r, "80°C,\ OH^-", "i\text{-PrOH},\ H_2"'] & {[Rh_4(CO)_{11}(\overset{\overset{O}{\|}}{C}OH)]^-} \arrow[d, "-CO_2"] \\ {[Rh_{13}(CO)_{25}H_3]^{2-}} & {[Rh_4(CO)_{11}(H)]^-} \arrow[l] \end{tikzcd}$$

$$\begin{tikzcd} Rh_4(CO)_{12} \arrow[r, "OCH_3^-,\ 25°C", "MeOH"'] & {[Rh_4(CO)_{11}(\overset{\overset{O}{\|}}{C}CH_3)]^-} \arrow[d, "-3OH^-"] \\ & {[Rh_4(CO)_{11}]^{2-} + MeOH + CO_3^{2-} + H_2O.} \end{tikzcd}$$

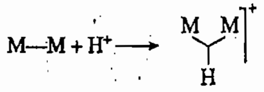
The clusters may undergo substitution of CO by other ligands when a wide variety of products are obtained through fragmentation :

$$Fe_3(CO)_{12} \xrightarrow{PPH_3} \left[\begin{array}{l} Fe_3(CO)_{11}(PPH_3) + \\ Fe_3(CO)_{10}(PPH_3)_2 + \\ Fe(CO)_5 + Fe(CO)_4(PPh_3) + \\ Fe(CO)_3(PPh_3)_2 + CO \end{array}\right.$$

At elevated temperatures and prolonged reaction time, only mono iron products are obtained. For heavier transition metals in *4d*- and *5d*- series, increased M—M bond strengths resist fragmentation and one may obtain substitution products of the cluster.

The M—M bonds in clusters undergo ready protonation to form *3c-2e* hydrogen-bridged species, e.g.,

$$[Fe_3(CO)_{11}]^{2-} \xrightarrow{H^+} [Fe_3H(CO)_{11}]^-$$



$$M\text{—}M + H^+ \longrightarrow \left[\begin{array}{c} M\quad M \\ \diagdown\diagup \\ H \end{array}\right]^+$$

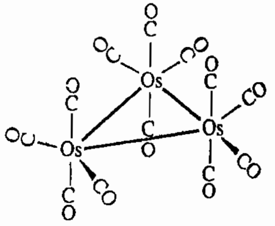
The hydrido compound may react with an additional proton, eliminating H_2. The net result is oxidation of the anionic cluster :

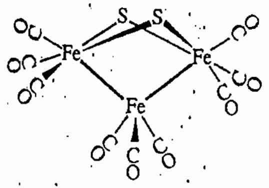
$$[Ir_4(CO)_{11}H]^- + H^+ \xrightarrow{CO} Ir_4(CO)_{12} + H_2$$

Certain oxidants may even coordinate to the cluster :

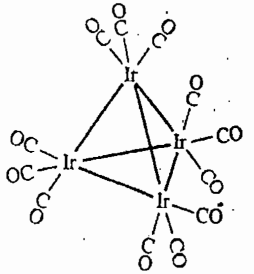
$$[Rh_6(CO)_{15}]^{2-} + I_2 \xrightarrow{THF} [Rh_6(CO)_{15}I]^- + I^-$$

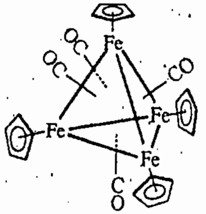
Like $Fe_3(CO)_{12}$ (28-XIX) and $Os_3(CO)_{12}$ (32.XX), most trinuclear clusters contain the metal atoms in a triangle. An open chain of three metal atoms is illustrated by $Fe_3(CO)_9S_2$ (32.XXI) with bridging S. These and similar clusters may also be considered as five atom heteronuclear clusters.

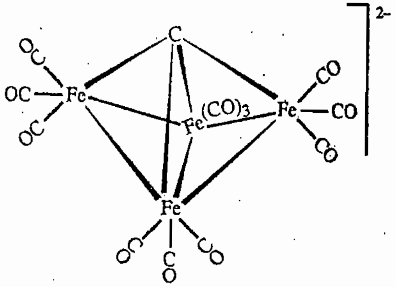

32-XX

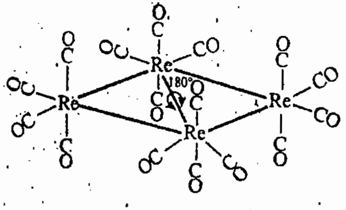

32-XXI

The majority of tetranuclear clusters contain an M_4 tetrahedron (often irregular) (32-XXII) but a "butterfly" structure is also common. In this latter structure the four metal atoms form two equilateral triangles sharing an edge like a hinge (32-XXIII). If the hinge is fully opened to make a dihedral angle of 180°, a square plane results (32-XXIV).

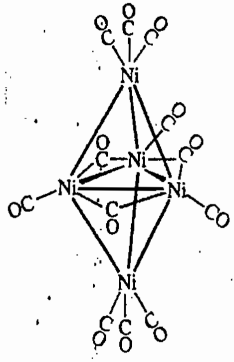

32-XXII(a) : $Ir_4(CO)_{12}$

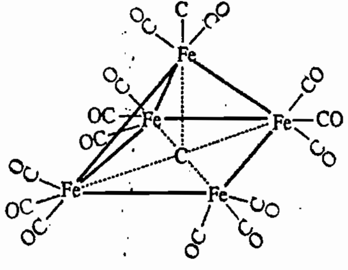

32-XXII(b) : $Fe_4(\eta^5\text{-}Cp)_4(CO)_4$


32-XXIII : $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$

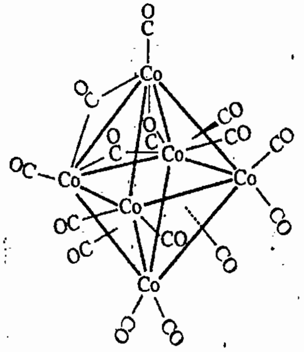

32-XXIV : $[Re_4(CO)_{16}]^{2-}$

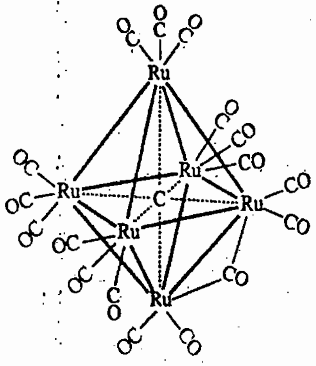
Pentanuclear clusters normally have the metals in a trigonal bipyramid arrangement (32-XXVa). A square pyramidal arrangement is present in $Fe_5(CO)_{15}C$ [32-XXV(b)] with a five-coordinate carbide carbon contributing four electrons to the cluster valence electrons.


32-XXV(a) : $[Ni_5(CO)_{12}]^{2-}$

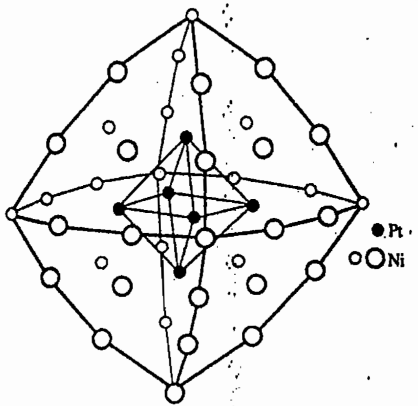

32-XXV(b) : $Fe_5(CO)_{15}C$

The most common geometry for hexanuclear clusters is again an M_6 octahedron but four other geometries are known : trigonal prism, capped square pyramid, a bicapped tetrahedron and a triangular planar network. Some typical skeletons are shown in 32-XXVI(a)-(b). Note the encapsulated carbon is 32-XXVI(b). $[Rh_6(CO)_{15}C]^{2-}$ similarly contains a carbon encapsulated in a trigonal prism of Rh atoms.

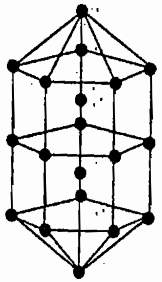

32-XXVI(a) : $[Co_6(CO)_{15}]^{2-}$


32-XXVI(b) : $[Ru_6(CO)_{17}C]$

Large clusters may be formed by linking M_6 octahedra, for example, the Ru_{10} cluster in $[Ru_{10}C_2(CO)_{24}]^{2-}$ is formed by edge-sharing of two Ru_6 octahedra; face sharing of two octahedra produce $[Rh_9(CO)_{19}]^{3-}$, fusion of three Rh_6 octahedra produce $[Rh_{11}(CO)_{23}]^{3-}$. Many large clusters with truncated octahedral structure are also known. The very large cluster $[Ni_{38}Pt_6(CO)_{48}]^{6-}$ whose synthesis has been described before, consists of a central Pt_6 octahedron surrounded by the nickel atoms in an overall octahedral symmetry (32-XXVII). Large clusters are known in other geometries also, for example, a truncated trigonal bipyramid in $[Ni_{12}(CO)_{21}H]^{3-}$ and bicapped pentagonal prism in $[Pt_{19}(CO)_{22}]^{4-}$ (32-XXVIII).



32-XXVII : $[Ni_{38}Pt_6(CO)_{48}]^{6-}$



32-XXVIII : $[Pt_{19}(CO)_{22}]^{4-}$

We have seen how the bonding and structure in smaller carbonyl clusters can be interpreted in terms of localized M—M and M—CO bonds and the 18-electron rule. The procedure does not work suitably for larger clusters containing 6 or more metal atoms (HNCC). The electron counting procedure for this latter class of clusters is duscussed separately.

It has been observed that the general behaviour of organometallic compounds may be largely related to organic molecules having similar distribution of valence orbitals, or more appropriately, frontier orbitals composed of the HOMO and LUMO. Such molecular species have been called isolobal (see later). The chemical analogy between two species is also prominent when they are isoelectronic or both isoelectronic and isolobal.

The isoelectronic relationship is self-explanatory. Some examples are

$Mn(CO)_5$ and $Re(CO)_5$

$Fe(CO)_3^-$ and $Co(CO)_3$

NiNO and $Co(CO)_2$

C_6H_6Cr and $Cr(CO)_3$.

Q. 32.15 *Select the isoelectronic pair(s) :*

$[Fe_5C(CO)_{14}]^{2-}$, $[FeC(CO)_{15}]^-$, $[Re_6C(CO)_{19}]^{2-}$, $[Mn_6C(CO)_{19}]^{2-}$.

The isolobal relationship is based on identical nature of the HOMO and LUMO, that is, the frontier orbitals of two molecular fragments. Isolobal fragments will have the same number of frontier orbitals with same spatial distribution and symmetry properties; their energies should also be comparable. Isolobality is expressed by the symbol $\underset{\bigcirc}{\longleftrightarrow}$. The molecular orbital energy levels and contour diagrams for many organic fragments have been calculated (Hoffmann and others) and isolobal relationship has been established with many organometallics. Thus, in both $Mn(CO)_5$ or $[MnH_5]^{5-}$, the ligands may be supposed to donate five electron pairs to five d^2sp^3 hybrid orbitals of Mn(0). Mn itself has seven electrons, six of which may be taken as paired in *d*-orbitals excluded from hybridization ("t_{2g}"). The seventh electron will occupy one of the hybrid orbitals on one side of the whole molecule. The situation is similar in CH_3 which has its fourth electron in an sp^3 hybrid orbital on one side (Fig. 32.21). In fact, both $[MnH_5]^{5-}$ and CH_3 have comparable contour diagrams and are isolobal. This is also true for $Mn(CO)_5$ which is isoelectronic and isolobal with $[MnH_5]^{5-}$.

[Sec. 32.4.1 *Carbonyl clusters*]

Some common reactions of CH_3 and $Mn(CO)_5$ are noted below :

(i) Ready formaton of dimer : C_2H_6; $Mn_2(CO)_{10}$

(ii) Reduction : CH_3^- (in CH_3MgX); $Mn(CO)_5^-$

(iii) Combination with other species having a single unpaired electron : RCH_3; CH_3I; $RMn(CO)_5$; $Mn(CO)_5I$

Some isolobal groups have been shown in Fig. 32.21. It may be noted that such pictorial consideration of isolobal relationship, though helpful in many cases, has its own limitations too. The "pictures" chosen for isolobality are in no way unique or obvious and one has to depend upon intuitive selection among several possible hybridization schemes. Thus, B—H and C—H systems may be viewed as consisting of two hybrid *sp* + two *p*-orbitals or four sp^3 hybrid orbitals. In either description, the frontier orbitals appear same. Similarly, two hybridization schemes may be applied to CH_2^- and NH_2.

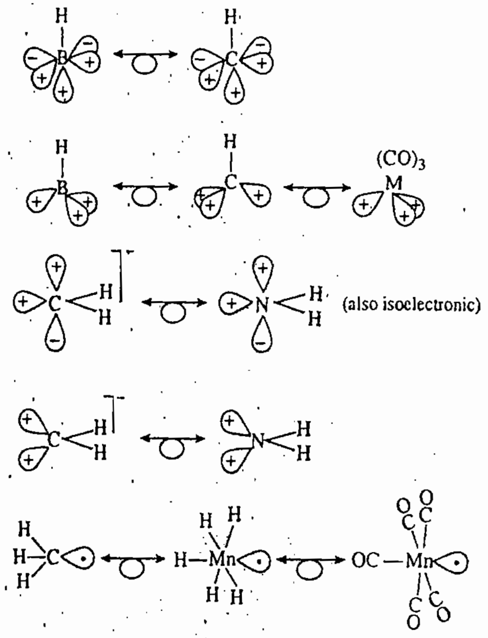


Fig. 32.21
Some isolobal fragments.

Some more isolobal species are shown in Table 32.11.

Table 32.11

Some isolobal moieties

CH_3	CH_2	CH
CH_2^-	CH^-	CH_2^+
	CH_3^+	
$Co(CO)_4$	$Cr(CO)_5$	$Mn(CO)_4$
$Mn(CO)_5$	$Fe(CO)_4$	$Co(CO)_3$
$CpCr(CO)_3$	$CpMn(CO)_2$	$CpCr(CO)_2$

It appears that an organic moiety with (8-*n*) electrons is isolobal with an organometallic fragment having (18-*n*) electrons. Addition or removal of a proton does not change the nature of frontier orbitals, for example, CH_3 and CH_2^-; CH_2 and CH_3^+ and so on.

In general, we may expect stable molecules of the same structure when one component is replaced by an isolobal group. The isolobality of BH (or CH) and $M(CO)_3$ fragments was exploited by Wade, Mingos and others to correlate the structures of polyhedral borane cages and metal carbonyl clusters.

To understand the basic relationship between the structure and the number of electrons available for cluster bonding we first consider the bonding in *closo*- $B_6H_6^{2-}$ which has an octahedral structure. Each B atom may be supposed to use one *sp*-hybrid orbital and one electron for the B—H link. This leaves each B atom with two electrons, one *sp*-hybrid orbital plus two tangential *p*-orbitals for the framework bonding. Six B-atoms contribute eighteen atomic orbitals which combine to produce a total of eighteen molecular orbitals. Of these, seven are bonding m.o.-s. Now, six B-atoms provide 6 × 2 = 12 electrons and the overall charge adds 2 more electrons, making a total of 14. These 14 electrons exactly fill the seven bonding m.o.-s, leaving a large HOMO-LUMO gap. Thus, a *closo*- structure with six vertices is formed by (6 + 1) or 7 pairs of electrons engaged in framework bonding. In general, $B_nH_n^{2-}$ anions may provide (*n* + 1) electron pairs in bonding framework m.o.-s to have a stable *closo*- polyhedron with *n* vertices. Since each face of the polyhedron has a triangular face (Greek delta, Δ), these are also called *deltahedral* structures.

Now we may remove one BH unit from $B_6H_6^{2-}$ retaining the electron pair to get $B_5H_5^{4-}$. The system still has seven skeletal bonding m.o.-s and exactly fourteen electrons to fill them. The structure is now a square pyramid formed by removal of one vertex of the octahedron of $B_6H_6^{2-}$ — the resulting open structure resembles a bird's nest and is called a *nido*-structure with five vertices. In general, *n* BH units providing (*n* + 2) skeletal electron pairs will have a *nido*-structure with *n* vertices i.e., one vertex missing from the (*n* + 1) *closo*-polyhedron.

Similar arguments show that the $B_4H_4^{6-}$ anion with seven skeletal electron pairs will adopt a more open structure with two adjacent vertices removed from the octahedron, that is, an *arachno*-structure. $B_nH_n^{6-}$ anions with (*n* + 3) electron pairs will thus have an *arachno*-structure with two adjacent vertices removed from an (*n* + 2) *closo* deltahedron.

The Polyhedral Skeletal Electron pair theory (PSEPT) for polyhedral metal clusters is based on the structure of $B_nH_n^{6-}$ anions and the isolobality of BH and $M(CO)_3$ fragments. A transition metal has nine valence orbitals (five *d*, one *s* and three *p*). It is now assumed that in the cluster three of these nine orbitals will be used as acceptor for the three CO ligands and three more will be low energy and essentially non-bonding. Each metal in a cluster is now left with three cluster-bonding orbitals — these are the frontier orbitals of the $M(CO)_3$ fragment : they consist of a radial *sp* and two tangential *pd* hybrids with orientations and symmetry properties similar to the BH unit. So an M_n polyhedral cluster will provide 3*n* orbitals for cluster bonding out of which (*n* + 1) will be low-lying bonding m.o.-s (compare $B_6H_6^{2-}$). We expect, in line with our observation on the borane anions, a *closo*-, *nido*- or *arachno*- structure depending on the number of electron pairs available for skeletal bonding.

Now let us take an account of the valence electrons of the transition metal. If the metal provides *m* electrons and the external ligands provide *l* electrons, we get a total of (*m* + *l*). Out of these (*m* + *l*), twelve electrons will be required to fill six orbitals not engaged in cluster bonding. Hence the contribution to cluster bonding comes out as (*m* + *l* − 12). Some calculations of cluster bonding electrons are shown in Table 32.12.

Table 32.12

Electrons available for cluster bonding (*m* + *l* − 12)

Metal	*m*	**CLUSTER UNIT** **M-Cp** (*l* = 5)	 **M(CO)$_3$** (*l* = 6)	 **M(CO)$_4$** (*l* = 8)
V, Nb, Ta	5	−2	−1	1
Cr, Mo, W	6	−1	0	2
Mn, Tc, Re	7	0	1	3
Fe, Ru, Os	8	1	2	4
Co, Rh, Ir	9	2	3	5
Ni, Pd, Pt	10	3	4	6

With the total number of cluster valence electrons, we can readily pair them. If *x* pairs of electrons are available, a closed deltahedron with (*x* − 1) vertices is indicated. If the number of metal atoms equals *x* − 1, the structure will be a *closo*- deltahedron. If the number of metal atoms is *x* − 2, that is one less than the deltahedron arrived at, the structure will be a *nido*-structure formed by removal of one vertex from the (*x* − 1) deltahedron. An *arachno* structure is predicted if *x* pairs of cluster electrons are provided by *x* − 3 metal atoms, again based on a polyhedron with (*x* − 1) vertices, with two adjacent vertices removed.

The *total electron count* (TEC) of a cluster is often useful in deciding the number of skeletal electron pairs. The total electron count is the sum of

(i) the number of valence electrons of all metal atoms plus any hetero atom and interstitial atom, if present;

(ii) two electrons for each CO group, irrespective of their mode of bonding (i.e., terminal, bridge etc.);

(iii) number of electrons to justify the overall charge of the cluster.

In terms of our argument developed earlier, the TEC should tally with the stucture of the cluster. Stated in terms of the number of vertex *n* of the polyhedron, we require (i) twelve non-skeletal electrons per metal atom plus (ii) a total of 2(*n* + 1) skeletal electrons to fill the bonding m.o.-s. In a *closo* structure, we have *n* metal atoms, giving a TEC of 12*n* + 2(*n* + 1). For a *nido* structure derived from the *n*-vertexed parent polyhedron, we have (*n* − 1) metal atoms giving a TEC 12(*n* − 1) + 2(*n* + 1). For an arachno structure, two metal atoms are short of the parent polyhedron, when we have a TEC 12(*n* − 2) + 2(*n* + 1).

closo $12n + 2(n + 1)$

nido $12(n - 1) + 2(n + 1)$

arachno $12(n - 2) + 2(n + 1)$.

Some examples of total electron count and structures are given in Table 32.13.

TABLE 32.13

Total electron count (TEC) and structure of some clusters on PSEPT

Cluster	TEC	No. of skeletal electron pairs (S)	No. of vertices of parent polyhedron (S − 1)	Structure expected
$Rh_6(CO)_{16}$	$9 \times 6 + 2 \times 16 = 86$	$\frac{1}{2}[86 - 6 \times 12] \div 2 = 7$	6	*closo* (octahedron)
$Os_5(CO)_{16}$	$5 \times 8 + 2 \times 16 = 72$	$\frac{1}{2}[72 - 60] \div 2 = 6$	5	*closo* (TBP)
$Fe_5C(CO)_{15}$	$5 \times 8 + 4 + 30 = 74$	$\frac{1}{2}(74 - 60) = 7$	6	*nido* (square pyramid)
$[Fe_4C(CO)_{12}]^{2-}$	$32 + 4 + 24 + 2 = 62$	$\frac{1}{2}(62 - 48) = 7$	6	*arachno*

In order to maintain consistency with the general rules, it is convenient to consider a tetrahedron as a *nido*- structure derived from a parent trigonal bipyramid by removal of one vertex. For example,

$$Co_4(CO)_{12} \ : \ TEC = 60 \quad S = 6$$

$$[H_3Ru_4(CO)_{12}]^- \ : \ TEC = 59 + 1 = 60 \quad S = 6$$

In eah case we expect a parent polyhedron with 5 vertices and 4 metal atoms, that is, *nido*- structures. However, there is often no advantage from the PSEPT approach for tetrahedral and planar triangular clusters. These have direct 2-electron M—M bonds directed along the edges and are electron-precise.

The structures of several clusters may be looked upon as a deltahedron with one or more extra metal atoms on their triangular faces. Such metal atoms, with their extra cluster fragments, appear as a cap on the polyhedral face. According to the *capping principle*, the skeletal electron count for a capped structure remains unchanged from that of its parent. Let us take $Os_7(CO)_{21}$ as an example :

$$Os_7(CO)_{21} \ : \ TEC = 56 + 42 = 98$$

$$\text{Skeletal electron pairs} = \tfrac{1}{2}(98 - 84) = 7.$$

We expect a polyhedron with six vertices. To accomodate the seven Os- atoms, we may consider a regular octahedron capped on one face by an $Os(CO)_3$ group. Similarly, $[Rh_7(CO)_{16}]^{3-}$ contains an $[Rh_7(CO)_3]^{3+}$ cap on an octahedral face of $[Rh_6(CO)_{13}]^{6-}$. Bicapped and tetracapped octahedrons are also known, as in $[Os_8(CO)_{22}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ respectively. Steric requirements of the CO groups presumably exclude the occurrence of capping on adjacent faces.

Like other bonding theories, the PSEPT model also has its limitations. It cannot rationalize many structures — particularly when the number of bonding m.o.-s are different from those predicted by the theory. Clusters of platinum, gold and similar metals toward the end of the transition series do not fit this model. The *p*-orbitals in these metals are much higher in energy (greater contraction of the lower energy orbitals) and do not form a part of the valence shell. $[Ni_5(CO)_{12}]^{2-}$, with a TEC = 76, is expected from the PSEPT to have an *arachno* structure derived from a polyhedron with seven vertices. Instead, it has an elongated trigonal bipyramid structure. When a regular trigonal bipyramid (72-electron) is axially elongated, two higher energy otherwise antibonding molecular orbitals are sufficiently lowered in energy to form a part of the bonding region and holds the four extra electrons.

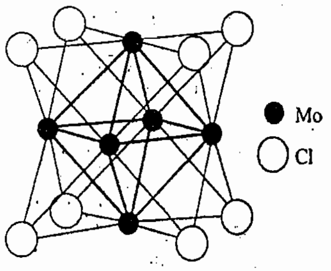
[Sec. 32.4.2
Halide
clusters]

The metal framework in many high nuclearity clusters resemble the close-packed structures (usually *hcp* or *ccp*) of many catalytically active metals. The course of a chemical reaction catalyzed by a metal surface may be visualized as chemisorption of small molecules at different sites, bond breaking where necessary, migration of reactive fragments to adjacent sites, reaction and finally desorption of the product. The activity depends critically on the nature of the metal surface and the extent of surface coverage. Detailed investigation of the interaction of small molecules on a heterogeneous (solid) catalyst surface is difficult since usual spectroscopic studies are not possible. Herein comes the importance of metal clusters — the large metal framewroks in these clusters may be used as a model for the metal surface. Large superclusters have been prepared whose surfaces present possiblities for binding small molecules to more than one atom simultaneously. This may modify the reactiviy of these small molecules paralleling their reactivity on metal surfaces. Again, both metal struetures and cluster structures are capable of incorporating nonmetal atoms (e.g., C or H) in their framework. Some reactions are known to be catalyzed by clusters, for example, reaction of CO and H_2 to give methanol is catalyzed by $Ir_4(CO)_{12}$ and to ethylene glycol is catalyzed by $Ru_2Rh(CO)_{12}$. It is likely that the C≡O bond is weakened by simultaneous coordination of CO to more than one metal when hydrogenation takes place readily.

32.4.2 Halide clusters

We have mentioned some of the halide clusters of 2nd and 3rd transition series elements in chapter 29. Mainly two structural types are predominant among such clusters — triangular and octahedral.

Numerous triangular clusters are formed by Mo, W, Nb and Re. As mentioned in section 29.5.7, Re(III) halides consist of Re_3X_9 clusters with halide bridges. The Re_3X_9 units are very stable with Re=Re double bonds. Octahedral clusters are formed by Zr, Nb, Ta, Mo and W, and others. The structure of M_6X_{12} type clusters has been shown in 29-VI (section 29.3.5). Another long-known M_6-cluster is represented by $[Mo_6Cl_8]^{4+}$ (32.XXIX). Each Mo is surrounded by four Cl^- in a square plane which may be supposed to be bonded by dsp^2 hybrid orbitals. A *pd* hybrid orbital is used for bonding additional ligands outside the metal framework. This leaves each metal with four atomic orbitals for framework bonding. The Mo_6^{12+} unit has 12 electron pairs which may be used to make 2-center M—M bonds along the 12 edges of the octahedron. The Nb_6^{14+} or Ta_6^{14+} cores have only 8 electron pairs which can form three-center bonds on the eight faces of the octahedron.



32-XXIX

SUMMARY

Introduction. Organometallic compounds contain at least one metal-carbon (M—C) bond, where M may also stand for nonmetals like B, Si, P or As.

The organometallic compounds may be broadly classified into two general categories — (i) compounds dominated by M—C bonds and (ii) compounds dominated by M—M bonds, i.e., metal clusters.

The compounds dominated by the nature of M—C bonds may be further classified as

(a) compounds of highly electropositive metals which are mostly ionic, for example $Ph_3C^-Na^+$ and $(C_5H_5)_2Ca$.

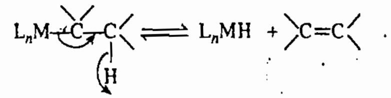
(b) compounds in which the M—C bond is a conventional σ-bond. These are formed by most of the nonmetals and a few metals like Sn, Pb, Zn, Hg etc.

(c) compounds formed by σ-donor and π-acceptor ligands like CO, NO, RNC etc.

(d) compounds formed by π-electron donors like the olefins and other π-systems.

σ-bonded organometallics of the transition metals like simple alkyls and aryls are mostly unstable under ordinary conditions — the M—C bonds are very reactive as the metal centers are usually coordinatively unsaturated. The M—C bond strength increases as one moves to heavier transition metals. Stability of the compounds is greatly enhanced when π-acid ligands such as CO, η^5-Cp or PR_3 etc. are present.

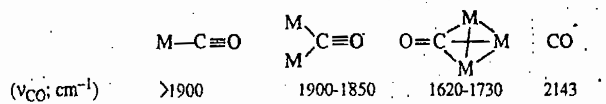
β-hydride transfer is the most important mode of decomposition of these σ-bonded organometallics :



The reverse process of β-elimination is the addition of alkenes to M—H bond (*hydrometalation*) — an important step in catalysis.

Carbonyl complexes. Carbon monoxide is an important π-acid ligand which stabilizes low oxidation states of transition metals. A large number of binary carbonyls as well as complexes with other ligands are known. The carbon to metal σ-bond is stabilized by back-donation of electron density from the metal into empty π* m.o. of CO and vice-versa.

CO may also act as a bridging ligand. Terminal and bridge CO may be distinguished by i.r. stretching frequencies.



Most carbonyl complexes conform to the 18-electron rule, $V(CO)_6$ (17 *e*) being an exception.

The CO groups in carbonyl complexes may be substituted by other ligands. Most metal carbonyls may be reduced to metal carbonylate anions by alkali or other reducing agents.

Nitrosyl complexes. NO has one more electron than CO and effectively acts as a three electron donor when it coordinates as NO^+. Complexes are mostly formed in combination with other ligands like $CO.Cr(NO)_4$ is an example of a pure binary nitrosyl. Terminal, linear and bent as well as bridge NO complexes are known. Terminal linear M—N—O groups (angle 165-180°) have N—O stretching modes in the infrared in the range 1650-1900 cm^{-1}. Linear nitrosyl complexes are formed by earlier transition metals with low-lying vacant orbitals suitable for accepting the lone pairs of electrons by the nitrogen. Later transition elements having filled orbitals may leave the lone pair on nitrogen which may coordinate in an sp^2 hybridized state and form bent MNO bonds. The N—O stretchings are usually in a lower range, 1525-1690 cm^{-1}.

Cyanide and Isocyanide complexes. The CN^- and RNC groups are stronger σ-donors and poorer π-acceptors compared to CO :

σ-donor : $CN^- > RNC > NO^+ \sim CO$

π-acceptor : $CN^- < RNC << CO < NO^+$

The mode of bonding of these ligands is essentially same as that in carbonyls but the importance of π-back bonding is less. In fact the isocyanide complexes need not derive their stability from back bonding and many complexes with metals in high oxidation states are known where the bonding is essentially σ-only.

Complexes of alkenes. Zeise's salt, $K[Pt(\eta^2\text{-}C_2H_4)Cl_3]$, known since 1827, may be readily prepared by reacting ethylene with K_2PtCl_4 in aqueous HCl. The anion of the complex contains the C=C bond perpendicular to the plane of the Pt and the 3 Cl^- ions. Bonding involves the filled π and empty π* m.o.-s of ethylene — back bonding results in slight increase (~3.8 pm) in the C—C distance compared to free ethylene. The M—C_2H_4 σ-bond offers little resistance to rotation of the alkene about the metal-olefin bond axis.

Complexes of carbocyclic π-donors. Ferrocene $(\eta^5\text{-}C_5H_5)_2Fe$ was the first example in which the delocalized π-electron cloud from an aromatic system $(C_5H_5^-)$ coordinates to a metal. It is a stable solid containing an iron atom sandwiched between two cyclopentadiene rings in staggered position. The molecule obeys the 18*e* rule and contains just sufficient electrons to complete the nine bonding/nonbonding m.o.-s. in the system. Bis(cyclopentadienides) of many other transition elements are known. Cyclopentadiene may also form compounds as a monohapto (η^1-) and trihapto (η^3-) ligand.

Compounds containing other aromatic systems like C_6H_6, $C_7H_7^+$ (tropylium cation) and $C_8H_8^{2-}$ (cyclooctatetraenide) are also numerous.

Organometallic compounds in catalysis :

Wilkinson's catalyst, $RhCl(PPh_3)_3$, was the first catalyst to ensure hydrogenation of olefins at ordinary temperature and pressure.

Addition of H_2 and CO to an olefin (*hydroformylation*; also known as the *oxo process*) is catalyzed in presence of finely divided cobalt (or rhodium). Cobalt is converted to $Co_2(CO)_8$ at the reaction condition (150°C, 200 atm); this is converted to $HCo(CO)_4$, supposed to be the effective catalyst. Trans-$HRh(CO)(PPh_3)_3$ is a superior catalyst as it operates ~100°C and 1 atm pressure and promotes linear aldehydes.

Methanol is manufactured by passing H_2 + CO (synthesis gas) at a pressure of 200 atm. over a catalyst bed consisting of Cu, Zn and Cr at 300°C.

Acetic acid may be produced from methanol by the action of CO by using rhodium carbonyl iodide as a homogeneous catalyst (*Monsanto process*).

Synthetic gasoline is produced by passing methanol vapour over the Zeolite catalyst ZSM-5. The older *Fischer-Tropsch proess* involves reaction of H_2 and CO over transition metal catalysts like Fe, Ru, Co, Ni etc.

EXERCISE

1. *Manganese carbonyl has the empirical formula $Mn(CO)_5$ and is dimeric (mol. wt.) in solution. The diamagnetic compound shows no i.r. absorption due to C—O stretching below 2000 cm^{-1}. What inferences can be drawn from these facts?*

   [Hint : $Mn_2(CO)_{10}$; Mn—Mn bond; no bridge carbonyl;]

2. *Starting from $Mn_2(CO)_{10}$, how are the following compounds prepared?*

   (i) $NaMn(CO)_5$ (ii) $MeMn(CO)_5$ (iii) $MeCOMn(CO)_5$ (iv) $CF_3COMn(CO)_5$ (v) $CF_3Mn(CO)_5$.

   [Hint : (i) Na/THF; (ii) MeI on i; (iii) CO on ii; (iv) $(CF_3CO)_2O$ in THF at 25°C on i; (v) heat iv at 130°].

3. *How are the following compounds prepared?*

   (a) $Ni(CO)_4$ (b) $Fe(CO)_5$ (c) $Fe_2(CO)_9$
   (d) $Fe_3(CO)_{12}$ (e) $H_2Fe(CO)_4$ (f) $Na[Co(CO)_4]$
   (g) $Co(CO)_3NO$.

4. *$C_{10}H_{10}Fe$ represents a stable orange diamagnetic solid. The compound shows zero dipole moment and a single strong C—H stretching band at 3080 cm^{-1}. It may be oxidized to a blue solution and acetylated with $CH_3COCl/AlCl_3$ in CS_2 to a red crystalline solid $C_{14}H_{14}O_2Fe$. Oxidation of this second compound gives an acid $C_{12}H_{10}O_4Fe$ having dissociation constants K_1 and K_2 approximately 10^{-7}, comparable to that of benzoic acid. Correlate.*

   [**Hint :** The acid is a symmetrical dicarboxylic acid (equal K_1, K_2) : $Fe(C_5H_4.COOH)_2$. Comparison with benzoic acid shows that the Cp rings have considerable aromatic character.]

5. *Comment*

   (i) *Although CO forms many complexes with transition metals in low oxidation states, it does not do so with the halides of B or Al which are themselves strong Lewis acids.*

   (ii) *$Fe_2(CO)_9$ is diamagnetic.*

   (iii) *Though copper is a transition metal, it does not form a stable carbonyl.*

   (iv) *The organometallics containing the following bonds show the order of thermal stability as shown ;*

   $$M—CF_3 > M\,COCH_3 > M—C_6H_5 > M—CH_3.$$

   (v) *$MnCp_2$ is paramagnetic with five unpaired electrons.*

   (vi) *Acid dissociation constants of the following hydrides in water are*

   $$HCo(CO)_4 \sim 1;\ HMn(CO)_5 \sim 10^{-7};\ HCo(CO)_3PR_3 \sim 10^{-7}.$$

   (vii) *Alkyl compounds of Zn and Cd inflame spontaneously in air but $HgMe_2$ is stable towards air and water.*

   (viii) *$Ni(CO)_4$ is tetrahedral while $Ni(CN)_4^{2-}$ is planar, though both are diamagnetic.*

   (ix) *The mean dissociation energies for the process $M(CO)_6\,(g) \longrightarrow M\,(g) + 6CO\,(g)$ are as follows :*

$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
126	151	176 kJ mol^{-1} approx.

   (x) *Metal-metal bonds in carbonyls are often shorter than metal atom diameters in pure metals.*

   (xi) *In the reaction*

   $$(O\overset{*}{C})_5MnCH_3 + CO \longrightarrow (OC)_5Mn\overset{*}{C}OCH_3\ (\overset{*}{C} = {}^{14}C)$$

   the acyl CO is derived from $(OC)_5MnCH_3$.

   [**Hint :** A 16*e* intermediate $CH_3COMn(CO)_4$ is probably formed via a cyclic three center transition state. This adds a molecule of CO to give the 18*e* product.]

   (xii) *The V—C bond lengths in $V(CO)_6^-$ and $V(CO)_6$ are 193 pm and 200 pm respectively.*

   (xiii) *The N—O distance in $[Co(diarsine)_2NO]^{2+}$ is 168 pm and the CoNO angle is 180°. Reaction of the complex with SCN^- forms $[Co(diarsine)_2(NCS)NO]^+$ in which N—O distance is 185 pm and CoNO angle is 135°.*

   (xiv) *$LiCo_3(CO)_{10}$ shows three distinct types of ν_{CO} in the regions 2080-2000, 1850 and 1600 cm^{-1}.*

6. (a) *Show different coordination modes of NO with examples.*

   (b) *NO^+ is a bad donor but good acceptor while CN^- is a good donor but bad acceptor—explain.*

7. (a) *The C—C stretching frequency in ethylene and acetylene are about 1650 cm^{-1} and 2000 cm^{-1} respectively. $Pt(PPh_3)_2(RC{\equiv}CR')$ shows a C—C stretching frequency at 1700 cm^{-1}. What should be your conclusion?*

   (b) *Ethylene complexes of transition metals show C—C stretching frequency around 1500 cm^{-1}.*

8. *Which of the following species are expected to be unstable and why?*

   (i) *diamagnetic $NiCl_4^{2-}$* (ii) *$Ti(CO)_4^{4+}$* (iii) *$Cd(CO)_3$* (iv) *$Fe_3(CO)_{12}$* (v) *$ZrCl_4$.*

   [**Hint :** (i) Repulsion between Cl in sq. planar arrangement (ii) back-bonding not possible (iii) high effective nuclear charge of Cd disfavours back bonding.]

9. *$[Fe(H_2O)_5NO]^{2+}$ shows N—O stretching frequency 1745 cm^{-1} and μ_{eff} = 3.9 B.M. What are your inferences regarding the bonding in this complex?*

10. *Find the number of x :*

    (i) *$H_2Ru_4(CO)_x$ (tetrahedral cluster)*

    (ii) *$H_3Os_4(CO)_xI$ (butterfly, I serving as a bridge between two extreme Os)*

    (iii) *$HFe_5N(CO)_x$ (square pyramid, N at center of basal plane)*

    [**Hint :** (i) 6 Ru—Ru bonds. Total excluding CO = 46. 72 − 46 = 26. *x* = 13.
    (ii) 5 Os—Os bonds. I contributes 3 electrons. Total excluding CO = 48. *x* = 12.
    (iii) 8 Fe—Fe bonds. N = 5. Total excluding CO = 62. *x* = 14.]

11. *Suggest likely structure for*

    (a) *$Fe(CO)_2(NO)_2$* (b) *$Mn(CO)_4NO$* (c) *$Fe(CO)_4C_2H_4$* (d) *$[Fe(CO)_4CN]^-$.*

    [**Hint :** See In-chapter Q. 32.11]

12. (a) *How will you prepare Zeise's salt from K_2PtCl_6?*

    (b) *Discuss the structure and bonding in Zeise's salt.*

    (c) *Explain :*

    (i) *the C—C bond in the coordinated olefin is greater than that in the free olefin.*

    (ii) *the C—C bond axis is perpendicular to the $PtCl_3$ plane.*

    (iii) *the Cl^- trans to C_2H_4 has larger Pt—Cl distance.*

    (d) *Do you expect any rotation of the ethylene molecule in Zeise's salt without hampering the stability of the complex? If possible explain it.*

13. (a) *Ferrocene, an 18e species, is diamagnetic; nickelocene, a 20e species, is paramagnetic (μ = 2.86 B.M.). Comment.*

    (b) *The m.o. diagram of ferrocene has 19 molecular orbitals. How many molecular orbitals do you expect for $(\eta^6\text{-}C_6H_6)_2Cr$ from a similar bonding model?*

    [**Hint :** (a) Last two electrons in a doubly degenerate level. See Fig. 32.17.
    (b) Each carbon atom in benzene contributes one π-orbital. Chromium has nine valence orbitals.]

CHAPTER THIRTYTHREE

BIOINORGANIC CHEMISTRY

OBJECTIVES

33.1 Essential elements in biological systems
    Introduction [33.1.1]
    Essential elements of life [33.1.2]
    Basic chemical processes in biological systems [33.1.3]
33.2 Metalloproteins and metalloenzymes
    Introduction [33.2.1]
    Iron proteins [33.2.2]
    Copper proteins [33.2.3]
    Zinc proteins [33.2.4]
33.3 Metal ions as charge carriers
    Introduction [33.3.1]
    Sodium-potassium pump [33.3.2]
33.4 Health concern of metals and nonmetals
    Introduction [33.4.1]
    Toxicity [33.4.2]
    Metals in medicine [33.4.3]

33

BIOINORGANIC CHEMISTRY

33.1 ESSENTIAL ELEMENTS IN BIOLOGICAL SYSTEMS

33.1.1 Introduction

Life originally appeared on earth in an overall reducing atmosphere. As shown by Miller and Urey (1953), lightning discharges through a mixture of CH_4, H_2O, NH_3 and H_2 produce significant amounts of amino acids essential to life processes. Abelson and others later showed (1960s) that solar uv radiation not filtered by the earth's ozonosphere acts on a mixture of CO, CO_2, nitrogen and a small amount of H_2 producing, among others, hydrogen cyanide. This molecule can subsequently give rise to glycine, adenine, and other biologically significant molecules. These compounds, formed in the primitive earth, might have undergone a series of complex chemical evolution over millions of years to produce living organisms which could replicate themselves and undergo biological evolutions (~ 3.5 billion years ago). Photosynthetic organisms appeared approximately 2.5 billion years ago when the atmosphere became gradually rich in dioxygen and ultimately sustained aerobic forms of life. The diverse biological world of today has largely developed with this form of life and is a unique example of nature's delicate balance between constructive and destructive oxidation by dioxygen. The amazingly complex and yet precisely synchronized biological processes involve, in addition to H, C, N, O, and P, other elements abundant on the earth, particularly a large number of metals, in both bulk and in trace. As more and more finer details regarding these roles get unveiled, the emphasis on a particular area of study generates new terminologies to justify the thrust area. Inorganic biochemistry or bioinorganic chemistry is such a terminology adapted in the last lap of the tewntieth century to cover studies on the biological functions of typically "inorganic elements",—the metals in particular. The major areas of study under this discipline may be broadly identified as :

(i) biological functions of different elements which are mostly known to form inorganic compounds — some authors even term them "inorganic elements";

(ii) investigation on the toxicity of these elements and their compounds and, of course, methods to overcome the toxic effects;

(iii) metal ion transport and storage in living systems;

(iv) use of metals as probes and drugs;

(v) other applications like microbiological extraction of metals (see Cu) and artificial fixation of nitrogen.

33.1.2 Essential elements of life

Essential elements

An element is considered essential when it has a specific role indispensable to sustain life in a living organism; absence or even deficiency of the element will lead to serious hindrance to the normal function of the living system.

About thirty elements appear essential to some form of life (Table 33.1). Hydrogen is by far the most abundant biological element (63% of the atoms in a human body). This is followed by oxygen (25.5%), carbon (9.5%) and nitrogen (1.4%). The following seven elements in order of their abundance in humans are Ca, P, Na, K, S, Cl and Mg; together they constitute about 0.6%. These eleven elements are *bulk* or *constituent elements* as they are required in the living body in relatively larger amounts (about 1-10^4 g-mole in 75 kg. adult human body).

Living systems also require small amounts of other elements shown in Table 33.1. The requirement of these elements may be very low (i.e., 10^{-4} g-mole or less in a 75 kg adult) or moderate (e.g., 10^{-1} g-mole). All these elements are classed as *essential trace elements*; iron, copper and zinc top this list. Elements present in exceedingly small amounts are called *ultra-trace elements*, for example, Mn, Mo, Co, Ni and V.

TABLE 33.1

Essential elements in living organisms

bulk elements : □; others are trace elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$\boxed{\text{H}}$												B	$\boxed{\text{C}}$	$\boxed{\text{N}}$	$\boxed{\text{O}}$	F
$\boxed{\text{Na}}$	$\boxed{\text{Mg}}$												Si	$\boxed{\text{P}}$	$\boxed{\text{S}}$	$\boxed{\text{Cl}}$
$\boxed{\text{K}}$	$\boxed{\text{Ca}}$			V	Cr	Mn	Fe	Co	Ni	Cu	Zn			As	Se	Br
					Mo								Sn			I
					W											

TABLE 33.2

Abundance of some metals in an adult human (g/75 kg)

Bulk metals		Trace Metals		Ultra-trace metals	
Na	70-120	Fe	4.5	V	15×10^{-3}
K	160-200	Zn	2-3	Mn	10×10^{-3}
Ca	1100	Cu	$80\text{-}120 \times 10^{-3}$	Mo	10×10^{-3}
Mg	25			Cr	2×10^{-3}
				Co	1.2×10^{-3}
				Ni	3×10^{-3}

It is interesting to note that the distribution of essential elements in the biosphere is not in harmony with the abundance of the elements in the earth's crust. About 88% of the earth's crust is made from the four most abundant elements oxygen, silicon, aluminium and iron. In living cells, more than 98% is derived from the four elements hydrogen, carbon, nitrogen and oxygen. On the other hand, the concentrations of different ions in sea-water show a parallelism with those in living systems, for example, the blood plasma. This reminds us that the evolution of life to its present form probably originated in the sea. The process of evolution continued with the relatively abundant elements which were found suitable for sustained development of the process. The metal ions chosen were able to form thermodynamically stable units in the active centers of proteins (metalloproteins) or other biomolecules. At the same time, they had to be kinetically labile, facilitating rapid assembly and disassembly under physiological conditions. Ti and Zr, in spite of their high abundance, are not found in living cells as the metals are readily precipitated as insoluble hydrated oxides at our body pH; also the metals have a uniform high +4 oxidation state unsuitable for reversible electron transfer and other reversible biological processes.

The criterion of essentiality of an element in living systems is determined by following the involvement of the metal in one or more essential life process — mere accumulation of an element in the body does not prove that it is really essential in some

[Sec.33.1.2 *Essential elements*]

vital physiological process. Several marine organisms can accumulate high concentrations of Ti, V, Cr etc. metals in their body from very small concentrations of these elements in sea water; but the exact biological functions of these elements are not clear. The essentiality of lithium and cadmium is similarly in dispute, though the metals are definitely involved in some biological processes. Cadmium binds to the animal protein *metallothionein* but this may well be due to a tendency of the living system for detoxification.

The health response of an organism to an essential element follows the general type of curve shown in Fig. 33.1; details of the curve vary from one element to another. At and around zero intake of the element, the condition may be anything between bare survival to death. As the dose is slowly increased, the organism gradually reaches a stage of smooth functioning. But an excessive dose will gradually result in toxicity by the same element and ultimately lead to death. For some elements, the safe dose and the toxic dose may be quite close — for example 50 to 200 µg for selenium (Table 33.3).

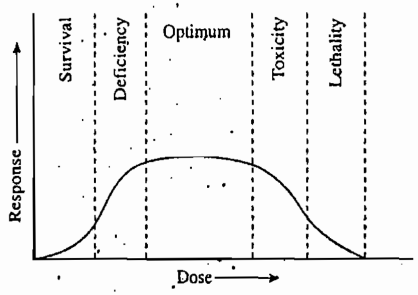


Fig. 33.1 : Nature of variation of response to increasing dose of an essential element.

TABLE 33.3

Recommended daily doses of some elements for an adult human being (~70 kg)

Element	Intake (Per day)	Element	Intake (Per day)
Iron	10 mg (male)	Fluorine	1.5-4.0 mg
	18 mg (female)	Molybdenum	150-500 µg
Zinc	15 mg	Iodine	150 µg
Manganese	2.5-5.0 mg	Chromium	50-200 µg
Copper	2.0-3.0 mg	Selenium	50-200 µg

Deficiency or excess of these elements may give rise to metabolic disorders, inhibited growth and other diseases. These will be mentioned in our subsequent discussions (33.4.2).

Sometimes one element strongly interferes with the uptake of another element (*antagonism*). The copper containing enzyme monoamine oxidase is involved in the cross-linking of polypeptide chains responsible for structural strength of arteries. As a consequence, copper deficiency in herbivorous animals causes anemia, loss of pigmentation and ultimately death owing to arterial lesions. However, even when the animals are supplied with pasture having a plentiful supply of copper, the uptake may be still hampered if the soil contains a high level of molybdenum — presumably owing to the formation of highly insoluble copper thiomolybdate in the gut.

We conclude this section with an overview of the nature of involvement of the essential elements in life processes, while specific functions played by some of the select elements will be discussed in later sections.

Roles of essential elements : an overview

The function of the elements in life processes involve a large number of biomolecules (see box). The manner in which nature selects and utilizes these elements for their specific roles in life in an extremely balanced and synchronized system has been a matter of great wonder to scientists, and will remain to be equally amazing for years to come.

The Biomolecules

As mentioned earlier, the living system started with simple molecules formed by carbon, hydrogen, nitrogen and oxygen. These molecules give rise to various molecular building blocks like the amino acids which, in turn, form more complex structural units like proteins. Proteins are polymers of amino acids linked by amide bonds and commonly called peptides and polypeptides. Nucleotides are formed by linking of bases (e.g., purines, pyrimidines) with carbohydrates and phosphates. Adenosine triphosphate is a representative example of such nucleotide which controls the energetics of the cell (see 22.3.5). The double helix of DNA (Fig. 7.45) is a polymer of nucleotides.

Metals, bulk and trace, are components of different biomolecules, both proteins or non-proteins. The non-protein sector includes the photoredox system (example chlorophyll) or those involved in storage and transport of metals like Na, K, Ca, Si and Fe. Among the protein sector of metallobiomolecules, metal-containing enzymes (metalloenzymes) cover a wide range of activities. They catalyze many biochemical processes through hydrolysis or cleavage of a variety of chemical bonds and have been named according to their activities with the suffix-*ase*. For example. *carboxypeptidase* functions to cleave a terminal carboxy group from peptide chains; *superoxide dismutases* (SOD) assist dismutation of *superoxide* and so on. Other metalloproteins are chiefly involved in oxygen management, metal management and electron transport. Some representative examples are given in Fig. 33.2.

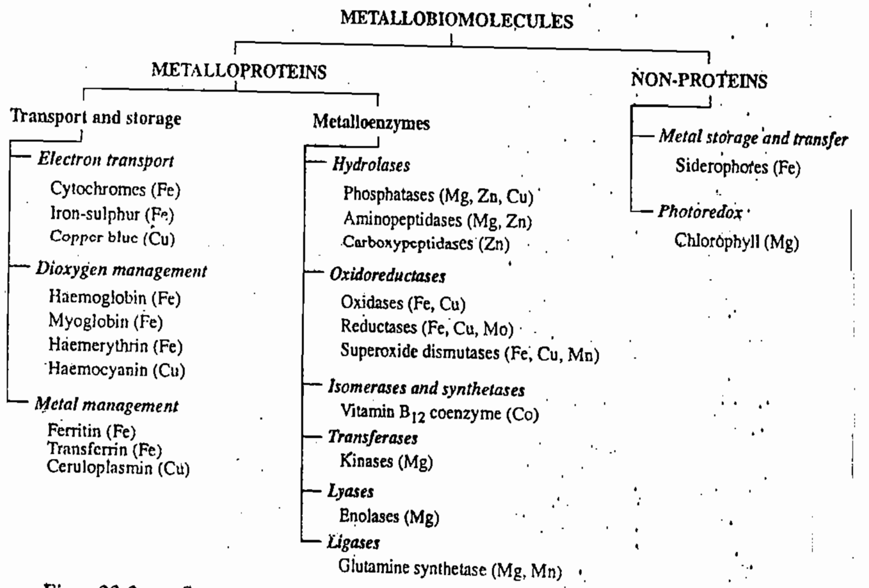


Fig. 33.2 : Some representative examples of different metallobiomolecules.

[Sec.33.1.2 *Essential elements (s-block)*]

The s-block elements :

H	
Na	Mg
K	Ca

Hydrogen

It is the most abundant element in the bio-sphere. The small atoms can effectively "seal" the residual valences of C, N, and O without any structural strain. When bonded to N and O, hydrogen can form hydrogen bond; the weak but extensive bonds are crucial in stabilizing many biological systems, for example, the double helix of DNA (chapter-7). The weakness of the bonds is an advantage in such systems since the helix must unwind during replication. The life supporting properties of water and many other functions like operations of several enzyme are also dependent on hydrogen bond. Protein folding, opening and encapsulation of the active site on hydrophilic and hydrophobic environment as and when required are thus controlled by hydrogen.

The other four elements in the s-block—Na, K, Ca and Mg, are the most abundant metal ions in living systems. They occur at fairly high concentration in most cells and constitute 99% of the metal content (more than 1% of the body weight) in man.

Sodium and Potassium

In spite of their established chemical similarity, the elements differ in their ability to penetrate cell membranes presumably due to their different ionic size. The metals also differ in their transport mechanism and efficiency to activate enzymes. Sodium ions are more abundant outside the cells, for example in the blood plasma and in the interestitial fluid surrounding the cells. They participate in transmitting nerve signals and regulate the flow of water across cell membranes. The transport of sugars and amino acids into cells is also influenced by Na^+ ions.

On the contrary, potassium ions occur at a higher concentration inside cells. They also activate many enzymes and participate in the oxidation of glucose to produce ATP. With sodium, K^+ ions are also involved in the transmission of nerve signals. The transport of these ions across cell membranes will be discussed in a separate section (33.3.2).

Calcium

It is the major constituent of bones and teeth. It is also important in neuromuscular function, interneuronal transmission, maintenance of cell membrane integrity and blood coagulation. The clacium in bones is mainly present as the hydroxyapatite, $Ca_5(PO_4)_3(OH)$. Bone is being continuously solubilized and redeposited in our body to the extent of about 400 mg. per day. The concentration of Ca^{2+} in plasma is closely maintained around 100 $mg \cdot L^{-1}$ by means of two hormones—calcitonin and parathyroid hormone. When the concentration of calcium in plasma falls, the parathyroid glands secrete parathyroid hormone. When the plasma level rises, thyroid secretion of calcitonin arrests resorption of bone. Parathyroid hormones also enhance gastrointestinal absorption of calcium from food and reduce loss of calcium via excretion.

During the period of growth, deposition of bone must exceed resorption. With ageing, resorption predominates and causes loss of about 15-30 mg per day. Vitamin D promotes deposition of bone. This vitamin is synthesized by the action of uv light on 7-dehydrocholesterol. So inadequate exposure to sunlight may result in diseases of the bone like ricket in childhood and softening of bones (osteomalacia) in later life.

Calcium ions in the cytoplasm of muscle fibrès (sarcoplasm) play an important regulatory role in muscle functioning. Clotting of blood is also influenced by the presence of Ca^{2+} ions. Blood contains prothrombin, a soluble protein. This is converted to the enzyme thrombin by the action of prothrombin activator in the presence of Ca^{2+} ion. Thrombin, again aided by Ca^{2+}, now clots the blood by converting its soluble fibrinogen into insoluble fibrin.

$$\begin{tikzcd} \text{Prothrombin} \arrow[r, "\text{Prothrombin activator}", "+Ca^{2+}"'] & \text{Thrombin} \arrow[d, "+Ca^{2+}"] \\ \text{Fibrinogen} \arrow[r] & \text{Fibrin} \end{tikzcd}$$

Magnesium

The involvement of magnesium in photosynthesis by plants is well-known (see below). Magnesium is also an essential element for animal physiology. 60% of the total magnesium present in an adult human (~25 g) is distributed in the skeleton while the remainder is mostly present inside cells. The Mg^{2+} ion in cells is the next most important cation after K^+. The small doubly charged cation has a high charge/size ratio and is strongly hydrated — mostly to $[Mg(H_2O)_6]^{2+}$ which binds the $ROPO_3H$—groups in nucleotides (ATP, ADP) and polynucleotides (DNA, RNA). The ion may form strong complexes with oxygens on various phosphate groups; such complexes appear to be important in storing energy and use of the same when necessary. All enzymes utilizing ATP in phosphate transfer require Mg^{2+} as cofactor.

Intracellular magnesium ions are also essential to keep ribosomes intact. Ribosomes are RNA-protein complexes of particle size ~200 Å diameter which occur in the cytoplasm and function as sites for protein synthesis.

Enzymes catalyzing replication and transcription of DNA require Zn^{2+} together with another divalent ion which is usually Mg^{2+} (sometimes Mn^{2+}). Nerve impulse transmissions, muscle contraction and metabolism of carbohydrates are also associated with the interaction of Mg^{2+} with nucleic acids.

Photosynthesis

Photosynthesis involves a series of complex reactions in the chloroplasts of plants with the overall conversion of water and carbon dioxide to carbohydrates and dioxygen. The overall reaction may be written as

$$xCO_2 + xH_2O \longrightarrow (CH_2O)_x + xO_2.$$

All the dioxygen come from oxidation of H_2O, as shown by the use of labelled $H_2\overset{*}{O}$ ($\overset{*}{O} = {}^{18}O$) :

$$xCO_2 + 2xH_2\overset{*}{O} \longrightarrow (CH_2O)_x + x\overset{*}{O}_2 + xH_2O$$

The reaction is endothermic to the extent of about 469 kJ per mole of CO_2 and is initiated by visible solar radiation in the range 600-700 nm. A part of the series of reactions may proceed in dark as well.

Plants absorb light with the help of chlorophylls which are magnesium porphyrine complexes (Fig. 26.1). Other variants of chlorophylls are also known in different algae.

The molecules are capable of absorbing photons around 700 nm and transmit the energy on to other species in the reaction sequence. The ability to absorb photon may be summarily associated with the conjugated polyene structure of the porphine ring system (Fig. 19-XII). Some chlorophylls (actually chlorophyll-protein complexes) act as antenna for solar radiation — also called light harvesting centres (LHC), which pass

the photon energy to the reaction site through excitation transfer within picoseconds. Other pigments like carotenoids may also be present in LHC; these respond to radiations not absorbed by chlorophylls.

The overall photosynthetic conversion is the outcome of a series of complex reactions and involves light absorption at two different regions of wavelength — photosystem-I (PS I) and photosystem-II (PS II). PS-I is based on a special form of chlorophyll-a having absorption maxima at 700 nm (P-700) while PS II utilizes another form of chlorophyll-a having maxima at 680 nm (P-680).

Photosystem-II : A manganese cluster (Mn_4) catalyzes the oxidation of water to dioxygen; the metalloenzyme is called oxygen-evolving complex (OEC) :

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e$$

The electrons are excited photochemically by P-680 to the primary electron acceptor pheophytin. Therefrom it is transferred to photosystem I via the intermediacy of (i) cytochrome b_3, (ii) plastoquinone (iii) Rieske's Fe-S protein (vi) cytochrome *f* and (v) plastocyanin.

Photosystem-I : The electron received from PS-II is further excited by P-700 and is ultimately used up in the reduction of CO_2 via (i) an Fe-S center (ii) Ferredoxin NADP reductase and (iii) NADPH. The electron flow also results in the formation of ATP from ADP.

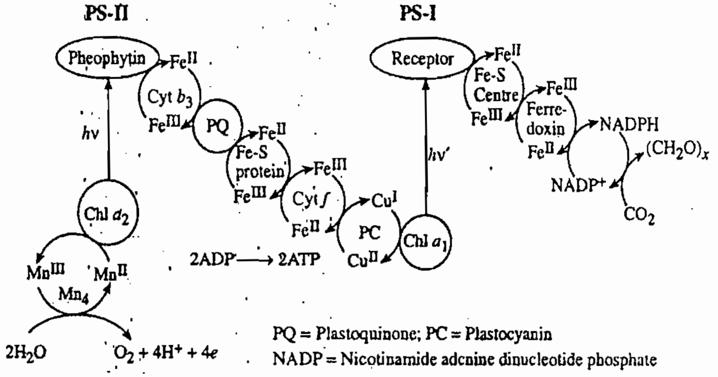


Fig. 33.3 : Schematic representation of the main steps in photosynthesis:

The main reactions may be summarily represented as

PS-II : $2H_2O \longrightarrow O_2 + 4H^+ + 4e\,] \times 6$

PS-I : $2NADP^+ + 2H^+ + 4e \longrightarrow 2NADPH\,] \times 6$

Dark reaction : $12NADPH + 12H^+ + 6CO_2 \longrightarrow 12NADP^+ + 6H_2O + (CH_2O)_6$

Net reaction : $6H_2O + 6CO_2 \longrightarrow 6O_2 + C_6H_{12}O_6$

The Mg^{2+} ion serves at least three purposes :

(i) it maintains the rigidity of the macrocyclic structure of chlorophyll and minimises molecular vibrations; hence energy is not readily lost by thermal vibrations.

(ii) the H_2O molecules co-ordinated to it mediates H-bonding between adjacent chlorophyll molecules in a stack.

(iii) the initial photon absorption gives rise to a short lived singlet state. The Mg^{2+} ion enhances the rate at which this singlet state is transformed into a triplet. This H-bonding, in turn, enhances the rate of electron transfer in the redox chain formed by the stack of chlorophyll molecules.

The initial excited state on light absorption is a shortlived singlet state which subsequently passes to a triplet state with relatively longer life. This triplet state is actually involved in the redox chain. The H-bonded system of several chlorophyll molecules can readily transmit the electrons without the formation of a bottleneck.

The p-block elements :

B	C	N	O	F
	Si	P	S	Cl
		As	Se	Br
	Sn			I

C, H, N and O comprise 99% (wt) of the human body and the major part of all living systems as water, organic compounds; carbohydrates, proteins and nucleic acids.

Phosphorus is also a major component of our body- about 85% of the 700 g of phosphorus in our body is present in the form of bones (and teeth). We have also seen (Ch. 7) how the PO_4 groups play a crucial role in bridging the sugar units of DNA and RNA. The involvement of ATP and ADP in energy storage and reproduction has been mentioned in section 22.3.5. Many other biological systems involve phosphorus, for example, the phospholipids present in cell membranes.

Space does not permit a complete discussion of the bio-chemistry of all these elements. A few select topics are briefly mentioned here; some others will be mentioned later in connection with metalloproteins and metalloenzymes.

Boron

It is an ultra-trace element essential for healthy plants but its detailed biochemical roles are not fully understood. It is known to be involved in the synthesis of nucleic acids, metabolism of carbohydrates, hormone action and membrane formation.

Neutron capture therapy

The high affinity of B-10 for capturing low-energy neutrons has been successfully used in the treatment of tumours, specially brain-tumours. After injection into patients, many boron compounds collect preferentially in growing tumours. Irradiation of the tumour area with low-energy neutrons leads to the release of high energy alpha particles according to the reaction

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{7}_{3}Li + \alpha.$$

The α-particles grown inside the tumour destroy the cancerous cells. Since the particles travel only short distances in tissue, they cannot damage healthy cells.

Aluminium, the third most abundant element in the earths crust (after O and Si), is not an essential element to life, the low solubility of its compounds around physiologial pH may be a likely explanation. On the other hand, the element is highly toxic, hampering brain function (section 33.4.2).

Carbon

Carbon is the key element to any form of life where its involvement is widespread. We have already discussed the conversion of carbon dioxide to carbohydrates during photosynthesis. Respiration supplies dioxygen for conversion of these carbohydrates and other organic molecules back to carbon dioxide. Organic compounds and CO_2 can also be interconverted via carbon monoxide. The enzymes carbon monoxide dehydrogenases catalyze the CO-CO_2 interconversion. In aerobic bacteria, these enzymes contain molybdenum, while in anaerobic bacteria, the enzymes contain FeS and Ni.

Essential elements (s-block)]

Methanogenesis and methylotrophy

Methanogenic bacteria catalyze the conversion of carbon dioxide to methane according to the reaction

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

The process, called methanogenesis, proceeds successively through the reduction steps — CO_2, —CHO, —CH_2OH and —CH_3. Various coenzymes including Mo or W-Fe (with S) and Fe-S proteins are active over these steps. The final reduction is catalyzed by methyl-S-coenzyme-M reductase, a coenzyme containing Ni(II)-tetrapyrrole complex.

$$\underset{\text{methyl-S-coenzyme-M}}{CH_3S(CH_2)_2SO_3^-} + H_2 \longrightarrow CH_4 + \underset{\text{coenzyme-M}}{HS(CH_2)_2SO_3^-}$$

Methane and air pollution

Such processes lead to the formation of methane in sediments in ponds, lakes, oceans, sludge from sewage plants and old unused wells (death-traps). Methanogens produce about 10^9 tons of methane per year all over the world and nearly half of this goes into the atmosphere.

The accumulation of methane in the atmosphere contributes to the greenhouse effect (section 21.3.5) and causes rise in temperature of the earth's atmosphere. O_2 and OH radicals (produced by sunlight on ozone layer) convert some methane to CO and CO_2. Burning of tropical rain forests adds substantial amounts of CO and CO_2 to the atmosphere. The increasing amount of CO largely consumes the OH radicals, leaving CH_4 untouched.

Methylotrophy is the reverse conversion of methane to carbon dioxide through CH_3OH, HCHO and HCO_2H as intermediates. The first step is catalyzed by soluble methyl monoxygenase (SMMO : contains iron) or particulate methyl monoxygenase (PMMO : contains copper). Conversion of methanol to formaldehyde is catalyzed by methanol dehydrogenase which contains a quinone co-factor. If a simple enzyme for the conversion of methane to methanol can be developed, we would be able to utilize the vast deposit of methane beneath ocean floors.

The carbon dioxide produced in our body is managed by the enzyme carbonic anhydrase present in red blood cells. Hydration of CO_2 is normally very slow ($t_{1/2}$ ~20s) at neutral pH and 25°C :

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

But the enzyme can dramatically reduce the half life to microseconds allowing both the take up of carbon dioxide from tissues like active muscle and its subsequent release in the lungs. As we shall see in the next section, the activity of the enzyme may be related to the presence of zinc.

Silicon

Though the second most abundant element (after oxygen) in earth's crust, silicon was not supposed to participate in any form of life owing to high insolubility of most silicon compounds. Photosynthesizing diatoms form their shells from silica which are silicon compounds. Photosynthesizing diatoms form their shells from silica which are more transparent compared to calcium carbonate. At present silicon has been shown to be involved in the structure of bone, cartridge, skin etc. connective tissues. The silicon is concentrated in proteoglycans in the connective tissues of animals (about 5g per kg. of proteoglycans); these are complexes containing proteins and acidic chains of repeating monosaccharide residues. Silicon is present at the active calcification sites during bone growth and its deficiency has been found to inhibit growth.

Nitrogen

As is well-known, nitrogen is an essential constituent of several biomolecules. Many inorganic nitrogen compounds are also involved in life processes — ammonia, nitric oxide, nitrite and nitrate ions being some ready examples. Nitrogen fixation by plants is a vivid example of nature's very own way of carrying out certain chemical changes which is yet to be followed by our present science.

Nitrogen fixation

A key reaction in the nitrogen cycle (section 22.1.3) concerns nitrogen fixation by nature using bacteria like Rhizobium present in the nodules in the roots of legumes such as peas, beans, soya etc. The conversion of dinitrogen to ammonia at ordinary temperature and pressure appears a sharp contrast to methods developed by human science using high temperature and pressure. It appears that the metalloenzyme nitrogenase present in the bacteria catalyze the reaction

$$N_2 + 8H^+ + 16MgATP + 8e \longrightarrow 2NH_3 + H_2 + 16MgADP + 16PO_4^{3-}$$

The ammonia produced is consumed for cell growth. The electrons required are supplied to nitrogenase by reduced forms of ferredoxins and flavodoxins. The enzyme nitrogenase may contain vanadium or iron or Fe-V or Fe-Fe or Fe-Mo metal centres. The most common form of the enzyme (also most investigated) contains two proteins (i) an Fe-Protein, molecular weight ~ 60,000, which includes an Fe_4S_4 cluster; (ii) an Fe-Mo protein, molecular weight ~2,20,000, a tetramer containing two Mo atoms, and 30-32 Fe atoms together with sulphur. Mg-ATP (and MgADP) binds to the reduced form of the Fe-protein about 20Å from the FeS cluster. For every two molecules of MgATP hydrolyzed, the Fe-protein tansfers an electron to the FeMo protein, possibly linked to it by salt bridge. When the FeMo protein accumulates enough electrons (eight electrons per N_2) these are transferred to N_2 with proton transfer from water.

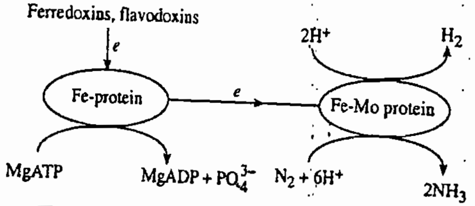
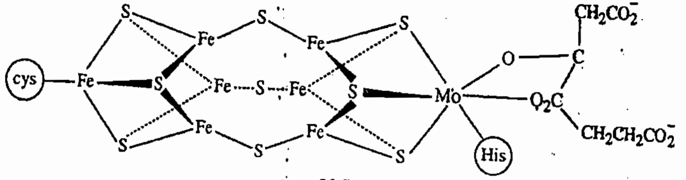


Fig. 33.4 Nitrogen fixation (schematic).

The site for binding of N_2 in the FeMo protein has been a point of much speculation. It was thought earlier that N_2 may initially co-ordinate to Mo by displacement of H_2 from a reduced metallo-hydride. Reduction of the co-ordinated N_2 may now proceed via a hydrazido(2–) intermediate : $Mo = \overset{\alpha}{N}—\overset{\beta}{N}H_2$. Multiple bond character progessively builds up between Mo and the α-N atom with concomitant protonation of the β-N. This gradually weakens the strong N≡N bond in dinitrogen.

The structure of the FeMo protein of nitrogenase has been determined by X-ray crystallography and a model has been proposed for the FeMo-cofactor (FeMoco; 33-I).



33-I

[Sec.33.1.2 *Nitrogen*]

The cofactor consists of two cuboidal fragments : one Fe_4S_3 fragment and one Fe_3MoS_3 fragment; these are linked by two sulphide bridges. The cluster is bound to the protein by a cysteine at one iron atom at the end and a histidine at the molybdenum atom at another end. The molybdenum is six-co-ordinated — its co-ordination numbers are fulfilled by the homocitrate ion at the extreme right (homocitric acid = 2-hydroxy-1, 2, 4-butanetricarboxylic acid). There is little change in the coordination of Mo during enzyme turnover. Also the iron atoms at the interface of the two cube fragments have open co-ordination sites. This observation has lead to the speculation that instead of Mo, these iron atoms might also serve as the site for binding dinitrogen [33-II(a) and (b)]. This hypothesis also fits the existence of nitrogenases which do not contain any molybdenum.

(a) (b)

33-II

A second point of interest in the nitrogen cycle is the formation of nitrates from lightning discharges. The nitrates are converted to ammonia using assimilatory nitrite and nitrate reductases.

$$NO_3^- \xrightarrow{Mo^{IV}\text{-oxotransferase}} NO_2^- \xrightarrow{Fe_4S_4 \text{ siroheme}} NH_3$$

The nitrate reductase is also a molybdenum containing enzyme.

$$(RS)_2\overset{VI}{Mo}(=O)=O \qquad (RS)_2\overset{IV}{Mo}=O$$

(a) oxidized form of nitrate reductase. (b) reduced form.

33-III

Nitric oxide

The role of nitric oxide as an important neurotransmitter has been established relatively recently. The molecule has been identified in the human brain and also in exhaled breath. It is generated even in a primitive species like the horseshoe crab, suggesting that its participation in life system must be at least 500 million years.

NO is formed in mammals from the guanidine N atom of *L*-arginine catalyzed by nitric oxide synthases (NOS). Its synthesis is regulated by calcium/calmodulin and its receptor is an iron porphyrin within the enzyme guanylate cyclase (converts guanine triphosphate to cyclic guanine monophosphate). At least three distinct NO synthases have been identified : (i) nNOS from neuronal tissue, (ii) eNOS from endothial cells and (iii) iNOS induced in macrophages (white blood cells).

Nitric oxide (i) takes part in the transmission of nerve impulses for many specific physiological functions; (ii) acts as a relaxant of vascular muscle through the activation of guanylate cyclases and thus reduces blood pressure. Sodium nitroprusside. $Na_2[Fe(CN)_5NO]$, ("nipride") acts as a vasodilator probably through the release of NO; (iii) it is also an effective blocker of cell multiplication and growth (cytostatic) as well as an efficient killer of cells (cytotoxic); (iv) NO is also involved in blood clotting.

Since NO is highly toxic and unstable, its release within the body must be carefully controlled. Production of excessive amounts of NO may lead to lethal dilation of blood vessels. This may be checked through NO synthetic inhibitors like *L*-thiocitrulline.

Detailed investigations on the involvement of NO in life processes present a fast developing area in bioinorganic chemistry. Some examples of biologically significant reactions of NO are :

(i) combination with O_2 to form NO_2;

(ii) combination with O_2^- to form ONO_2^-, a potent oxidant;

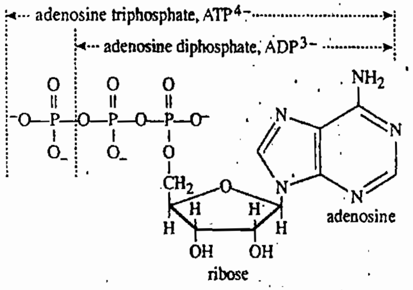
(iii) reactions with thiols to give nitrosothiols ($RSH \longrightarrow RSNO$);

(iv) adduct formation with heme.

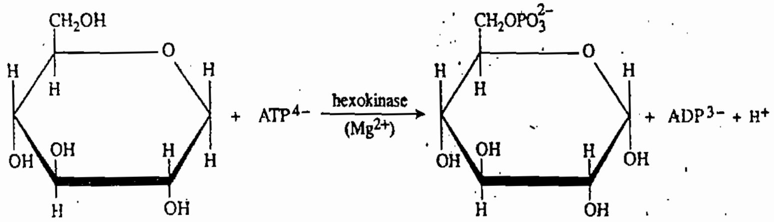
Phosphorus

Phosphorus, as PO_4 group, acts as a bridge between sugar units in DNA and RNA (see H-bond, section 7.3.3). The phosphate group plays a crucial role during cell replication. The recycling of phosphorus in the biosphere has been mentioned in chapter 22 (The phosphorus cycle; sec. 22.1.3).

We have also mentioned earlier (See 22.3.5) the role of adenosine triphosphate, ATP (33-IV) as the major source of energy for all biological processes. ATP can transfer a phosphate group, usually the terminal one, to glucose under the influence of the enzyme hexokinase (aided by Mg^{2+}) to produce ADP and glucose 6-phosphate; the energy released in the process supplies the energy necessary for all biological processes like muscle movement. It has been estimated that a man consumes about 40 kg of ATP per 24 hours during rest but the figure may rise to as high as 30 kg. per hour under stress. The ATP is continuously generated by the glycolytic and oxidative metabolism of food via ADP and phosphate ions.

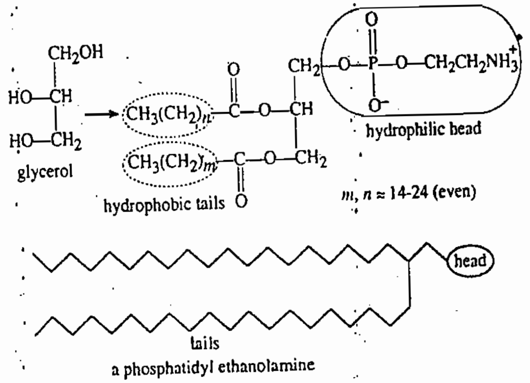


33-IV



Phospholipids

Phospholipids constitute another class of important biophosphorus compounds. These are mostly derived from glycerol : two hydroxyl groups being esterified by long chain fatty acids and the third hydroxyl group by phosphoric acid. A further alcohol such as ethanolamine forms an ester with the phosphate group (33-V).



33-V

The carboxylic acid may have a double bond in the chain. In any case, the skeleton consists of (i) a hydrophilic end or head (33-V) containing ionic groups which can interact with dipoles of water and (ii) two hydrophobic tails containing water-repelling hydrocarbon groups.

Most cell membranes contain such phospholipids (and glycolipids having similar shape) together with cholesterol and proteins. The hydrophilic heads of the phospholipids project outward in the aqueous environment of cells while the hydrophobic tails interact via van der Waals interaction to form double layers about 4.5 nm thick (Fig. 33.5).

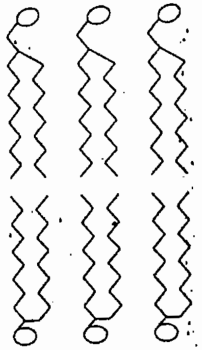


Fig. 33.5
Double-layer formed by phospholipids.

Lipid molecules are free to diffuse sideways in the plane of the bilayer. Various metalloproteins embedded within the cell membranes act as enzymes and perform various functions including transport of ions across the organic barrier.

The membrane phospholipids are being continuously hydrolyzed by phospholipases and replaced. Deficiency of these enzymes result in accumulation of undegraded phospholipids in nerve tissue, causing mental retardation.

Phospholipases are a group of digestive enzymes which catalyze the hydrolyis of membrane phospholipids. They are present in intestinal juices and venoms. The catalytic function involves Ca^{2+}.

About 85% of the 700 g (approx) phosphorus in our body is present as the bones. The bony skeleton of vertebrates is made up mainly of a fibrous protein (collagen) and crystals of calcium phosphate (hydroxyapatite, $Ca_5(PO_4)_3OH$). The triply charged phosphate ion PO_4^{3-} combines with divalent calcium ion to form ionic solids with high lattice energy and consequent low solubility. Tooth enamel is mostly hydroxyapatite.

Arsenic

Contrary to popular beliefs, this element has also been identified as an essential element. Animals fed on an arsenic-free diet showed rough fur, poor growth and low fertility rates; sudden heart failure was observed in lactating goats. However, no specific function of the element is known but in mammals it may be involved in arginine and zinc metabolism. Some marine organisms also contain arsenolipids. Methyl arsenicals, specially those with Me_3As^+ groups, originate in several biological changes. Some microorganisms can methylate inorganic arsenic compounds to trimethylarsine, Me_3As.

$$AsO_3^{3-} \longrightarrow MeAsO_3^{2-} \longrightarrow Me_2AsO^{2-} \longrightarrow Me_3AsO \longrightarrow Me_3As.$$

Oxygen

The initimate association of oxygen with our life processes needs little description. Only some small animals and plants receive their necessary oxygen from diffusion of O_2 across cell membranes. In others, uptake and storage of dioxygen involves sophisticated systems which will protect themselves from the oxidizing power of O_2 and release it in a controlled manner as and when necessary. As we have seen in chapter 28 (section 28.7.5) this function is carried out by the metalloproteins haemoglobin and myoglobin in our body. We shall discuss these proteins further in the next section. Besides the haemoglobin-myoglobin family, there are two other dioxygentransport proteins hemocyanins and hemerythrins. In haemoglobin the iron-porphyrin site undergoes a structural change upon binding of the dioxygen. In the other two proteins, the O_2 molecule binds to an iron or copper center.

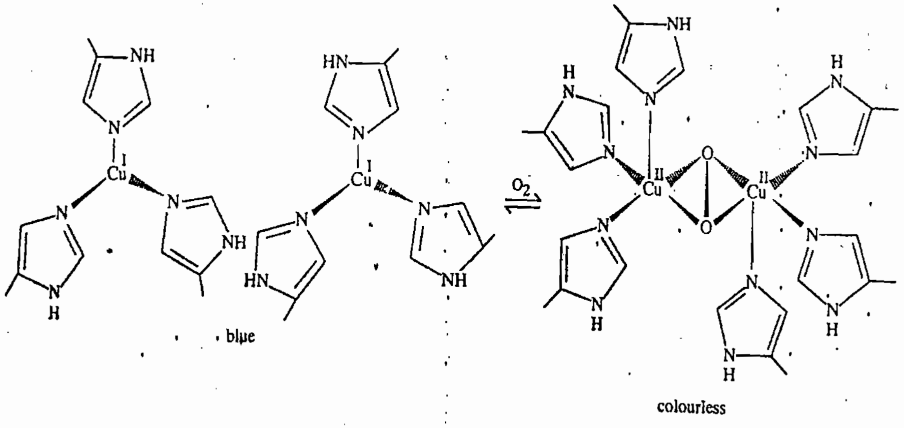


Fig. 33.6
Dioxygen uptake by haemocyanin. (see sec. 33.2.3)

Haemocyanin (HC) is found in several invertebrates, e.g., mollusks (snails, octopus) and arthropods (lobsters, crab). The dioxygen binds reversibly between two copper atoms.

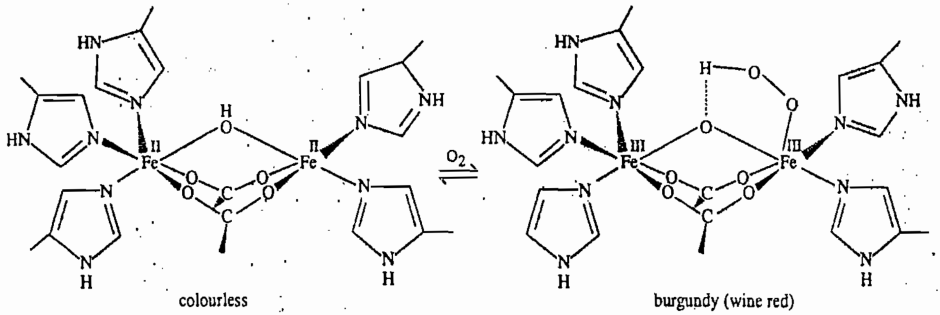


Fig. 33.7 : Dioxygen uptake by hemerythrin.

Hemerythrin (Hr) is found in marine invertebrates e.g., sipunculids (peanut marine worms). The dioxygen molecule coordinates to an iron atom in the Fe_2 unit (sec. 33.2.2).

In both hemocyanin and hemerythrin, a bimetallic unit serves the same function as a metalloporphyrin unit in hemoglobin or myoglobin.

The dioxygen received and stored in the body is ultimately reduced to water. The oxygen is used in the bio-synthesis of many compounds in the metabolic chain and to convert some lipid-soluble molecules to water soluble ones suitable for excretion. Different redox couples of oxygen are associated with these conversions :

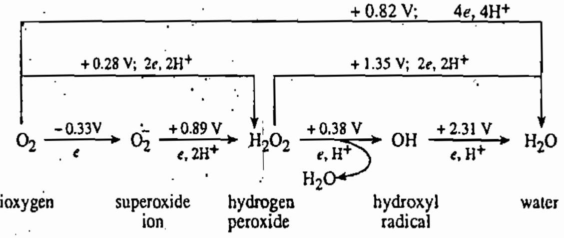


Fig. 33.8 : Standard reduction potentials (volt) for oxygen systems ($E^{\circ\prime}$ at pH = 7, 25°C).

Direct reduction of O_2 to H_2O is thermodynamically favourable ($E^{\circ\prime}$ = + 0.82 V) but the four-electron step does not take place readily. Stepwise reduction of O_2 to H_2O is also rendered difficult at the very first step to superoxide with a negative $E^{\circ\prime}$ (–0.33 V).

The main kinetic barrier to the direct reaction of an organic substrate with dioxygen arises from spin restrictions. In the ground state, the dioxygen molecule has two unpaired electrons and is in a triplet state (section 23.2.1). Typical bioorganic molecules contain no unpaired elecrons and so also are the products of their oxygenation — that is, they have singlet ground states. The time required for triplet to singlet transition being longer than the time of reaction, each elementary step of a chemical reaction must involve the same number of unpaired electrons before and after reaction. Representing electron spins with arrows (↑or↓), the spin states in the reactants and products in an elementary reaction of dioxygen may be symbolically represented as :

$$\frac{1}{2}\ {}^3O_2(\uparrow\uparrow) + {}^1X(\downarrow\uparrow) \longrightarrow {}^1XO(\downarrow\uparrow)$$

The process cannot be a fast, concerted step owing to spin restrictions. Likely pathways to overcome this restriction may be

$$\text{(i)}\quad \frac{1}{2}\,{}^3O_2(\uparrow\uparrow) + {}^1X(\downarrow\uparrow) \longrightarrow {}^3XO(\uparrow\uparrow) \xrightarrow{\text{slow}} {}^1XO(\uparrow\downarrow)$$

$$\text{or (ii)}\quad {}^3O_2(\uparrow\uparrow) \longrightarrow {}^1O_2(\uparrow\downarrow) \xrightarrow{{}^1X(\uparrow\downarrow)} {}^1XO(\uparrow\downarrow)$$

Both paths require high energy of activation. In path (i), excited triplet states of even unsaturated organic molecules are typically 150-300 kJ/mol higher than the ground state; the separation should be still higher in saturated hydrocarbons.

In path (ii), the conversion of triplet O_2 to singlet O_2 requires at least 92 kJ mol^{-1} (section 23.2.1, singlet O_2). It appears that metalloenzymes can overcome these barriers. For example, cytochrome *c* oxidase (section 33.2.2) bypasses the inconvenient reduction to O_2^- by binding O_2 to two paramagnetic metal ions and reduces O_2 to O_2^{2-} (peroxide ion) in a two electron step. The reaction occurs in a controlled manner and the energy released in the reduction of dioxygen can be used to produce ATP.

Two electron reduction of O_2 to O_2^{2-} or H_2O_2 takes place more readily than the formation of superoxide. Further reduction occurs to the hydroxyl radical which is readily converted to water (Fig. 33.8).

$$H_2O_2 + H^+ + e \longrightarrow H_2O + OH$$

An important aspect of dioxygen chemistry is the slowness of its reactions under ordinary conditions in absence of catalysts. Even pure dioxygen itself in high concentrations (5 atm, say) can be dangerous to mammals. All the reduction intermediates of it, that is, species like O_2^-, O_2^{2-} and OH radicals formed within the living body (*in vivo*) are highly toxic as they may cause uncontrolled, indiscriminate oxidation during the short span for which they exist. Arthritis, rapid ageing, Alzheimer's disease and a lot of neurological problems have been associated with such toxic effects. The superoxide and peroxide ions can further promote the formation of OH radicals :

$$O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH$$

The OH radical is a strong, non-selective oxidant which abstracts protons from other species and can damage cellular constituents like lipids, proteins and DNA. The last one is particularly vulnerable to attack at the base or at the sugar. Attack at the ribose ring can lead to scission of the DNA strand, forming faulty genes.

Nature has devised a number of tactics to achieve a delicate balance between the constructive and destructive oxidation by dioxygen. There are enzymes and non-enzymes which direct and control the oxidation of substrates for producing energy or for *biosynthesis* — these are generally known as anti-oxidants. Moreover, the oxidative reactions have been designed to occur in a stepwise manner in different parts of the body; any toxic by-product of dioxygen reaction can be eliminated easily.

Metalloenzymes like catalase, peroxidase and superoxide dismutase (SOD) catalyze disproportionation and reduction of H_2O_2 and the superoxide ion :

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (\textit{dismutation}, \text{ catalyzed by } \textit{catalase})$$

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \quad (\textit{reduction}, \text{ catalyzed by } \textit{peroxidase})$$

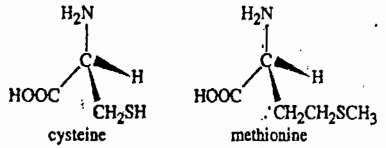
$$2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2 \quad (\textit{dismutation}, \text{ catalyzed by SOD})$$

The enzymes catalase and peroxidase contain Fe(III)-porphyrin system at their active sites; superoxide dismutase (SOD) contains Cu—Zn or Mn at their active sites. Cu—Zn SOD and peroxidases are present in the mitochondria.

Some of the non-enzyme anti-oxidants are ascorbic acid, glutathiol (both present in cytosol) and vitamin E (present in lysosomes, together with vitamin C).

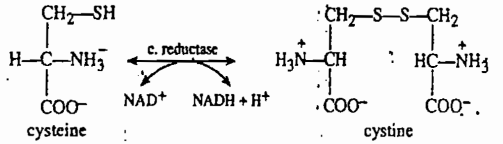
Sulphur

Sulphur is an important constituent of plant and animal bodies. Proteins contain the sulphur amino acids cysteine, cystine and methionine. Methionine and cysteine, besides being present in proteins, are involved in many important metabolic reactions.



33-VI

Cysteine and cystine are interconvertible by an NAD$^+$-dependent cystine reductase :

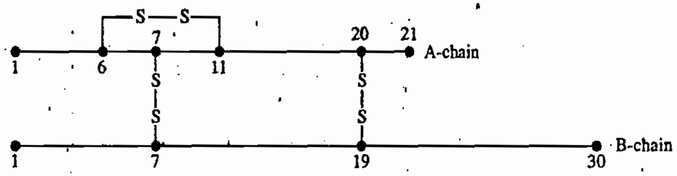


33-VII

Plants prepare cysteine using SO_4^{2-} as the source of sulphur. Animals must obtain cysteine from plants. Humans consume nearly 1 to 2 g of sulphur daily through animal proteins and vegetables. The sulphur is ultimately excreted in urine mainly as sulphates, together with small amounts of organic esters and thiocyanates. Biological decay of organic matter in marshes and estuaries produces H_2S. This is oxidized in the atmosphere (or by oxygen dissolved in water) to sulphates. At the bottom of the Black sea, the dissolved oxygen is used up by the huge amount of organic pollutants carried by rivers; so bacteria have to feed on sulphates producing large quantities of H_2S. Some green and purple bacteria use H_2S from dead organic matter for photosynthesis of carbohydrates :

$$6CO_2 + 12H_2S \longrightarrow C_6H_{12}O_6 + 12S + 6H_2O.$$

The ability of sulphur for catenation has been used by nature to link two separate protein chains or two parts of the same chain. The hormone insulin contains such disulphide bridges between two polypeptide chains (33-VIII).

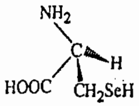


33-VIII

The potential Lewis base character of the sulphur atom in amino acids or as sulphide ion is manifest in various metallo-enzymes containing iron, copper, zinc or molybdenum coordinated by one or more cysteine sulphur. We have already mentioned such iron-sulphur proteins (ferredoxins; section 23.3.8). We shall discuss them again in the next section.

As expectd for a soft **Lewis base**, sulphur binds preferentially to soft metal ions. In the transport protein metallothionein, nearly one-third of the amino acid residues are cysteines whose —SH (sulf-hydryl) groups bind soft metal ions like Cd^{2+}, Hg^{2+}, Pb^{2+} and Tl^+. Human metallothionein from liver contains zinc almost exclusively; that from kidney may also contain cadmium and copper. While the protein provides an efficient storage mechanism for zinc, its affinity for cadmium (~1000 times more effective than zinc) and other softer metal ions may be a part of the defence mechanism of the body to protect cells against toxic effects of these metal ions.

Selenium



33-IX

Selenium, once thought to be toxic to animals, has been recognized as an essential element in the 1950s. Selenium often replaces sulphur in the amino acid residues of proteins, for example selenocysteine (33-IX) is present in the enzyme glutathione peroxidase (M.W. ~ 84000). The enzyme is probably effective in protecting lipids in cell membranes, especially those in the liver from unwanted oxidation by peroxides and also other oxygen radicals. Selenium also protects animals from carcinogenic chemicals though its precise role in cancer prevention in humans is yet to be established. The element is also able to bind other toxic heavy metals like Cd and Hg. Along with vitamin E, selenium prevents the development of hepatic necrosis and muscular dystrophy.

Though an essential element, excessive selenium may be toxic causing *selenosis*. It is manifest in weight loss, emotional disturbance, loss of hair, diarrhea and garlic smell in exhaled breath (due to dimethyl selenide). In animals, continued intake of fodder containing high selenium levels (> 100 ppm) has been found to cause impaired vision, respiratory failure, paralysis and eventually death.

Fluorine

Fluorine occurs mostly in bone and teeth where the fluoride ion (r = 129 pm) partially substitutes the hydroxide ion (r = 133 pm) in hydroxyapatite, $Ca_5(PO_4)_3OH$. Lower solubility of the fluorapatite partly prevents decay of tooth enamel and hence resists dental caries. However, the actual role of fluoride in this respect may be more complex. Fluorides inhibit the bacterial enzymes and reduces the production of acids. It has been generally observed that drinking water containing less than 0.5 ppm fluoride causes dental caries in children. But excessive fluoride in toothpastes may cause more harm than the benefits gained and hence such formulations are no more encouraged.

Similarly, though fluoride is supposed to be necessary for the proper development of bones, excessive intake of fluoride, through drinking water, say, may lead to *fluorosis*. Excess fluoride inhibits the function of enzymes such as enolase and pyrophosphatase — may be due to substitution of an OH group by F near the active site. Continuous exposure to excess fluoride in drinking water (> 2 ppm or 2 mg per liter; particularly >5 ppm) may cause weakening of tooth enamel and discolouration of teeth (brown or yellow patches; known as dental fluorosis). An intake of fluoride above 20 ppm causes pathological changes in the bones (osteosclerosis) in which nearly 50% of the —OH groups in apatite may get substituted by fluorine. In advanced stages of skeletal fluorosis, hypercalcification, increasing density of the bones of limbs, pelvis and spine, is a characteristic feature. Even the ligaments of spine and collagen of bones get calcified and neurological disturbances are observed. In the long run the patients are crippled due to stiff joints.

The fluoride content of water in some parts of **Andhra Pradesh**, Delhi, Punjab, Karnataka and Assam is quite high (sometimes 15 mg per liter). **Recently** West Bengal has also joined the list. Widespread regions of Birbhum and even **Bankura** and Purulia are suspected to contain excessive fluoride in groundwater. **Dangerous levels** of 19 g/dm^3 have been recently located in the Nalhati block of Rampurhat. Scores **of people** in the village Nashipur have been crippled for want of proper diagnosis at **the beginning**. Of the 29 countries known to have excess fluoride in their drinking water, **India has the highest** number of people suffering from fluorosis. **In** 1995, an estimated 62 **million people in India** over 17 states — which includes six million children, were affected with **dental**, skeletal and non-skeletal forms of fluorosis and associated health complaints (**Fluorosis Research** and **Rural Development** Foundation, Delhi). The fluoride contamination **originates in the** underground rock. Fluoride is generally found as fluorapatite in granite and **granite** metamorphosed gneiss depositions and as dissolved hydrofluoric acid in hot springs. The **village** Nashipur and much of adjoining area lie over basaltic rocks. It is likely that hydrofluoric acid is trapped in gaseous form in the crevices of the basaltic rock formations and gets dissolved in water from these aquifers. Workers in local stone quarries drink such contaminated water. Even tubewell water penetrating the basaltic bedrock at depths below 50-60 metres is unfit for human or animal consumption.

Chlorine

Chlorine is a bulk constituent of our body in the form of chloride ion accompanying sodium and potassium ions. **Chloride** ions are involved in the formation of HCl in the gastric juice as well as **regulation** of acid base equilibrium, fluid balance and osmotic pressure control. The **enzyme** salivary amylase is activated by chloride.

Chloride ions are also a major constituent of **plasma** and cerebrospinal fluid (CSF). The normal plasma concentration of chloride is **95-105** milliequivalents per dm^3 (liter). In CSF, where the protein content is lower, this **figure** is slightly higher at 125 meq dm^{-3}, necessary to maintain Donnan membrane **equilibrium**.

Bromine

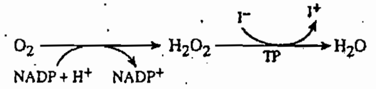
The element is not considered essential for **bacteria**, plants or animals. Human tissues contain bromide ions to the extent of **1-9 ppm** and there appears to be some relation between sleep pattern and **concentration of bromide** ion in serum. Some seaweeds contain the enzyme bromoperoxidase **which** contains vanadium at its active site; the enzyme can brominate organic compounds.

Iodine

A full grown human body contains about 20 **mg iodine**, most of which (~ 80%) is bound to the protein thyroglobin (~ 660,000) in **the thyroid** gland. Some amount of iodine is also present in the muscle, salivary **glands and** ovaries.

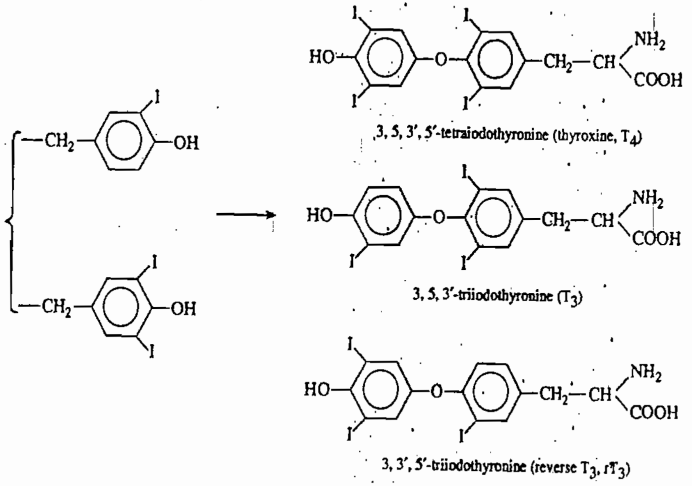
The dietary requirement of 100-150 μg **iodine per** day (200 μg for pregnant women) is mostly supplied through sea foods, **drinking water**, vegetables and fruits. In high altitudes, both soil and water are deficient **in iodine** and so also are plant and animal foods. Supplementary iodine in the form **of iodized** salt is essential for these regions.

Most of the iodine is absorbed through the **small intestine** as iodide. In the thyroid, the I^- is oxidized to I^+ by H_2O_2 catalyzed by the **enzyme thyroperoxidase** (TP).



$$O_2 \xrightarrow[NADP + H^+ \quad NADP^+]{} H_2O_2 \xrightarrow[TP]{I^- \quad I^+} H_2O$$

The iodine binds to tyrosine residues of the protein thyroglobin and ultimately produces three thyroid hormones T_3, T_4 and reverse T_3.



The ratio of T_3 to T_4 in thyroglobulin is usually around 1 : 10, but T_3 is nearly ten times more active than T_4 in binding to the receptors. rT_3 has negligible biological activity. Stimulated by thyroid stimulating hormone (TSH), T_3 and T_4 are released into the bloodstream where they bind to specific thyroxine binding proteins for transportation. The hormones influence metabolic rate, protein synthesis, carbohydrate metabolism, lipid utilization and maintenance of electrolyte balance. Deficiency of iodine results in goitre (enlargement of the thyroid gland and swelling of the neck), mental sluggishness, lack of energy and other disorders.

Iodine-131, produced in nuclear tests and accidents in nuclear power plants, offers the risk of concentrating in thyroids where it may cause cancer.

The d-block elements :

V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Mo						
	W						

General discussion

The *d*-block elements are present in the body as trace elements; among them V, Cr, Mn, Co, Ni and W are ultratrace. These elements are present in the biological system as co-ordination complexes of various ligands — ranging from H_2O in cells, small organic molecules and porphyrins to the side chains of amino acids. They differ from the alkali and alkaline earth metal ions in showing a wide range of oxidation states and co-ordination number. Most of these metals thus show a rich redox chemistry. Iron is the leading metal in this respect, followed by copper and molybdenum. V, Cr, Co and Mn are much less used. Zinc has only the +2 oxidation state but it has other important roles. We shall come across some important redox metalloenzymes (oxidoreductases) containing these metals in the next section.

Non-redox reactions are also catalyzed by certain metalloenzymes containing the *d*-block metal ions like, Zn^{2+}, Mn^{2+} (stable d^{10} and d^5 configurations) and Ni^{2+}. These metal ions are co-ordinated by different protein fragments, usually together with a molecule of water. The water molecule bound to a bivalent metal ion of the first transition series is labile (half-life of exchange ~10^{-3} to 10^{-6}s) and its substitution by a substrate is often a necessary step in the enzyme activity. We shall discuss zinc-containing enzymes in the next section.

Vanadium, Chromium and Manganese

Vanadium is probably an essential element in man but it is certainly essential for healthy growth of chicks and rats. The blood of some marine species like tunicates have protein bound vanadium at a concentration 10^6 times that in the surrounding water. Some nitrogenases may also contain vanadium instead of molybdenum.

Chromium is primarily involved in the action of insulin in glucose metabolism. It is also involved in lipoprotein metabolism and transport of amino acids into the cells (heart and liver). An adult usually consumes about 10-100 μg Cr per day, mostly through foods like grains, cereals, cheese and meat.

Chromium deficiency may disturb carbohydrate, lipid and protein metabolism. In excess, several chromium compounds are toxic, damaging the liver and kidney.

Manganese is an essential constituent (cofactor) of several enzymes, e.g., arginase, pyruvate carboxylase, superoxide dismutase (mitochondrial) and peptidase. It acts as a cofactor along with glucose-5-phosphate dehydrogenase. The metal is also required in the formation of bone — about 25% of the 10-20 mg manganese present in the human body is found in the skeleton. Manganese is involved in a number of other biological processes like reproduction, proper functioning of the nervous system, hemoglobin synthesis, cholesterol bio-synthesis and synthesis of mucopolysaccharides and glycoproteins. About 2 mg Mn per day is recommended for intake by an adult human. It is present in cereals, nuts, leafy vegetables and specially tea. Deficiency of the metal in animals gives rise to retarded growth, sterility, accumulation of fat in liver, increased activity of serum alkaline phosphatase and diminished activity of β-cells of pancreas (low insulin). In certain cases of managanese deficiency, magnesium seems to take over the activation role.

Miners who inhale large amount of manganese ores through dusts develop hapatolenticular degeneration resembling Parkinson's disease.

Iron

An adult human contains about 4-5 g iron in the body; about 75% of this is present in the erythrocytes of blood as a constituent of hemoglobin, 20% is stored as non-heme iron in ferritin and hemosiderin, transferrin etc.; 3-4% is present in myoglobin of muscles and the rest in other hemoproteins like cytochromes, xanthine oxidase, peroxidase etc.

An adult man requires about 10 mg iron per day, the figure being higher for menstruating women (18 mg) and pregnant or lactating women (40 mg). Meat, pulses, leafy vegetables are the sources of iron in the ferric form bound to proteins or organic acids. The Fe^{3+} ion is released from food in the acid medium provided by gastric HCl. Reducing substances like ascorbic acid (vitamin C) and cysteine convert the Fe(III) to Fe(II). The ferrous form is readily absorbed by the body (mainly stomach and duodenum).

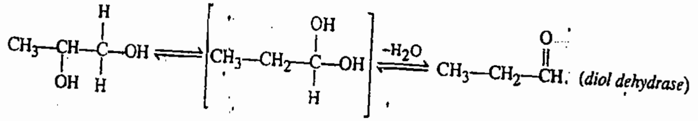
The Fe(II) entering the mucosal cells by absorption is oxidized by the enzyme ferroxidase to Fe(III). This combines with apoferritin to form ferritin which is the temporary storage form of iron. The liver and bone marrows contain most of the ferritin. The iron is stored in cavities of proteins as the micro-crystalline hydrate 5 Fe_2O_3, $9H_2O$ with phosphates. When the supply of iron is in excess of body demands, hemosiderin, a water soluble protein, serves as another storage devise for iron in the spleen and liver.

Iron is very efficiently utilized in the body, mainly in oxygen transport and storage process in higher animals. (We shall discuss the proteins hemoglobin and myoglobin in the next section). Iron is not excreted during the course of metabolic function and hence excessive intake of iron can be dangerous.

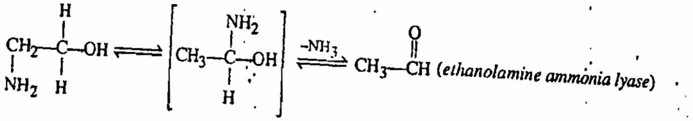
Cobalt

The structure of cyanocobalamin or vitamin B_{12} in its isolable form is given in Fig. 26.2 followed by a discussion under cobalt (Sec. 28.8.7). Though essential for all growing tissues in humans the vitamin is produced exclusively by certain micro-organisms. As already explained, the isolable form of the vitamin is cyanocobalamin which is converted into adenosyl cobalamin and methyl cobalamins under physiological conditions. The former of these provides a rare example of a naturally occuring organometallic compound with a Co—C σ-bond (Fig. 28-XXII a). About 5 mg cobalamin is present in an adult human body, the cobalt content is only about 4% of this. Deficiency of the vitamin causes anemia owing to decreased production of red blood cells (pernicious anemia), neurological disorder and other problems. As little as 1-2 μg of B_{12} containing 0.045-0.09 μg cobalt is sufficient to maintain normal bone marrow function in pernicious anemia.

Enzymes that catalyze 1, 2 carbon shifts require vitamin B-12 or one of its derivatives as a cofactor (28-XXII b); for example,

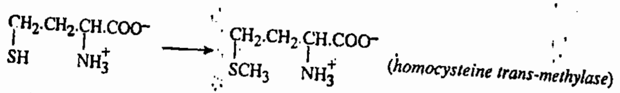


$$CH_3—CH(OH)—CH(OH) \rightleftharpoons [CH_3—CH_2—CH(OH)—OH] \xrightleftharpoons{-H_2O} CH_3—CH_2—CHO \text{ (diol dehydrase)}$$



$$CH_2(NH_2)—CH_2—OH \rightleftharpoons [CH_3—CH(NH_2)—OH] \xrightleftharpoons{-NH_3} CH_3—CHO \text{ (ethanolamine ammonia lyase)}$$

Several redox reactions are also promoted by the coenzyme B-12, for example, the reduction of ribonucleoside to deoxyribonucleoside triphosphates. Methyl transfer reactions are also known; for example, methylcobalamine acts as the coenzyme in the conversion (*S*)-homocysteine to methionine.



$$CH_2(SH).CH_2.CH(NH_3^+).COO^- \longrightarrow CH_2(SCH_3).CH_2.CH(NH_3^+).COO^- \text{ (homocysteine trans-methylase)}$$

The role of cobalt may involve homolysis of the Co—C bond forming the deoxyadenosyl radical.

Vitamin B-12 derivatives, particularly methylcobalamin, can pose environmental hazard as they facilitate conversion of mercury to CH_3Hg^+ and $(CH_3)_2Hg$ (section 30.4).

Prolonged administration of cobalt is toxic as it results in increased RBC in blood (polycythemia).

Nickel

The natural biological role of nickel was established only in 1975 with discovery of the metal in the enzyme jack bean urease. The enzyme is present in a number of plants and bacteria, catalyzing hydrolysis of urea :

$$CO(NH_2)_2 + H_2O \longrightarrow H_2NCOO^- + NH_4^+ \longrightarrow CO_2 + 2NH_3$$

It appears that the enzyme contains nickel in the uncommon oxidation state III. A redox-inactive Ni_2^{III} unit containing octahedral nickel acts as a Lewis acid for substrate

binding. Redox active nickel centres are present in other enzymes, found mainly in bacteria, e.g.,

Hydrogenase (Ni, Fe) $2H_2 + O_2 \longrightarrow 2H_2O$

CO dehydrogenase (CODH; Ni, Fe) $CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e$

Methyl-S-coenzyme M reductase (Ni) $CO_2 \longrightarrow CH_4$.

Hydrogenases from methanogenic bacteria give EPR signals consistent with the unusual Ni(III) oxidation state (low spin d^7). The nickel may have an octahedral coordination from nitrogen (or oxygen) and sulphur donors. Ni(III) is also present in CODH, together with 4Fe—4S clusters. The methylcoenzyme M reductase catalyzes reduction of the methyl group of methylcoenzyme M, 2-(methylthio)ethanesulphonate to methane :

$$CH_3SCH_2CH_2SO_3^- + H_2 \longrightarrow CH_4 + HSCH_2CH_2SO_3^-$$

It has a prosthetic group (see sec. 33.2.1) consisting of a redox-sensitive planar Ni^IN_4 macrocyclic moiety.

Ashes from the Australian shrub, *Hybunthus floribundus* can sometimes contain upto 20% nickel when grown in nickel-rich soil. Such abnormal uptake of the metal by plants can be used in its biogeochemical prospecting when the metal-bearing layer is not deeply buried under soil.

Nickel is one of the most cancer-causing metals. Ni_2S_3 found in many nickel ores has been shown to be carcinogenic in humans and other animals.

Copper

About 60-100 mg of copper is present in an adult human distributed over various organs. The metal is an essential constituent of several proteins and enzymes, e.g., ceruloplasmin, hemocyanine, cytochrome *c* oxidase, catalase, superoxide dismutase, ascorbic acid oxidase etc. Copper is thus involved in a number of metabolic functions. We shall discuss hemocyanin and ceruloplasmin in the next section.

The dietary requirement of copper is nearly 2-3 mg per day, supplied by green leafy vegetables, cereals, nuts, liver, kidney, meat, egg etc. It is absorbed in the intestines and carried to the liver. Most of the copper is now incorporated into ceruloplasmin which enters the blood stream and functions for a long term (see later). Deficiency of copper causes demineralization of bones, anemia, fragility of arteries, decolouration of skin and hair and several other disorders. Poor intestinal absorption of the metal from genetic disorder leads to *Menke's disease* : anemia, depigmentation and spiralling (kinky) of hair, decreased copper in urine and plasma. In *Wilson's disease*, copper is deposited in liver, kidney and other parts of the body, probably due to failure in synthesizing ceruloplasmin or the binding of the metal to this protein (see metal toxicity, section 33.4.2).

Microbiological mining

As mentioned earlier (section 28.10.2), biotechnology has developed methods using microbes for the extraction of copper from very low grade sulfide ores. Acidophilic bacteria such as *Thiobacillus ferrooxidans* can leach insoluble copper sulphide minerals by oxidation, either directly by O_2 or indirectly via Fe(III) formed from Fe(II) by them. Growing at temperatures from 30° to 70°C, the bacteria generate acid, and can attain a pH as low as 1. The overall process

$$CuS + 2O_2 \longrightarrow CuSO_4$$

helps leaching of copper sulfate from billions of tonnes of otherwise uneconomical low grade ore. Hence, the bacteria are called "rock eating" (*chemolithotrophic*). The dilute copper sulfate solution is processed as usual and copper precipitated by scrap iron. About one-quarter of the total copper produced in the world is obtained in this manner and the figure is likely to increase as the deposits of higher grade ores get exhausted.

Zinc

About 2g of zinc is present in an adult human as an essential constituent of several enzymes : carbonic anhydrase, alcohol dehydrogenase, alkaline phosphatase, carboxypeptidase, superoxide dismutase and so on. The metal is stored in the kidneys and liver in metallothionein. The prostate gland is very rich in zinc (100 μg/g). Meat, fish, egg, milk, beans and nuts are sources of the metal which should supply the dietary requirement of 10-15 mg/day (50% more in pregnancy and lactation). Cereals containing high proportion of phytic acid (inositol hexaphosphate) inhibits uptake of zinc.

The biochemical function of zinc is based on its Lewis acid character. It has a strong preference for the tetrahedral conformation in Lewis acid-base complexes formed; this fact is used in stabilizing many biological structures. In certain enzymes, the coordination environment of the metal is highly strained, giving rise to a distorted tetrahedral geometry. Such strained or 'entatic' four-coordinated zinc may approach an alternative coordination environment — a fact that underlies the catalytic activity of the metal. We shall find such a behaviour in the discussion on the zinc containing enzyme carbonic anhydrase (section 33.2.4).

Zinc fingers

The structural role of zinc ions has been ingeniously utilized by Nature in forming metalloproteins, nucleic acid assemblies and other natural products containing the metal ion that interact with DNA and RNA. Several families of eukaryotic regulatory proteins that monitor the expression of genes contain zinc. The proteins bind to the recognition sequence of the appropriate gene. The first example of this type was discovered in 1983 in the nucleic acid binding transcription factor IIIa (TFIIIa) from *Xenopus Laevis* (an African clawed frog). TFIIIA, required for the accurate transcription of 5S ribosomal RNA genes*, has the Zn^{2+} ion bound tetrahedrally to two cysteine and two histidine residues. The coordination around zinc appears to monitor the folding and three-dimensional structure of the protein scaffolding about it — which ultimately forms series of spiral loops or 'fingers' which can function singly or in tandem to recognize their complementary structure on the nucleic acid polymer and thus fit into major grooves of DNA. TFIIIA has nine fingers, but there are many more such regulatory proteins with different zinc binding patterns which may contain any number from 2–40 fingers capable of interacting with nucleic acid strands in a number of ways. The yeast transcription factor GaL 4 has two zinc atoms coordinated by six cysteine groups, two of which are shared along a common tetrahedral edge ("Zinc cluster'). On the other hand, the glucocorticoid receptor (GR) has two zinc atoms each coordinated by four cysteines ('zinc twist'). Other motifs are also known.

Q. 33.1 *What should be the likely reason(s) for Nature's selection of zinc in nucleic-acid binding proteins?*

Hint : (a) high natural abundance; (b) zinc is redox insensitive, hence not expected to damage the DNA (unlike Fe^{II} or Cu^{II}); (c) it is also unlikely to coordinate to bases in DNA; other softer, heavier metal ions might bind preferentially to the DNA bases. (Sec. 33.2.4)

Zinc atoms providing catalytic sites as well as monitoring structure are present in the dimeric enzyme liver alcohol dehydrogenase (LAD) which oxidizes ethanol in the liver to acetaldehyde. It has four zinc atoms : (a) two structure forming Zn^{2+} ions in a regular tetrahedral array of four cystein sulphurs and (b) two catalytically active zinc sites in a more distorted tetrahedral coordination from two cysteine sulphurs, one water molecule and one histidine nitrogen.

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* RNA is synthesized on a DNA template. Messages encoded in the genetic material are copied or transcripted in the RNA produced. Proteins are made on the RNA template, keeping the same amino acid sequence as the nucleotide sequence of RNA.

Zinc deficiency is associated with retarded growth, anemia, loss of appetite and taste sensitivity, and a lot of other metabolic disorders. Zinc toxicity is often observed among welders who frequently inhale zinc oxide fumes. It is manifested by nausea, gastric ulcer, pancreatitis, anemia and excess salivation.

Molybdenum

Molybdenum is the only element in the second transition series which has natural biological functions. More than thirty enzymes in microorganisms, plants and animals are known to contain the metal. Nitrogen fixation enzyme nitrogenases contain a characteristic polymetallic cluster, the iron-molybdenum cofactor (FeMoco). Other enzymes functioning as oxidases, reductases, dehydrogenases have variants of molybdenum cofactor (Moco).

TABLE 33.4

Some molybdenum containing enzymes

1. **Nitrogenases** (M.W. ≈ 220,000)	Bacteria and blue green algae	$N_2 \longrightarrow NH_3$
2. **Aldehyde oxidase** (M.W. ≈ 270,000)	Pig's liver	$RCHO \longrightarrow RCOOH$ (2Mo, $4Fe_2S_2$, 2FAD*)
3. **Nitrate reductase** (M.W. ≈ 200,000 – 360,000)	Fungi, algae, bacteria, plants	$NO_3^- \longrightarrow NO_2^-$ (2Mo, $2Cyt_b$, 2FAD)
4. **Sulfite oxidase**	Mammalian liver, bacteria	$SO_3^{2-} \longrightarrow SO_4^{2-}$ (2Mo, $2Cyt_b$)
5. **Xanthine oxidase** (M.W. ≈ 300,000)	Cow milk, mammalian liver	Xanthine ⟶ uric acid (2Mo, $4Fe_2S_2$, 2FAD)
6. **Formate dehydrogenase**	Fungi, bacteria, plants	$HCOOH \longrightarrow CO_2 + H_2O$ (Mo, Se, Fe_nS_n)

*FAD = Flavin adenine dinucleotide

Xanthine oxidase is a dimer in which each subunit has two Fe_2S_2, one molybdenum and one flavine adenine dinucleotide. It has one terminal Mo = O group in the oxidized form and its catalytic activity involves transfer of the O atom to the substrate.

$$Mo^{VI}O + Sub \rightleftharpoons Mo^{IV} + O\ Sub$$

The molybdenum cycles back and forth from Mo^{IV} to Mo^{VI} via oxo-transfer. Similar considerations apply to other oxotransferases. The FeMoco in nitrogenases has been discussed earlier.

Excessive molybdenum in the body impairs growth, diminishes intestinal absorption of copper and may cause diarrhea and anemia (***molybdenosis***).

Tungsten

Tungsten is the only element in the third transition series with established natural biological functions. Proteins containing tungsten are, however, rare and are mainly found in thermophilic anaerobes. For example, the enzyme aldehyde ferredoxin oxidoreductase is isolated from the anaerobe *Pyrococcus furiosis* which grows optimally at 100°C; the enzyme itself is also highly thermally stable. Tungsten also occurs in several enzymes together with molybdenum. The mode of functioning of the metal centre in these enzymes is comparable to the molybdenum containing enzymes, involving oxotransfer from W(VI) to the substrate.

33.1.3 Basic chemical processes in biosystems

The foregoing discussion on photosynthesis, nitrogen fixation and some other systems amply illustrate that living systems involve the same basic chemical processes as are commonly encountered in non-living systems, namely, redox, acid-base, rearrangement and so on. While this will be further supplemented in all discussions to follow, it will be worthwhile to mention a few points of interest regarding chemical processes in biosystems.

Life on our planet earth is dependent on the sun and photosynthesis may be taken as the starting point in our discussion. As already seen, the entire process involves a number of metalloproteins acting over several stages in collaboration and is more complex than apparent from the overall reaction written for reduction of CO_2 to carbohydrates. The process ultimately stores solar energy as chemical bond energy in the carbohydrates. The process is endothermic and is accompanined by a net decrease in entropy.

Respiration, the most vital activity of all living systems, is again dependent on a number of chemical processes, viz., dioxygen uptake and transport by metalloproteins like hemoglobin, hemocyanin etc.; storage of the dioxygen in myoglobin; and its controlled release as and when necessary for oxidation of food nutrients (e.g., the carbohydrates) and oxidative phosphorylation of ADP. Here we are again confronted with a number of steps, each utilizing a number of metalloproteins. The carbon dioxide released in such processes is rendered soluble by hydration to HCO_3^- so that it may be transported through blood (hence the pH of blood ≈7.2). The HCO_3^- is finally dehydrated in the lungs before being released in breathing. The hydration-dehydration process is catalyzed by the zinc enzyme carbonic anhydrase (sec. 33.2.4). This is an example of hydrolytic reaction. Hydrolysis of a terminal phosphate group in ATP and its transfer to a substrate provides the energy required by the muscles to perform various forms of work.

Biological oxidation in our body may also lead to the formation of peroxide and superoxide radical ions from partial reduction of O_2. As already discussed, these indiscriminate oxidizing agents are harmful to the body; these are removed from our body by the metalloenzymes catalases, peroxidases (both contain Fe^{III}) and superoxide dismutases (Cu^{II} and Zn^{II}).

Besides these basic processes like redox, acid-base, hydrolysis and dismutation reactions, the living system also displays other reaction types, for example, 1, 2-shifts catalyzed by vitamin B-12 or its derivatives (sec. 33.1.2, under cobalt).

The main chemical processes in biological systems may be summarized as follows :

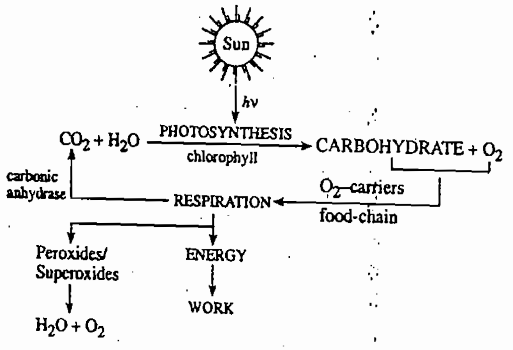


Fig. 33.9
Basic chemical processes in biological systems.

[Sec.33.2 *Metalloproteins & Metalloenzymes*]

The foregoing overview helps us to make the following generalizations regarding biologically significant chemical processes :

(i) electron transfer : single, pair or multipair;

(ii) atom or group transfer, including transport;

(iii) coupled electron-atom or electron-proton transfer.

Examples in each category are frequent throughout the text. The main distinctive features of these reactions in biological systems are

(i) the reactions are irreversible and kinetically controlled; thermodynamically the reactions are mostly unfavourable.

(ii) the reactions are catalyzed by natures own catalysts; the enzymes, which usually have a metal at their active site, are extremely selective in their action.

(iii) The reactions can take place with the reactants at very low concentrations and under ambient conditions acceptable to living organisms.

(iv) the courses of the reactions are monitored by the bio-environment usually provided by the protein. The role of the globin portion in reversible binding of dioxygen to hemoglobin provides a ready example (section 33.2.2). The redox behaviours of the metals are also influenced significantly by the biomolecules.

(v) Quite related to the influence exerted on the redox system of metals, many biological processes involve otherwise uncommon oxidation states of metals. As we shall see in the next section, catalytic activity of cytochrome P-450 is believed to proceed via Fe^{IV} and/or Fe^{V} intermediates. The involvement of Ni(I) and Ni(III) in several nickel enzymes has been mentioned in the last section

(vi) Metal ions as Lewis acids often play the key role in most biochemical reactions of which we shall mention only a few in our subsequent discussion on metalloproteins and metalloenzymes. As we shall soon appreciate, the metals influence both structure as well as function of the proteins, their folding, cross-linking and overall participation in the chemical process (for example, see carbonic anhydrase, section 33.2.4). The metal and the protein part thus mutually regulate one another to provide the unique features of biochemical reactions.

The role of metals in metalloproteins and metalloenzymes has been discussed in section 33.2.

33.2 METALLOPROTEINS AND METALLOENZYMES

33.2.1 Introduction

This section is intended to have glimpses of the functioning of some metallobiosites — a few selected metalloproteins and metalloenzymes. As noted earlier, a metalloprotein is formed when a protein incorporates one or more metal atoms as an integral part of its structure. In many cases it is possible to remove the metal atom from its site and then restore it or replace it with another metal keeping the protein structure intact. In such cases, the metal-deficient protein is called the *apoprotein*; it reverts to the active metalloprotein when the metal is restored.

An apoprotein can be generally obtained by removing the metal ion from the metalloprotein by gentle dialysis against a solution containing a chelating ligand (pH ≈ 5.5 – 7.5). Addition of the metal ion restores the original activity of the protein. Sometimes a different metal ion is added to the apoprotein to obtain information regarding the metal environment. For example, Zn^{2+} ions have poor spectroscopic features, but zinc ions in zinc-proteins may be substituted by Co^{2+} to get clues about the role of the metal ion.

A large subclass of the metalloproteins is formed by the metalloenzymes — enzymes that strongly bind one or more metal ions which serve as the active site during the functioning of the enzyme. Structure and function of these metal sites have been elucidated in many cases through a wide range of spectroscopic studies like uv-visible absorption, Raman, NMR, circular dichroism, Mössbauer, electron paramagnetic resonance (EPR), extended x-ray absorption fine structure (EXAFS) and single crystal x-ray diffraction. These informations are augmented by magnetic, kinetic and redox studies on the natural as well as model versions of the biomolecules. However, a lot remains to be done.

Metalloproteins

The activity of a metalloprotein is jointly contributed to by the nature of the metal ion and the polypeptide environment provided by the protein. Nevertheless, we may artificially divide our discussion into separate roles for the two components — the protein and the metal.

The role of protein

(i) The main role of the protein is to provide the coordinated ligands and set the appropriate environment around the metal ion. The protein environment is crucial to the function of metal site as we shall presently find in the function of haemoglobin. We shall also see how the redox potential of the metal system is largely influenced by the presence of the proteins. Hydrophobic pockets or H-bonding facilities offered by the protein may also facilitate binding of the substrate and the reactions taking place — examples of which are found in connection with carbonic anhydrase and cytochrome *c* peroxidase (see later).

(ii) The protein may provide a suitable path of protected entry of the substrate to the active metal site. The metallobiosite in many metalloproteins is buried deep inside the protein. A charged substrate can be guided electrostatically by the amino acid side chains forming a 'channel' leading to the metal site. The copper(II) centre in Cu—Zn superoxide dismutase is approachable by a conical channel of amino acid ends. In some metalloproteins, a transient broadening of the channel is required for substrate entry.

(iii) Proteins also facilitate the transport and storage of metal ions. Though lower organisms use mainly nonproteins for the purpose, vertebrates use only proteins. For example, transferrin and ferritin are used in animals for transport and storage of iron respectively. The transport of Na^+, K^+ etc. ions across the central hydrophobic region of a membrane is made possible with the help of membrane proteins (ionophores) which are strong chelating ethers (see later).

The role of metal

(i) Metals play a vital, structural role by stabilizing the biomolecule. Mg^{2+}, Ca^{2+} and Zn^{2+} ions are prominent examples of this type. The DNA and RNA helices are stabilized by the Mg^{2+} ion and most enzyme catalyzed reactions involving DNA and RNA polymerases require Mg^{2+}. Some proteins are stabilized by Ca^{2+}, e.g., thermolysin. Zinc is also present in this protein but it has a catalytic role. Zinc ions monitor the folding of protein chains in transcription factor IIIA ('zinc fingers'). However, a number of other factors like H-bonding, surface-to-volume ratio etc. may also contribute to the overall stability of a protein.

(ii) Metal ions can promote essential conformational changes in proteins necessary for initiating the enzyme activity. Ca^{2+} binds to the inactive proteins calmodulins (small proteins with glutamic and aspartic acid residues) and changes its conformation in such a way that it can reorganize, bind and activate an enzyme (e.g., NO synthase, phosphorylase kinase and ATPases).

Localized structural changes triggering muscle contraction are also brought about by metals.

(iii) Metal ions can modify the function of a biomolecule.

(iv) Metal ions can also function as cofactors. For example, K^+ ions are essential for the activity of pyruvate kinase. The K^+ ion (or some other +1 ion) probably links the substrate to the enzyme surface.

Metalloenzymes

Enzymes are biocatalysts synthesized by Nature in living cells. They are very specific in their action.

Though mostly protein in nature, it has been found (1983) that some RNA molecules can also function as enzymes in *ribonuclease P*; such ribozymes (RNAs) might have played the role of catalysts during evolution before the formation of proteins.

The Enzyme Commission (EC) set by the International Union of Biochemistry (IUB) recommends classification of enzymes into six major classes in the order shown in Table 33.5. Each enzyme is assigned an EC number showing its class, sub-class etc. However, the trivial names are still more common.

TABLE 33.5

Classification of enzymes

Class	Function	Example
(i) *Oxidoreductases*	Oxidation-reduction	alcohol dehydrogenase (E.C. 1.1.1.1)
(ii) *Transferases*	Transfer of functional group from one substrate to another.	hexokinase (E.C. 2.7.1.1)
(iii) *Hydrolases*	Hydrolysis of, e.g., peptide bonds, phosphate esters etc.	lipase (E.C. 3.1.1.3)
(iv) *Lyases*	Addition or removal of H_2O, CO_2, NH_3 etc.	aldolase (E.C. 4.1.2.7)
(v) *Isomerases*	Interconversion of isomers	triose phosphate isomerase (E.C. 5.3.1.1)
(vi) *Ligases*	Bond formation coupled with break down of ATP.	glutamine synthetase (E.C. 6.3.1.2)

The first letter in each class in proper order forms the world OTHLIL.

The acitivity of a number of enzymes depends upon a non-protein entity. Such enzymes are referred to as a *holoenzyme*' which consists of an *apoenzyme* (protein part) and a coenzyme (non-protein part).

$$\underset{(active)}{\text{Holoenzyme}} \equiv \underset{\text{(protein part)}}{\text{Apoenzyme}} + \underset{\text{(non-protein part)}}{\text{Coenzyme}}$$

When the non-protein moiety is tightly bound to the apoenzyme, it is called a *prosthetic group*. By dialysis, one can strip the enzyme of its coenzyme but not of the prosthetic group. A loosely bound coenzyme is also called a *cofactor*.

Metalloenzymes catalyze specific spontaneous biological processes by factors of several powers of ten (usually $10^6 - 10^{10}$). Some enzymes can even enhance the reaction by a factor as large as 10^{17}. (*Abzymes*, or antibodies, which are large proteins, can also catalyze a wide variety of chemical reactions but usually by a much lower factor, e.g., $10^3 - 10^6$ fold over the uncatalyzed (reaction). The metal ions in metalloenzymes can function in a number of ways :

(i) Play a structural role comparable to that outlined earlier in connection with metalloproteins. Bivalent cations like Ca^{2+}, Mg^{2+} and Zn^{2+} often serve a structural as well as catalytic role. Zn^{2+} in liver alcohol dehydrogenase has two zinc ions in its dimer : one zinc ion plays a structural role while the other catalyzes the reaction

$$C_2H_5OH + NAD^+ \longrightarrow CH_3CHO + NADH + H^+.$$

(ii) A metal atom may serve as a point of rendezvous for the reactants. When one reactant is intimately associated with the metal centre, presumably through coordination, another reactant located near it with correct orientation will be able to interact leading to the desired product.

(iii) The acidity of a coordinated ligand may be enhanced by the positive charge on the metal. A coordinated water molecule, for example, will leave a hydroxide ion on the metal. Being a stronger nucleophile than water, the hydroxide ion makes the metal centre more susceptible to nucleophilic attack at neutral physiological pH.

(iv) The metal ion can serve as a redox centre and facilitate electron transfer.

Examples of these roles will be found in our subsequent discussions.

33.2.2 Iron Proteins

Iron proteins are versatile in nature and occurrence. They mostly belong to four categories :

(i) *Iron-porphyrin proteins*, e.g., hemoglobin, myoglobin, cytochrome P_{450}; all of them contain one or more iron-porphyrin units. They are mostly involved in O_2-transfer and storage or electron-transfer.

(ii) *Non-heme iron proteins*, e.g., transferrin, ferritin, hemosiderin; they are mostly involved in iron storage and transport.

(iii) *Non-heme diiron oxobridged species*, e.g., hemerythrin, methane monooxygenase (Sec. 33.2.1) and ribonucleotide reductase.

(iv) *Non-heme proteins containing iron-sulfur clusters*, e.g., nitrogenase, ferredoxins and rubredoxins.

The principal iron-proteins found in humans are shown in Table 33.6.

TABLE 33.6

Major Fe-proteins in an adult human (Total Fe-4g)

Function	Protein (M.W.)	% of total body iron	No. of Fe per molecule
O_2-transport	Hemoglobin (64,500)	65	4 Fe^{II} (heme)
O_2-storage	Myoglobin (17,000)	6	1 Fe^{II} (heme)
Fe-transport	Transferrin (76,000)	0.2	2 Fe^{III} (non-heme)
Fe-storage	Ferritin (444,000)	13	0-45,000 Fe^{III} (non-heme)
	Hemosiderin	12	5000 Fe^{III} (non-heme)
Metabolism of H_2O_2	Catalase (280,000)	0.1	Fe^{II} (heme)
	Peroxidase (44,100)	—	— (heme)
Terminal oxidation	Cytochrome *c* (12,500)	0.1	1 Fe^{II}–Fe^{III} (heme)
	Cytochromes and oxidases	<0.5	Fe^{II}–Fe^{III} (heme)

Hemoglobin and Myoglobin

An adult human contains about 5 litre of blood, each millilitre of which contains 5000 million blood cells; each cell contains 2.5×10^5 (0.25 million) hemoglobin molecules. Red blood cells have a relatively short life span of 100–120 days and hence about 1% of these hemoglobin molecules is replaced daily (2.5×10^{16}).

While hemoglobin is essential for dioxygen transport, myoglobin is engaged in storage of O_2 in muscle tissues for controlled release for oxidative phosphorylation as and when necessary. The site of reversible binding of O_2 in both is heme (or haem) — an Fe(II) complex of the macrocyclic ligand protoporphyrin IX (Fig. 33.10).

In hemoglobin, a high-spin Fe(II) is coordinated by the four N-atoms of protoporphyrin IX and the fifth coordination position is bound to nitrogen atom of an imidazole group in the histidine residue F8.

The entire heme unit is encapsulated in a water-repelling pocket of protein chains. Hemoglobin has four protein chains each with a heme pocket, packed in the form of a roughly tetrahedral $\alpha_2\beta_2$ cluster : the α chains have 141 amino acid residues and the β chains 146. Myoglobin has a long protein chain of 153 amino acid residues folded intricately to create the hydrophobic pocket for each heme group.

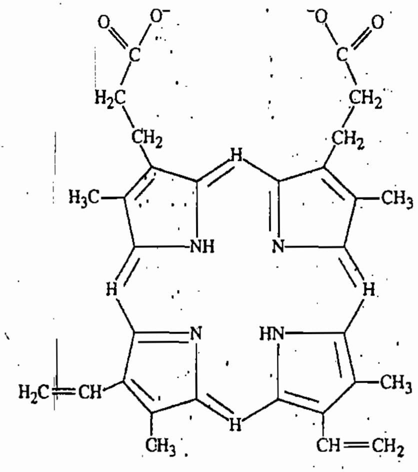


Fig. 33.10 : Protoporphyrine IX.

It has four pyrrole rings linked by —CH— bridges. The two NH protons are lost on binding Fe^{2+}, and an uncharged complex is obtained.

In absence of O_2, the iron(II) (high spin) in hemoglobin (i.e., deoxyhemoglobin) is about 36–40 pm out of the plane of the N atoms in the direction of the histidine group (Fig. 33.11).

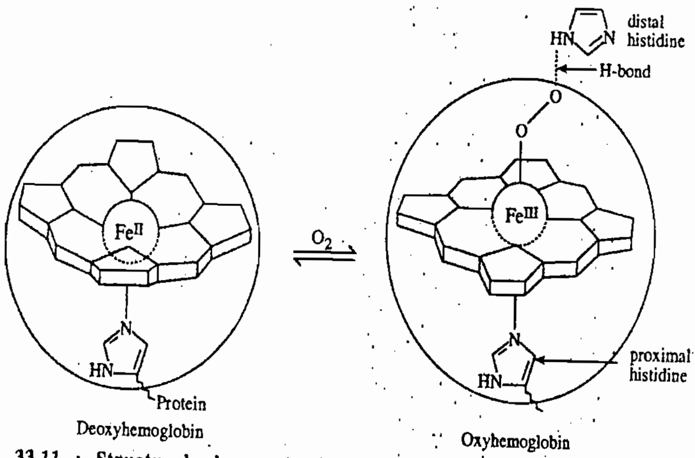


Fig. 33.11 : Structural change in hemoglobin on reversible binding of O_2.

Upon binding of dioxygen, the iron atom moves within ~ 13 pm of the plane and at the same time pulls the histidine with it, thus commencing a cooperativity shown by the four subunits in hemoglobin towards binding of O_2 (in myoglobin, this change is not so pronounced). The dioxygen, bound in a bent, end on fashion to the iron, makes a further H-bond to an N—H bond in a histidine residue on the side away from the coordinated imidazole base (distal side).

The O—O stretching band of the coordinated O_2 lies at ~ 1105 cm^{-1}, close to the value characteristic of the superoxide ion (Table 23.12, section 23.3.8). So the iron in the oxygenated complex may be taken as low spin Fe(III). Magnetic coupling between the superoxide ions forms a diamagnetic ground state ($S = 0$). The covalent radius of the high spin Fe(II) is presumably too large to fit the space in the plane of the four nitrogen atoms. Formation of the $Fe^{III}—O_2^-$ adduct reduces the effective size of the iron atom which can now move closer into the plane of the porphyrin ring.

The motion of the out-of-plane iron toward the plane of the porphyrin ring upon conversion to oxyhemoglobin serves as a "trigger" for cooperative binding of O_2 to the four subunits in hemoglobin. In absence of O_2, the subunits interact between themselves to constrain the proximal (basal) histidine to resist movement of the 5-coordinate Fe(II) toward the plane of the porphyrin ring. This conformation is designated as T (for 'tense'). When a molecule of O_2 is bound to a heme unit, the proximal histidine is moved by about 80 pm, so causing conformational changes in the protein which is somehow relaxed to the R ('relax') state; binding of O_2 to the remaining subunits is now facilitated in a concerted action. The four heme groups react cooperatively—at first the α and then the β hemes become oxygenated; conformational changes caused by the bound oxygen make it easier to bind more oxygen (allosteric effect).

The oxygen affinity of the hemoglobin tetramer rises with increasing oxygen saturation. Hemoglobin is less efficient in O_2 uptake compared to myoglobin under low oxygen pressures, as is the situation in muscle tissues. Here a thermodynamically favourable transfer of dioxygen to the myoglobin takes place.

Binding of dioxygen by deoxyhemoglobin leads to release of protons; hence dioxygen release is favoured by a decrease in pH. In active muscles, O_2 is converted to

CO_2 which releases protons under the action of carbonic anhydrase (see zinc); this, in turn, facilitates release of dioxygen from hemoglobin (The Bohr effect; after the biologist Christian Bohr, father of Niels Bohr). Such pH-dependence is not observed with myoglobin.

To serve as an ideal carrier of O_2, oxyhemoglobin must be able to release the dioxygen at the cell to which the O_2 is to be delivered. This is achieved by the globin protein surrounding the heme unit. When an aqueous solution of free heme (i.e., without globin) comes in contact with O_2, it is readily oxidized to a μ-oxo dimer known as hematin. The steps involved may be summarily represented as follows (P ≡ porphyrin):

$$\begin{tikzcd}
P—Fe^{II} \arrow[r, "O_2"] & P—Fe^{III}—O_2^- \arrow[r, "P—Fe^{II}"] & P—Fe^{III}—O—O—Fe^{III}—P \arrow[d] \\
\underset{\text{hematin}}{P—Fe^{III}—O—Fe^{III}—P} & & 2P—Fe^{IV}=O \arrow[ll, "P—Fe^{II}"']
\end{tikzcd}$$

Globin, which is generaly nonpolar and can flex suitably in response to changing coordination of iron, presumably prevents the irreversible oxidation by exerting some kind of steric congestion : the heme units are so far apart that one oxoheme unit cannot be attacked by a second heme leading to the peroxobridged dimer (as it happens in case of free heme).

This interpretation of the function of hemoglobin and myoglobin finds support from a number of ingeniously designed model complexes.

Such model complexes for reversible binding of dioxygen have been designed with several points in mind, for example,

(i) the model should also be five-coordinate in absence of O_2; (ii) it should provide a nonpolar environment for coordinated O_2; (iii) pathways leading to irreversible formation of a μ-peroxo dimer should be sterically hindered; (iv) acidic protons and nucleophiles should be excluded from the O_2 binding site; (v) low temperature will stabilize the dioxygen complex.

Two models in which the formaion of a six-coordinate Fe(II)—porphyrin may be arrested by introducing steric congestion in the ligand are shown in Fig. 33.12.

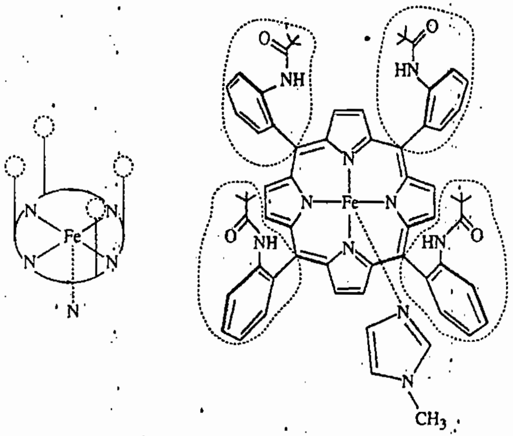


Fig. 33.12(a) : A picket fence porphyrin iron(II) complex*.

The analogy to the pickets of a fence is shown on the left.

**meso*-tetra (α, α, α, α-*o*-pivalamidophenyl) porphyrin.
2-methylimidazole as axial ligand, $\nu_{O-O} = 1159\ cm^{-1}$. O—O dist = 125 pm.

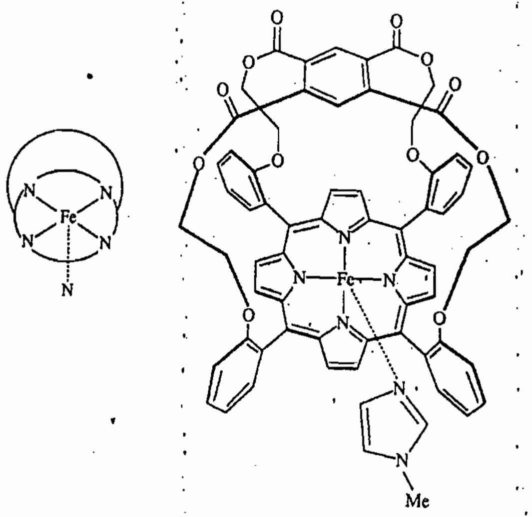


Fig. 33.12(b) : A capped porphyrin-iron(II) complex.
The analogy to a cap is shown on the left.

Cytochromes

Cytochromes are a group of heme proteins which act as one-electron carriers to effect oxidation by dioxygen. They operate by shuttling between Fe(II) and Fe(III) at their active sites. A large number of cytochromes (>50) have been characterized, differing from one organism to another or even from one cell to another in the same species. Four major groups of cytochromes are

(i) *cytochromes a* : the heme has a formyl group replacing a methyl group.

(ii) *cytochromes b* : the same heme group as in hemoglobin and myoglobin but the protein is not bonded to the heme.

(iii) *cytochromes c* : these have covalent links between the protein and the heme.

(iv) *cytochromes d* : these have the dihydroporphyrin group present.

Cytochrome *c* has been studied very extensively among these redox proteins. The folded protein chain, while creating the heme pocket, also provides the iron with two strong field axial ligands—an imidazole nitrogen from histidine and a sulfur from methionine. The iron is six coordinate and has no position for further coordination (unlike the hemes used in oxygen transport and enzyme activity). So they interact only by an electron-transfer mechanism. The iron-ligand distances are virtually identical in both the oxidized (Fe^{III}) and reduced (Fe^{II}) forms of cytochrome *c* and the metal is low-spin in each case. The activation energy of any ensuing redox process is thus kept low. Electrons released from oxidation of carbohydrates is transferred to dioxygen in the mitochondrion of cells via a series of steps involving various cytochromes, e.g.,

$$NAD^+ \longrightarrow \text{Flavoprotein} \longrightarrow \text{Cyt } b \longrightarrow \text{Cyt } c_1 \longrightarrow \text{Cyt } c \longrightarrow \underset{\text{oxidase}}{\text{Cyt } c} \longrightarrow O_2$$

The chemical potential energy derived from the process is used in the conversion of ADP to ATP.

Cytochrome *c* oxidase involved in the final steps of the chain is an enzyme — it is a large protein with two copper and two heme irons, and catalytically reduces O_2 to H_2O in four steps :

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O.$$

One copper atom (Cu_A) and one heme (cytochrome *a*) participate in electron transfer processes while the reduction of O_2 to H_2O is carried out by the second heme (cytochrome a_3) together with the other copper atom (Cu_B).

They also act as proton pump across the membrane. Since the heme iron atoms are buried within the protein chain in both cytochrome *c* and cytochrome *a* (of cytochrome c oxidase) an inner-sphere mechanism for electron transfer between the two appears unlikely. However, cytochrome *c* has one edge of the heme surface exposed and an attractive suggestion is that a positive surface charge near this exposed edge forms an encounter complex with a similar negatively charged area on the oxidase. During thermally induced vibrations or distortions, the π-systems of these two interacting heme units approach close enough to allow electron transfer via an outer-sphere mechanism.

The reaction of dioxygen with the enzyme is less understood. Some cytochrome *a* types have 5-coordinate iron in contrast to cytochrome *c*; at some stage the dioxygen may coordinate to this site forming a heterobimetallic complex (with Cu_B) of the type $Fe^{III}—O_2^{2-}—Cu^{II}$.

The unusual toxicity of the cyanide ion may be associated with its strong binding to the sixth coordination position of Fe(III) in cytochromes *a*. The Fe(III) is so stabilized that it can no more be reduced; electron shuttling along the chain thus stops. Cyanides can also bind to hemoglobin at the site of dioxygen binding but the effect is less serious than inhibition of cytochrome *a* activity.

Cytochromes P-450

These are mononuclear heme enzymes which function as mono-oxygenases, i.e., catalyze reactions in which one O-atom of dioxygen is inserted into the substrate while the second O-atom is reduced to water (in dioxygenases both O-atoms are inserted into the substrate) :

$$RH + O_2 + 2H^+ + 2e \longrightarrow ROH + H_2O$$

The CO-adducts of the enzyme have absorption bands at 450 nm and hence the name. They form a large family of enzymes catalyzing hydroxylations at C, S and N.

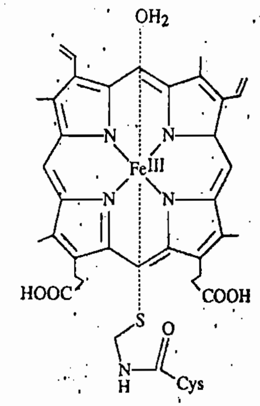


Fig. 33.13
The metallobiosite in Cytochrome P-450.

The iron in the heme group of cytochrome P-450 is coordinated to the protein by a cysteine sulfur group (Fe—S = 220 pm). The sixth coordination position of the low spin iron(III) is probably occupied by a molecule of water or hydroxide ion.

The currently accepted mechanism for the catalytic action of cytochrome P-450 in the oxidation of hydrocarbons may be summarized in the following steps (Fig. 33.14):

(i) The 6-coordinate Fe(III) (low spin, LS) in the resting enzyme loses the coordinated H_2O. Weakening of the ligand field results in a 5-coordinate high spin (HS) Fe(III).

(ii) The substrate binds to a hydrophobic region of the protein near the heme iron centre. The Fe(III) is out of plane, high spin, 5-coordinate.

(iii) An electron (from, say, NADH or $FADH_2$) reduces the Fe(III) to Fe(II), 5-coordinate, high spin, out of plane. The protein is now ready to bind O_2. (FAD = Flavine adenine dinucleotide).

(iv) Dioxygen binds to the iron as $Fe^{II}—O_2$ or $Fe^{III}—O_2^-$. The six-coordinate Fe^{III} is now in-plane (low spin).

(v) A second electron (from $FADH_2$) now probably forms a peroxo complex — the Fe(III) is in-plane, 6-coordinate, low-spin.

(vi) The peroxo bond is now cleaved to form an *oxenoid* moiety, variously represented as

$$P.Fe^{III}—O^{\circ} \longleftrightarrow P.Fe^{IV}—O^- \longleftrightarrow PFe^V—O^{2-} \quad (P \equiv \text{porphyrin}).$$

The π-system of the porphyrin ring can also be oxidized to a cation radical ($\dot{P}^+$) and the $PFe^V—O^{2-}$ or $PFe^V\!=\!O$ forms can be assigned the alternative representation $\dot{P}^+Fe^{IV}\!=\!O$. The Fe(IV) is in-plane, 6-coordinate, low-spin.

(vii) The oxenoid species now reverts to the resting enzyme with oxidation of the substrate. The C—H bond is most probably cleaved homolytically.

$$R—H + PFe^V\!=\!O \longrightarrow [\dot{R} + PFe^{IV}—OH] \longrightarrow ROH + PFe^{III}$$

Presumably the alcohol remains briefly attached to the Fe^{IV} porphyrin before its release to the solution.

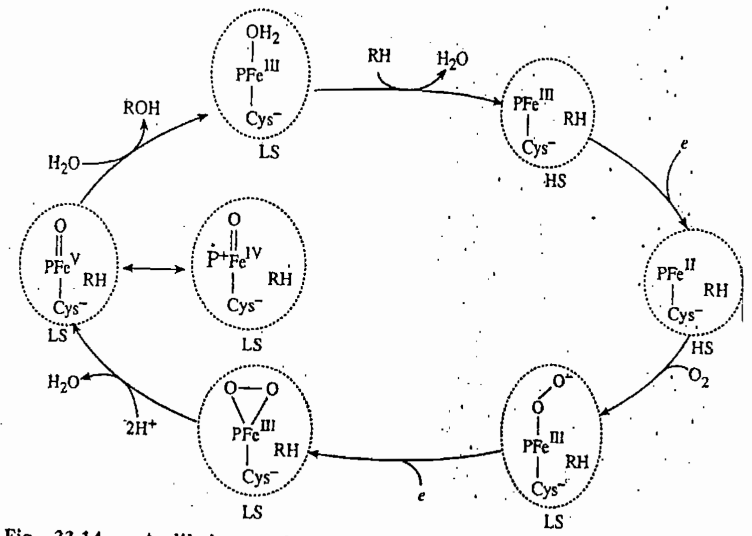


Fig. 33.14 : A likely catalytic cycle for Cytochrome P-450 (schematic).
The protein environment is marked by dotted circles. P = porphyrin.

[Sec. 33.2.2 *Iron proteins*]

Several aspects of the cytochrome P-450 reaction mechanisms have been confirmed by single crystal, EXAFS, isotope labelling and synthetic model studies. Mg^{2+} and Zn^{2+} ions are also found to be present in this enzyme, but their roles are not known.

Peroxidases and Catalases

These protective metalloenzymes help removal of H_2O_2 through reduction or disproportionation :

$$H_2O_2 + H_2\,Sub \longrightarrow 2H_2O + Sub \quad \textit{(Peroxidase)}$$

$$H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2 \quad \textit{(Catalase)}$$

Horseradish peroxidase, found in the roots of horseradish, has been extensively studied. The active site contains an iron(III) in protoporphyrin(IX) with an axial N-atom from histidine. The sixth coordination site usually contains a water molecule. The Fe(III) is high spin at low pH and low spin at high pH. A low-spin $Fe^{IV}\!=\!O$ unit is believed to supply one electron in the two-electron reduction process of H_2O_2 to $2H_2O$; the other electron comes from the porphyrin ring to yield a cation radical species.

Cytochrome *c* peroxidase from yeasts catalyze cleavage of the peroxo link :

$$ROOH + 2H^+ + 2e \longrightarrow ROH + H_2O$$

Like horseradish peroxidase, the axial ligand is again histidine; the other side is unoccupied in the resting state.

Chloroperoxidases catalyze the oxidation of chloride ions in the halogenation of a range of substrates :

$$Cl^- + H_2O_2 \longrightarrow ClO^-; \quad Sub\text{-}H + ClO^- \longrightarrow Sub\text{-}Cl + OH^-$$

In contrast to the previous peroxidases, the axial ligand is a cysteine thiolate.

An $Fe^{IV}\!=\!O$ unit at the heme centre is again the active species in both these enzymes. In chloroperoxidase, the porphyrin ring supplies an electron as in the case of horse radish peroxidase. But in cytochrome *c* peroxidase, this electron is supplied by a protein side chain.

Catalases Catalases are multisubunit enzymes (M = 250,000) with heme units at their active sites. Catalases from beef liver have been structurally characterized. The heme unit contains high-spin Fe(III) with one axial position occupied by the deprotonated phenolic oxygen from a tyrosine residue. The other axial position appears free to bind the substrate. H-bonding to amino acid side chains on this distal side appears essential for the catalytic function of the enzyme. A binuclear Mn-form is also known.

The enzyme catalyzes disproportionation of H_2O_2 according to the overall reaction

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2.$$

The process occurs in two steps (PFe represents the iron at heme centre).

$$PFe^{III} + H_2O_2 \rightleftharpoons \text{compound I} + H_2O$$

$$\text{compound I} + H_2O_2 \rightleftharpoons PFe^{III} + H_2O + O_2$$

The compound I is stable only for a few hundred milliseconds and has the $Fe^{IV}\!=\!O$ unit as in the case of peroxidases and cytochrome P-450. The oxenoid unit can also oxidize formate, nitrite, and ethanol in addition to H_2O_2.

Hemoglobin, peroxidases and catalases — all contain the same heme unit. The difference in their properties depends largely on the different electrostatic effects exercised by the different protein environments on the iron centre.

Non-heme proteins

Hemerythrin

Hemerythrin (Fig. 33.7), the dioxygen carrier in marine invertebrates, is an example of numerous carboxylate-bridged non-heme iron proteins. The diiron core in hemerythrin (deoxy form) contains two Fe(II) roughly 325-350 pm apart and bridged by two carboxylate groups and a hydroxy group. One iron is linked to the protein chain by two histidine units and is five-coordinate; the other iron has three histidine units linking the protein chain and is six coordinate. Dioxygen binds to the vacant site in five-coordinate iron, takes two electrons from the Fe_2^{4+} core, and gets reduced to peroxo group with a proton from the bridge-hydroxo group.

Methane monooxygenase

Though the diiron core exemplified in hemerythrin is most common, several non-heme proteins with multiple iron centres are known which participate in various redox (e.g., purple phosphatase and methane monooxygenase) and non-redox processess (e.g., ribonucleotide reductase). Methane monooxygenase (MMO) mentioned earlier (see carbon) catalyzes the oxidation of methane to methanol in an NADH-coupled process :

$$CH_4 + O_2 + H^+ \xrightarrow[\text{NADH} \quad \text{NAD}^+]{} CH_3OH + H_2O$$

One oxygen atom of O_2 is transferred to the substrate while the other is converted to water.

Two kinds of MMO are known : a membrane-bound type containing copper and a water soluble type which contains the non-heme iron. The soluble MMO in many methanotrophs has three constituents — a hydroxylase, a reductive protein and a coupling protein. The metal centre responsible for hydroxylation of methanol appears to be the diiron centre in hydroxylase — bridged by hydroxo, alkoxo or carboxylate bridges. Details of the structure vary from species to species.

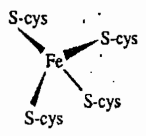
Ferritin

Formation of the ferritin core as an iron-reservoir is an example of *biomineralization* : synthesis of 'minerals' by organisms from simple substances; formation of shells, skeleton and teeth are other examples of this process. In animals as well as plants (and some bacteria) iron is stored in the form of non-toxic hydrated iron(III) oxide (with some phosphate) inside protein shells of ferritin. In humans, ferritin occurs in high concentration (~ 0.1 *M*) in liver, spleen and bone marrow and consists of a protein shell having twentyfour subunits. The hollow shell, ~65—70 pm inner diameter, (~ 130 pm outer diameter) can accomodate upto 4500 iron atoms present as microcrystalline particles of iron(III) oxide/hydroxide comparable to rust. Various compositions like $5Fe_2O_3.9H_2O$ or $[FeO(OH).H_2O]$, comparable to that of the mineral *ferrihydrite* have been proposed for the core. Another represention including some phosphate ions is approximately $[FeO(OH)]$ $[FeO(H_2PO_4)]$. The Fe^{III} ions are octahedrally coordinated and joined by bridging oxide and/or hydroxide ions; Fe—Fe distance ~330 pm. The iron atoms occupy octahedral interstices in a close-packed array of oxide and hydroxide anions. Iron in the core is received in the form of aqueous iron(II) through hydrophillic channels in the protein and is subsequently oxidized by O_2. This is followed by a number of steps like formation of diiron-oxo dimers to oligomers and larger aggregates and clusters.

Iron-sulfur proteins

The iron-sulphur proteins occur extensively in all living organisms and take part in a wide range of electron-transfer processes, either as redox centres (e.g., ferredoxins, rubredoxins) or as catalysts (e.g., hydrogenase, nitrogenase, sulfite reductase etc.). In these non-heme proteins, the iron is always bound by sulphur atoms, either from cysteinyl residues present in the protein or by inorganic sulphide. Structurally, these may conveniently be designated in terms of the number of iron atoms and the *suphide sulphurs*.

1Fe—0S proteins



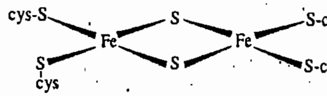
33-X

The simplest type of iron-sulphur proteins are rubredoxins found in bacteria. They can act as one-electron donor-acceptors and have the iron-atom bound to four cysteinyl residues in a distorted tetrahedral manner (33-X). Fe—S distance (Fe^{III} form) lies between 224 and 233 pm.

$$E^0\ (Fe^{III} - Fe^{II}) = -0.060\ V.$$

Ferredoxins are the most important family of iron-sulphur proteins. Three major categories of ferredoxins are [2Fe—2S]; [3Fe—4S] and [4Fe—4S]; the last one is the most common.

2Fe—2S proteins



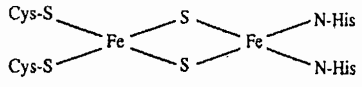
33-XI

Isolated from mammals, plants and bacteria. Dinuclear structure (33-XI) — two tetrahedra share a common edge containing inorganic sulphur atoms. Fe^{III}—Fe^{III} = 269 pm. Both are high spin; but strong antiferromagnetic coupling gives a diamagnetic cluster.

The cluster transfers and accepts only one electron to form an Fe^{II}—Fe^{III} cluster containing high-spin d^6-high-spin d^5 pair.

$$E^0 \sim -0.150\ V\ to - 0.450\ V$$

A non-symmetrical structure (33-XII) is found in *Rieske proteins* isolated from bovine mitochondria.



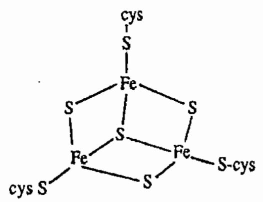
33-XII

$$E^{0'} \sim -0.10\ V\ to - 0.40\ V.$$

[3Fe—4S] proteins

First found in *Azobacter vinlandii* and *Desulfovibrio gigas*; also present in aconitase from pig heart. Structure may be derived from that of Fe_4S_4 unit (33-XIII) by removing one Fe. All three iron are Fe^{3+} in oxidized form; reduced form has two Fe^{3+}, one Fe^{2+}.

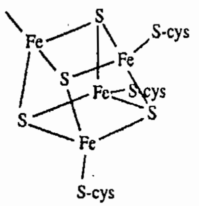
$$E_0 \sim -0.070\ V\ to\ -0.460V.$$



33-XIII

[4Fe—4S] proteins

Distorted cubic structure (33-XIV) with iron atoms at alternate corners of cube; other corners occupied by S (cysteine).

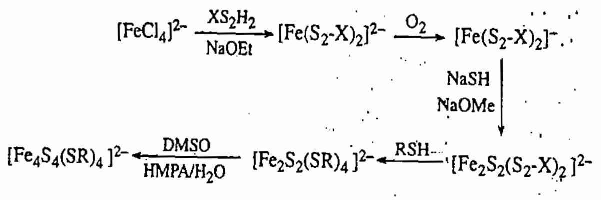


33-XIV

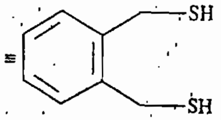
The iron has an average oxidation number of +2.5, formally consistent with two Fe^{III} and two Fe^{II} in the oxidized state and three Fe^{II} and one Fe^{III} in the reduced state.

E^0 (Fe^{III}–Fe^{II}) = – 0.400 V. Another high potential form present in some bacteria has $E^{0'}$ = + 0.350 V.

Several synthetic analogues of the iron-sulpur proteins have been prepared with thiolato, sulfido and other ligands attached to the iron centre; an elegant synthetic scheme is as follows :



HMPA = hexamethylphosphoramide; XS_2H_2 ≡



Electrochemical studies on these model systems provide valuable clues regading electron transfer processes in natural systems.

33.2.3 Copper proteins

Copper occurs in all forms of life providing the active metal centre in a large number of enzymes (Table 33.7).

TABLE 33.7

Some common copper-containing enzymes

Enzyme (molecular wt)	Metal centre	Main function (catalytic)
Ceruloplasmin (132,000)	8 Cu	Oxidase : release of iron from liver
Superoxide dismutase (2 × 16,500)	2 Cu—2 Zn	Disproportionation of superoxide
Cytochrome oxidases (~150,000)	2 Cu + 2Fe (heme)	Reduction of oxygen to water
Plastocyanin (10,500)	1 Cu	Electron transfer in plants, algae and bacteria,
Tyrosinase (4 × 32,000)	4 Cu	Hydroxylation of tyrosine
Amine oxidases (2 × 90,000)	2 Cu	Oxidation of primary amine to aldehyde $—CH_2NH_2 \longrightarrow —CHO.$

Ceruloplasmin accounts for 70-90% of the total copper in normal human plasma. The intense blue protein is associated with the glycoprotein of the α_2-globulin fraction of mammalian blood; it has 1064 amino acid residues with eight (or seven) copper atoms per molecule. It is a long term copper transporter in plasma; several vital copper enzymes receive their copper through this enzyme.

Ceruloplasmin is involved in several other processes, for example,

(i) release of iron from liver storage sites and its oxidation prior to complexation by transferrin;

(ii) as an antioxidant in blood serum;

(iii) regulation of serum biogenic amines; growth promoter in some cells;

(iv) stimulation of angiogenesis in cornea and in cell culture.

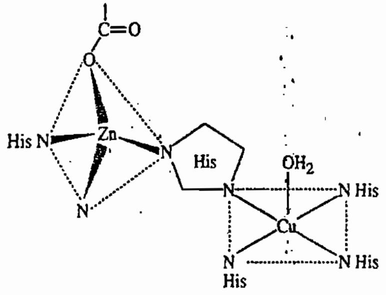
Acute deficiency of the enzyme in serum (< 10^{-9} M) reduces mobilization of iron from liver storage sites and hence results in anemia. However, such anemia arising from copper deficiency is uncommon in humans, but may be found in farm animals.

The blue colour of the enzyme arises from intense absorption (ε >3000 M^{-1} cm^{-1} at 600 nm) arising from cysteine-S to Cu(II) charge transfer.

The copper-zinc superoxide dismutase (CuZnSOD) is a rather small enzyme (MW ~ 16,000) with both copper and zinc at active sites. The enzyme catalyzes the reaction

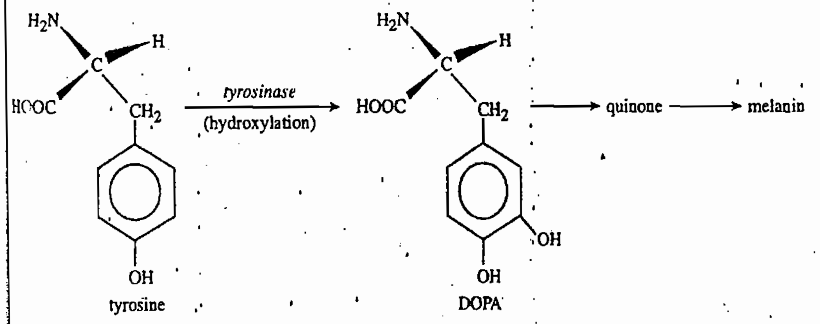
$$2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2$$

It has two identical sub-units, each having a binuclear active site with the Cu^{2+} and Zn^{2+} coordinated to separate N atoms of a common imidazole group of histidine 61 (33-XV). The Zn^{2+} can be replaced by Co^{2+} or Cd^{2+} with insignificant loss of activity (30 – 0%) but the activity disappears in absence of copper. This suggests that the functional role is played by copper while zinc plays a supportive structural role; probably it holds the bridging imidazolate group in place.



33-XV

Tyrosinase acts as a monooxygenase catalyzing the *o*-hydroxylation of monophenols to *o*-diphenols (***cresolase activity***). It also acts as a two electron oxidase catalyzing the oxidation of *o*-diphenols to *o*-quinones (***catecholase activity***). The enzyme has a coupled dinuclear active site which binds an O_2 molecule, reduces this to peroxide and utilizes one oxygen atom to form a hydroxyl group. This is subsequently oxidized to quinones. Oxidation of the essential amino acid tyrosine to dihydroxyphenylalanine (DOPA) by tyrosinase forms the inital steps for synthesis of the pigment melanin :



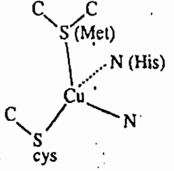
Hemocyanin, the dioxygen carrier protein in the blood of molluscs and arthropods, has a similar dinuclear active site (Fig. 33.6). The high molecular weight protein has many subunits — each subunit has a dinuclear copper(I) core (in deoxy form). Each Cu(I) is coordinated by three histidine residues at an internuclear distance around 370 pm (±30 pm). An empty cavity between the metals accommodates the dioxygen molecule, possibly involving cooperativity among various subunits.

In oxyhemocyanin the two Cu(II) ions (d^9) are strongly antiferromagnetically coupled resulting in diamagnetism and no epr signal. The (μ-peroxo)dicopper(II) centre is supported by the O—O stretching vibration at 745-750 cm^{-1} in the resonance Raman spectrum. Further support to the bridging peroxo group came from studies on a model complex compound containing two Cu(II) ions linked by η^2, η^2-peroxide followed by crystal structure determination of horseshoe crab hemocyanin (oxy form).

Oxyhemocyanin owes its blue colour to the intense optical transition at 345 nm arising from ligand to metal charge transfer.

Copper-containing enzymes are conveniently classified according to the structural and spectroscopic characteristics of the copper complex at the active site. Three principal types of Cu(II) complexes are generally found at the active site (Table 33.8).

TABLE 33.8
Main structural types of copper enzymes

Type	Example	Characteristics
Type 1	Plastocyanin. Found in higher plants and green algae, it is a representative of the "*blue copper proteins*". Its intense blue colour arises from strong absorption in the visible region (ε ∼ 3000 M^{-1} cm^{-1}, 600 nm), assigned to S(cysteine) ⟶ Cu(II) charge transfer.	Cu(II) in an unusual geometry : two histidine N and one cysteine thiolate S donors lying nearly in the plane of the metal; a long out-of-plane axial Cu—S bond to a thioether unit of methionine residue. Anomalous epr spectra. 
Type 2	Cu—Zn SOD	'Normal' tetragonal coordination of Cu^{2+}.
Type 3	Coupled 2—Cu (or multicopper) oxygenases, e.g., tyrosinase. Also, the respiratory enzyme hemocyanin.	EPR silent— antiferromagnetic coupling between two copper sites results in diamagnetism and abnormal visible spectra.

All three types of copper are present in proteins such as laccase and ascorbate oxidase (Fig. 33.15). These enzymes catalyze the four electron reduction of dioxygen to water and an one-election oxidation of a reducing substrate. In ascorbate oxidase, the Type 1 copper receives electrons from ascorbate and transfers them to the triangular array of Type 2 and Type 3 copper atoms. Dioxygen binding occurs within this triangular site with close interaction and rapid spin exchange with all three copper atoms.

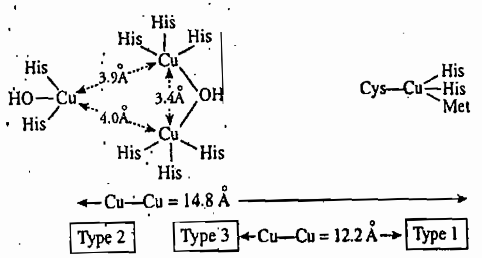


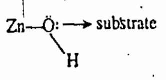
Fig. 33.15 : Copper sites in ascorbate oxidase.

33.2.4 Zinc proteins

More than 300 enzymes are known to contain zinc, which is also the second most abundant trace element in man. As mentioned earlier, the metal ion offers an ideal metallobiosite owing to its potential Lewis acid character and redox insensitivity.

Zn^{2+} is a good Lewis acid in bioinorganic systems, specially in low coordination numbers. The $3d^{10}$ configuration provides no ligand field stabilization and the metal shows no preference for a particular geometry. The coordination number is determined primarily by the balance of inter-ligand repulsion and bond energies. Both metal-donor distance and interligand repulsion (steric as well as electronic) increase with increasing coordination number. The metal is in a low coordination number in enzymes, mostly tetrahedral (often distorted), where it can bind a fifth ligand with little energy barrier and then another ligand can dissociate. Similarly, a six-coordinate complex can readily dissociate a ligand to form a five-coordinate complex with little loss of energy. These facts place zinc in a favourable position for functioning as a catalyst.

The electrophilicity of the zinc ion, summarily ascribed to its high charge-size ratio, is of paramount importance in determining the bioinorganic role of zinc. The pK_a of coordinated water molecules in zinc complexes is substantially lowered, favouring release of a proton with the formation of Zn—OH bonds. The nucleophilicity of the Zn—OH species is greater than either free H_2O or M^{2+}—OH_2. The Zn—OH bond can be attacked by a substrate, a behaviour to be found in the action of the zinc enzyme carbonic anhydrase. In the enzyme carboxypeptidase which cleaves peptide linkages (and esters), the zinc ion polarizes a carbonyl (>C=O) bond when the oxygen coordinates to the zinc ion in the beginning of the catalytic cycle.



The lack of preference of the Zn^{2+} ion for any given geometry also makes its complexes labile, allowing rapid exchange of coordinated ligands, particularly water. This factor also favours the catalytic behaviour of the zinc ion.

Carbonic anhydrase

The enzyme catalyzes the reaction

$$CO_2\,(aq) + OH^- \rightleftharpoons HCO_3^-$$

at physiological pH (around 7); without the catalyst, the reaction occurs appreciably only above pH 9. At pH = 7, the hydration of CO_2 takes place very slowly at room temperature in absence of any catalyst :

$$CO_2\,(aq) + H_2O \rightleftharpoons HCO_3^- + H^+ \quad (p_{CO_2} = 1\text{ atm};\ k \sim 10^{-1}s^{-1})$$

The enzyme human carbonic anhydrase (HCA) enhances the rate of hydration of CO_2 by a factor of about 10^7. The enzyme can also catalyze hydrolysis of esters and aldehydes.

In the red blood cells, the enzyme performs the important role of receiving carbon dioxide from tissues such as active muscle and releasing it in the alveoli of the lungs. Each molecule of carbonic anhydrase can hydrate about one million molecules of CO_2 per second at body temperatue (~37°C).

Different closely related forms of carbonic anhydrase are found in mammals, each having molecular weight ~ 30,000 and a roughly ellipsoidal shape. The zinc ion, situated in a small cleft about 12 Å from the surface, is co-ordinated by the imidazole nitrogens of three histidine residues and a molecule of water; the geometry is distorted tetrahedral. The catalytic action of the zinc-site is initiated by conversion of a coordinated water molecule to give a Zn—OH bond through participation of a neighbouring histidine and a buffer medium. This is followed by a nucleophilic attack on the carbon atom of CO_2 (Fig. 33.16). It is possible that the OH group is properly oriented for the attack through a hydrogen bond with a threonine residue in the protein chain (Thr 199). Dehydration of $HC^{18}O_3^-$ leaves an ^{18}O on the zinc, suggesting that at some stage during the reaction sequence, the $HC^{18}O_3^-$ ion must have been directly coordinated to the metal.

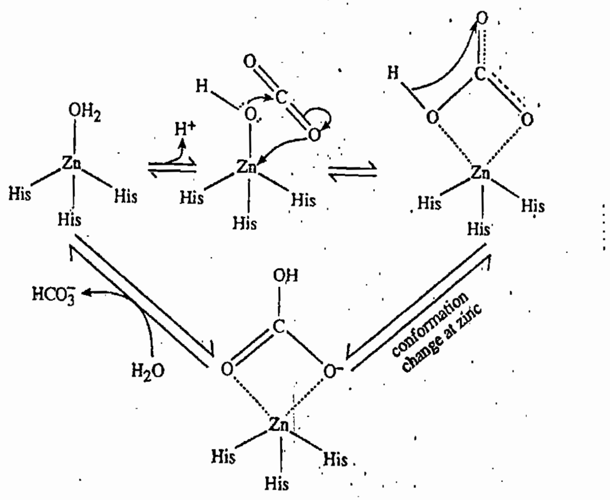
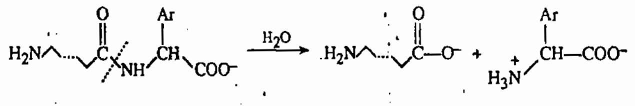


Fig. 33.16 : Catalytic path (schematic) for hydration of CO_2 by HCA.

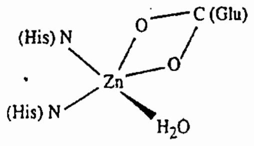
Since the zinc ion (d^{10}) can not be studied by EPR, uv and visible spectroscopy, the metal site in the enzyme has been replaced by other metal ions like Co^{2+}, Cd^{2+}, Mn^{2+}, Cu^{2+} and Ni^{2+} (apoenzyme + M^{2+}). The Co^{2+}-reconstituted enzyme retains about 50% of the activity, presumably due to the ability of Co^{2+} to adopt the tetrahedral geometry. The Cu^{2+} and Ni^{2+}-enzymes show slight activity but the activity is negligible in case of other metals.

Carboxypeptidases

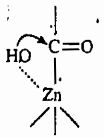
These are mammalian digestive enzymes, synthesized in the pancreas as inactive procarboxypeptidase and is activated by trypsin in the small intestine. Peptidases belong to the class of enzymes called *hydrolases* which are involved in the degradation of proteins. Peptidases are so called because they specifically cleave the peptide bonds. *Endopeptidases* (proteases) attack the internal peptide bond and release peptide fragments (e.g., pepsin, trypsin). *Exopeptidases* act on the peptide bonds of terminal amino acids. Carboxypeptidases are exopeptidases which act on C-terminal amino acids; aminopeptidases act on N-terminal amino acids. The overall reaction catalyzed by carboxypeptidase may be represented as :



Carboxypeptidase A from the pancreas of cattle (bovine) was the first zinc enzyme characterized crystallographically. The zinc ion, well inside the protein surface, is pentacoordinate — ligated by the imidazole nitrogen atoms of two histidine residues, a water molecule and a bidentate carboxylate group of a glutamate residue (33-XVI). In presence of substrates or inhibitors, the glutamate carboxylate group coordinates more or less as a unidentate group (*carboxylate shift*), keeping the coordination number unchanged on substrate binding. The coordinated water molecule forms hydrogen bond with the glutamate residue. The enzyme has a preference toward substrates possessing large, hydrophobic C-terminal side chains, e.g., phenylalanine; the aromatic ring protrudes into a hydrophobic pocket near the active site. Several arginine and tyrosine residues near the active site assist in substrate binding.



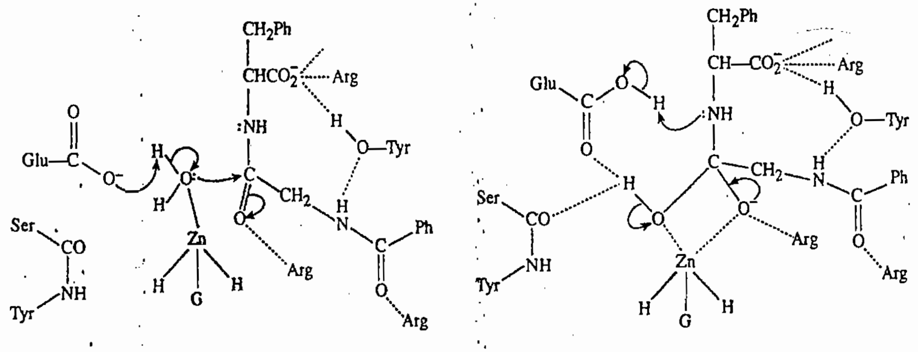
33-XVI



33-XVII

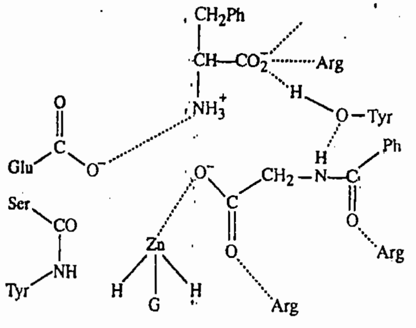
The enzyme carboxypeptidase A (CPA) and human carbonic anhydrase (HCA) have the same common mode of initiation of their catalytic activity — attack by a zinc-bound hydroxide at the substrate C=O bond. The nucleophilic adduct in case of HCA is the product while in case of CPA, it is an intermediate (33-XVII).

A probable mechanistic path for the function of the enzyme is shown in Fig. 33.17.



(a)

(b)



(c)

Fig. 33.17 : Proposed mechanistic path for the function of CPA (simplified).

(a) A peptide substrate (with terminal phenylalanine residue) near the active zinc site; note the extensive H-bonding network (dotted). The carbonyl group undergoing fission is polarized by an arginine residue.

Nucleophilic attack by water (zinc-bound) is promoted by the carboxylate end of Glu.

(b) The intermediate containing pentacoordinate zinc. Proton donation from Glu leads to the product-complex in (c).

(c) Formation of product-complex from the intermediate. This subsequently releases the product carboxylate.

33.3 METAL IONS AS CHARGE CARRIERS

33.3.1 Introduction

A resting human uses nearly 200 ml O_2 (STP) per minute; this is used to supply the free energy change for the life process in terms of the electron-transfer process :

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O.$$

Each molecule of O_2 consumes four electrons in the process. 200 ml O_2 makes about 9 millimoles, and hence involves 36 millimols of electrons per minute. This is equivalent to 0.6 millimols of electrons per second, that is 60 amperes of electric curent! This huge quantity of charge is carried in our body by the ions H^+, Na^+, K^+, Ca^{2+} and Mg^{2+}. As mentioned earlier, the last two metals also contribute to structure formation. The proton alone takes a large share of this charge transport but it is beyond our scope to discuss this aspect. We shall briefly mention metal ion transport.

The alkali and alkaline earth metal ions can be transported in serum as their aquated ions since they are soluble at the pH of the body. The concentrations of these ions inside and outside a cell maintain a steep gradient, as shown by the following typical values (approximate) :

	Na^+	K^+	Ca^{2+}	Mg^{2+}
$\dfrac{[M^{x+}]_{in}}{[M^{x+}]_{out}}$	0.1	20	0.0001	100

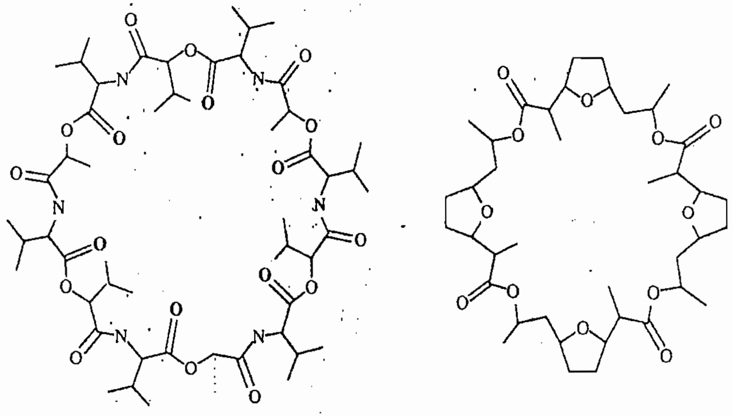
This suggests that the metal ions must be transferred constantly across the plasma membrane surrounding the cell to maintain healthy functioning. But the passage of the hydrophilic metal ions through hydrophobic regions in the membrane poses some difficulty. Gas molecules (e.g., O_2, N_2) or organic molecules may pass through the membrane in which they are soluble, other small molecules or ions (e.g., H_2O, urea, Cl^- etc.) can also move through transient gaps or tunnels in the membrane, but how do the ions like Na^+, K^+ etc. would move through the membrane? And that too, most of the time against the direction of the concentration gradient?

How does water move from a lower level to a higher level? The obvious answer : with the aid of a pump. The process requires energy. Similarly, ion pumps send ions across a membrane at the cost of ATP-energy. This is called 'active' ion transport. A large number of different ion-pumps operate at various locations in the body. For lack of space, we shall discuss only the Na^+—K^+ pump in section 33.3.2.

Passive transport of metal ions may occur in two ways : (a) the cation may be encapsulated within a macrocyclic ion-carrying ligand (ionophores) having organic groups outside; a hydrophobic sheath helps the complex dissolve in nonpolar regions of the cell and diffuse across fatty membranes; (b) The metal may pass through an ion-permeable channel extending through the membrane.

(a) **Ionophores** : Some naturally occurring molecules have the ability to encapsulate a metal ion from several coordination sites and at the same time provide a layer of organic groups outside the complex. Such ligands are known as *ionophores*. Valinomycin and nonactin are such cyclic proteins (Fig. 33.18); their analogy with crown ethers is at once evident.

Valinomycin, a cyclic protein with 12 peptides, has three repeated sequences L-valine-D-α-hydroxyvaleric acid-D-valine-L-lactic acid. The resulting 36 membered flexible macrocycle can adopt various geometries depending upon the polarity of surrounding medium and the presence or absence of a metal ion within its cavity. The different conformations are stabilized by H-bonds between different parts of the molecule and/or to the solvent. It forms an 1 : 1 complex with K^+, which fits nicely into the cavity, with the six carbonyl O-atoms pointing inward in an approximately octahedral coordination around the metal. The potassium complex is nearly 1000 times stronger than that made by the Na^+ ion, which is only loosely held within the cavity.



Valinomycin
(a)

Nonactin
(b)

Fig. 33.18 : (a) valinomycin; (b) nonactin.

Before coordination by the encapsulating ligand, the hydration sheath around the metal must be removed. This requires energy (~ 322 kJ mol⁻¹ in case of K^+) but the energy spent is more than compensated by the formation of six strong ion-ligand interactions. The process of removal of the water layer is perhaps initiated by the oxygen atoms lying on the outer side of free valinomycin and is continued as the metal is gradually and completely trapped by the serpentine ligand.

Nonactin is another naturally occurring ionophore which also resembles a crown ether – in fact it is a polyester. In the metal-free crystalline form, the carbonyl oxygens point outward and the four oxygens from the four tetrahydrofuran rings form nearly a square at the centre. On coordination to an alkali metal ion or NH_4^+, the conformation changes to form a nearly cubic arrangement of four carbonyl O and four ether O around the cation providing, at the same time, an extremely nonpolar periphery around the whole moiety.

Several ionophores have been described, obtained mostly from fungi and marine organisms. They can carry both Na^+ and K^+ ions through the nonpolar cell membrane in either direction. This may disrupt the ion balance in the cells — a situation that may be fatal for single cell species like bacteria. The ionophores thus possess the potentiality of antibiotics (*transport antibiotics*). But they are therapeutically useless as they cannot distinguish microbial cells from the host animal's cells. Some limited veterinary applications are reported. For example, monensin (a charged ionophore) can practically blow up the cells of *coccidia*, an internal poultry parasite, by replacing H^+ ions by Na^+ ions.

(b) **Transport through channels :** Some molecules form ion-permeable channels extending through the membranes. Gramicidin A, a linear polypeptide containing 15 amino acid residues produced by *Bacillus brevis*, forms such a channel in phospholipid membranes (Fig. 33.19).

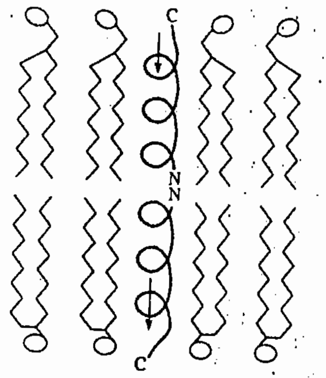


Fig. 33.19 : Gramicidin A channel passing through a membrane.

The channel consists of dimers of singlestranded β-helical monomers of gramicidin joining end-to-end. About 50 Å in length, the channel is about 4Å wide in the inactive state. When passing a cation, the channel may be widened to about 6.8 Å through molecular conformational changes. It allows the passage of univalent cations (including H^+)—about 10^7 cations are transported in one second.

33.3.2 The Na^+-K^+ ion pump

The steep concentration gradient between Na^+ and K^+ (and between Ca^{2+} and Mg^{2+}) across the cell wall membranes is largely maintained by the Na—K pump. According to one estimate by Streyer, the Na—K pump consumes more than one-third of the ATP used by a resting animal—approximately 15 kg per day in a resting adult human.

The ion pump works with a membrane-bound enzyme Na^+-K^+ ATPase which catalyzes the movement of Na^+ and K^+ ions in opposite directions; the overall process may be summarily represented as (*intra* = intracellular, *extra* = extracellular).

$$3Na^+ (intra) + 2K^+ (extra) + Mg^{2+}\text{-}ATP^{4-} + H_2O \longrightarrow$$
$$3Na^+ (extra) + 2K^+ (intra) + Mg^{2+}\text{-}ADP^{3-} + HPO_4^{2-} + H^+$$

Two K^+ ions enter the cell with the expulsion of three Na^+ ions; the energy is derived from hydrolysis of ATP catalyzed by Mg^{2+}.

The Na^+-K^+ ATPase is a "tetrameric" protein—it has two α subunits (M.W. around 95,000) and two β subunits (M.W. ~40,000). The larger α-units are in contact with each other and protrude right through the membrane. Details of the molecular structure and exact mode of action of the enzyme are not yet known. A likely mechanism is outlined below (Fig. 33.20).

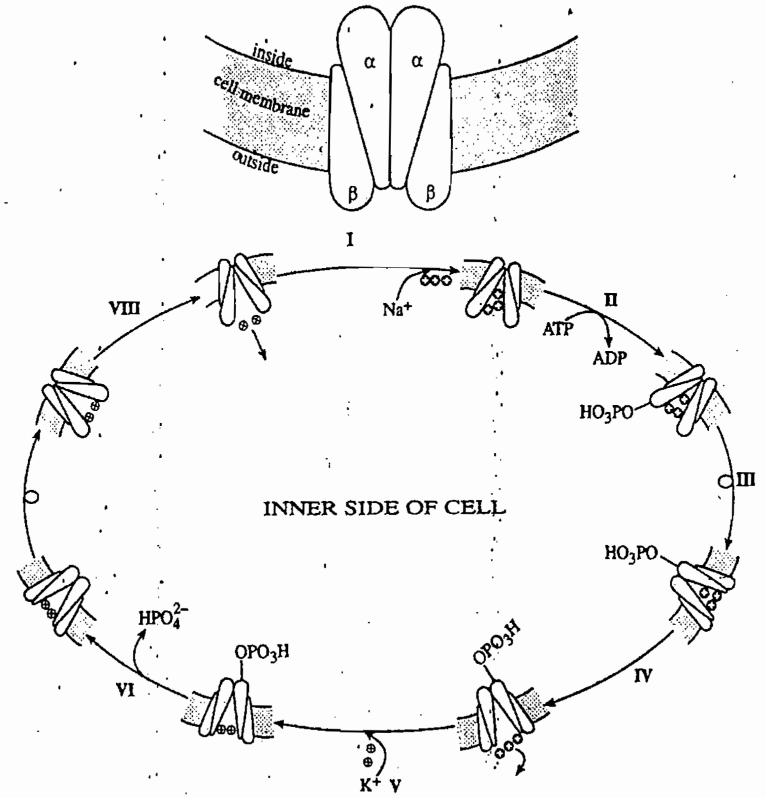


Fig. 33.20 : Functioning of the Na^+-K^+ pump (schematic).

I. Inside the cell, the enzyme binds three Na^+ ions to sites on the α units consisting probably of six O-atoms.

Coordination of the Na^+ ions changes local polarities in a manner that favours coordination of an ATP (in presence of Mg^{2+}) into the enzyme.

II. The ATP is hydrolyzed by the enzyme to ADP and a covalently bound phosphate ester. One of the α-unit aspartyl groups in the enzyme is phosphorylated.

III. The conformation of the α-units changes on phosphorylation, turning them inside out (eversion; shown by $\curvearrowright$).

IV. The Na^+ ions, now weakly bound to the enzyme, are lost to the extracellular fluid.

V. Two K^+ ions are bound to the outer side of the enzyme.

VI. Binding of the K^+ ions facilitates dephosphorylation of the α-units; the monophosphate is lost to the intracellular fluid.

VII. The enzyme reverts to its original conformation (eversion, $\curvearrowright$).

VIII. The K^+ ions; now bound loosely to this changed conformation, are lost to the intracellular fluid. The ATPase reverts to its original form for accepting Na^+ ions.

Transmission of nerve impulse

Transmission of nerve impulses through the network of nerve cells, neurons, takes place through electrical signals induced by the flow of Na^+ or K^+ ions. A neuron is an irregular star-shaped cell with several receiving ends (*dendrite*) and one transmitting extension called *axon*. The axon of one cell meets the dendrite of another cell at a junction called *synapse* where the signal is relayed to another cell.

Like other cells, a nerve cell or neuron also has a higher concentration of K^+ inside and Na^+ outside. At rest, a nerve cell membrane is slightly permeable to K^+ but not to Na^+ or the negative protein molecules associated with the K^+ inside cell. Hence outward leakage of K^+ through these channels in the membrane make the inner side of the cell negatively charged. At one stage the protein charge opposes further loss of cation from the cell. The negative membrane potential so created is about 60-95 mV (the potential outside is taken as zero).

If an outside stimulus originating in the nervous system or at a sense organ site now removes the potential, the membrane becomes highly permeable to Na^+ ions. The ions now enter the cell and make the inner side of the cell positively charged (about +30 mV). This takes about 1 millisecond and involves only a small amount of Na^+ ions. In the following few milliseconds the membrane becomes again permeable to K^+ ions, which now move outward to bring back the resting potential. The Na^+-K^+ pump now restores the original cation ratio in the cell. During this entire operation, the voltage changes excite the neighbouring parts of the membrane where the same cycle of events is repeated. The original stimulus is thus relayed from one end of the cell to the other, in particular to the long drawn terminal or axon. The nerve impulses thus pass along the axon in the form of electrical signals induced by the flow of Na^+ or K^+ ions across the axon membrane. The axon ends in a knob at the junction with the next cell (the synapse). As the electrical impulse arrives at the knob, it releases certain specific transmitter chemicals (neurotransmitters) which now travel the gap between two cells, the synaptic gap or cleft (~ 200 Å), to reach suitably oriented receptor sites on the next cell. In this manner, the stimulus is transmitted from one cell to another. Different cell junctions provide different transmitter chemicals like serotonin, catecholamines (epinephrine, norepinephrine), acetyl choline etc.

33.4 HEALTH CONCERN OF METALS AND NON-METALS

33.4.1 Introduction : metal and nonmetal deficiency

The involvement of various essential elements in life processes is intimate as well as intricate and inter-dependent. We have already mentioned the essential principal roles played by these elements in section 33.1 and abnormalities which develop from their deficiency or excess. We devote this section to a summary review of this latter aspect of the elements followed by a short exposure to the application of metals in medicine.

We have already seen that either deficiency or excess of the essential elements may dirsupt normal functions of the body and result in ailments. Table 33.9 summarizes some common ailments and diseases with deficiency or excess of an element.

[Sec. 33.4.1 *Metal deficiency*]

TABLE 33.9

Some common ailments and diseases caused by deficiency or excess of some essential elements

Element	Deficiency	Excess
Arsenic	Inhibited growth.	Toxicity (chapter 22)
Calcium	Rickets, osteomalacia and osteoporosis.	Calcification of tissues, formation of stone and cataract.
Chromium	Disturbance in carbohydrate, protein and lipid metabolism.	Lung disease; Toxicity (liver and kidney damage).
Cobalt	Anemia	Heart failure; Polycythemia (increased RBC).
Copper	Anemia, Wilson's disease, Menke's disease (discussed below).	Wilson's disease.
Fluorine	Dental caries in children	Fluorosis
Iodine	Goitre	Goitre
Iron	Anemia	Hemosiderosis, Hemochromatosis (bronze diabetes).
Magnesium	Convulsion, neuromuscular irritation.	
Manganese	Inhibited growth; low insulin; accumulation of fat in liver.	Psychiatric disorder.
Molybdenum	Inhibited growth.	Molybdenosis (impaired growth, anemia, diarrhea)
Silicon	Inhibited growth.	Lung diseases
Sodium	Hyponatremia—reduced blood pressure and circulatory failure.	Hypernatremia — increase in blood pressure, hypertension.
Zinc	Inhibited growth, anemia.	Toxicity—nausea, gastric ulcer, pancreatitis, anemia etc.

A few select cases of metal and nonmetal deficiency are summarized below :

Calcium

As already mentioned, the metal not only plays a major structural role but also plays crucial regulatory functions like muscle contraction, nerve transmission, blood coagulation and so on. The blood calcium level is maintained within a narrow range (9-11 mg/dl or 4.5-5.5 meq/l) by several hormones like parathyroid hormone, calcitonin and calcitriol (homeostasis of Ca). In *hypercalcemia*, the serum calcium level is elevated, due mainly to enhanced activity of parathyroid glands. This is associated with decrease in serum phosphate, increase in alkaline phosphatase activity and increase in urinary excretion of calcium and phosphorus. The last effect may also lead to formation of urinary calculi (stones).

Hypocalcemia, characterized by a fall in serum calcium below 7 mg/dl is more serious and threatening compared to hypercalcemia. It gives rise to *tetany*, whose symptoms include neuromuscular irritability, spasms and convulsions. Hypocalcemia occurs mostly due to underfunctioning of parathyroid glands or due to an autoimmune disease.

Rickets may result from low levels of vitamin D in the body or due to insufficient intake of Ca or P or both. This gives rise to defective calcification of bones. *Renal rickets* is caused by an inherited defect in the reabsorption of phosphate in the renal tube and does not respond to normal vitamin D therapy. The disease is more appropriately known as *familial hypophosphatemic rickets*.

Oseteoporosis, or demineralization of bone is common in elderly people, particularly in postmenopausal women. It results in frequent bone fracture. Reduced production of calcitriol (hormone) from vitamin D and deficiency of other hormones may be some of the principal factors behind osteoporosis.

Iron

Iron deficiency anemia is the most prevalent nutritonal disorder all over the world, in both developed and underdeveloped countries. It may be caused by inadequate dietary intake or some defect in the absorption system. Chronic blood loss, repeated pregnancy and hookworm infection may also cause such anemia. It is characterized by lower hemoglobin content of blood (< 12 mg/dl), retarded growth, loss of appetite, sluggish metabolic activities and dull or inactive attitude.

Another type of anemia is observed in rare individuals having a mutant variety of hemoglobin (HbS) in which the sixth position of the β subunit is occupied by valine instead of glutamic acid. This results in sickling of RBC and the deoxy HbS polymerizes into soluble, ordered fibrous structures. This lowers the ability of the blood to transport O_2 effectively to the tissues.

Hemosiderosis occurs due to an excess deposit of iron in the body, commonly in persons receiving repeated blood transfusions over years. Since iron is not excreted from the body, excessive intake of iron in long term or short term may lead to deposition of iron in the body. The Bantu tribe in South Africa are prone to hemosiderosis as they have high intake of iron from cooking food in iron pots and their stable diet corn.

Hemochromatosis is characterized by deposition of iron in liver, spleen, pancreas and skin. It may result in cirrhosis of liver, pancreatic fibrosis and bronze pigmentation of the skin (hence also the name *bronze diabetes*).

Iodine

As explained earlier, both deficiency or excess of iodine lead to abnormal functioning of the thyroid gland. This in turn, may cause several diseases.

Goiter is an abnormal increase in the size of the thyroid gland to compensate the decreased synthesis of thyroid hormones. Simple endemic goitre is common in geographical regions away from sea coast where people generally have low intake of iodine in their food. Consumption of iodized salt may supplement this deficiency.

Certain *goitrogenic substances* interfere with production of thyroid hormones, for example, thiocyanates, nitrates, perchlorates and drugs like thiourea, thiouracil etc. Cabbage, cauliflower and turnip contain much thiocyanates and are not recommended for patients of goiter.

Hypothyroidism occurs due to impairment in the function of thyroid gland and is characterized by slow heart rate, low BMR, weight gain, sluggish behaviour, fatigue, dry skin etc. Physical and mental retardation in children due to hypothyroidism is known as *cretinism*.

Hyperthyroidism, also known as thyrotoxicosis, is associated with over production of thyroid hormones. It is characterized by high BMR, nervousness, irritability, anxiety, rapid heart rate, weakness, sweating, sensitivity to heat and protrusion of eyeballs.

Copper

As discussed earlier, large amounts of copper metalloenzymes are required to maintain the high metabolic rate of heart and brain. Severe deficiency of copper causes demineralization of bones, anemia (cytochrome oxidase is required for blood formation), fragility of arteries, hypopigmentation of skin, greying of hair, myocardial fibrosis and several other disorders. Defective intestinal absorption of copper gives rise to *Menke's disease*; the lack of absorption may be trapping of the copper by metallothionein in the intestinal cells. The disease is characterized by lowered copper in plasma and urine, anemia and depigmentation and kinking of hair.

Wilson's disease results from abnormal copper metabolism due to failure to synthesize ceruloplasmin (see last section) or any impairment of the binding of copper to this protein. As a result, free copper in the plasma enters different tisues, binds with the proteins and gets deposited (liver, kindney, brain). The main manifestations of Wilson's disease are

(i) Low levels of copper and ceruloplasmin in plasma and increased excretion of copper in urine.

(ii) High intestinal absorption of copper.

(iii) Deposition of copper in liver and lenticular nucleus of brain. This may result in hepatic cirrhosis and brain necrosis.

(iv) Renal damage due to deposition of copper in the kidneys. This leads to increased excretion of amino acids, glucose, peptides and hemoglobin in urine.

Patients of Wilson's disease are treated with the copper chelating agent penicillamine (see later).

Zinc

Deficiency of zinc is associated with retardation of growth, anemia, loss of appetite and taste sensation, poor wound healing etc.

Inhalation of zinc oxide fumes (particularly by welders) may lead to zinc toxicity. It is characterized by nausea, gastric ulcer, pancreatitis, excessive salivation and loss of body hair.

33.4.2 Toxic effects of metals

It was mentioned earlier (Fig. 33.1) that an essential element may become toxic at a large dose. We have discussed in the last section how the friendly metals iron and copper may become toxic when present in large amounts either due to any metabolic disorder or due to accidental ingestion when the normal absorption and distribution of the metal is impaired. The toxic effects of other essential elements have also been mentioned in appropriate places and summarized in Table 33.9.

Another broad class of metal toxicity results from entry of non-essential metals into the body from the environment — through food, respiration or skin absorption. These are parts of environmental pollution.

All toxic elements are chemically similar to an essential element and hence will impair the function of the latter. The similarity may arise from their positions in the periodic table or from comparable sizes of their ions. Besides, some radioactive isotopes like Sr-90 and Pu-239 are also highly toxic.

Some common toxic metals are mentioned below. Treatment for the removal of these metals are discussed in the next section.

Aluminium : The Al^{3+} ion is a hard cation and will bind strongly to N- and O- donor ligands in any biomolecule and thus deactivate them. Since Al^{3+} can replace Fe^{3+}, it will cause anemia, dementia and death. The metal is also probably involved in the etiology of Alzheimer's disease and other neurological disorders. It also replaces Mg^{2+} and binds more strongly to the same ligands. Lower pH in soils increases the bioavailability of Al^{3+}.

Beryllium : The small Be^{2+} cation can easily interfere with Mg^{2+}. In fact, it is the most toxic of all elements. Ingestion of beryllium compounds leads to lung cancer.

Cadmium : Cd^{2+} can replace Zn^{2+} in S-containing enzymes and Ca^{2+} in bone. It may cause gastrointestinal, neurological and kidney toxicity. It is bound to metallothioneins which may act as clearing agents provided by the defence mechanism of the body.

Chromium : Evidences for toxic effects of Cr(III) are not well established but Cr(VI) is highly toxic as it possesses carcinogenic and mutagenic properties. In cells, CrO_4^{2-} is reduced to Cr(III) via Cr(V) and Cr(IV) intermediates, probably through reaction with SH groups of peptides, e.g., glutathione. The Cr(V) intermediates can coordinate to phosphate units in DNA where they may be reduced to Cr(III) forming a kinetically inert complex. This causes DNA strand cleavage and DNA protein cross-links. Interestingly, the metal cannot readily enter cells in the +2 and +3 states which are not known to be carcinogenic.

Lead : Toxic effects similar to Cd^{2+}. Organolead compounds may cross the blood-brain barrier and attack the central nervous system. Pb^{2+} also inhibits heme synthetase which catalyzes the incorporation of iron in porphyrin and thus leads to anemia.

Mercury : The elemental form of mercury is reportedly non-toxic but Hg^{2+} and RHg^+ are highly toxic as they bind strongly to sulphhydryl groups in proteins — leading to neurological disease and kidney failure. Hatters in the 19th century used $Hg(NO_3)_2$ for cleaning felt hats and eventually became victims to it and were called "mad hatters".

Nature has invented a novel way to detoxify mercury by converting Hg(II) and RHgX to Hg(0) in some bacteria. The bacterial mercury resistance mechanism involves at least five gene products — MerT, MerP, MerB, MerA and MerR. The metalloregulatory protein MerR controls transcription of the *mer* genes. In absence of Hg(II), MerR binds strongly to DNA and prevents transcription of other mer genes. Hg(II), even in low concentrations (nM), preferentially and firmly binds to DNA-bound MerR and promotes some unwinding. The changed conformation now allows binding of RNA polymerases and transcription of the detoxifying genes begins. A 3 cys site in a trigonal plane in MerR appears to offer an unusual geometry specific for the binding of Hg(II) but not other soft metal ions like Zn(II) or Ag(I).

Molybdenum : The metal is antagonistic to copper and diminishes intestinal absorption of copper. Toxic effects include impaired growth, diarrhea and anemia (Molybdenosis). Skin diseases, loss of hair and gout-like syndromes are also reported.

Strontium-90 : Sr^{2+} accumulates in the mineralized portion of bone where it is retained for a long period and affects bone marrow function. Complexing ligands for Ca^{2+} like EDTA promote removal of Sr^{2+}.

Thallium : The stable Tl^+ ion, having a radius comparable to that of K^+, can substitute K^+ in many cases. Hence the metal acts as a neurotoxin.

Toxic metal cleanup by plants

Plutonium : Fast growth of nuclear power plants presents the threat of poisoning from plutonium and other radioactive metals, specially when the memory of Chernobyll disaster has not completely faded out. ^{239}Pu, for example, may be ingested as small particles of PuO_2 at the site of nuclear power plants. The ^{239}Pu may be transported by transferrin to different tissues where the high energy α-emitter can lead to malignancies of bone, liver, lung and lymph nodes. Plutonium is one of the most toxic metals, its maximm tolerated dose being 1.5 μg. Salts of diethylenetriaminepentaaccetic acid (DTPA) and other designed ligands which will encapsulate the eight coordinate Pu(IV) have been recommended as treatment.

Nature has also provided its own way of toxic metal cleanup from soil. Some plants can concentrate many heavy metals from soil upto several percent of their dry weight before they face death. Such hyperaccumulating plants use phytochelatins which are small peptides containing cysteine-glutathione; organic acids or amino acids such as histidine are also used by the plants. These complexing agents sequester heavy metal ions like Cd^{2+}, Cu^{2+} etc. Deaths of trees and heavy metal deposits in soil appear interrelated and this has prompted trials for development of plant species which would recover abandoned mines (Zn, Pb contaminated) and municipal waste sites (Cu, Hg, Pb). Mustard plant (*Brassica juncea*) and alpine pennycress (*Thlaspi caerulescens*) have shown promising results in this respect. Once the gene responsible for hyperaccumulation gets identified, it may be transferred to fast growing plants which are non-edible to small herbivorous animals. Even recovery of the metals may be possible from ashes of the plants.

[**Sec. 33.4.2** *Chemical speciation*]

Chemical Speciation

Studies on the toxic effects of different metals and nonmentals naturally present the task of detection and estimation of these elements in their common modes of occurrence in the environment. And obviously, these modes of occurrence of the elements in the environment are significantly different from those in which the elements occur in bulk in their minerals or from the pure compounds which we handle in the laboratory for their routine analysis. The essentiality and toxicity of an element is also intimately associated with the very nature of the chemical species in which it interacts with the living world. The identification of these chemical species — inorganic, organic or organometallic (molecule or ion) is summarily known as chemical speciation. By chemical species we mean any atom or chemically distinct group of atoms (molecule or ion or radical) in a given conformation which may be consistently present in different systems. An element often occurs in different chemical species in air, water, sediments and soil. The underlying reason is also not difficult to understand — the principal interacting agencies in these different phases are different. In air : action of solar radiation and dioxygen; in surface water : hydrolytic pattern, dissolved air, other organic/inorganic chemicals and bacteria; in underground water the geochemical composition of sub-soil layers and so on. Microbial action becomes prominent in soils and sediments in the ocean-bed, examples of which we have found in our foregoing discussion. The availability and mobility of an element among the biosphere depend critically on its speciation.

Sophisticated methods are necessary for proper chemical speciation of an element, mostly available in traces only. Electrochemical techniques, particularly anode stripping voltametry, solvent extraction, chromatography, ion-exchange and inductively coupled plasma-mass spectrometry are only a few to be mentioned in this connection. Chemical speciations of a few elements are briefly mentioned below.

Arsenic : In water, $HAsO_3^{2-}$ and $HAsO_4^{2-}$ (plus some $H_2AsO_4^-$) appear dominant. In upper parts of lakes, marshes etc. arsenate (V) is more important. With decline of dissolved oxygen with depth, arsenites (arsenate(III)) are present in significant amount. These are converted to insoluble As_2S_3 by the action of HS^-; the As_2S_3 collects in sediments. Also important in the sediments are the insoluble arsenates of Fe(III), Cr(III), Ba(II) and similar ions. These are partly methylated by bacteria to $(CH_3)_3As$. Organoarsenic compounds are also found in the body of aquatic animals and plants. Some As(V) in sediments is reduced by bacteria to As(III) and returned to water. Needless to say, all these processes are highly pH-dependent.

Arsenic in ground water is mostly As(III) originating from arsenopyrites. In soils, this is partly methylated by bacteria.

Copper : $Cu(OH)_2$ and $CuCO_3$ are the principal species in seawater, together with minor quantities of Cu^{2+}, $CuOH^+$ and $CuHCO_3^+$. In fresh water, the list is extended by humic-

Box continued next page

acid complexes. Non-filterable forms of copper bound to different substances can be selectively extracted by different reagents, for example,

Cu bound to carbonates : 1*M* sodium acetate
Cu bound to Fe-Mn hydrated oxides : 0.04 *M* $NH_3OH^+Cl^-$ in 25% acetic acid, 96°C.
Cu bound to organic matter : H_2O_2 in ammonium acetate and 20% HNO_3.
Cu in residual matter : HF + $HClO_4$.

In the filterable form, various forms may be distinguished by ion-exchange separation.

Cadmium : In water, Cd^{2+} (*aq*) may be present but with increase in pH, $Cd(OH)^+$ and $Cd(OH)_2$ become important. In sea-water, $CdCl^+$, $CdCl_2$, $CdCl_3^-$ etc. dominate in pH 7-9; $CdCO_3$ appears at higher pH. In reducing condition and also in polluted water, $CdHS^+$ and organocadmium compounds become significant. Humic acid complexes are also present appreciably in fresh water.

Aerosols contain appreciable amount of cadmium from smelters—the principal species being Cd, CdS, CdO and $Cd(OH)_2$. These ae partly returned to the soil through the action of rain.

Chromium : As mentioned earlier, chromium(VI) is toxic. This may enter water bodies from chromates added to water in cooling towers (to control corrosion) or metal plating baths etc. and subsequent discharges. Normal level of Cr(VI) in drinking water is 3–40 ppb—the permissible limit being 50 ppb.

Lead : In fresh water, $PbCO_3$ and $Pb(CO_3)_2^{2-}$ are the major species while in sea water $PbCl^+$ and $PbCl_2$ are main (40-80%) followed by $Pb(OH)^+$ and $Pb(OH)_2$ (10-25%). Carbonates increase with increase in pH between 6-8; at higher pH the hydroxy species dominate.

Lead is a major pollutant of the atmosphere, entering mainly from smelters and car exhausts. Smelters send PbS, $PbSO_4$, PbO etc. while car exhausts add a long list : Pb, PbO, PbClBr, Pb(OH)Cl, $PbSO_4$, $Pb_3(PO_4)_2$ together with R_4Pb and R_3PbCl and so on. With ageing of the aerosol, the halo compounds gradually change to oxy-compounds. Biomethylation also adds an appreciable amount of tetraalkyl lead to the atmosphere.

Lead carbonates (and basic carbonates) are found in sediments in rivers, lakes and oceans. These are gradually converted to PbS. Lead compounds are also sorbed by iron-manganese oxides.

Mercury : In fresh water, $Hg(OH)_2$ is the main form of mercury, together with some $Hg(OH)^+$, humic acid complex and others. In saline water, chlorocomplexes are the major species. Under anaerobic conditions, some mercury is precipitated as HgS. Part of this is returned to water by the action of O_2 and bacteria.

Methyl cobalamin and bacteria convert Hg(II) in water and sediments to $(CH_3)_2Hg$ and CH_3Hg^+. Volatile $(CH_3)_2Hg$ enters the atmosphere and join other volatile species like Hg(0), $HgCl_2$ and CH_3HgCl.

Selenium : Selenium(IV) as SeO_3 and $HSeO_3^-$, together with some selenates(VI), are present in both fresh water and sea water. Bio-methylation produces various species like $CH_3SeO_2(OH)$, $CH_3SeO(OH)$, $(CH_3)_2SeO_2$, $(CH_3)_3Se^-$, $(CH_3)_2Se_2$ and $(CH_3)_2Se$. Both bacteria (e.g., *Flavobacterium sp* and *Pseudomonas sp*) and fungi (e.g., Penicillium chrysogenum) carry out the methylation. S-adenosyl-methionine appear to be the principal methylating agent.

33.4.3 Metals in medicine

Introduction

The use of gold, mercury and other metals in medicine is described in the Ayurveda. Modern medical science also includes a large number of metal compounds for both diagnostic and therapeutic purposes. The present development of bioinorganic chemistry aims to add a new dimension to the use of metal compounds in medicine from an understanding at the atomic-molecular level.

The various applications of metals and metal compounds in medicine may be broadly classified as follows :

(i) *metal compounds as diagnostic aids;*

(ii) *chelation therapy*, which, in turn, may be subdivided into two classes

  (a) use of chelating agents or ligands to remove toxic metals from the body

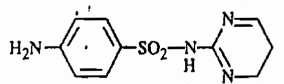
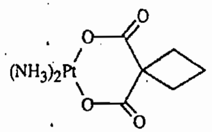
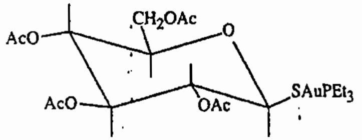
  (b) use of metal chelates.

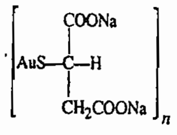
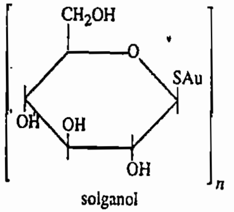
(iii) *miscellaneous metal compounds* in medicine.

A few metal compounds used in medicine are shown in Table 33.10.

TABLE 33.10

Some metal compounds used in medicine

Compound	Use
(i) Zinc oxide/carbonate	Antimicrobial and antifungal skin applications.
(ii) Ag(I) sulphadiazine  (sulphadiazine)	Antibacterial, particularly for severe burns.
(iii) *cis*-$[Pt(NH_3)_2Cl_2]$ (*cis*-diamminedichloro-platinum(II); *cis*-DDP or cisplatin)	Anticancer
(iv) Carboplatin  (carboplatin)	Second generation anticancer drug, less toxic
(v) Lithium carbonate	Treatment of manic-depressive behaviour.
 (vi) 2, 3, 4, 5-tetra-*O*-acetyl-1-1-β-D-thioglucose(triethylphosphine)gold(I)	Oral medicine for rheumatoid arthritis ("auranofin").
(vii) 2, 3-dimercaptopropanol (BAL, Fig. 26-XV)	Wilson's disease, heavy metal toxicity.
(viii) $K_2CaEDTA$	Wilson's disease, heavy metal toxicity.
(ix) $[Tc(CNR)_6]^+$ [R = $CH_2C(CH_3)_2OMe$]	Imaging heart abnormalities ("cardiolite").
(x) $[Gd(DTPA)(H_2O)]^{2-}$ (DTPA = diethylenetriaminepentaacetate anion; Table 26.3)	Improvement of magnetic resonance imaging scans.

Compound	Use
(xi)  myochrisin	Antiarthritic (injectable).
(xii)  solganol	Antiarthritic (injectable).

(i) *Metals and metal compounds for diagnosis*

The use of barium sulphate in imaging the gastrointestinal tract is quite old. We are familiar with the current techniques like ultrasonography, computerized tomography (CT) and magnetic resonance imaging (MRI) for detailed investigation on various organs. We have also seen how B-10 may be used in the detection of tumours (sec. 33.1.2; neutron capture therapy). Metal complexes containing radioactive nuclei help us a lot in such investigations on tumours, organs and other tissues where they are selectively bound. The choice of a radioisotope for such purposes lies with those nuclides which will not damage normal tissues :

(a) they should be short-lived;

(b) they should emit only low-energy γ-photons and no α or β particles;

(c) they should be available in the form of suitable compounds which can be easily ingested into the body of the patient; here the compound should be stable enough for distribution among affected parts.

(d) finally, the compound or its degradation product(s) must be easily excreted from the body.

Several radionuclides are available for the purpose (Table 33.11).

TABLE 33.11

Some common radionuclides used in medicinal diagnosis

Nuclide (Half-life)	Energy (keV)	Nuclide (Half-life)	Energy (keV)
^{57}Co (271 d)	836	^{123}I (13 h)	1230
^{67}Ga (78 h)	1001	^{169}Yb (32 d)	207
^{99m}Tc (6 h)	140	^{197}Hg (64 h)	159
^{111}In (67 h)	172,247	^{201}Tl (72 h)	135,167
^{113m}In (104 m)	392		

^{99m}Tc (section 29.5.2) is the most suitable diagnostic metal for this purpose — the emitted γ-photons can penetrate tissues but not damage them. The metal offers different oxidation states which are kinetically stable in the body (*in vivo*). Different Tc-complexes localize in specific tissues and cells; for example the species $[Tc(CNR)_6]^+$ (R = *t*-Bu, $CH_2CO_2Bu^t$ etc; Table 33.10) are selectively taken up by heart tissues and hence their use in heart-imaging. Phosphonates (contain the $—CH_2PO_3R^-$ group) have a high affinity for growing bones. The ^{99m}Tc methylenediphosphonate complex has been used in imaging bone malformities.

Magnetic resonance imaging (MRI) is based on NMR spectroscopy. The presence of paramagnetic metal ions in tissues brings about a difference in the water proton relaxation time around the tissue which can be probed by NMR spectroscopy. The distribution of metal ions in normal and abnormal tissues being different, this provides a means of diagnosis. Mn(II), Fe(III) and Gd(III) ions have been found to produce good proton-relaxation enhancements in humans. $[Gd(DTPA)(H_2O)]^{2-}$ (Table 33.10) has been successfully used in the diagnosis of brain tumours.

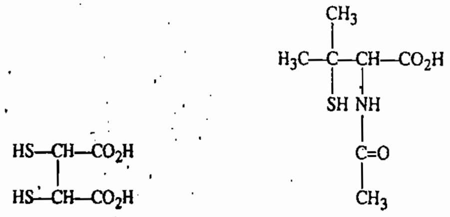
(ii) *Clinical use of chelating ligands*

Some chelating ligands used in medicine have been described in section 26.1.6 : BAL (26-XV); penicillamine and trien (26-XVI); desferrioxamine (26-XVII) and Na_2Ca(edta).

> **Q. 33.2** *EDTA or its commonly available disodium salt are not used in the treatment of heavy metal toxicity. Explain.*
>
> **Hint :** See section 26.1.6.

2, 3-Dimercaptosuccinic acid (33.XVIIIa) and 2, 3-dimercapto-1-propanesulphonate (unithiol) show the same efficiency against a range of heavy metals as BAL but they do not allow (unlike BAL) the passage of Hg(II) into brain. BAL forms a neutral complex with Hg(II) which is soluble in lipids and hence can easily permeate the brain cell-membranes (cell membranes are made up of protein and phospholipids). The complex of unithiol with Hg(II) is charged and hence lipid-insoluble; the water-soluble complex concentrates in the liver and kidneys before being excreted.

N-acetyl-D-penicillamine (33-XVIIIb) is less toxic than D-penicillamine and is the preferred treatment for removal of methylmercury(II) from brain.

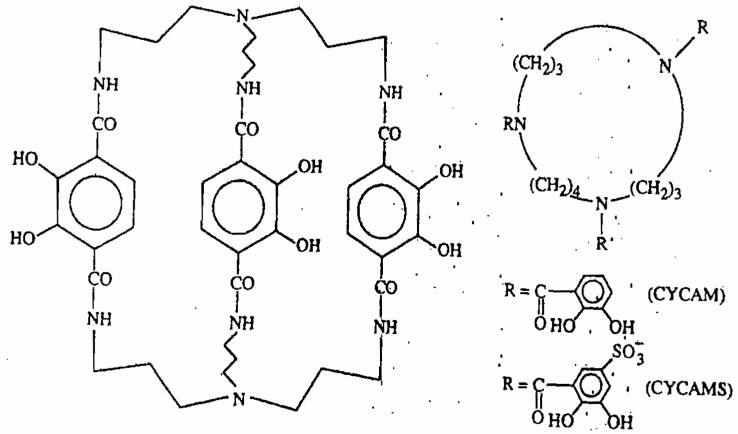


2, 3-dimercaptosuccinic acid (a)

N-acetylpenicillamine (b)

33-XVIII

Desferrioxamine B is used in the chelation therapy against unwanted iron deposit in the body (sec. 26.1.6). Here we use a natural siderophore—low molecular weight non-protein chelating ligands used by aerobic bacteria to make soluble and transport Fe(III). The siderophores chelate Fe(III) strongly with O-donors, the formation constants being greater than 10^{30} M^{-1}. They are usually of two types according to the nature of the chelating group — hydroxamate or catecholate. Desferrioxamine B contains three hydroxamate groups (Fig. 26-XVII) — the metal-free siderophore is used as injections as it is poorly absorbed in the gut. Some allergic responses in individuals are reported. Several synthetic analogues of this and other tris-catecholate containing siderophores have been synthesized (33-XIX) and are being tried as an alternative to desferrioxamine B.



33-XIX

However, the hydroxamates are hydrolyzed in the acid environment of the stomach and the catecholate siderophores form charged complexes which can trap some iron intracellularly. So scientists are looking for simpler and neutral ligands which will form neutral complexes with iron and being small, will be easily absorbed by the gut. 1, 2-dimethyl-3-hydroxypyridine-4-one has been found to be effective in removal of iron and is under clinical trial. The compound has the extra advantage of being orally active.

Choice of ligands in chelation therapy

Several points of concern appear important in the search for a ligand ideal for chelation therapy. Some of these are

(a) Identification of the site of action of the toxic element. In developing BAL, Sir Rudolph Peters observed that the arsenic in Lewisite inactivated the —SH groups of enzymes responsible for the metabolism of pyruvate.

(b) Identification of the donor groups which bind the metal — the hard soft acid base principle is often useful in this respect.

(c) Looking for chelating agents with similar donor groups as those in the binding site for the toxic metal.

(d) The resulting complex should be able to free the inhibited site and be able to carry the metal upto its excretion stage. This requires that the complex should be stable, should not be metabolized and be water soluble.

The action of BAL on Lewisite-affected enzyme is shown in Fig. 33.21,

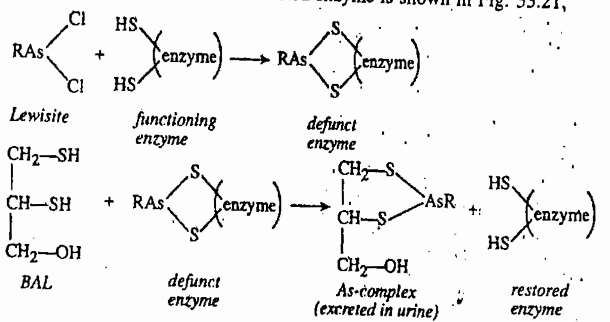


Fig. 33.21 : Action of BAL (schematic).

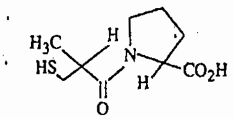
(e) The ligand should be non-toxic itself and should specifically bind the toxic metal. The tolerance limit of a ligand is conveniently expressed in terms of LD_{50} value (Table 33.12) which is the statistical estimate of the dosage level of the compound which results in 50% mortality in a large animal population. The desired LD_{50} for a compound is equal to or greater than 400 mg/kg.

TABLE 33.12

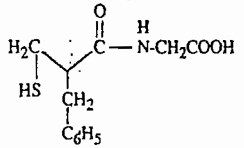
Some LD_{50} values of common chelating agents used in medicine

Compound	LD_{50} mg/kg	Species applied
$Na_2CaEDTA$	3800	rat
D-penicillamine	334	mouse
N-acetyl-D-penicillamine	1000	rat
Unithiol	2000	mouse
BAL	105	rat
Na-2, 3-dimercaptosuccinate	5000	mouse

Ligands may also be used to target metalloenzymes and inhibit their undesirable activity which appear at the root of many physiological disorders. For example, the zinc-enzyme ACE (angiotensin converting enzyme) may catalyze the cleavage of decapeptide (angiotensin I) to octapeptide (angiotensin II) which tends to raise the blood pressure (hypertensive). The hypertension may be controlled by EDTA or captopril which bind the zinc and controls hypertension (vasodilator). Similarly, the enzyme enkephalinases catalyzes cleavage of neuropeptides in enkephalins to inactive fragments, resulting in loss of pain level control. Thiorphan binds to the zinc and deactivates the enzyme, acting as an analgesic.


captopril

33-XX


thiorphan

33-XXI

(iii) *Coordination compounds as drugs*

Therapeutic uses of coordination compounds are numerous, some of which we have already mentioned in connection with respective metals, for example, gold complexes as anti-arthritis and platinum complexes as anti-cancer agents. The efficacy of many organic drugs is also enhanced through metal binding, for example, the painkiller ibuprofen is more effective as its zinc complex; the anticancer drug bleomycin is activated as an Fe(II) complex. For space limitation, we shall mention only one or two representative examples in this category.

Anticancer drugs

Cis-diamminedichloroplatinum(II) (*cis* DDP, cisplatin) is the best-known example of the application of coordination compounds in medicine. In the mid-1960's, Rosenberg and his collaborators (Michigan State University) were studying the effects of electric fields on the growth of *E. coli* cells in culture. They observed that the electric field inhibited normal division of the cell but not their growth. The cells showed an unusual filamentous growth of the bacteria (to about 300 times their normal length). The origin of this phenomenon was ultimately traced to the formation of platinum(II and IV) amminehalo complexes from the platinum electrode used and the NH_4Cl buffer in the medium. After much investigation it was established that *cis*-DDP was responsible for the inhibition of cell division. Through years of tenacious investigations and series of rigorous screenings it was finally established as an anticancer agent in 1979. It is not active against all types of cancers, but is particularly effective against testicular cancers and active against cancers of ovary, lung, bladder, head, neck and cervix.

Cisplatin is administered as i.v. injection every few weeks—solutions are usually given in physiological saline (NaCl). Kidney toxicity, nausea, vomitting and drug resistance are some of the adverse side effects of the drug. Kidney toxicity can be largely avoided by administering large amount of water by i.v. injection to the patients, together with osmotic diuretic agents (like D-mannitol). This will flush the kidney and reduce the toxicity. Other side effects can be treated symptomwise. Chemoprotector drugs like sodium diethyldithiocarbamate are also used to reduce the toxicity, particularly to the kidneys and bone marrow.

The mode of action of cisplatin rests on its capacity to bind to DNA and block replication. Since the chloride ion concentration in extracellular fluids is large, the chloride ligands in cisplatin are not significantly substituted by water outside the cell. The chloride concentration being much less inside the cell, the chloride ligands in cisplatin are replaced by water, forming products like $[Pt(NH_3)_2(OH_2)_2]^{2+}$ and $[Pt(NH_3)_2(OH)_2]$. The Pt(II) now binds to two nitrogen atoms (N-7) of two adjacent guanine bases—mostly in the same strand, to form a chelated intrastrand cross-link (Fig. 33.22). Interstrand cross-links also occurs to a lesser extent; similarly, interaction with adenine bases are also found to be small.

The interaction of platinum with adjacent guanine bases may be due to the strongly preferred square planar coordination by Pt(II) (d^8). The cross linking sharply changes the angle between the planes of the base molecules which were formerly parallel. The axis of the helix kinks by an angle ranging from 40°-70° (estimated) toward the major groove. This kink essentially sterically prevents replication of the DNA and thus inhibits growth of the tumour cells. *Trans*-DDP can form intrastrand cross-links, but its geometry will not permit bonding with adjacent bases. The predicted bend angle from molecular modelling is only ~18°.

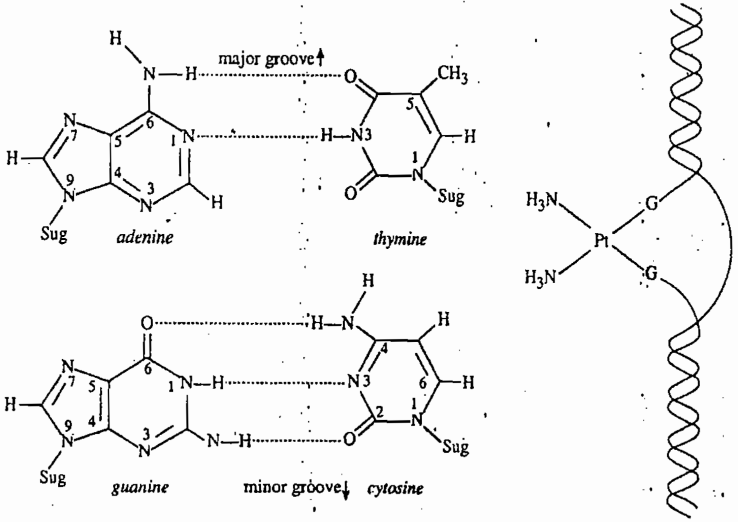


Fig. 33.22 : Intrastrand cross-link by cisplatin in DNA (schematic). H-bonded base-orientations are shown on the left. (Also see Fig. 7.45)

[Sec. 33.4.3 *Metals in medicine*]

In DNA replication, the H-bonds linking the two strands of a DNA molecule break apart; each strand now collects nucleotides (the sugar-phosphate moiety) from the nucleus to synthesize a complementary strand. This produces two daughter molecules, each identical to the mother DNA. During transcription, the DNA acts as a template for the synthesis of messenger RNA which carries the genetic code.

It seems that cisplatin disturbs all these processes by blocking a strand in the DNA. The DNA polymerase enzymes normally move along a strand to assemble its complements. But the sharp kink produced by binding of cisplatin presumably do not sterically allow the enzymes to pass the coordinated site and function normally.

The body has evolved sophisticated DNA repair mechanisms to restore its normal function. A "damage recognition protein" binds to the abnormal DNA at the damage site. The damaged site may be expelled by excision — the sugar-phosphate backbone on either side of the damaged part gets hydrolyzed and removed. The remaining strand is now used for new DNA synthesis.

Probably related to this repair mechanism, cisplatin-treated patients develop drug resistance, that is, tolerance to the drug, after repeated doses of drug therapy. Other factors, of course, contribute to such drug resistance which is still not clearly understood. For example, an S-donor ligand, a soft base favouring Pt(II), may intervene the intra-strand cross-linking. It is known that *cis*-platin-treated cells show higher concentrations of —SH groups, particularly in glutathione, a tripeptide containing cystein. The efficiency of the repair mechanism may also be enhanced to arrest the action of the drug.

Second generation platinum anticancer drugs with less side effects have been developed, for example carboplatin (Table 33.10) diammine(1,1-cyclobutanedicarboxylato)platinum(II), which is more slowly aquated than cisplatin. Several metallocenes and their halides, notably those of Ti, V, and Fe are also reported to show significant activity against animal tumours. The compounds include $[(C_5H_5)_2TiX_2]$ (X = Cl, Br, Cl_3CO_2); $[(C_5H_5)_2MCl_2]$ (M = V, Nb, Mo) and $[(C_5H_5)_2Fe]^+$ salts.

Q. 33.3 *Au(III), isolectronic with Pt(II), forms isostructural complexes with the latter. But Au(III) compounds are not used as anticancer agents. Comment.*

Hint : (i) Au(III) complexes readily undergo ligand substitution reactions.

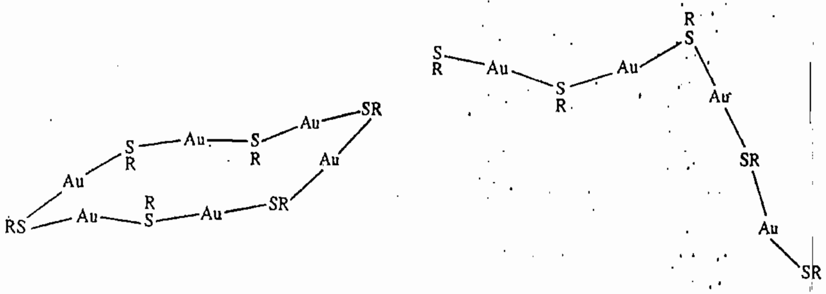
(ii) Aqua complexes of Au(III) are highly acidic.

(iii) Au(III) complexes are oxidizing in nature. $AuCl_4^-$ can oxidize methionine and cystine disulphides.

(iv) *cis*-diamminedihalogold(III) has not been characterized. $[Au(NH_3)_3X]^{2+}$ reacts with X^- to give only the trans product.

Antiarthritic drugs

Modern use of gold in medicine (chrysotherapy) was initiated in 1929 by the French physician Forestier who used gold(I) thiolates for the treatment of rheumatoid arthritis. Myochrisin (sodium aurothiomalate), solganol (aurothioglucose) are now used as intramuscular injection in curing arthritis. The compounds are polymeric involving chains and rings (33-XXII). (Table 33.10), Auranofin another potential antiarthritic agent, is administered orally. The mode of action of these antiarthritic gold drugs may involve binding of the gold(I) to —SH and —S—S— units of proteins, for example, the blood serum albumin. The protein carries the gold compounds throughout the body. Prolonged treatment is necessary before any beneficial effect is observed. But these are the only class of pharmaceuticals known to halt the progreses of rheumatoid arthritis.



33-XXII

Lithium compounds in manic depression

Lithium carbonate is widely used in the treatment and prevention of manic-depressive behaviour. A 0.5 to 2.0 mM concentration range in blood is found to be effective, outside which it may be either ineffective or toxic. Doses may vary from 250 mg to 2g per day.

In the manic state, neuronal communication becomes high. One neurotransmission path is based on inositol 1, 4, 5-triphosphate and 1, 2-diacylglycerol. According to one theory, the Li^+ ion possibly binds to inositol phosphates whereby their degradation to inositol is reduced. This, in turn, lowers the content of inositol-containing phospholipids and suppresses neuronal communication. However, this theory does not explain the antidepressive action of the drug. It is also possible that Li^+ disturbs neurotransmission by inhibiting the formation of the key signalling molecule adenosine monophosphate. Inormation transduction involves a class of guanosine triphosphate (GTP) binding proteins (G-proteins). Li^+ may displace Mg^{2+} from GTP or from other protein-binding sites—thereby hampering their required activation.

SUMMARY

Essential elements. About thirty elements appear essential to some form of life. The bulk or constituent elements are H, O, C, N, Ca, P, Na, K, S, Cl and Mg (in their decreasing order of abundance); these are required in the living body in relatively larger amounts — about 1-10^4 gmole in a 75 kg adult human.

B, Si, Sn, As, Se, F, Br, I and the transition elements V, Cr, Mo, W, Mn, Fe, Co, Ni, Cu and Zn occur in very low (10^{-4} gmole or less in a 75 kg adult) or moderate (10^{-1} gmole); these are classed as essential trace elements. Fe, Cu and Zn top this list. Elements present in exceedingly small amounts are called ultratrace elements, e.g., Mn, Mo, Co, Ni and V.

The essentiality of an element is determined by following its involvement in one or more essential life processes required for maintainance of living mechanisms.

Metalloproteins and metalloenzymes. Metals, bulk and trace, are components of different biomolecules — both proteins and nonproteins. Metalloproteins serve a variety of functions like

(i) *electron transport*, e.g., cytochrome, Fe—S proteins and blue copper proteins.
(ii) *dioxygen management*, e.g., hemoglobin, myoglobin, haemerythrin and haemocyanine.
(iii) *metal management*, e.g., ferritin, transferrin and ceruloplasmin.

In many cases it is possible to remove the metal atom from its site. The metal-deficient protein is called the apoprotein.

A major class of metalloproteins act as catalysts in various life processes — these are called metalloenzymes which contain the metal at their active site.

They are of different types according to their function :

(i) *Hydrolases* (hydrolysis) : Phosphatases, Aminopeptidases, Carboxypeptidases.
(ii) *Oxidoreductases* (redox) : Oxidases, Reductases, Superoxide dismutases, Hydrogenases.
(iii) *Isomerases and synthetases* (isomerisation) : Vitamin B_{12} enzyme.

The activity of a metalloprotein is jointly contributed to by the nature of the metal ion and the polypeptide environment provided by the protein. The main role of the protein is to provide the coordinated ligands and provide a protein environment around th metal ion. Hydrophobic pockets or H-bonding facilities provided by the protein may facilitate binding of the substrate. The protein may also provide a suitable path of guided entry of the substrate to the active metal site. Proteins also facilitate the transport and storage of metal ions.

Metals play a vital structural role by stabilizing the biomolecule. They may also promote essential conformational changes in proteins necessary for initiating the enzyme activity. They can modify the function of a biomolecule and also act as cofactors.

Enzymes are biocatalysts synthesized by Nature in living cells. They are very specific in their action. Though mostly protein in nature, some RNA molecules (non-protein) can also function as enzymes.

The activity of a number of enzymes depends upon a non-protein entity. Such enzymes are referred to as a *holoenzyme* which consists of an *apoenzyme* (protein part) and a *coenzyme* (non-protein part). When the non-protein moiety is lightly bound to the apoenzyme, it is called a *prosthetic group*. A loosely bound coenzyme is also called a *cofactor*.

The metal ions in metalloenzymes play structural role as well as a site for assembly of the reactants. They can also regulate the function of a coordinated ligand and serve as redox centres.

Iron-proteins mostly belong to four categories :

(i) *Iron-porphyrin proteins*; e.g., hemoglobin, myoglobin, cytochrome P_{450}. All of them contain one or more iron-porphyrin units. They are mostly involved in dioxygen transfer and storage or electron transfer.

(ii) *Non-heme iron proteins*, e.g., transferrin, ferritin and hemosiderin. They are mostly involved in iron transfer and storage.

(iii) *Non-heme diiron oxobridged species*, e.g., hemerythrin, methane monooxygenase and ribnucleotide reductase.

(iv) *Non-heme proteins containing Fe—S clusters* : e.g., nitrogenase, ferredoxins and rubredoxins.

In hemoglobin, a high spin Fe(II) is coordinated by the four N-atoms of protoporphyrin IX and the fifth coordination site is bound to the N-atom of an immidazole group in the histidine residue F8. This comprises the heme unit which is encapsulated in a water-repellant pocket of protein chains (globin). Myoglobin has a different protein chain and is used to store O_2 in muscle tissue for controlled release as and when necessary.

In absence of O_2, the the Fe(II) in hemoglobin is about 36-40 pm out of plane of the N-atoms. Upon binding O_2, the iron atom moves with ~13 pm of the plane. The O_2 is attached in a bent position and the O—O stretching band. (~1105 cm^{-1}) is close to the value for a superoxide ion. Formation of the $Fe^{III}—O_2^-$ adduct reduces the effective size of the iron atom which can now move close into the plane of the porphyrin ring.

Copper enzymes. Copper forms the active metal centre in a number of vital enzymes. *Ceruloplasmin* (8 Cu) is an oxidase responsible for release of iron from liver. *Cytochrome oxidases* (2Cu + 2Fe-heme) catalyze reduction of dioxygen to water. *Hemocyanin* (2Cu) is the dioxygen carrier in the blood of molluscs and arthropods.

Zinc enzymes. Zinc forms more than 300 vital enzymes and offers an ideal metalobiosite owing to its potential Lewis acid character and redox insensitivity. *Carbonic anhydrase* catalyzes the hydration of CO_2 as a step in CO_2 management. *Carboxypeptidases* catalyze the degradation of proteins by cleaving peptide bonds as a part of the digestive system.

The Na^+-K^+ pump. Reduction of O_2 to H_2O in life processes requires considerable amount of charge transport across the cell membranes. This is mostly accomplished by H^+ and the metal ions Na^+, K^+, Ca^{2+}, Mg^{2+}. In *active transport*, the ions are "pumped" across the cell membrane at the cost of ATP energy. Various ion-pumps perform this job. The Na-K ion pump works with a membrane-bound enzyme Na^+-K^+ ATPase which catalyzes the movement of Na^+ and K^+ ions in opposite directions. The concentration of K^+-ions is higher (~20 times) inside cells while that of Na^+ ions is higher outside (~10 times).

In *passive transport*, the metal ion may (i) either pass through an ion-permeable channel through the membrane or (ii) be transported through *ionophores*—naturally occurring molecules which can encapsulate a metal ion from several coordination sites and at the same time provide an outside "coating" of organic molecule. Valinomycin and nonactin are such ionophores resembling macrocyclic crown ether ligands.

Deficiency or excess of the essential elements leads to malfunctioning of various organs as well as specific ailments. Deficiency of calcium results in underdevelopment of boney skeleton while its excess may promote calcification of tissues. Deficiency or excess of copper may produce *Wilson's disease* : copper is deposited in the body (liver, brain, kidney). Patients may be treated with a copper chelating ligand like penicillamine.

Chelation therapy : Chelating ligands, for example, Na_2Ca-edta, penicillamine, 2, 3-dimercaptosuccinic acid etc. may be used to remove excess of toxic metals from the body. Accumulated iron in thalassemia patients in removed by desferrioxamine.

Preformed metal chelates are also effective against many diseases. *Cis*-diamminedichloroplatinum(II) (*cis*-DDP or cisplatin) is an effective anticancer. Gold thiolate complexes (e.g., Auranofin) are useful anriarthritic agent.

EXERCISE

1. *Name an essential trace element in each of the following category : (a) p-block of the periodic table; (b) second transition series; (c) halogens.*
2. *Ti and Zr, in spite of their relatively high abundance, are not found in living cells—comment.*
3. *The first row transition elements (except Ti) are all very abundant in living systems but second or third row transition elements are almost absent (except Mo and W). Suggest an explanation.*
4. *Name the element(s) or compound(s), typicaly "inorganic", which are associated with the following functions of living systems (a) respiration; (b) muscle contraction; (c) control of pH in blood; (d) cell division; (e) blood pressure and blood coagulation control.*

   (a) Fe, Cu; (b) Ca, Mg; (c) Zn, CO_2; (d) Ca, Fe, Co; (e) Na, Cl, Ca, NO.

5. *Select the metal ion(s) which are expected to favour coordination from (i) O-donors; (ii) S-donors; (iii) O, N, S donors.*

   Zn^{2+}, Ca^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}.

6. *What are apoproteins and holoproteins?*

   The metal from a specimen of carbonic anhydrase was removed by 1, 10-phenanthroline. Co(II) was now added, when 50% activity of the enzyme was restored. d-d spectra of the new product indicated the presence of 5-coordinate Co(II) in acid and tetrahedral Co(II) in basic (active) form. Comment.

7. *Suggest alternative metal ions which may be used to study proteins containing Mg^{2+} and Ca^{2+}.*

   [**Ans. :** Mn^{2+} for Mg^{2+} (EPR); Tb^{3+} for Ca^{2+} (fluorescence)]

8. *What information(s) are supplied by the following observations on oxyhemocyanin?*

   (a) *ν_{O-O} in the range 744–752 cm^{-1} (resonance Raman spectroscopy).*

   (b) *Absorption bands at 580 nm ($\varepsilon = 10^3\ M^{-1}\ cm^{-1}$) and 340 nm ($\varepsilon = 2 \times 10^4\ M^{-1}\ cm^{-1}$).*

   (c) *No EPR signal nor magnetic splitting in the Mössbauer spectrum. $-J < 300\ cm^{-1}$. Cu—Cu distance 3.5–3.7 Å (EXAFS).*

   [**Hint :** (a) O_2 molecule bound symmetrically as peroxide. (b) intense absorptions due to LMCT. (c) strong antiferromagnetic coupling of the bridged copper ions.

9. *Give very short answers to the following :*

   (a) *Give an example of a naturally occurring M—C σ-bonded species.*

   (b) *Name an essential trace element of the 4th period which acts as an "anti-oxidant".*

   (c) *What is the O_2-carrier in lobsters and crab?*

   (d) *What is the nature of the metal centre in (c)?*

   (e) *Which metal centres are usually present in nitrogen-fixing enzymes?*

   (f) *What is the nature of the active site in the O_2-storage protein in human?*

   (g) *Name a non-heme iron protein and state its function.*

   (h) *Write down the overall reaction catalyzed by cytochrome c oxidase.*

   (i) *The average O. N. of Fe in 4Fe—4S proteins is +2.5.*

   (j) *Name a 'transport antibiotic'.*

   (k) *Name the metal whose deficiency is related to Menke's disease.*

   (l) *Which oxidation state of chromium is toxic?*

   (m) *Tl^+ readily acts as a neurotoxin—explain.*

   (n) *Which metal is associated with "mad hatters" of the 19th century?*

   (o) *What are the common forms of arsenic contamination in water?*

   (p) *What is the importance of gadolinium as a diagnostic aid?*

   (q) *Name the enzyme involved in the build-up of a higher concentration of K^+ ions inside cells.*

   (r) *Name an enzyme containing tungsten.*

   (s) *Sodium nitroprusside acts as a vasodilator—explain.*

   (t) *Name an enzyme present in methanogenic bacteria. What is the overall reaction catalyzed by the enzyme?*

10. *Give moderately short answers to the following questions.*

    (i) *What is neutron capture therapy?*

    (ii) *What is the nature of the dioxygen binding site in hemoglobin? How do you conclude that the protein part of hemogloboin is also involved in the reversible binding of O_2?*

    (iii) *How does cisplatin act as an anticancer agent?*

    (iv) *What is fluorosis?*

    (v) *Give two examples of use of chelating ligands in the treatment of metal toxicity.*

    (vi) *Mention the special features of zinc which make it an ideal metallobiosite.*

    (vii) *Explain why Pd(II) and Ni(II) are not likely targets for trial anticancer compounds.*

    [**Hint :** Ni(II) does not torm square planar complexes with weak ligands. The Pd(II)-complex would undergo much faster ligand substitution reactions; ~10^5 times compared to cisplatin.]

    (viii) *Describe the nature of the active site in cytochrome P-450. Why is the enzyme so named?*

(ix) *"A small molecule model of the functional site of an enzyme may accurately reproduce the physicochemical properties of a site but may not be able to respond in a truly functional manner."—justify.*

[**Hint :** The model site lacks the environment of the folded protein chain and the influence of this environment on the function.]

(x) *When the oxidized form of an electron-transfer protein is reduced with $[Cr(H_2O)_6]^{2+}$, the Cr(III) is found to be tightly bound to the protein — explain.*

[**Hint :** $[Cr(H_2O)_6]^{3+}$ is kinetically very inert. Exchange rates for water molecules from the first coordination spheres drops sharply : K_1 (25°C) = $10^9\ s^{-1}$ for Cr^{2+}; = $2 \times 10^{-6}\ s^{-1}$ for Cr^{3+}.

11. At a Cys_2His_2 *site,* Zn^{2+} *binds approximately two orders of magnitude more tightly than does* Cd^{2+}*; but at a* Cys_4 *site,* Cd^{2+} *binds two to three orders of magnitude more tightly. Comment.*

[Cys = Cysteine (S-donor); His = Histidine (N-donor)].

[**Hint :** Cd^{2+} is softer than Zn^{2+}.]

12. (a) *The metal zinc can play both structural as well as catalytic roles in proteins. What distinctive feature in its coordination environment may be used to distinguish between these two functions?*

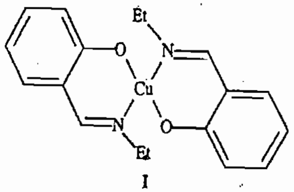
(b) *Distinguish the structural and catalytic zinc sites in the following metalloproteins.*

$Zn(Cys)_4$, $[Zn(Cys)(His)]$, $[Zn(His)_3(H_2O)]$, $[Zn(Cys)_2(His)(H_2O)]$, $[Zn(Cys)_2(His)_2]$, $[Zn(His)_2(Glu)(H_2O)]$.

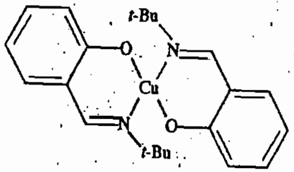
[**Hint :** A coordination position should be always open at a catalytic zinc site. In the resting enzyme, this coordination site may be occupied by a water or hydroxide ligand. The latter may function directly or may be displaced by the substrate or both.

In structural sites, the tetrahedral coordination site of each metal ion are saturated with ligands from the protein. The presence of two or more cysteinate ligands strongly suggests a stable tetrahedral coordination with little urge for expansion.]

13. *Which of the two copper(II) complexes shown below will be more difficult to reduce and why?*



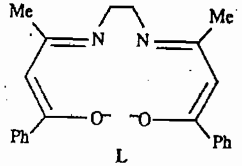
I



II

[**Hint :** Cu(I), d^{10}, is expected to prefer tetrahedral coordination. Cu(II) complexes are typically square planar (with distant axial ligands). The bulky group in **II** is more suited to tetrahedral environment, making reduction to Cu(I) easier.]

14. *A Schiff base is the imine product from the condensation reaction of a primary amine and a carbonyl compound, e.g.,* L. *If a Co(II) complex of* **L** *is allowed to react with* O_2 *in a coordinating solvent (e.g., DMSO) or in a non-coordinating solvent in presence of pyridine, rapid and reversible uptake of* O_2 *takes place at 0°C or below giving* $[Co(L)(py)O_2]$.

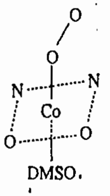


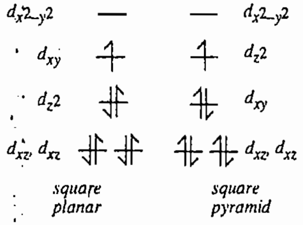
L

In absence of pyridine, the reversibility is lost and an oxy-bridged dimer is obtained. Explain.

[**Hint :** The presence of the base pyridine (or the coordinating solvent) changes the coordination environment around Co(II) from square planar to square pyramid. This change is vital for end-on coordination of O_2. In the square planar geometry, the HOMO is a d_{xy} orbital which cannot interact with an O_2 approaching along the z-axis. Addition of the base raises the d_{z^2} orbital, which is well-suited for interaction.

X-ray crystal structure of $[Co(L)(DMSO)O_2]$ shows a Co—O—O angle 125° and O—O distance 126 pm consistent with $Co(III)—O_2^-$.





15. (a) Zn^{2+} *is common in several non-redox enzymes while* Cu^{2+} *and* Fe^{2+} *are comon in most redox enzymes — comment.*

(b) *CuZnSOD remains almost fully active even when the zinc is replaced by other bivalent metals — explain.*

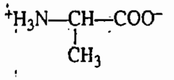
(c) *Give specific examples to illustrate the application of the SHAB principle in the choice and uptake of metals in the biosystem.*

(d) *Lozenges containing* $Cr^{III}(pic)_3$ *(pic = picolinate) are consumed in many countries (believed to reduce fat). Do you think this may lead to any toxic effect?*

(e) *Name the elements whose deficiency/excess may be related to the following ailments :*

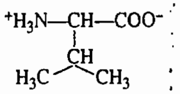
(i) bronze diabetes; (ii) tetany; (iii) cretinism.

Some common amino acids mentioned in the text



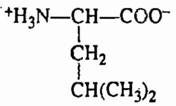
$^{+}H_3N—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COO^-$

alanine (Ala)



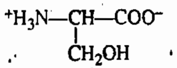
$^{+}H_3N—\underset{\displaystyle H_3C\ \ CH\ \ CH_3}{\underset{|}{CH}}—COO^-$

valine (Val)



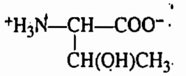
$^{+}H_3N—\underset{\displaystyle \underset{\displaystyle CH(CH_3)_2}{\underset{|}{CH_2}}}{\underset{|}{CH}}—COO^-$

leucine (Leu)



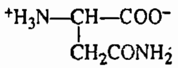
$^{+}H_3N—\underset{\displaystyle CH_2OH}{\underset{|}{CH}}—COO^-$

serine (Ser)



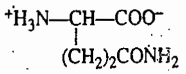
$^{+}H_3N—\underset{\displaystyle CH(OH)CH_3}{\underset{|}{CH}}—COO^-$

threonine (Thr)



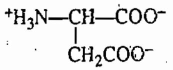
$^{+}H_3N—\underset{\displaystyle CH_2CONH_2}{\underset{|}{CH}}—COO^-$

asparagine (Asn)



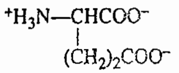
$^{+}H_3N—\underset{\displaystyle (CH_2)_2CONH_2}{\underset{|}{CH}}—COO^-$

glutamine (Gln)



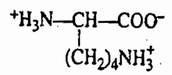
$^{+}H_3N—\underset{\displaystyle CH_2COO^-}{\underset{|}{CH}}—COO^-$

aspartate (Asp)

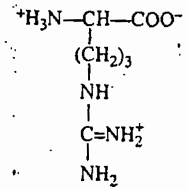


$^{+}H_3N—\underset{\displaystyle (CH_2)_2COO^-}{\underset{|}{CH}}COO^-$

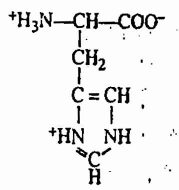
glutamate (Glu)



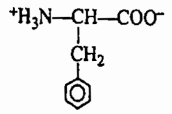
lysine (Lys)



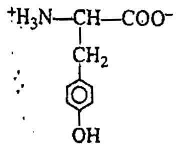
arginine (Arg)



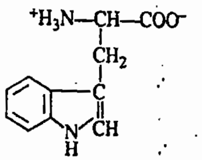
histidine (His)



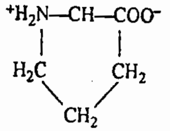
phenylalanine (Phe)



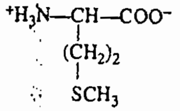
tyrosine (Tyr)



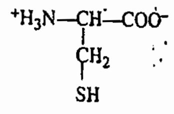
tryptophan (Trp)



proline (Pro)



methionine (Met)



cysteine (Cys)

Appendix

Some common structural types adopted by different compounds

Hydrides		
MH	M = Cr	NiAs (p 464)
MH_2	M = Ti, Cr, La, Er, Gd	Fluorite (p. 150, 463)
	= Mg	Rutile (p. 150, 463)
Oxides		
M_2O	M = Li, Na, K, Rb	Antifluorite (p. 463)
	M = Cs	Anti-$CdCl_2$ (see below)
MO	M = Mg, Ca, Sr, Ba V, Mn, Co, Ni, Cd Nb, Mo, Ta, Zr La, Eu, Ce, Yb, Pu	NaCl (Fig. 6.8, Part-I)
	M = Be, Zn	Wurtzite (p. 147, 463)
MO_2	M = Zr, Bi, Ce, U	Fluorite
	M = Ge, Sn, Pb V, Cr, Mn Nb, Mo, Ru, Rh, Pd Ta, Re, W, Os, Ir, Pt	Rutile
Hydroxides		
$M(OH)_2$	M = Mn, Fe, Co, Ni, Zn, Cd	Anti-$CdCl_2$
Fluorides		
MF	M = Ag	NaCl
MF_2	M = Ca, Sr, Ba, Pb Cd, Ag, Hf, Eu	Fluorite
	= Mg, V, Cr, Fe, Co, Ni, Cu, Zn	Rutile
Chlorides		
MCl	M = Li, Na, K, Ag	NaCl
	= Cs, Tl, NH_4	CsCl (Fig. 6.9, Part-I)
MCl_2	M = Cr	Rutile
	= Mg, Mn, Fe, Co, Ni, Cd	$CdCl_2$ (see below)
	= Ti, V	CdI_2 (see below)
Bromides		
MBr	M = Li, N, K, Ag	NaCl
	= Cs, Tl	CsCl
MBr_2	M = Mg, Ti, V, Cr, Fe, Cd	CdI_2

contd. next page

Iodides		
MI	M = Li, Na, K	NaCl
	= Cs	CsCl
MI_2	M = Mg, Ti, V, Cr, Fe, Cd	CdI_2
Sulfides/Selenides		
M_2S	M = Li, Na, K	Anti-fluorite
MS	M = Mg, Ca, Sr, Ba, Pb, Cd, Mn, Zr, La, Eu, U, Th, Pu	NaCl
	M = Co	NiAs
	M = Be, Mn, Zn	Zinc blende (p. 463)
MS, MSe	M = Mn, Zn	Wurtzite
	M = V, Cr, Fe, Ni	NiAs
MSe, MTe	M = Zn, Cd, Hg	Zinc blende
MS_2	M = Ta	$CdCl_2$
MS_2, MSe_2	M = V, Zr, Hf, Pt, Sn	CdI_2
Nitride, Phosphide, Arsenide		
MN	M = Sc, Ti, V, Cr, Zr, Hf, Nb, Re La, Pu	NaCl
	M = B, Al, Ga, In	Wurtzite
MP, MAs	M = B	Zinc blende
MP, MAs, MSb	M = Al, Ga, In	Zinc blende
MAs, MSb	M = Mn, Fe, Ni	NiAs

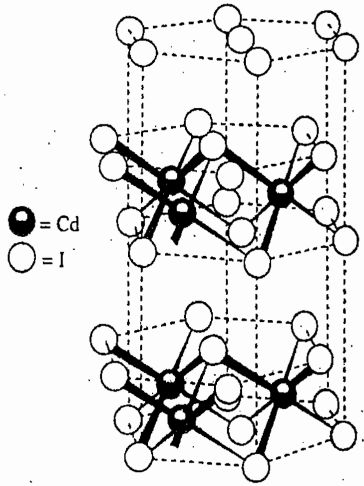


Fig. A-1
Structure of CdI_2

Hexagonal close-packing of I atoms with Cd atoms in octahedral sites.

In $CdCl_2$, the individual composite layers are identical but their arrangement gives rise to cubic close packing of Cl atoms.

List of sourcebooks

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2. Atkins, P. W. ... Physical Chemistry (Oxford)
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43. Winter, M.J. ... d-Block Chemistry (Oxford)

Periodic Table of the Elements

(with ground-state electronic configurations)

Table of Standard Atomic Weights given separately

Periods ↓ / Groups →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $[He]2s^1$	4 **Be** $[He]2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $[Ne]3s^1$	12 **Mg** $[Ne]3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $[Ar]4s^1$	20 **Ca** $[Ar]4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $[Kr]5s^1$	38 **Sr** $[Kr]5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $[Xe]6s^1$	56 **Ba** $[Xe]6s^2$	57 * **La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $[Rn]7s^1$	88 **Ra** $[Rn]7s^2$	89 ** **Ac** $6d^17s^2$	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Uun**	111 **Uuu**	112 **Uub**						

*	58 **Ce** $4f^15d^16s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
**	90 **Th** $6d^27s^2$	91 **Pa** $5f^25d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^86d^17s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

*/** The ground-state configurations for some lanthanide and actinide elements are uncertain

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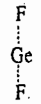
Relative Atomic Masses (^{12}C = 12.000)

Actinium	(227.03)	Hafnium	178.49	Radium	(226)
Aluminium	26.982	Hassium	(269)	Radon	(222)
Americium	(241.06)	Helium	4.003	Rhenium	186.21
Antimony	121.76	Holmium	164.93	Rhodium	102.91
Argon	39.948	Hydrogen	1.00794	Rubidium	85.47
Arsenic	74.922	Indium	114.82	Ruthenium	101.07
Astatine	210	Iodine	126.904	Rutherfordium	(261)
		Iridium	192.217		
Barium	137.33	Iron	55.845	Samarium	150.4
Berkelium	(249.08)			Scandium	44.96
Beryllium	9.012	Krypton	83.80	Selenium	78.96
Bismuth	208.98	Lanthanum	138.91	Silicon	28.086
Bohrium	(264)	Lawrencium	(262)	Silver	107.868
Boron	10.811	Lead	207.19	Sodium	22.9898
Bromine	79.904	Lithium	6.941	Strontium	87.62
		Lutetium	174.97	Sulphur	32.066
Cadmium	112.411	Magnesium	24.305	Tantalum	180.95
Calcium	40.08	Manganese	54.938	Technetium	(98)
Californium	(251)	Meitnerium	(268)	Tellurium	127.60
Carbon	12.0107	Mendelevium	(258)	Terbium	158.92
Cerium	140.12	Mercury	200.59	Thallium	204.38
Cesium	132.905	Molybdenum	95.94	Thorium	232.04
Chlorine	35.453	Neodymium	144.24	Thulium	168.93
Chromium	51.996	Neon	20.18	Tin	118.71
Cobalt	58.933	Neptunium	(237)	Titanium	47.87
Copper	63.546	Nickel	58.69	Tungsten	183.84
Curium	(247)	Niobium	92.91		
Dysprosium	162.50	Nitrogen	14.0067	Ununnilium	(269)
		Nobelium	(259)	Unununium	(272)
				Ununbium	(277)
				Uranium	238.03
Einsteinium	(252)	Osmium	190.23	Vanadium	50.942
Erbium	167.26	Oxygen	15.9994		
Europium	151.96	Palladium	106.42		
		Phosphorus	30.97	Xenon	131.29
Fermium	(257)	Platinum	195.08		
Fluorine	18.998	Plutonium	(244)	Ytterbium	173.04
Francium	(223)	Polonium	(210)	Yttrium	88.91
		Potassium	39.098		
Gadolinium	157.25	Praseodymium	140.91		
Gallium	69.72	Promethium	(145)	Zinc	65.39
Germanium	72.61	Protactinium	231.04	Zirconium	91.22
Gold	196.967				

(Values in parenthesis refer to most stable isotopes).

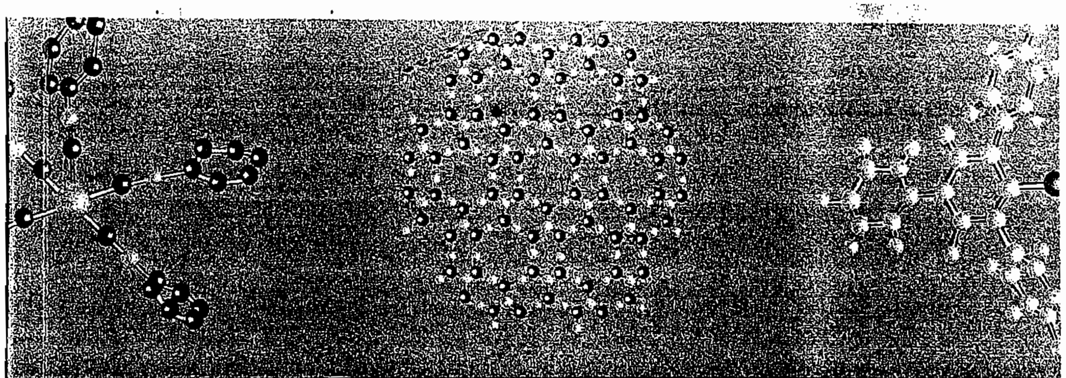
ERRATA

(Few minor printing mistakes not mentioned)

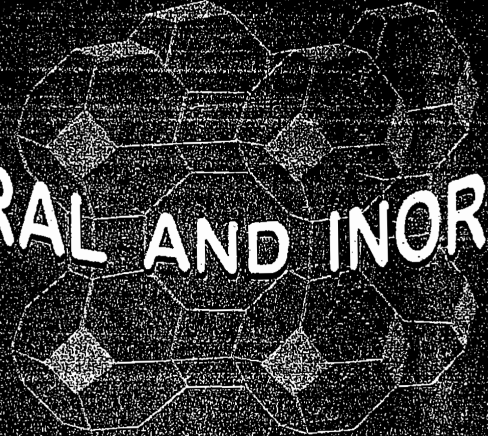
Page/line	Read (Correct form)	instead of (as printed)
1. Contents (2) line 6	(Chapter Nineteen) Summary 158 Exercise 159	Summary 132 Exercise 133
2. Contents (5) line 11	(Chapter Thirtyone) Elements of the f-block	Elements of the f-block
3. 69 line 8	17.1.1. Abundance and Isotopes	17.1.1. Abudance and Isotopes
4. 260 Fig. 21-VII	Bonds to axial F-atoms should be dotted lines  $F\cdots Ge\cdots F$	Bonds shown by solid lines
5. 260 line 4 from bottom	van der Waals	van der walls
6. 269 line 3	$CCl_4 + 4C_2H_5I \longrightarrow CI_4 + 4C_2H_5Cl$	$\cdots\longrightarrow Cl_4 + 4C_2H_5Cl$ ↑
7. 276 line 18	$GeCl_2 \underset{-HCl\ (70°)}{\overset{+HCl\ (20°)}{\rightleftharpoons}} GeHCl_3$	$\cdots\rightleftharpoons GeCl_3$
8. 285 Caption to Fig. 21.10	Combination of carbon–2s and ………	Combination of carbon–2p_z ↑
9. 296 line 23 (under clay minerals)	$KAlSi_3O_8 \longrightarrow Al_2O_3\ldots$	$KALSi_3O_8 \longrightarrow A\lambda_2O_3$
10. 297 line 7 from bottom	**Delete** *and technique colloidal silica*	—
11. 309 line 6	though MeSCN……	through MeSCN
12. 405 line 6 from bottom	ONO bond angles equal to 120°	……180°……
13. 485 line 23 (center)	$4Na_2S_2O_3 = 3Na_2SO_4 + \ldots$	$2Na_2S_2O_3 = \ldots\ldots$
14. 487 Fig. 23-XXI(b)		 —
15. 487 line 11	*add* : after action of I_2 (Spring's reaction).	
16. 867 Fig. 28.22	Relevant values of *nE* are V(II) –2.26; V(III) –2.52 V(IV) –2.18; V(V) –1.18	
17. 495 line 2 from bottom	biphenyl	bipheyl
18. 880 Fig. 28.29 legend	$Cr^{3+} + 3e = Cr$	$Cr^{3+} + 2e = Cr$
19. 937 Fig. 28-XVIII	*add* : one more bridging CO.	Only two bridging CO shown.

Index

Index (supplement)



GENERAL AND INORGANIC



CHEMISTRY

[Part II]

R. Sarkar

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