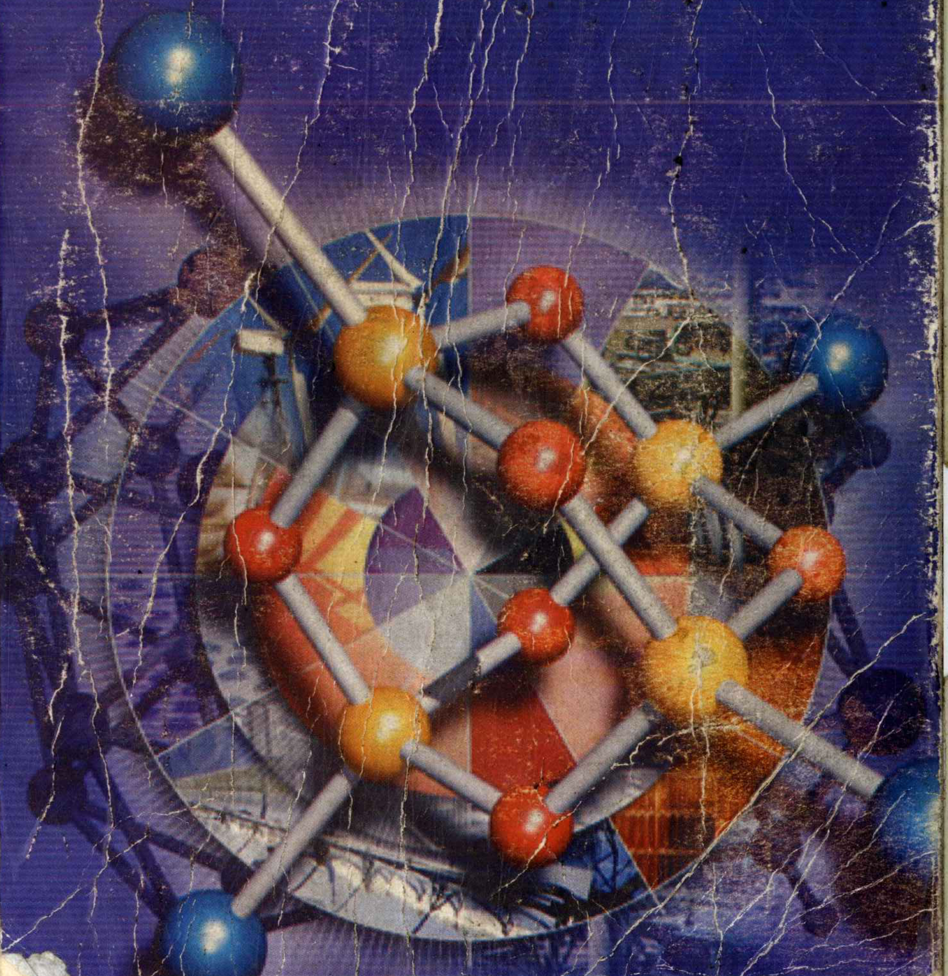
Selected Topics In Inorganic Chemistry

(For B.Sc (Hons.) and M.Sc Students)



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SELECTED TOPICS IN INORGANIC CHEMISTRY

[*For B.Sc. (Hons.) and M.Sc. students*]

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Preface to the Seventh Edition

In this edition the style of the presentation and arrangement of different topics of sixth edition has been kept unchanged.

Main Features:

Main features of this new edition are:

- In this edition a new chapter entitled as "*Electrode Potential and Their Applications*" (Chapter 22) has been added at the end of the book. This chapter has been introduced by many Indian Universities in the syllabus of their B.Sc. (Honours) Course. The study of this chapter is very important since the knowledge of electrode potentials has been used to predict whether a given redox reaction will take place in the forward direction or not.
- In Chapter 22 a large number of numerical problems, along with their solution, has also been given. Solving these problems involves the use and application of various concepts studied in this chapter.
- The printing mistakes noted so far have been corrected.

Acknowledgement:

We express our sincere thanks to our students and fellow-teachers who have been sending us their valuable suggestions for the improvement of the book. We are extremely grateful to our respected Managing Director, Shri Ravindra Kumar Gupta, Shri R.S. Saxena (Advisor), Shri Navin Joshi, General Manager (Sales & Marketing), and Shri Dharmendra Jha (Asstt. Editor), S. Chand & Company Ltd. for the valuable and active cooperation they have extended during the publication of this new edition.

Our thanks are also due to Shri Virender Singh, DTP operator who has taken pains in composing and designing the book according to our instructions and to our complete satisfaction. He has thorough knowledge of composing chemistry books.

A Request:

We humbly request our students and chemistry teachers to send us their constructive criticism and suggestions which we shall be using in the publication of the next edition.

Authors

Delhi
June, 2001

Preface to the First Edition

During the last few years, the Boards of Studies in Chemistry of the various universities in India have been trying to overhaul and modernise the syllabi at the under-graduate and post-graduate level. There has accordingly been a distinct change in approach and content with the result that a shortage of suitable texts written on these lines was being keenly felt. The authors seek justification in presenting the present volume in the sincere attempts that they have made to fill up the gap.

Considerable thought has been given to the selection of topics for discussion. As the book has been written primarily for the use of B.Sc. (Hons.) and M.Sc. students, most of the topics deal with the theoretical aspects of Inorganic Chemistry. Great care has been taken to elucidate the fundamentals and the approach to discussion is modern throughout. Particular mention may be made in this connection of the Chapters on Structure of the Atom, Chemical bonding, Inner Transition elements and Coordination Chemistry.

A special feature of the book is that the text has been illustrated with a large number of line diagrams and the data presented in the form of numerous tables for reference and comparison.

In the preparation of the text, standard works and reviews by renowned authors have been freely consulted and the references given chapter-wise at the end of the book will be found useful by those who wish to make a more detailed study of the topics discussed.

The authors wish to thank all those who helped in the preparation of the text and illustrations. Since drawbacks and better methods of presentation are always there, suggestions for improvement and criticism will be gratefully received and acknowledged.

November 20, 1975 AUTHORS

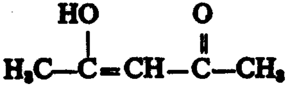
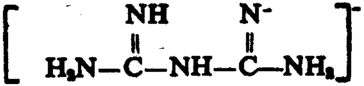
Contents

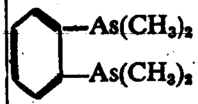
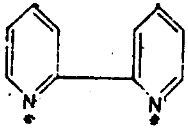
Chapter *Pages*

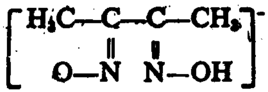
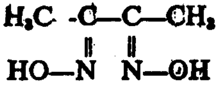
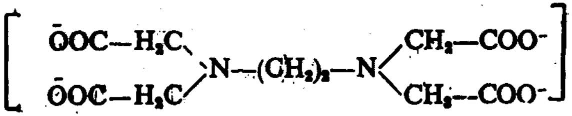
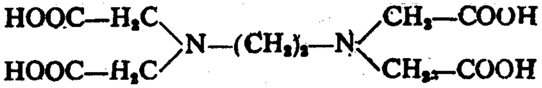
Chapter *Pages*

List of Abbreviations and Important Relations

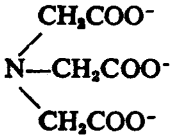
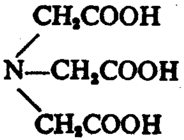
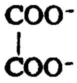
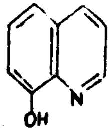
(A) Abbreviations of Chemicals, Ligands, Radicals, etc.

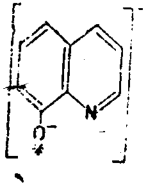
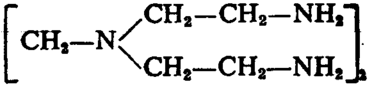
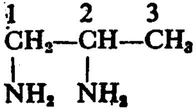
Abbreviations	*Name of the chemical, ligand, radical, etc.*	*Structure*
acac⁻	Acetylacetonato ion	 $\left[H_3C\cdots\overset{:\dot{O}^-}{\overset{\vert}{C}}=CH\cdots\overset{O:}{\overset{\Vert}{C}}-CH_3\right]^-$
*acac*H	Acetyl acetone	 $H_3C-\overset{HO}{\overset{\vert}{C}}=CH-\overset{O}{\overset{\Vert}{C}}-CH_3$
am	Ammonia (occasionally as *ammine*)	NH_3
aq	Aquated	H_2O
Big	Biguanido ion	 $\left[H_2N-\overset{NH}{\overset{\Vert}{C}}-NH-\overset{N^-}{\overset{\Vert}{C}}-NH_2\right]^-$
*Big*H	Biguanide	 $H_2N-\overset{NH}{\overset{\Vert}{C}}-NH-\overset{NH}{\overset{\Vert}{C}}-NH_2$

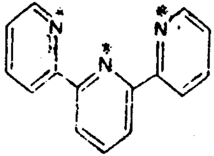
bn	Butylene diamine	$H_2\ddot{N}-CH(CH_3)-CH(CH_3)-\ddot{N}H_2$
Cp	Cyclopentadienide ion	$C_5H_5^-$
chxn	*trans*-1, 2-cyclohexane diamine	—
diars or D	*o*-phenylene-*bis* (dimethyl arsine)	 or $(CH_3)_2As.C_6H_4.As(CH_3)_2$
dien	Diethylen triamine	$\ddot{N}H_2.(CH_2)_2\ddot{N}H(CH_2)_2\ddot{N}H_2$ or $(\ddot{N}H_2-CH_2-CH_2)_2\ddot{N}H$
diphos	—	$R_2\ddot{P}(CH_2)_2\ddot{P}R_2$
dipy	2 : 2′—Dipyridyl or 2, 2′—dipyridine	

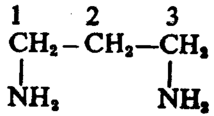
dl-bn	*dl*-butylene diamine	*dl*—$NH_2—CH(CH_3)—CH(CH_3)—NH_2$
dmg or DMG⁻	Dimethylglyoximato ion	 $\left[\begin{matrix} H_3C—C—C—CH_3 \\ \Vert \quad \Vert \\ O—N \quad N—OH \end{matrix}\right]^-$
*dmg*H or DMGH	Dimethylglyoxime	 $\begin{matrix} H_3C—C—C—CH_3 \\ \Vert \quad \Vert \\ HO—N \quad N—OH \end{matrix}$
(*d*-tart)$^{2-}$	*d*-tartrate ion	—
(*dtp*)	Diethyldithiophosphate	$[PO_2S_2(C_2H_5)_2]^-$
EDTA^{4-} or Y^{4-}	Ethylenediaminetetraacetato ion	
$EDTAH_4$ or YH_4	Ethylenediaminetetraacetic acid	
en	Ethylenediamine	$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$
Et	Ethyl	C_2H_5

eten	N-ethylethylenediamine	$NH_2-(CH_2)_2-NH(C_2H_5)$
gly$^-$	Glycinato ion	$H_2N-CH_2-COO^-$
*gly*H	Glycine	H_2N-CH_2-COOH
glyme	Ethyleneglycoldimethyl ether	$CH_3\ddot{O}CH_2CH_2\ddot{O}CH_3$
i-bn	Isobutylenediamine	$H_2\ddot{N}-C(CH_3)_2-CH_2-\ddot{N}H_2$
$(IDA)^{2-}$	Imido-diacetato ion	$^-OOC-CH_2-NH-CH_2-COO^-$ or $[NH(CH_2COO)_2]^{2-}$
$IDAH_2$	Imido-diacetic acid	$HOOC-CH_2-NH-CH_2-COOH$ or $NH(CH_2COOH)_2$
Me	Methyl	CH_3
Me$_6$*tren*	*Tris*-(2-methylaminoethylamine)	$(NMe_2-CH_2-CH_2)_3N$
meen	N-Methylethylenediamine	$NH_2-(CH_2)_2-NH(CH_3)$

m-bn	*meso*—butylenediamine	*meso*-$NH_2—CH(CH_3)—CH(CH_3)—NH_2$
n-pren	N-propyl ethylene diamine	$NH_2—(CH_2)_2—NH(n\text{-}C_3H_7)$
$(NTA)^{3-}$	Nitrilotriacetato ion	 or $[N(CH_2COO)_3]^{3-}$
$NTAH_3$	Nitrilotriacetic acid	 or $N(CH_2COOH)_3$
ox^{2-}	Oxalato ion	 $\begin{array}{c}COO^-\\ \vert \\ COO^-\end{array}$ or $C_2O_4^{2-}$
oxH_2	Oxalic acid	 $\begin{array}{c}COOH\\ \vert \\ COOH\end{array}$ or $H_2C_2O_4$
*oxin*H or *oxinate*H	8-hydroxyquinoline	

(oxin)⁻ or *(oxinate)*⁻	8-hydroxyquinolinato ion or oxinato ion	
penten	*Tetrakis* (Aminoethyl)ethylene diamine	 $\left[CH_2-N\begin{matrix}CH_2-CH_2-NH_2\\CH_2-CH_2-NH_2\end{matrix}\right]_2$ or $(NH_2CH_2CH_2)_2.NCH_2.CH_2N.(CH_2CH_2NH_2)_2$
Ph	Phenyl	C_6H_5
phen or *o-phen*	1, 10-phenanthroline or *o*-phenantholine	
pn	Propylenediamine or 1, 2-diamino propane	 $\overset{1}{C}H_2-\overset{2}{C}H-\overset{3}{C}H_3$ with NH_2 on C1 and C2: $\underset{NH_2}{CH_2}-\underset{NH_2}{CH}-CH_3$
pr	Propyl group	C_3H_7

py	Pyridine	 or C_5H_5N
QAS	*Tris* (*o*-diphenylarsinophenyl)arsine	$As(o\text{-}C_6H_4AsPh_2)_3$
R	Alkyl or aryl group	—
R_5*dien*	—	$(NR_2—CH_2—CH_2)_2NR$
TAP	*Tris*-(3-dimethylarsinopropyl) phosphine	$P(CH_2CH_2CH_2AsMe_2)_3$
terpy or *trpy*	2, 2′, 2″-terpyridine	
tetraen	Tetraethylenepentamine	$NH_2—(CH_2)_2—NH—(CH_2)_2—NH—(CH_2)_2—NH—(CH_2)_2—NH_2$ or $NH(CH_2—CH_2—NH—CH_2—CH_2—NH_2)_2$

tetrameen	Tetramethyl-ethylenediamine	$H_2\ddot{N}—C(CH_3)_2—C(CH_3)_2—\ddot{N}H_2$
THF	Tetrahydrofuran	C_4H_8O
tn	1. 3-diaminopropane	 $\underset{NH_2}{\overset{1}{CH_2}}-\overset{2}{CH_2}—\underset{NH_2}{\overset{3}{CH_2}}$
tren	Triaminotriethylamine or *Tris*-(2-aminoethyl)amine	$(NH_2—CH_2—CH_2)_3N$
trien	Triethylenetetramine	$H_2N—(CH_2)_2—NH—(CH_2)_2—NH—(CH_2)_2—NH_2$ or $(CH_2NHCH_2CH_2NH_2)_2$
TSP	*Tris*-(*o*-methylthiophenyl)phosphine	—
tu	Thiourea	$NH_2.CS.NH_2$
X	Halogen	Cl, Br, etc.

(B) Miscellaneous Abbreviations and Important Relations

These are given chapter-wise as follows :

Chapter 1. Structure of the Atom

Abbreviations :

h	Plank's constant ($= 6{\cdot}62 \times 10^{-27}$ ergs)
cm^{-1}	Wave number
Hz	herz, sec^{-1}
ν (*Nu*, न्यू)	Frequency (cm^{-1} or Hz)
c	Velocity of light
λ (Lambda, लैम्डा)	Wave length
$\bar{\nu}$	Wave number
E	Energy
R_H	Rydberg constant or Rydberg number for hydrogen ($= 109{,}679\ cm^{-1}$)
A° or A	Angstrom unit (1 A° $= 10^{-8}$ cm)
pm	picometer
nm	nanometer
r_n	Radius of the *n*th orbit of hydrogen atom
r_1	Radius of the *1st* orbit (called *Bohr radius*)
E_n	Energy of an electron revolving in the *nth* orbit
E_1	Energy of an electron revolving in the *1st* orbit
n	Principal quantum number
l	Azimuthal quantum number (Also called *orbital angular momentum quantum number*)
m	Magnetic quantum number (*m* also denotes the mass of an electron)
s	Spin quantum number (Also called *spin angular momentum quantum number*)
S	Resultant spin angular momentum quantum number
L	Resultant orbital angular momentum quantum number
J	Resultant inner quantum number (also called *angular momentum quantum number*)
t_{2g} or d_ϵ	A set of orbitals consisting of d_{xy}, d_{yz} and d_{zx} atomic orbitals) (These are called *non-axial orbitals*)
e_g or d_γ	A set of orbitals consisting of $d_{x^2-y^2}$ and d_{z^2} atomic orbitals. (These are called *axial orbitals*).

Relations :

(1) Einstein's mass-energy relationship : $E = mc^2$

(2) Plank's equation : $E = h\nu$

(3) Rydberg's formula : $\overline{\nu} = \frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$ cm^{-1}

(4) Angular momentum of an electron, $mvr = n\frac{h}{2\pi}$

This equation represents the *principle of quantisation of angular momentum* of an electron with mass m and revolving in an orbit of radius r with velocity v

(5) Radius of *nth* orbit, $r_n = \frac{n^2h^2}{4\pi^2me^2}$

(6) Radius of the first orbit of hydrogen atom (called *Bohr radius*), r_1 (or r_H or a_0) = 0·53 A°

(7) r_n and r_1 are related as :
$r_n = (r_1 \times n^2)$ A° = $(0{\cdot}53 \times n^2)$ A°

(8) Centrifugal force = $+\frac{mv^2}{r}$

(9) Centripetal force = $-\frac{e^2}{r^2}$

(10) Energy of an electron revolving in the *nth* orbit,

$$E_n = -\frac{2\pi^2me^4}{n^2h^2}$$

(12) Energy of an electron revolving in the *first* orbit,

$$E_1 = -21{\cdot}79 \times 10^{-12} \text{ ergs/atom}$$
$$= -13{\cdot}6 \text{ eV/atom}$$
$$= -313{\cdot}6 \text{ kcal/mole}$$

(13) E_n and E_1 are related as .

$$E_n = -E_1 \times \frac{1}{n^2} \text{ eV/atom}$$

$$= -13{\cdot}6 \times \frac{1}{n^2} \text{ eV/atom}$$

(14) $(\mathrm{R_H})_{cal} = \frac{2\pi^2\epsilon^4m}{h^3c} = 109{,}679$ cm^{-1}

(15) $\nu = \frac{2\pi^2e^4m}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(16) $\overline{\nu} = \frac{1}{\lambda} = \frac{2\pi^2e^4m}{h^3c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

or $$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $$\bar{\nu} = \frac{1}{\lambda} = 109{,}679\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

(17) Principal quantum number, $n = 1, 2, 3, \ldots\ldots, n$

Azimuthal quantum number, $l = 0, 1, 2, \ldots\ldots, (n-2), (n-1)$

Magnetic quantum number, $m = 0, \pm 1, \pm 2, \ldots\ldots, \pm l$

Spin quantum number, $s = +\frac{1}{2}, -\frac{1}{2}$

(18) Multiplicity $= 2S+1 = 2 \times \frac{n}{2} + 1 = n+1$

(19) Ground state term of an atom or an ion

$$= \text{L}_\text{J}^{\text{Multiplicity}} = {}^{2S+1}\text{L}_\text{J} = {}^{n+1}\text{L}_\text{J}$$

(20) Heisenberg's uncertainty relation : $\Delta x \times \Delta p > \frac{h}{2\pi}$

or $\Delta \text{E} \times \Delta \text{T} > \frac{h}{2\pi}$

(21) Schrodinger wave equation :

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2 m}{h^2}(\text{E}-\text{P.E.})\,\Psi = 0$$

Laplacian operator, $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

Schrodinger wave equation for hydrogen atom :

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2 m}{h^2}\left(\text{E} + \frac{e^2}{r}\right)\Psi = 0$$

(22) Order of energy of various atomic orbitals for poly-electron atoms (*Aufbue Principle*)

$$\xrightarrow{\text{Energy increasing}}$$

$1s < 2s < 2p < 3s < < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7s < 8s$.

(23) Order of filling of atomic orbitals with electrons :

$$\xrightarrow{\text{Orbitals being filled}}$$

$1s^2$ (He$_2$), $2s^2$ (Be$_4$), $2p^6$ (Ne$_{10}$), $3s^2$ (Mg$_{12}$), $3p^6$ (Ar$_{18}$), $4s^2$ (Ca$_{20}$), $3d^{10}$ (Zn$_{30}$), $4p^6$ (Kr$_{36}$), $5s^2$ (Sr$_{38}$), $4d^{10}$ (Cu$_{48}$), $5p^6$ (Xe$_{54}$), $7s^2$ (Ba$_{56}$), $5d^1$ (La$_{57}$), $4f^{14}$ (Lu$_{71}$), $5d^{2 \text{ to } 10}$ (Hf$_{72}$ tc Hg$_{80}$),......

Chapter 2. Extended or Long Form of Periodic Table

n	Number of the period
TE's	Transitional Elements
Z	Atomic number.

Chapter 3. Periodic Properties

Abbreviations :

r_A	Radius of an atom A (called *atomic radius*)
r^{c+}	Radius of a cation, c^+ (called *cationic radius*)
r_a^-	Radius of an anion, a^- (called *anionic radius*)
ca	Approximately
d_{A-B}	Internuclear distance between atoms A and B (called *bond length*)
x_A	Electronegativity of atom A
$(Z_{eff})^{c+}$	Effective nuclear charge acting on the cation, c^+
C.N.	Coordination Number
R_r	Radius ratio
I_A or $(IP)_A$	Ionisation potential (or ionisation energy) of atom A
E_A or $(EA)_A$	Electron affinity of atoms A
E_{A-B}	Energy of A—B bond
Δ_{A-B}	Ionic-resonance energy of A—B bond
Kcal	Kilo calories
e*V*	Electron volts
MeV	Million electron volts
KJ mol^{-1}	Kilojoules per mole
ccp	Cubic close packed
hcp	Hexagonal close packed

Relations :

(1) $d_{A-A} = r_A + r_A = 2r_A$

(2) Schomaker and Stevenson equation :

$$d_{A-B} = r_A + r_B + 0{\cdot}09\,(x_A - x_B)$$

(3) Radius ratio, $R_r = \dfrac{r_c^+}{r_a^-}$

(4) Pauling's scale of electronegativity :

$$x_A - x_B = 0{\cdot}208\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]^{\frac{1}{2}}$$

(5) % ionic character in A—B bond $= 16\,(x_A - x_B) + 3{\cdot}5\,(x_A - x_B)^2$

Chapter 4. Chemical Bonding

Abbreviations :

$(U)_{MX}$	Lattice energy (also called *crystal energy*) of MX crystal
n	Born exponent
b	Repulsion coefficient
z_+, z_-	Charges carried by cations and anions respectively
A	Mandelung constant
$\phi_{M^{n+}}$	Ionic potential (also called *charge density*) of cation, M^{n+}
(s)	Solid state
(l) or (liq)	Liquid state
(g)	Gaseous state
$\left(\Delta H_{for}\right)_{MX}$	Heat of formation of MX crystal
$\left(\Delta H_{sub}\right)_{M}$	Heat of sublimation of one mole of solid M
$\left(\Delta H_{diss}\right)_{X_2}$	Heat of dissociation of one mole of X_2.

Relations :

(1) Born-Lande equation : $U = \frac{NAe^2 z_+ z_-}{r_0}\left(1-\frac{1}{n}\right)$

(2) Born-Haber cycle equation for MX crystal :

$$\left(\Delta H_{for}\right)_{MX} = \left(\Delta H_{sub}\right)_{M} + \frac{1}{2}\left(\Delta H_{diss}\right)_{X_2} + (IP)_M + (EA)_X + (U)_{MX}$$

(3) Ionic potential (or charge density), $\phi = \frac{\text{Charge on cation}}{\text{Radius of cation}}$

Chapter 5. Nature of Covalent Bond and Shapes of Molecules.

Abbreviations :

VBT	Valence Bond Theory
MOT	Molecular Orbital Theory
LCAO	Linear Combination of Atomic Orbitals
AO	Atomic Orbital
MO	Molecular Orbital
σ^b-MO	Sigma bonding molecular orbital
σ^*-MO	Sigma anti-bonding molecular orbital
π^b-MO	*pi* bonding molecular orbital
π^*-MO	*pi* anti-bonding molecular orbital
VSEPR	Valence Shell Electron Pair Repulsion

bp	Bonding pair of electrons
lp	Lone pair of electrons
B.O.	Bond Order (Also called *bond multiplicity*)
n_b	Number of electrons in bonding molecular orbitals
n_a	Number of electrons in antibonding molecular orbitals
(2*c*—2*e*) bond	Two-centre-two-electron bond
(3*c*—2*e*) bond	Three-centre-two-electron bond

Relations :

(1) Bond order, B.O. $= \frac{1}{2}(n_b - n_a)$

(2) Order of energy of molecular orbitals of a homonuclear diatomic molecule (A_2 type molecule) :

$$\xrightarrow{\text{Energy increasing}}$$

$$\sigma_{2s}^{b} < \sigma_{2s}^{*} < \pi_x^{b} = \pi_y^{b} < \sigma_z^{b} < \pi_x^{*} = \pi_y^{*} < \sigma_z^{*}$$

(3) Order of the magnitude of the repulsive force existing between electron pairs :

$(lp-lp) > (lp-bp) > (bp-bp)$

Chapter 6. Modern Concepts of Acids and Bases

(1) SHAB Principle of Soft and Hard Acids and Bases

(2) *Conjugate acid-base pair* :

Conjugate acid-base pair

$$\begin{array}{ccccccc} \text{Acid}_1 & + & \text{Base}_2 & \rightleftharpoons & \text{Acid}_2 & + & \text{Base}_1 \\ (e.g.\ \text{HCl}) & & (e.g.\ \text{H}_2\text{O}) & & (\text{H}_3\text{O}^+) & & (\text{Cl}^-) \end{array}$$

Conjugate acid-base pair

(3) *A salt containing (hard acid+hard base) or (soft acid+soft base) is more stable than that containing (hard acid+soft base) or (soft acid+hard base)*

Chapter 8. Transition Elements (*d*-Block Elements)

Abbreviations

TE's	Transition elements
I	Magnetic moment per unit volume
B	Total magnetic induction or magnetic flux
H	Strength of a magnetic field
P	Magnetic permeability
χ (Chi, काई)	Volume susceptibility

χ_g	Gram, specific or weight susceptibility
χ_M	Molar susceptibility
χ_p	Paramagnetic susceptibility
μ (*Mu*, म्यू)	Magnetic moment in Bohr magnetons
μ_{eff}	Effective magnetic moment
B.M.	Bohr magneton (1 BM)
C	Curie's or Weiss constant$\left(=\frac{N\mu_{eff}^2}{3k}\right)$
N	Avogadro's number
k	Boltzman constant
T	Absolute temperature
θ (थीटा)	Weiss constant
$2S+1$	Spin multiplicity
g	Lande splitting factor
n	Number of unpaired electrons
S	Resultant *spin* angular momentum quantum number
L	Resultant *orbital* angular momentum quantum number
J	Resultant angular momentum quantum number (also called *resultant inner quantum number*)

Relations :

(1) Magnetic permeability, $P = B/H$

(2) Volume susceptibility, $\chi = I/H$

(3) Total magnetic induction,

$$B = H + 4\pi I$$

or $$\frac{B}{H} = 1 + 4\pi\frac{I}{H}$$

or $$P = 1 + 4\pi\chi$$

(4) Gram susceptibility, $\chi_g = \frac{\chi}{d}$ (d = density)

(5) Molar susceptibility, $\chi_M = \chi_g \times M$ (M = molecular weight)

(6) Paramagnetic susceptibility,

$$\chi_p = \frac{N\mu^2}{3kT}$$

(7) Curie's equation :

$$\chi_M^{corr} \times T = C = \frac{N\mu_{eff}^2}{3k}$$

or $${}^{corr}_{M} \times T = \frac{N\mu^2_{eff}}{3k}$$

or $$\mu_{eff} = \sqrt{\frac{3k}{N}} \cdot \sqrt{\chi_M^{corr} \times T} \text{ B.M.}$$

or $$\mu_{eff} = 2{\cdot}84 \sqrt{\chi_M^{corr} \times T} \text{ B.M.}$$

(8) Curie-Weiss equation :

$$\chi_M^{corr} \times (T-\theta) = C$$

Also $$\mu_{eff} = 2{\cdot}84 \sqrt{\chi_M^{corr} \times (T-\theta)} \text{ B.M.}$$

(9) $1 \text{ B.M.} = \frac{eh}{4\pi mc} = 9{\cdot}27 \times 10^{-21}$ ergs/gauss

(10) $S = n/2$

(11) Spin multiplicity $= 2S+1 = 2 \times \frac{n}{2} + 1 = n+1$

(12) Lande splitting factor,

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

(13) Ground state term of an atom or ion

$$= {}^{2S+1}L_J = {}^{n+1}L_J$$

(14) (*a*) When the spin-orbit (L—S) coupling of unpaired electrons is *strong* as in case of tripositive ions of lanthanides (with the exception of Sm^{3+} and Eu^{3+} ions), effective magnetic moment, μ_{eff} is given by :

$$\mu_{eff} = \mu_J = g\sqrt{J(J+1)} \text{ B.M.}$$

(*b*) When spin-orbit (L—S) coupling is *weak* as in case of some ions of the metals of first transition series, effective magnetic moment, μ_{eff} is given by ;

$$\mu_{eff} = \sqrt{L(L+1)+4S(S+1)} \text{ B.M.}$$

(*c*) For the ions which have S ground state terms [*e.g.* Mn^{2+} (${}^6S_{5/2}$), Fe^{3+} (${}^6S_{5/2}$), La^{3+} (${}^1S_0$), Gd^{3+} (${}^8S_{7/2}$) and Lu^{3+} (${}^1S_0$)], $L = 0$ and hence μ_{eff} is given by :

$$\mu_{eff} = \mu_{S+L} = \sqrt{L(L+1)+4S(S+1)} \text{ B.M.}$$
$$= \mu_{S+0} = \sqrt{0 \times (0+1)+4S(S+1)}$$
$$= \mu_S = \sqrt{4S(S+1)} = \sqrt{4 \times \frac{n}{2}\left(\frac{n}{2}+1\right)}$$
$$= \sqrt{n(n+2)} \text{ B.M.}$$

or $$\mu_{\text{spin only}} \left.\begin{aligned} &= \sqrt{4S(S+1)} \text{ B.M.} \\ &= \sqrt{n(n+1)} \text{ B.M.} \end{aligned}\right\} \text{(Spin-only formula)}$$

Chapter 10. Actinides (5*f*-block elements)

Molar susceptibility, χ_M of an actinide ion is given by :

$$\chi_M = \frac{Ng^2\beta^2J\,(J+1)}{3kT} + N\alpha$$

where N = Avogadro's number, g = Lande splitting factor, β = Bohr magneton, J = Total angular momentum of atom = $|\,L+S\,|$, k = Boltzman constant, T = Absolute temperature and α = Small, temperature independent term due to second order Zeeman effect.

Chapter 11. Basic Concepts of Coordination Chemistry

C.N.	Coordination number (or ligancy of the central metal cation)
IUPAC	International Union of Pure and Applied Chemistry
EAN concept	Effective Atomic Number concept (also called *Noble Gas Rule*)

Chapter 12. Nature of Metal-Ligand Bonding in Complexes

Abbreviations :

VBT	Valence Bond Theory
CFT	Crystal Field Theory
LFT	Ligand Field Theory
MOT	Molecular Orbital
ACFT	Adjusted Crystal Field Theory
n	Number of unpaired electrons
μ_{exp}	Experimental value of magnetic moment
M^{n+}	Central metal cation
L	A monodentate ligand
Δ_o or Dq	Energy difference between t_{2g} and e_g sets of orbitals in octahedral complexes (Δ_o or Dq is called *octahedral crystal field splitting energy* or *orbital separation*)
Δ_t	Energy difference between t_2 and e sets of orbitals in tetrahedral complexes
Δ_{sp}	Energy difference between the highest $d_{x^2-y^2}$ orbital and lowest d_{xz}, d_{yz} pair of orbitals is square planar complexes
S	Resultant spin
P.	Energy required to pair two electrons in the same orbital (called *average or mean pairing energy*)
HS	High spin
LS	Low spin
sym	symmetrical
unsym	unsymmetrical
CFSE	Crystal Field Stabilisation Energy

Relations :

(1) Splitting power of the following common ligands to split the *d*-orbitals into t_{2g} and e_g sets increases from left to right

$$\xrightarrow{\text{Splitting power increasing}}$$

$I^- < Br^- < Cl^- \sim SCN^- \sim N_3^- < (C_2H_5O)_2PS_2^- < F^- < (NH_2)_2CO < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < NH_2CH_2CO_2^- < NH_3 \sim C_5H_5N < en < SO_3^{2-} < NH_2OH < NO_2^- < o\text{-phen} < < CH_3^- < CN^-, CO.$

This series is called **spectro-chemical series** or **Fajans-Tsuchida series**

(2) Resultant spin, $S = \frac{n}{2}$

(3) $10\ Dq = \triangle_0$

(S) CESE for an ion having $t_{2g}^{q}e_g^{p}$ configuration

$$= [-0{\cdot}4p+0{\cdot}6\,q)\,\triangle_0$$

$$= [-4p+6q]\,Dq$$

(5) Order of MO's and AO's of an octahedral complex of a cation from 3*d*-series

(*a*) *When the ligands are strong(er)*

$$\xrightarrow{\text{Energy increasing}}$$

$\sigma_s^b < \sigma_x^b = \sigma_y^b = \sigma_z^b < \sigma_{x^2-y^2}^{b} = \sigma_{z^2}^{b} < 3d_{xy} = 3d_{yz} = 3d_{zx} < \sigma_{x^2-y^2}^* = \sigma_{z^2}^* < \sigma_s^* < \sigma_x^* = \sigma_y^* = \sigma_z^*$

(*b*) *When the ligands are weak(er)*

$$\xrightarrow{\text{Energy increasing}}$$

$\sigma_s^b < \sigma_x^b = \sigma_y^b = \sigma_z^b < \sigma_{x^2-y^2}^{o} = \sigma_{z^2}^{b} < 3d_{xy} = 3d_{yz} = 3d_{zx} = \sigma_{x^2-y^2}^* = \sigma_{z^2}^* < \sigma_s^* < \sigma_x^* = \sigma_y^* = \sigma_z^*$

Chapter 13. Isomerism Among Inorganic Complexes

(+) or *d*-form	Dextro-rotatory form
(−) or *l*-form	Levo (or Laevo) rotatory form
dl or (±) form	Recemic form
(AA)	A symmetrical bidentate ligand having two A atoms as donor atoms
(AB)	An unsymmetrical bidentate ligand having A and B as donor atoms

Chapter 14. Stability of Complexes in Aqueous Solution

[M], [L], [ML]	Concentration of M, L and ML respectively
K_1, K_2, K_n	Stepwise or successive formation (or stability) constants

$\beta_1, \beta_2, \ldots\ldots \beta_n$	Overall (or cumulative) formation (or stability) constants
β_n	*nth* overall (or cumulative) formation (or stability) constant
$1/K$	Instability constant
E_a	Activation energy
Oct	Octahedral
squ. py.	Square pyramidal
pent. bipy.	Pentagonal bipyramidal
tbp	Trigonal bipyramidal
ΔG°	Standard free energy change
R	Gas constant
T	Absolute temperature
ΔH°	Enthalpy (or heat) change
ΔS°	Entropy change
A	Absorbance or optical density
ε	Mole extinction coefficient
l	Length of the absorption cell
c	Concentration of the complex (in moles/litre)

Relations :

(1) The *nth* stepwise stability constant, K_n for the equilibrium : $ML_{n-1} + L \rightleftharpoons ML_n$ is given by :

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$

(2) The *nth* overall stability constant, β_n for the equilibrium : $M + nL \rightleftharpoons ML_n$ is given by :

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n}$$

(3) With few exceptions the values of stepwise stability constants are in the order :

$$\xrightarrow{\text{Values decreasing}}$$

$$K_1 > K_2 > K_3 > \ldots\ldots K_{n-1} > K_n$$

(4) β_n and $K_1, K_2 \ldots\ldots K_n$ are related as :

$$\beta_n = K_1 \times K_2 \times \ldots\ldots \times K_{n-1} \times K_n$$

or

$$\log_{10}\beta_n = \log_{10} K_1 + \log_{10} K_2 + \ldots\ldots \log_{10} K_{n-1} + \log_{10} K_n$$

(5) Natural order (also called *Irving-William order*) of stability of the high-spin complexes of the ions between Mn^{2+} and Zn^{2+} with a given ligand is as follows :

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

(6) $-RT\ln\beta = \Delta G^\circ = \Delta H^\circ - T\,.\Delta S^\circ$ (ΔH° is *negative*)

(7) Absorbance, A, of a complex $= \varepsilon\, l\, c$ (*Beer's Law*)

Chapter 15. Ligand Substitution Reactions in Octahedral Complexes

ΔH	Reaction energy
X...Y...Z	Transition state or activated complex
S_N	Nucleophilic or ligand substitution reactions
S_E	Electrophilic or metal substitution reactions
$S_N{}^1$	Substitution (*S*) nucleophilic (*N*) uni-molecular or first order (1) reactions (Also called *dissociation unimolecular reactions*)
$S_N{}^2$	Substitution (*S*) nucleophilic (N) bimolecular or second order (2) reactions (Also called *association or bimolecular displacement reactions*)
CB	Conjugate base

Values of some physical constants

One Bohr magneton (IBM)
$= 9{\cdot}27 \times 10^{-21}$ ergs/gauss

Planck's constant (gas constant per molecule) (*h*)
$= 6{\cdot}6256 \times 10^{-27}$ ergs-sec

Rydberg's constant for hydrogen (R_H)
$= 109{,}679\ cm^{-1}$

Boltzman constant (*K*)
$= 1{\cdot}38 \times 10^{-16}$ ergs/deg/mole

Universal gas constant (R)
$= 1{\cdot}9872$ cal/deg/mole
$= 8{\cdot}31434$ Joule/deg/mole

Radius of :

Hydrogen atom (*Bohr radius*) (r_1 or r_H or a_0)
$= 0{\cdot}5297$A°
$= 0{\cdot}5291 \times 10^{-8}$ cm

Proton $= 10^{-13}$ cm (calculated)

Electron $= 10^{-13}$ cm (calculated)

Rest mass of :

neutron, ${}^1n_0$ (m_n) $= 1{\cdot}675 \times 10^{-27}$ kg
$= 1{\cdot}0087$ *amu*
$= 939{\cdot}6$ MeV

proton, ${}^1p_1$ or ${}^1H_1$ (m_p)
$= 1{\cdot}67 \times 10^{-27}$ kg
$= 1{\cdot}0073$ *amu*
$= 938{\cdot}3$ MeV

electron, $^{0}e_{-1}$ (m_e) = 9·11 × 10^{-31} kg
= 5·487 × 10^{-4} *amu*
= 0·511 MeV

Helium nucleus, $^{4}He_{2}$
= 4·0028 *amu*

Charge on :

electron = 4·80298 × 10^{-10} *esu*
= 1·60210 × 10^{-19} coulombs

proton = 1·60210 × 10^{-19} coulombs

Velocity of light in vacuum (*c*)
= 2·997225 × 10^{10} cm/sec

Avogadro's number (N)
= 6·023 × 10^{23} per g-mole or g-atom
= 6·023 × 10^{26} per kg-mole or kg-atom

1 Atomic mass unit (*amu*)
$= \frac{1}{N}$ = 1·66 × 10^{-27} kg
= 931 MeV

Energy of the electron revolving in the *1st* orbit (E_1)
= −21·79 × 10^{-12} ergs/atom
= −13·6 *eV*/atom
= −313·6 kcal/mole

pi(π) = 3·14

Energy Conversion Factors

1 kcal/mole = 350·00 cm^{-1} (wave number)
= 0·0483 *eV*/particle
= 6·9468 × 10^{-24} ergs/mole
= 4·1840 Joules/mole

1 cm^{-1} (wave number)
= 2·8593 × 10^{-3} kcal/mole
= 1·239 × 10^{-4} *eV*/particle
= 1·986 × 10^{-16} ergs/mole
= 11·963 Joules/mole

1 *eV*/particle = 23·060 kcal/mole
= 8065·7 cm^{-1}

$= 1{\cdot}602 \times 10^{-12}$ ergs/mole

$= 1{\cdot}602 \times 10^{-19}$ Joules/mole

1 erg/mole $= 2{\cdot}390 \times 10^{-11}$ kcal/mole

$= 5{\cdot}0348 \times 10^{15}$ cm^{-1}

$= 6{\cdot}242 \times 10^{11}$ eV/particle

$= 10^{-7}$ Joules/mole

1 Joule/mole $= 0{\cdot}239$ kcal/mole

$= 0{\cdot}0835$ cm^{-1}

$= 6{\cdot}242 \times 10^{18}$ eV/particle

$= 10^{7}$ ergs/mole

1 kJ/mole $= 83{\cdot}54$ cm^{-1}

Length Conversion Factors

1 angstrom (1Å or 1A

$= 10^{-8}$ cm

1 nanometer (1 *nm*) $= 10$Å $= 10^{-7}$ cm

1 picometer (1 *pm*) $= 10^{-2}$Å $= 10^{-10}$ cm.

Numerical prefixes

(The prefixes in parentheses are less used)

$\frac{1}{2}$—hemi or semi ; 1—mono or uni ; $1\frac{1}{2}$—sesqui ; 2—Di or Bi (*bis*) ; 3—tri or ter (*tris*) ; 4—tetra or quadri (*tetrakis*) ; 5—penta or quinque (*pentakis*) ; 6—hexa or sexa (*hexakis*) ; 7—hepta or septa ; 8—octa ; 9—nona or ennea ; 10—deca or decena ; 11—undeca or henadeca ; 12—dodeca ; etc.

Prefixes for naming multiples and sub-multiples of units

Factor	*Prefix*	*Symbol*	*Factor*	*Prefix*	*Symbol*
10^{12}	tetra	T	10^{-2}	centi	*c*
10^{9}	giga	G	10^{-3}	milli	*m*
10^{6}	mega	M	10^{-6}	micro	μ
10^{3}	kilo	*k*	10^{-9}	nano	*n*
10^{2}	heotc	*h*	10^{-12}	pico	*p*
10^{1}	deka	*da*	10^{-15}	fento	*f*
10^{-1}	deci	*d*	10^{-18}	atto	*a*

Greek Alphabets

Α	α	Alpha	Ν	ν	Nu
Β	β	Beta	Ξ	ξ	Xi
Γ	γ	Gamma	Ο	ο	Omicron
Δ	δ	Delta	Π	π	Pi
Ε	ε	Epsilon	Ρ	ρ	Rho
Ζ	ζ	Zeta	Σ	σ	Sigma
Η	η	Eta	Τ	τ	Tau
Θ	θ	Theta	Υ	υ	Upsilon
Ι	ι	Iota	Φ	ϕ, φ	Phi
Κ	k	Kappa	Χ	χ	Chi
Λ	λ	Lambda	Ψ	ψ	Psi
Μ	μ	Mu	Ω	ω	Omega

1

Structure of the Atom

QUANTUM MECHANICAL AND WAVE MECHANICAL APPROACH

PLANK'S QUANTUM THEORY OF RADIATION AND EINSTEIN'S EXTENSION.

Plank in 1901 studied the energy of light of different frequencies radiated from hot (black) bodies and on the basis of these studies he put forward a theory known as *Plank's Quantum Theory of Radiation* according to which *a black body emits (i.e. radiates) or absorbs the energy such as light and heat not continuously but in whole number of small packet of energy called a quantum.* The energy of each quantum is equal to the product of Plank's constant, h ($=6{\cdot}62\times10^{-27}$ erg-sec) and the frequency, ν of radiation. Thus :

$$E=h\nu \text{ or } F=\frac{hc}{\lambda}\left(\because \quad \nu=\frac{c}{\lambda}\right) \text{ or } E=hc\bar{\nu}$$

$$\left(\because \quad \bar{\nu}=\frac{1}{\lambda}\right)$$ where c = velocity of radiation (cm/sec)

λ = wavelength (in cms) and $\bar{\nu}$ = wave number.

In 1905 Einstein extended the quantum theory by postulating that the energy, *like light, is not only emitted or absorbed in packets but is also propagated in space in packets.* Each packet he called a photon. *According to this extension light has wave as well as particle characteristics.* The energy, E and the mass, m of a photon, are given by : $E=h\nu$ and $E=mc^2$ where c = velocity of light. The relation between the mass and energy is called **Einstein's mass-energy relationship.**

THE HYDROGEN SPECTRUM.

When an electric current is passed through hydrogen gas kept at low pressure, we get hydrogen spectrum which is found to consist of a number of lines in the visible ultraviolet and infra-red regions. Each line of the spectrum corresponds to a particular frequency.

It was found that these lines could be grouped into a definite number of spectral series. These are five series and are known after the names of their discoverers : (*i*) *Balmer series* (1885) appearing in the *visible region* (*ii*) *Paschen series* (1896) (in the *infra-red region*) (*iii*) *Lyman series* (1896) (in the *ultra-violet region*) (*iv*) *Brackett series* (1922) (in the *infra-red region*) (*v*) *Pfund series* (1925) (in the *infra-red region*)

Balmer's formula. In 1885 Balmer, while analysing the hydrogen spectrum in the visible region (Balmer series), found that the wavelength, λ and the wave number, $\bar{\nu}$ of each spectral line of Balmer series is given by :

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where R_H=constant known as **Rydberg constant** or **Rydberg number for hydrogen** and n=an integral. n=3, 4, 5 and 6 for H_α, H_β, H and H_δ lines respectively in the hydrogen spectrum. (See Fig. 1·1).

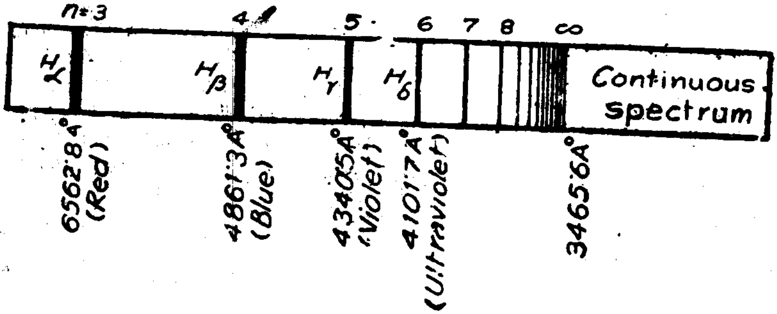


Fig. 1·1. Balmer series of atomic hydrogen in the excited state. The dark lines show the bright emission lines of the spectrum.

The experimental value of R_H for the visible lines of hydrogen spectrum has been found to be equal to 109,678 cm^{-1}.

Rydberg's formula. Balmer's formula as given above served as a valuable clue to Rydberg who made a detailed study of the spectrum and gave in 1889 a general relationship for the wave number $\bar{\nu}$ for the spectral lines. This formula, known as Rydberg's formula, can be written in a simple form as :

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \text{ cm}^{-1}$$

where R_H=Rydberg's constant and m and n are two integers called Rydberg's integers. For a given spectral series m remains constant and n varies from line to line in the same series, *e.g.* for the six lines of Balmer series, m=2 and n for the successive six lines is 3, 4, 5, 6, 7 and 8.

The values of *m* for various series and those of *m* for the successive lines in the same series are given below in Table 1·1.

Table 1·1 Values of *m* and *n* for various series

Spectral Series	*Value of m*	*Value of n* [$n=(m+1), (m+2), \ldots$]	*Spectral Region*
Lyman Series	1	2, 3, 4, 5...	Ultra-violet region
Balmer Series	2	3, 4, 5, 6...	Visible region
Paschen Series	3	4, 5, 6, 7...	Infra-red region
Brackett Series	4	5, 6, 7, 8...	Infra-red region
Pfund Series	5	6, 7, 8...	Infra-red region

Thus by assigning suitable values to *m* and *n* as indicated in the Table we can calculate the value of the wave number, $\bar{\nu}$ and the wavelength, λ of the spectral lines.

Ritz Combination Principle. This principle states that *by combining the two terms that occur in Rydberg's or Balmer's formula, other relations can be obtained which will represent new lines and even new spectral series, e.g.* series other than that of Balmer in the hydrogen spectrum were predicted even before they were actually discovered by Paschen and Brackett. Considering the first two lines *viz* H_α and H_β of the Balmer series, we can get the wave number of a new line as follows:

$$\bar{\nu}_\alpha = R_H\left(\frac{1}{2^2}-\frac{1}{3^2}\right) \text{ and } \bar{\nu}_\beta = R_H\left(\frac{1}{2^2}-\frac{1}{4^2}\right)$$

Thus $$\bar{\nu}_\beta - \bar{\nu}_\alpha = R_H\left(\frac{1}{3^2}-\frac{1}{4^2}\right)$$

This equation gives the wave number, $(\bar{\nu}_\beta - \bar{\nu}_\alpha)$ of a new line which is actually the first line in a new series namely Paschen series appearing in the infra-red region. Similarly it can be shown that the wave number of the second line of the same series is equal to $\bar{\nu}_\gamma - \bar{\nu}_\alpha$ and so on. In the same manner another series namely Brackett series discovered by Bracket can be obtained.

BOHR'S ATOMIC MODEL—QUANTUM MECHANICAL CONCEPT

Rutherford's planet-like model of the atom was contested by

Bohr in 1913 on two grounds:

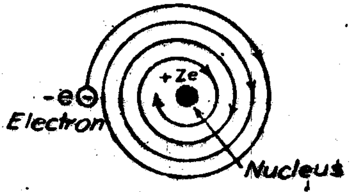


Fig. 1·2. An electron in the Rutherford Atomic Model spirals into the nucleus as it radiates energy due to acceleration.

(*i*) According to classical mechanics, whenever a charged particle is subjected to acceleration, it emits radiation and loses energy. An electron revolving round the nucleus would, therefore, be continually accelerated towards the centre of the orbit and consequently emitting radiation. The result of this would be that the radius of curvature of its path (*i.e.* orbit) would go on decreasing and due to spiral motion, the electron would finally fall into the nucleus when all its rotational energy has been spent on the electromagnetic radiation and the atom would collapse. (*See* Fig. 1·2). No such thing is, however, observed.

(*ii*) If the electrons lose energy continuously, the observed atomic spectra should be *continuous*, consisting of *broad bands* **merging one into the other.** **The observed atomic** spectra, however, consists of well-defined lines of definite frequencies.

To overcome these two objections and also to explain the spectra of hydrogen atom he proposed a *quantum mechanical model* of the atom based on **Quantum Theory** of Radiation.

Postulates of Bohr's Theory. (*i*) Each orbit round the nucleus is associated with a definite amount of energy and the orbits are, therefore, are called **energy levels** or **main energy shells.** These shells are numbered as 1, 2, 3,......starting from the nucleus and are designated by capital letters : K, L, M......respectively. *The energy associated with a certain energy level increases with the increase of its distance from the nucleus.* Thus, if E_1, E_2, E_3......denote the energies associated with the energy levels numbered as 1 (K-shell), 2 (L-shell), 3 (M-shell)......, these are in the order :

$$E_1 < E_2 < E_3 < \ldots\ldots$$

Thus an outer energy level has higher energy than an inner energy level.

While revolving round the nucleus in a fixed orbit, the electron neither loses (*i.e.* emits) nor gains (absorbs) energy, *i.e.* its energy remains constant as long as it is revolving in a particular orbit. Under this condition the atom as a whole is said to be in a **stationary energy state** or simply in **stationary state.**

Energy is, however, emitted or absorbed by an atom when an electron jumps from one energy level to the other. The amount of energy (ΔE) emitted or absorbed in this type of jump of the electron is given by Plank's equation. Thus :

$$\Delta E = h\nu$$

where ν is the frequency of the energy (radiation) emitted or absorbed.

(*ii*) Although there is an infinite number of circular concentric orbits in which an electron may be expected to move about the nucleus, *the electron can move only in that orbit in which the angular momentum of the electron* (mvr) *is quantised*, i.e. *the angular momentum of the electron is a whole number multiple of* $h/2\pi$. This is known as *principle of quantisation of angular momentum* according to which

$$mvr=n.\frac{h}{2\pi}$$

where m = mass of the electron, v = tangential velocity of electron in its orbit, r = distance between the electron and nucleus and n = a whole number which has been called **principal quantum number** by Bohr. It is the number of the orbit in which the electron is revolving and can have the values 1, 2, 3......for the main energy levels numbered as 1 (K-shell), 2 (L-shell), 3 (M-shell),......starting from the nucleus.

BOHR'S THEORY FOR HYDROGEN ATOM

By applying the concept of quantisation of energy and the laws of classical mechanics, Bohr in 1913 worked out a number of mathematical expressions such as those of radius of *n*th orbit, energy of an electron in the *n*th orbit etc. These expressions gave a satisfactory explanation for the hydrogen spectrum etc.

(1) **Radius of the *nth* orbit (r_n).** Imagine nucleus of a hydrogen atom having one proton of charge $+e$ The electron with charge equal and opposite to $+e$ (*i.e.* with $-e$) revolves round this nucleus in an orbit of radius, r. Let v be the tangential velocity and m the mass of the revolving electron.

Evidently on the revolving electron two types of forces are acting: (*i*) *Centrifugal force* which is due to the motion of the electron and tends to take the electron away from its orbit. It is equal to $+mv^2/r$ and acts outwards from the nucleus. (*ii*) *Centripetal force* (also called *electrostatic force of attraction*) which exists between the revolving electron and the nucleus and tends to pull the electron towards the nucleus. It is given by Coulomb's inverse square law and is, therefore, equal to $-e\times e/r^2=-e^2/r^2$. It acts towards the nucleus.

In order that the electron may keep on revolving in its orbit, these two forces, which act in opposite directions must balance each other, *i.e.*

$$\frac{e^2}{r^2}=\frac{mv^2}{r}$$

or

$$v^2=\frac{e^2}{mr}$$

From the principle of quantisation as applied to the revolving electron, we know that $mvr=nh/2\pi$ or $v^2=n^2h^2/4\pi^2m^2r^2$. Comparing this equation with the above equation we get

$$\frac{e^2}{mr}=\frac{n^2h^2}{4\pi^2m^2r^2}$$

or
$$r=\frac{n^2h^2}{4\pi^2me^2}$$

or
$$\boxed{r_n=\frac{n^2h^2}{4\pi^2me^2}}$$

where r_n=radius of the *nth* orbit.

Since all the terms on the right hand side of the above equation, except n, are fixed, radius of the *nth* orbit is proportional to n^2 (*i.e.* $r_n \propto n^2$).

On putting $n=1$ in the above expression of r_n we get the radius of the first orbit of hydrogen atom which is represented as r_1, r_H or a_0 and is called **Bohr radius.** Thus :

$$\boxed{r_1\ (r_H \text{ or } a_0)=\frac{h^2}{4\pi^2me^2}}$$

On putting $h=6{\cdot}6256\times10^{-27}$ erg-sec,
$\pi=3{\cdot}14$, $m=9{\cdot}109\times10^{-28}$ gm,
$e=4{\cdot}8\times10^{-10}$ e.s.u.

in the above expression for r_1 we get the value of r_1 as :

$$r_1=\frac{(6{\cdot}625\times10^{-27})^2}{4\times(3{\cdot}14)^2\times(9{\cdot}109\times10^{-28})\times(4{\cdot}8\times10^{-10})^2}$$

or
$$\boxed{r_1\ (r_H \text{ or } a_0)=0{\cdot}53\times10^{-8}\text{ cm}=0{\cdot}53\text{ Å}}$$

Relation between r_n and r_1. On dividing the equations giving the values of r_n and r_1, we get

$$\frac{r_n}{r_1}=\frac{n^2h^2}{4\pi^2me^2}\times\frac{4\pi^2me^2}{h^2}=n^2$$

or
$$\boxed{r_n=r_1\times n^2=0{\cdot}53\times n^2\text{ Å}}$$

Thus the values of r_2, r_3......(in Å) in terms of r_1 are given as :

$r_2=0{\cdot}53\times2^2=2{\cdot}12$Å, $r_3=0{\cdot}53\times3^2=4{\cdot}77$ Å,
$r_4=0{\cdot}53\times4^2=3{\cdot}48$ Å, $r_5=$......

(2) **Energy of the electron in the *nth* orbit (E_n).** Energy (E_n) of an electron moving in the *nth* orbit is the sum of its kinetic energy (K.E.) and potential energy (P.E). K.E. which is due to the motion of the electron is equal to $mv^2/2$ and P.E. which is because of the fact

that the electron lies in the field of the positive nucleus is equal to $-e^2/r$. Thus :

$$E_n = \frac{1}{2} mv^2 - \frac{e^2}{r}$$

Again we know that in order to keep the electron revolving in its orbit the centrifugal force $(=+mv^2/r)$ and the centripetal force $(=-e^2/r^2)$ acting on the revolving electron must balance each other, *i.e.* $e^2/r^2 = mv^2/r$ or $mv^2 = e^2/r$. On putting mv^2 equal to e^2/r in the above expression of E_n, we get

$$E_n = \frac{e^2}{2r} - \frac{e^2}{r} = -\frac{e^2}{2r}$$

Now put $r = n^2h^2/4\pi^2me^2$ in the above equation to get

$$E_n = -\frac{e^2}{2} \times \frac{4\pi^2me^2}{n^2h^2}$$

or

$$\boxed{E_n = -\frac{2\pi^2me^4}{n^2h^2}}$$

From this equation of E_n the following conclusions emerge :

(*i*) Since all the quantities except n on the right hand side of the above equation are constant, E_n will depend only on n. It means that so long as the electron is moving in a particular orbit (*i.e.* n does not change), its energy will remain constant.

(*ii*) The negative sign occurring in the above equation implies that $E_n \propto n^2$. Thus if the energies associated with 1st, 2nd, 3rd, ... nth orbits are $E_1, E_2, E_3, \ldots E_n$, these will be in the order :

$$E_1 < E_2 < E_3 < \ldots < E_n$$

The concept of negative value of E_n can be explained as follows : Suppose there is an electron at infinity from the positively charged nucleus. In this case, there is no electrical attraction between the electron and the nucleus and the energy of the electron may be supposed to be zero. Now let the electron move closer and closer to the nucleus. No work needs be done on the electron, since it can move by itself on account of electrical attraction and work is done by the electron itself as a result of which its energy falls and E_n becomes negative. When one wants to remove the electron from the orbit, energy known as ionisation energy must be supplied.

Energy (E_1) of the electron moving in the *1st* Bohr orbit is obtained by putting $n=1$ in the energy expression of E_n. Thus

$$\boxed{E_1 = -\frac{2\pi^2me^4}{h^2}}$$

Putting the values of π, m, e and h in the above expression of E_1 we get the numerical value of E_1 as :

$$E_1 = -\frac{2 \times (3{\cdot}14)^2 \times (9{\cdot}109 \times 10^{-28})(4{\cdot}8 \times 10^{-10})^4}{(6{\cdot}6256 \times 10^{-27})^2}$$

$$= -21{\cdot}79 \times 10^{-12} \text{ ergs/atom} = -13{\cdot}6 \; eV\text{/atom}$$

$$= -313{\cdot}6 \text{ Kcal/mole}$$

(Note that 1 erg $= 6{\cdot}2419 \times 10^{11}$ *eV*, 1 *eV* $= 23{\cdot}06$ Kcal)

Relation between E_n and E_1. Evidently

$$\frac{E_n}{E_1} = \frac{2\pi^2 me^4}{n^2 h^2} \times \frac{h^2}{2\pi^2 me^4}$$

or

$$\boxed{E_n = E_1 \times \frac{1}{n^2} = -\frac{13{\cdot}6}{n^2} \; eV\text{/atom}}$$

Thus the values of E_2, E_3, E_4, E_5 etc. (in *eV*) in terms of E_1 are given as :

$$E_2 = -13{\cdot}6/2^2 = -3{\cdot}4 \; eV\text{/atom},$$

$$E_3 = -13{\cdot}6/3^2 = -1{\cdot}51 \; eV\text{/atom},$$

$$E_4 = -13{\cdot}6/4^2 = -0{\cdot}85 \; eV\text{/atom},$$

$$E_5 = -13{\cdot}6/5^2 = -0{\cdot}54 \; eV\text{/atom}.$$

From these values of E_1, E_2, E_3 etc. the following points are obvious :

(*i*) The energy levels converge as *n* increases, *i.e.*, the difference in energy between two successive energy levels decreases with the increase of *n*, *e.g.* $E_2 - E_1 > E_5 - E_4$. This means that as the value of *n* goes on increasing, the energy values for the orbits become closer to each other and as *n* approaches infinity, the levels become closely packed and reach a series limit.

(*ii*) An electron in a hydrogen atom can have only certain definite energies and no energies in between are possible, *e.g.* hydrogen electron cannot have an energy between $-13{\cdot}6$ *eV*/atom ($=E_1$) and $-3{\cdot}4$ *eV*/atom ($=E_2$).

(*iii*) The lowest energy state corresponding to $n=1$ for an atom (or an ion or a molecule) is called the **ground state.** The first higher energy state (*i.e.* the state with $n=2$) above the ground state ($n=1$ state) is called the **first excited state** while the next higher state (*i.e.*, state with $n=3$) is called the **second excited state.**

(3) **Frequency (ν), Wave number ($\bar{\nu}$) and wavelength (λ) of the spectral lines of hydrogen atom.** We have already stated that energy is *emitted* or *absorbed* by an atom only when an electron jumps from one energy level to the other. When an electron jumps from an outer energy level, n_2 of energy, E_{n_2} to an inner energy level, n_1 of energy the E_{n_1}, energy equal to $(E_{n_2} - E_{n_1})$ is emitted (*i.e.* given out or radiated) which is equal to $h\nu$ (Plank's equation) where ν is the frequency of the energy emitted (Note $E_{n_2} > E_{n_1}$). Thus

$$(\Delta E)_{n_2 \rightarrow n_1} = E_{n_2} - E_{n_1} = h\nu$$

In this type of jump which is represented as $n_2 \longrightarrow n_1$ or $E_{n_2} \longrightarrow E_{n_1}$ jump the spectral line with the wavelength λ given by the above equation is *emitted* from the light falling on it and we get **emission spectrum.**

In the reverse jump (represented as $n_1 \longrightarrow n_2$ or $E_{n_1} \longrightarrow E_{n_2}$) in which the electron passes from an inner level to an outer level, energy equal to $(E_{n_2}-E_{n_1})$ is *absorbed*, and we get **absorption spectrum.** The wavelength of the spectral line is given by the same expression as given above.

Now since $E_{n_1}=-\dfrac{2\pi^2e^4m}{n_1^2h^2}$ and $E_{n_2}=-\dfrac{2\pi^2e^4m}{n_2^2h^2}$,

the above equation reduces to :

$$(\Delta E)_{n_2\to n_1}=-\frac{2\pi^2e^4m}{n_2^2h^2}-\left(-\frac{2\pi^2e^4m}{n_1^2h^2}\right)=h\nu$$

or

$$h\nu=\frac{2\pi^2e^4m}{h^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

or

$$\boxed{\nu=\frac{2\pi^2e^4m}{h^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)} \qquad \ldots(i)$$

or

$$\bar{\nu}c=\frac{2\pi^2e^4m}{h^2}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad (\text{since } \nu=\bar{\nu}c)$$

or

$$\bar{\nu}=\frac{2\pi^2e^4m}{h^2c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

or

$$\boxed{\bar{\nu}=\frac{1}{\lambda}=\frac{2\pi^2e^4m}{h^2c}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)} \left(\text{since } \bar{\nu}=\frac{1}{\lambda}\right)$$

or

$$\boxed{\bar{\nu}=\frac{1}{\lambda}=R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)}$$

where R$_H$ is Rydberg's constant and is equal to $2\pi^2e^4m/h^2c$. Its calculated value, $(R_H)_{cal}$ is thus given by

$$(R_H)_{cal}=\frac{2\times(3\cdot14)^2\times(4\cdot8\times10^{-10})^4\times(9\cdot109\times10^{-28})}{(6\cdot625\times10^{-27})^3\times(3\times10^{-10})}=109{,}679\text{cm}^{-1}$$

The above equation thus reduces to

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = 109{,}679\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{cm}^{-1}} \qquad \ldots(ii)$$

With the help of equations (*i*) and (*ii*) we can calculate the frequency (ν), wave number ($\bar{\nu}$) and wavelength (λ) respectively of the lines observed in the hydrogen spectrum, provided that we know the values of n_1 and n_2. The values of n_1 and n_2 are fixed from the electronic transitions.

ELECTRONIC TRANSITION AND ORIGIN OF 1HE SPECTRAL LINES OF HYDROGEN ATOM

Although hydrogen atom contains only one electron, its spectrum gives a large number of lines. This is because any given sample

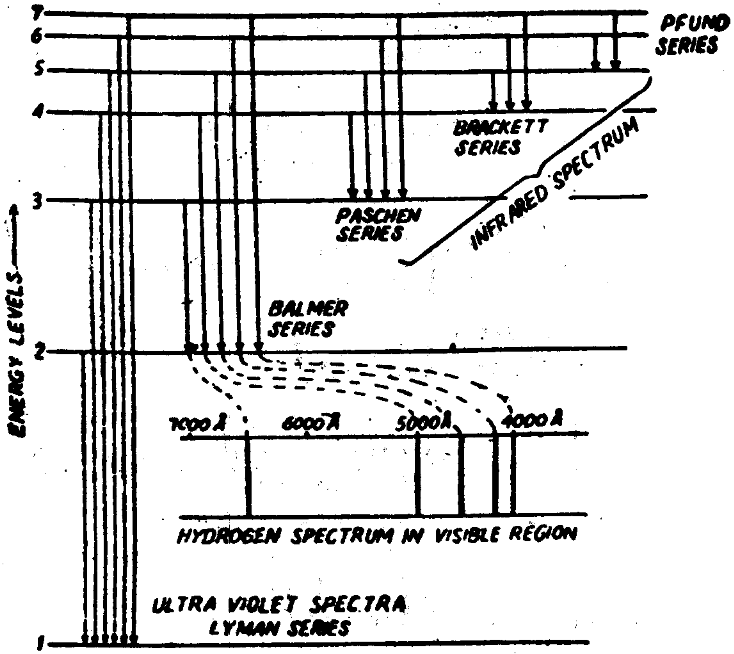


Fig. 1·3. Energy level diagram for the observed hydrogen spectrum.

of hydrogen contains almost infinite number of atoms. Under the normal conditions the electron of each hydrogen atom remains in the ground state near the nucleus, *i.e.*, in the energy level with $n=1$ (K-shell). When energy is supplied to this sample of hydrogen gas by passing an electric discharge through the gas in the discharge tube, individual atoms absorb different amounts of energy. Some atoms absorb such amount of energy as to shift their electron to, say, the third energy level (*i.e.*, M shell with $n=3$) while some others may absorb larger amount of energy to shift their electron to the fourth ($n=4$ level), fifth ($n=5$ level), sixth ($n=6$ level) and seventh energy level ($n=7$ level). The electrons in higher energy levels are relatively unstable and hence drop back to the lower energy level and in this process of dropping back, energy is emitted in the form of line spectrum containing various lines of particular frequency and wavelength. With the help of these electronic transitions (*i.e.*, the process of dropping back of electrons from the higher energy levels to the lower energy levels) we can fix the values of n_1 and n_2, *e.g.* Balmer series which appears in the visible region arises when the electrons jump from the 3rd, 4th, 5th,......energy levels (which are higher energy levels) to the 2nd energy level (which is lower energy level) (*see* Fig. 1·3). Thus for this series $n_2=3, 4, 5,...$ and $n_1=2$. Values of n_1 and n_2 determined from the electronic transitions of the type mentioned above for all the five series with the region in which they appear are given in Table 1·2.

Table 1·2. Electronic transitions and values of n_1 and n_2 for various spectral series of hydrogen spectrum

Series of lines	*Electron jumps to an energy level with n_1 =*	*Electron jumps from energy level with n_2 = (n_1+1), (n_1+2)...*	*Spectral region*	*Wavelength (λ) (A°)*
Lyman Series	1	2, 3, 4, ...etc.	ultraviolet	Less than 4000A°
Balmer Series	2	3, 4, 5..... etc.	visible	between 4000A° and 7000A°
Paschen Series	3	4, 5, 6......etc.	Near infra-red	more than 7000A°
Brackett Series	4	5, 6, 7..... etc.	Far infra-red	more than 7000A°
Pfund Series	5	6, 7, 8......etc.	far infra red	more than 7000A°

The wavelengths of various spectral lines can be calculated by making use of the following equation

$$\bar{v}=\frac{1}{\lambda}=109{,}679\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

For example, for the **Lyman series**, we have

$n_1=1$ and $n_2=2, 3, 4...$and hence

(*i*) When $n_2=2$, $\frac{1}{\lambda}=109{,}679\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\text{cm}^{-1}$

$$=\frac{3}{4}\times 109679$$

or
$$\frac{4}{3\times 109679}\ \text{cm}^{-1}=1216\text{A}^\circ$$

(*ii*) When $n_2=3$, $$\frac{1}{\lambda}=109{,}679\left(\frac{1}{1^2}-\frac{1}{3^2}\right)\text{cm}^{-1}$$

$$=\frac{8}{9}\times 109679$$

or
$$\lambda=\frac{9}{8\times 109679}\ \text{cm}^{-1}=1026\ \text{A}^\circ$$

(*iii*) The spectral lines of Lyman series converge to a limit at $n_2=\infty$. Thus

When $n_2=\infty$,

$$\frac{1}{\lambda}=109679\left(\frac{1}{1^2}-0\right)\text{cm}^{-1}$$

$$=109679\ \text{cm}^{-1}$$

or
$$\lambda=\frac{1}{107679}\ \text{cm}^{-1}=912\ \text{A}^\circ$$

The spectral lines of Lyman series lie in the ultra-violet region of the spectrum.

λ values of the lines of other series can similarly be calculated by adopting the above calculations.

Facts in favour of Bohr's Theory. The points in favour of the validity of Bohr's theory may be summarised as follows :

(*i*) The frequencies of the spectral lines of the hydrogen spectrum, as determined experimentally, are in close agreement with the frequencies of the same lines calculated with the help of Bohr's theory.

(*ii*) The value of Rydberg constant for hydrogen, R_H, as calculated from Bohr's theory ($R_H=109{,}679\ \text{cm}^{-1}$) is in full agreement with experimental value ($=109{,}678\ \text{cm}^{-1}$) obtained from spectroscopic studies.

(*iii*) The emission and absorption spectra of hydrogen-like atoms is explained nicely by Bohr's concept of stationary states of electrons.

(*iv*) The radii and energies of the permissible orbits in hydrogen atom as calculated on the basis of Bohr's theory are in good agreement with the experimental values.

Limitations of Bohr's Theory. (*i*) According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit, but how this radiation occurs is not explained by Bohr.

(*ii*) Bohr Theory had explained the existence of various lines in H-spectrum, but it predicted that only a series of lines exist. At that time this was exactly what had been observed. However, as better instruments and techniques were developed, it was realised that the spectral line that had been thought to be a single line was actually a collection of several lines very close together (known as spectrum). Thus for example, the single H_α spectral line of Balmer series consists of many lines very close to each other (see Fig. 1·4).

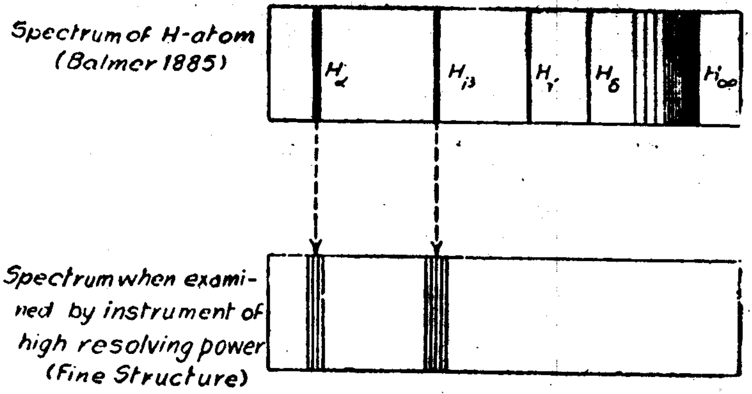


Fig. 1·4. Splitting of the lines of hydrogen spectrum when examined by instruments of high resolving power (*fine structure*)

Thus the appearance of the several lines implies that there are several energy levels which are close together for each quantum number *n*. This would require the existence of new quantum numbers.

(*iii*) Whereas Bohr's theory has successfully explained the observed spectra for hydrogen atom and hydrogen like ions (*e.g.* He^+, Li^{2+}, Be^{3+} etc.), it cannot explain the spectral series for the atoms having a large number of electrons.

(*iv*) There was no satisfactory justification for the assumption that the electron can rotate only in those orbits in which the angular momentum of the electron ($m\,v\,r$) is a whole number multiple of $h/2\pi$, *i.e.* he could not give any explanation for using the principle of *quantisation of angular momentum* and it was introduced by him arbitrarily.

(*v*) Bohr assumes that an electron in an atom is located at a definite distance from the nucleus and is revolving round it with definite velocity, *i.e.* it is associated with a fixed value of momentum. This is against the **Heisenberg's Uncertainty Principle** according to which *it is impossible to determine simultaneously with certainty the position and the momentum of a particle.*

(*vi*) **No explanation for Zeeman Effect** : If a substance which gives a line emission spectrum, is placed in a magnetic field, the lines of the spectrum get split up into a number of closely spaced lines (Fig. 1·5).

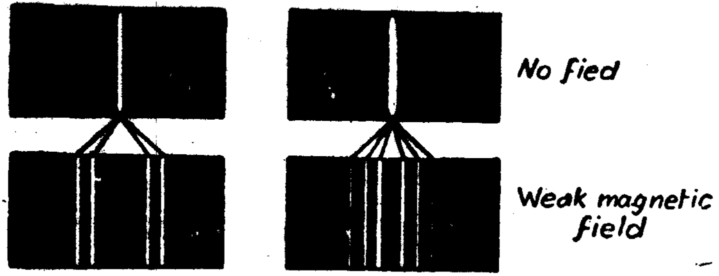


Fig. 1·5. Zeeman Effect for sodium. Principal doublet in the presence of a weak magnetic field.

This phenomenon is known as **Zeeman effect**. Bohr's theory has no explanation for this effect.

(*vii*) **No Explanation of the Stark Effect :** If a substance which gives a line emission spectrum is placed in an external electromagnetic field, its lines get split into a number of closely spaced lines. This phenomenon is known as **Stark Effect**. Bohr's theory is not able to explain this observation as well.

BOHR-SOMMERFELD'S ATOMIC MODEL

To account for the *fine structure* in the spectrum of hydrogen atom Sommerfeld extended Bohr's theory in 1915 and suggested *that the moving electron might describe, in addition to the circular orbits, elliptical orbits as well with the nucleus situated at one of the foci.*

It is well known that in a circle, the only coordinate that changes is the angle of revolution, ϕ while the radial coordinate, r (*i.e.* the radius) remains constant. In an elliptical orbit, however, both the polar coordinates *viz.* radius vector, r (which is the distance of the electron from the nucleus situated at one of the foci) and the vectorial angle, ϕ known as azimuthal angle (which is the angle between the radius vector and the major axis of the ellipse) change. Accordingly, an electron moving in an elliptical orbit *has two degrees of freedom*, ϕ and r and corresponding to these two degrees of freedom *two quantum numbers would be required to represent the electronic motion.* According to Sommerfeld, these two quantum numbers are : (*i*) **Radial quantum number**, n_r and (*ii*) **Azimuthal quantum number**, n_ϕ and these are related as : $n = n_r + n_\phi$ where n is the **total quantum number**. n and n_ϕ are related to the geometry of the ellipse as

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{Length of the major axis } (a)}{\text{Length of the minor axis } (b)}$$

It may be seen from the above expression that :

(*i*) When $n_\phi = n$, a becomes equal to b and the orbit becomes circular. Circular orbit thus is a special case of elliptical orbit.

(*ii*) When $n_\varphi < n$, the orbit will remain elliptical.

For a given value of n, the azimuthal quantum number, n_φ may have n values. Thus $n_\varphi = 1, 2, 3, \ldots, (n-1), n$, e.g. for $n=3$, $n_\varphi = 1, 2, 3$. Corresponding to these values of n_φ we have three possible orbits : one circular (for which $n_\varphi = 3$) and two elliptical ($n_\varphi = 1$ and $n_\varphi = 2$). These are shown diagramatically in Fig. 1·6.

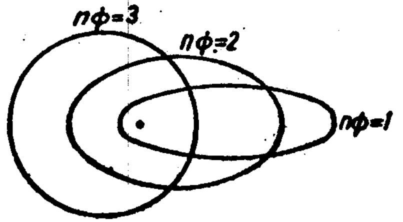


Fig. 1·6. Three possible orbits for $n=3$

Applying the principle of quantisation of momentum to the electron moving in an elliptical orbit. Sommerfeld deduced the energy of the electron in the hydrogen atom as :

$$E_n = -\frac{2\pi^2 e^4 m}{(n_\varphi + n_r)^2 h^2}$$

Thus we find that the energy depends not only on the principal quantum number, n but also to some extent on the azimuthal quantum number, n_φ. The frequency of the radiation emitted as a result of transition of an electron from a level of energy E_2 to a level of energy E_1 ($E_2 > E_1$) would, therefore, vary, depending on the various values of n_φ and as a result a group of closely spaced lines would appear instead of a single line in the spectrum of hydrogen atom or hydrogen like atoms.

The concepts advanced by Sommerfeld evidently postulate the existence of sub-energy level for electrons in each of the principal energy levels of the atom.

Weakness of Sommerfeld's model. Experimental observations and theoretical treatment based on wave mechanics show that the different values of azimuthal quantum number are : $0, 1, 2, 3, \ldots\ldots, (n-2), (n-1)$ (total n values) and not $1, 2, 3, \ldots\ldots (n-1), n$ (total n values). The new quantum number beginning with zero and ending at $(n-1)$ has been represented by l in order to avoid the confusion with n_φ. Thus l and n_φ are related as : $l = n_\varphi - 1$ and $l = 0, 1, 2, \ldots\ldots (n-2)\ (n-1)$.

Sommerfeld's theory can not give the correct number of lines observed in fine structure. Moreover, it gives no information about the relative intensities of the "*fine lines*". Further, the exact definition of position and momentum is contrary to the uncertainty principle.

QUANTUM NUMBERS

We have seen that Bohr's Theory could not explain the existence of fine structure in the *H*-spectrum. The appearance of several lines in the *H*-spectrum, therefore, indicates that only one quantum number, n, suggested by Bohr, is not sufficient for specifying the various lines. There is now clear evidence in favour of the fact that four quantum numbers are needed to explain the various spectra.

These quantum numbers are the **identification numbers** for an individual electron in an atom, since these fully describe the position and energy of an electron in an atom.

1. Principal Quantum Numbers (n). *This quantum number denotes the energy level or the principal shell to which an electron belongs.* It is denoted by n.

Permitted values of n. It can have only integral value from 1 to ∞, but 1 to 7 have so far been established. The letters K, L, M... are also used to designate the values of n. These letters stand to show the major energy level and correspond to $n=1, 2, 3$......respectively.

Thus when $n=1, 2, 3, 4$..., the letter designations used are K, L, M, N, ... respectively. If for an electron $n=3$, it resides in the M-shell. n gives an idea of the size of the shell and is the same integral as suggested by Bohr in $mvr=n.\frac{h}{2\pi}$.

2. Azimuthal Quantum Number (l). This quantum number is denoted by letter l. It is also called *angular momentum quantum number, orbital quantum number* and sometimes *subsidiary quantum number.* As already stated, this quantum number was introduced by Sommerfeld in his atomic model and gives the angular momentum of the electron in its "precessional" elliptical movement round the nucleus and accounts for the fine structure in the H-spectrum. *It gives an idea of the shape of the orbital.*

Permitted values of l for a given value of n. l can have any value from 0 to $(n-1)$ for a given value of n *i.e.*

$$l=0, 1, 2, \ldots\ldots (n-2), (n-1).$$

The total number of different values of l is equal to n. Thus, if $n=1$, $l=0$ (Only one value), $n=2$, $l=0$, 1 (Two values), $n=3$, $l=0$, 1, 2 (Three values), $n=4$, $l=0$, 1, 2, 3 (Four values).

Total values of l for a given value of n gives the total number of sub-shells into which a main shell (*e.g.* K, L, M...) is divided, *e.g.* only one value of l (*viz.* $l=0$) for $n=1$ (K-shell) shows that there is only one energy state in K-shell which is represented as (1 0) or 1s state. In 1s designation the number 1 stands for the value of n and the latter s denotes $l=0$. Similarly $l=0$, 1 for $n=2$ (L-shell) indicates that L-shell is divided into two sub-shells which are designated as (2 0) or 2s and (2 1) or 2p.

Different values of $l=0, 1, 2, 3$,... are symbolised by the letters s, p, d, f... These letters designate the old spectral terms : *sharp, principal, diffuse* and *fundamental* respectively.

3. Explanation of Zeeman Effect and the Magnetic Quantum Number (m). We have already seen that Bohr could not explain the splitting of a single spectral line into a number of closely spaced lines in presence of a magnetic field (*Zeeman Effect*) or in presence of electric field (*Stark Effect*). According to Linde, the presence of more lines in the spectrum in a magnetic field or in an electric field indicates that the energy levels are further sub-divided by the field and an additional quantum number, which he called **magnetic quantum number, m,** is needed to specify these energy sub-levels. Linde postulated that the electron producing the original line has in a magnetic field several possible space orientations for the same angular momentum vector (*i.e.*, for the same value of l). Thus m is the quantum number corresponding to the component of the orbital angular momentum along a reference direction for a single electron.

Permitted values of m. Total possible values of m depend on the values of l. m can have the following values for a given value of l :

$m=0, \pm1, \pm2, \pm3, \ldots \pm l$ giving a total number of values of m equal to $(2l+1)$. Thus if $l=0$ (s-sub-shell), $m=0$ (one value only), $l=1$ (p-sub-shell), $m=0, \pm1$ (total three values), $l=2$ (d-sub-shell), $m=0, \pm1, \pm2$ (total five values), $l=3$ (f-sub-shell), $m=0, \pm1, \pm2, \pm3$ (total seven values).

Total values of m for a given value of l gives the total number of space orientations of s, p, d, f etc. sub-shells. In other words total number of values of m for a given value of l gives the total number of sub-sub-shell (*orbitals*) into which s, p, d, f sub-shells are sub-divided, *e.g.* five values of m *viz.*, $m=0, \pm1, \pm2$ for $l=2$ (d-sub-shell) indicate that d-sub-shell is sub-divided into five sub-sub-shells (orbitals) which are d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. All these five orbitals are *energetically identical* (*i.e.*, *degenerate*) in an atom except when it is placed in a steady magnetic field or is in combination with other atoms in a molecule.

4. **Spin Quantum Number (s).** When spectral lines of H, Li, Na and K etc. were observed by means of the instruments of high resolving power, each line of the spectral series was found consisting of a pair of lines (known as **doublets or double-line structure**). Here it should be understood clearly that this doublet is different from fine structure which consists of closely-spaced fine lines (not widely-separated ones).

To account for these doublets Uhlenbeck and Goud-Smith (1925) suggested that *the electron, while moving round the nucleus in an orbit, also rotates* (or *spins*) *about its own axis either in a clockwise direction or in an anti-clockwise direction* and this spinning of the electron about its own axis adds to the angular momentum of the electron *i.e.*, the angular momentum of the electron is not only due to the motion of the electron round the nucleus but also due to the spinning of the electron. Accordingly, the angular momentum of the electron under this condition is called **spin angular momentum** and is equal to $\sqrt{s(s+1)} \cdot \frac{h}{2\pi}$ where s stands for the absolute value of spin quantum number *i.e.* without sign.

Permitted values of s. s can have two values *viz* $+\frac{1}{2}$ (corresponding to the spinning of the electron in the clock-wise direction) and $-\frac{1}{2}$ (corresponding to the spinning in anti-clock-wise direction). Clock-wise and anti-clock-wise spinnings are represented as ↑ and ↓ respectively.

Two electrons with the same sign of spin quantum numbers are said to have *parallel spins* (shown as ↑ ↑), while those having opposite signs of spin quantum numbers are said to have *opposite spins* or *anti-parallel spins* (↑ ↓). Two electrons having opposite spins are said to be *paired up electrons.*

Relation between different quantum numbers *viz.* n, l, m and s is given in Table 1·3 from which the following points one obvious.

(*i*) The main shells K, L, M, N etc. are divided into *one* (*viz* 1*s*), *two* (2*s*, 2*p*), *three* (3*s*, 3*p*, 3*d*), *four* (4*s*, 4*p*, 4*d*, 4 *f*) sub-shells etc. respectively.

(*ii*) (*a*) Only one value of m (*viz* $m=0$) for $l=0$ (s-sub-shell) shows that s-sub-shell has no sub-sub-shell and is present in all the main shells. Thus K-shell ($n=1$) has only one sub-shell *viz* 1*s*.

(*b*) Three values of m (*viz* $m=0, \pm 1$) for $l=1$ (p-sub-shell) shows that p-sub-shell which begins with $n=2$ (*i.e.* L main shell) is divided into three sub-sub-shells which are $2p_x$, $2p_y$, and $2p_z$. Thus L shell ($n=2$) has four sub-sub-shells *viz* $2s$, $2p_x$, $2p_y$ and $2p_z$.

(*c*) Similarly M-main shell ($n=3$) has nine sub-sub-shells *viz* $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$.

In general a main energy level with a given value of n has n^2 sub-sub-shells.

(*iii*) Since each sub-sub-shell can contain two electrons, the total number of electrons in a main shell is equal to $2n^2$. Thus maximum number of electrons in K ($n=1$), L($n=2$), M($n=3$) etc. shells is equal to 2 ($=2\times1^2$), 8 ($=2\times2^2$), 18 ($=2\times3^2$) etc.

(*iv*) Maximum number of electrons in s, p, d, f etc. sub-shells is equal to $2(2l+1)$. Consequently these sub-shells have 2, 6, 10, 14 electrons respectively.

PAULI'S EXCLUSION PRINCIPLE

The distribution of quantum numbers among the electrons in a given atom is governed by Pauli's Exclusion principle which states that "*It is impossible for two electrons in a given atom to have all the four quantum numbers identical*" *i.e.*, in an atom, two electrons

Table 1.3. Relation between quantum numbers.

Value of n and main shell designation	Values of l and sub-shell designation (nl)	Value of m and sub-sub-shell designation	Value of s	Total number of electrons in s, p, d, f sub-shells $=2(2l+1)$	Total number of electrons in main shells $=2n^2$
$n=1$ (K-shell)	$l=0(1s)$	$m=0(1s)$	$+\frac{1}{2}, -\frac{1}{2}$	2	$2\times1^2=2$
$n=2$ (L-shell)	$l=0(2s)$	$m=0(2s)$	$+\frac{1}{2}, -\frac{1}{2}$	2	$2\times2^2=8$ or $2+6=8$
	$l=1(2p)$	$m=0(2p_x)$	$+\frac{1}{2}, -\frac{1}{2}$	2	
		$=+1(2p_y)$	$+\frac{1}{2}, -\frac{1}{2}$	2 } 6	
		$=-1(2p_z)$	$+\frac{1}{2}, -\frac{1}{2}$	2	
$n=3$ (M-shell)	$l=0$	$m=0(3s)$	$+\frac{1}{2}, -\frac{1}{2}$	2	$2\times3^2=18$ or $2+6+10=18$
	$l=1$	$m=0(3p_x)$	$+\frac{1}{2}, -\frac{1}{2}$	2	
		$=+1(3p_y)$	$+\frac{1}{2}, -\frac{1}{2}$	2 } 6	
		$=-1(3p_z)$	$+\frac{1}{2}, -\frac{1}{2}$	2	
	$l=2$	$m=0(3d_{xy})$	$+\frac{1}{2}, -\frac{1}{2}$	2	
		$=+1(3d_{yz})$	$+\frac{1}{2}, -\frac{1}{2}$	2	
		$=-1(3d_{zx})$	$+\frac{1}{2}, -\frac{1}{2}$	2 } 10	
		$=+2(3d_{x^2-y^2})$	$+\frac{1}{2}, -\frac{1}{2}$	2	
		$=-2(3d_{z^2})$	$+\frac{1}{2}, -\frac{1}{2}$	2	

can have maximum three quantum numbers (n, l and m) the same and the fourth (s) will definitely be having a different value. Thus if $s=+\frac{1}{2}$ for one electron, s should be equal to $-\frac{1}{2}$ for the other electron. In other words the two electrons in the same orbital should have opposite spins (↑ ↓).

Uses of the principle

The greatest use of the principle is that it is helpful in determining the maximum number of electrons that a main energy level can have. Let us illustrate this point by considering K and L shells.

(*a*) **K-shell.** For this shell $n=1$. For $n=1$, $l=0$ and $m=0$. Hence s can have a value either equal to $+\frac{1}{2}$ or $-\frac{1}{2}$. The different values of n, l, m and s given above give the following *two* combinations of the four quantum numbers, keeping in view the exclusion principle. Combination (*i*) is for one electron and combination (*ii*) is for the other electron.

(*i*) $n=1$, $l=0$, $m=0$, $s=+\frac{1}{2}$ (1st electron)
(*ii*) $n=1$, $l=0$, $m=0$, $s=-\frac{1}{2}$ (2nd electron)
} (Two electrons in $l=0$ sub-shell *i.e.*, 1s-orbital).

These two combinations show that in K shell there is only one sub-shell corresponding to $l=0$ value (s-sub-shell) and this shell contains only two electrons with opposite spins.

(*b*) **L-shell.** For this shell $n=2$. For $n=2$ the different values of l, m and s give the following *eight* combinations of four quantum numbers.

(*i*) $n=2$, $l=0$, $m=0$, $s=+\frac{1}{2}$
(*ii*) $n=2$, $l=0$, $m=0$, $s=-\frac{1}{2}$
} **Two electrons in $l=0$ sub-shell (*i.e.* 2s-orbital)**

(*iii*) $n=2$, $l=1$, $m=0$, $s=+\frac{1}{2}$
(*iv*) $n=2$, $l=1$, $m=0$, $s=-\frac{1}{2}$
(*v*) $n=2$, $l=1$, $m=+1$, $s=+\frac{1}{2}$
(*vi*) $n=2$, $l=1$, $m=+1$, $s=-\frac{1}{2}$
(*vii*) $n=2$, $l=1$, $m=-1$, $s=+\frac{1}{2}$
(*viii*) $n=2$, $l=1$, $m=-1$, $s=-\frac{1}{2}$
} **Six electrons in $l=1$ sub-shell (*i.e.*, 2p orbitals : $2p_x$, $2p_y$, and $2p_z$**

Eight combinations given above show that L shell is divided into two sub-shells corresponding to $l=0$ (s sub-shell) and $l=1$ (p sub-shell) and this shell cannot contain more than 8 electrons, *i.e.*, its maximum capacity for keeping the electrons is eight.

RUSSEL-SAUNDER'S OR L-S COUPLNG SCHEME AND DETERMINATION OF THE GROUND STATE TERMS OF FREE ATOMS OR IONS.

According to this coupling :

(*i*) All the *l* vectors (*l=orbital angular momentum quantum number*) of the electrons couple together *electrostatically* to give the resultant vector L, called *resultant orbital angular momentum quantum number.* Different values of L define the state of the free atom or ion as a whole while those of *l* define the state of the electrons only.

L is always an integer, including zero, *i.e.*, L may be 0, 1, 2, 3,...etc. Different values of L are represented by capital letters as shown :

Values of	L=0	1	2	3	4	5
Capital letters	=S	P	D	F	G	H

L value for the electrons in any of the filled *s*, *p*, *d* etc. orbitals is zero, *e.g.*, for the six electrons in a completely filled *p* orbital for which $l=1$, the value of L is zero as shown below :

$$L=+\underbrace{1+1}_{p_x}+\underbrace{0+0}_{p_y}\underbrace{-1-1}_{p_z}=0,$$ where +1, +1, 0, 0, −1 and −1 represent the *m* values for the electrons numbered as (1), (4), (in p_x orbital), (2), (5) (in p_y orbital), and (3), (6) (in p_z orbital) (*see* Fig. 1·7).

p_x-orbital	p_y-orbital	p_z-orbital
$m=+1$	$m=0$	$m=-1$
$s=+\frac{1}{2}$	$s=+\frac{1}{2}$	$s=+\frac{1}{2}$
↑	↑	↑
(1)	(2)	(3)
(4)	(5)	(6)
↓	↓	↓
$m=+1$	$m=0$	$m=-1$
$s=-\frac{1}{2}$	$s=-\frac{1}{2}$	$s=-\frac{1}{2}$

Fig. 1·7. Different *m* and *s* values for the six electrons in three *p* orbitals.

The calculation of L values for d^n configurations (for *d*-orbitals $l=2$ and hence $m=+2, -1, 0, -1$ and -2) has been shown below in Table 1·4.

Table 1·4. Calculation of L values for d^n configurations

d^n configuration	$d_{x^2-y^2}$ $(m=+2)$	d_{yz} $(m=+1)$	d_{xy} $(m=0)$	d_{xz} $(m=-1)$	d_{z^2} $(m=-2)$	Resultant L and term symbol
d^1	$(+2)$					$=2$(D)
d^2	$(+2)$	$+(+1)$				$=3$(F)
d^3	$(+2)$	$+(+1)$	$+(0)$			$=3$(F)
d^4	$(+2)$	$+(+1)$	$+(0)$	$+(-1)$		$=2$(D)
d^5	$(+2)$	$+(+1)$	$+(0)$	$+(-1)$	$+(-2)$	$=0$(S)
d^6	$(+2+2)$	$+(+1)$	$+(0)$	$+(-1)$	$+(-2)$	$=2$(D)
d^7	$(+2+2)$	$+(+1+1)$	$+(0)$	$+(-1)$	$+(-2)$	$=3$(F)
d^8	$(+2+2)$	$+(+1+1)$	$+(0+0)$	$+(-1)$	$+(-2)$	$=3$(F)
d^9	$(+2+2)$	$+(+1+1)$	$+(0+0)$	$+(-1-1)$	$+(-2)$	$=2$(D)
d^{10}	$(+2+2)$	$+(+1+1)$	$+(0+0)$	$+(-1-1)$	$+(-2-2)$	$=0$(S)

(*ii*) Similarly all s vectors (s = *spin angular momentum quantum number*) also combine to give the *resultant spin angular momentum quantum number*, S. S is an *integer* or *half-integer* depending on the number of electrons involved and the direction of the spin vectors. S is always equal to half the number of unpaired electrons (*i.e.*, $S=n/2$). S value for the electrons in any of the completely filled s, p, d etc. orbitals is zero, *e.g.* for a completely filled p-orbital for which $l=1$, S is equal to zero as shown below :

$$\begin{array}{ccccccc} & (1) & (4) & (2) & (5) & (3) & (6) \\ S= & +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2}=0 \end{array}$$

(Also *see* Fig. 1·7).

The calculation of S values for d^n configuration has been shown in Table 1·5.

The quantity $(2S+1)$ is known as *multiplicity* of L state. This quantity gives the permitted values of J for a given value of L(J = resultant inner quantum number obtained by coupling L and S vectors).

(*iii*) Finally L and S vectors couple together to give a resultant vector J which is called *resultant inner quantum number* or *total angular momentum quantum number* of the atom. The process of L-S coupling can be symbolically represented as :

$$(s_1+s_2+s_3+\ldots)+(l_1+l_2+l_3+\ldots)=S+L=J$$

Table 1.5 : Determination of multiplicity, J values and ground state terms for d^n configurations.

d^n configuration	n	$S=\frac{n}{2}$	Multiplicity $=2S+1=n+1$	Values of L from Table 1·4	Different J values	Several possible terms	Ground state terms
d^1	1	1/2	2	2(D)	5/2, 3/2	$^2D_{5/2}$, $^2D_{3/2}$	$^2D_{3/2}$
d^2	2	2/2 = 1	3	3(F)	4, 3, 2	$^3F_4$, $^3F_3$, $^3F_2$	$^3F_2$
d^3	3	3/2	4	3(F)	9/2, 7/2, 5/2, 3/2	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	$^4F_{3/2}$
d^4	4	2	5	2(D)	4, 3, 2, 1, 0	$^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$	$^5D_0$
d^5	5	5/2	6	0(S)	5/2	$^6S_{5/2}$	
d^6	4	2	5	2(D)	4, 3, 2, 1, 0	$^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$	$^5D_4$
d^7	3	3/2	4	3(F)	9/2, 7/2, 5/2, 3/2	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	$^4F_{9/2}$
d^8	2	1	3	3(F)	4, 3, 2	$^3F_4$, $^3F_3$, $^3F_2$	$^3F_4$
d^9	1	1/2	2	2(D)	5/2, 3/2	$^2D_{5/2}$, $^2D_{3/2}$	$^2D_{5/2}$
d^{10}		0	1	0(S)	0	$^1S_0$	$^1S_0$

Possible number of values of J is (2S+1) when $L \geqslant S$ and (2L+1) when $L < S$.

When L=0, J can have only one value *viz.* J=S. J is *positive* and *never negative.* Different values of J vary in integral steps between (L+S) and (L−S), *i.e.* J can have the following values.

$$J=(L+S), (L+S-1), (L+S-2), \ldots, 0, \ldots, (L-S+1), (L-S)$$

Different J values for d^n configurations have been calculated on the basis of the above rules and tabulated in Table 1·5.

To write the ground state terms of atoms or ions. The ground state term of an atom or ion is represented by :

$$\text{Ground state term} = {}^{\text{multiplicity}}L_J = {}^{2S+1}L_J = {}^{n+1}L_J$$

While writing the ground state terms the following rules must be observed :

(*i*) The ground state term will be that which has the highest value of spin multiplicity or, which has the maximum number of unpaired electrons.

(*ii*) If there are several terms with the same spin multiplicity possible for an atom or ion, the term having the largest value of L will be the ground state term.

(*iii*) For a half-filled or less than half-filled shell, the ground state term is that which has the lowest value of J and for a more than half-filled shell, the ground state is that which has the highest value of J.

On the basis of these rules the ground state terms for d^n configurations have been determined and are given in Table 1·5.

WAVE MECHANICAL CONCEPT OF THE ATOM

Particle and wave nature (dual nature) of an electron. We have seen that Bohr in his theory has assumed that *an electron is a material particle revolving round the nucleus in circular orbits.* But de-Broglie pointed out in 1924 that the *electron, like light, behaves both as a material particle and as a wave, i.e. the electron has a dual character.*

de-Broglie's Equation. de-Broglie derived an expression for calculating the wavelength, λ of the wave associated with the electron.

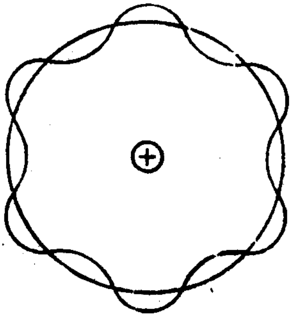


Fig. 1·8. An electron wave extending round the nucleus.

Let an electron of mass *m* move with a velocity *c* round the nucleus and be associated with a wave of wavelength λ (*see* Fig. 1·8). With the help of the equations *viz* $E=h\nu$ (Planck's equation) and $E=mc^2$ (Einstein's mass-energy relationship) (E=energy of the electron, h=Planck's constant, ν=frequency), it can be shown that

$$mc^2 = h\nu \qquad \ldots(i)$$

Now since Wavelength(λ)×frequency (ν)=Velocity of the wave (c)

or
$$\lambda\nu = c$$

or
$$\nu = \frac{c}{\lambda}$$

Equation (i) reduces to

$$mc^2 = h\nu = h.\frac{c}{\lambda}$$

or
$$mc = \frac{h}{\lambda}$$

or
$$\lambda = \frac{h}{mc}$$

or
$$\lambda = \frac{h}{\text{momentum of electron } (p)}$$

The above equation is called **de-Broglie's equation** and the wavelength λ is called **de-Broglie's wavelength.** From this equation it is evident *that the momentum* (p) *of the moving electron is inversely proportional to the wavelength* (λ).

Similarity between de-Broglie's wave character of the electron and Bohr's theory.

Bohr's quantum conditions which have been assumed by Bohr arbitrarily in his theory can be derived in a more natural way by considering the wave-like properties of the electron in an atom.

According to de-Broglie the electron is not a solid particle revolving round the nucleus in a circular orbit, but it is a standing wave extending round the nucleus in a circular orbit.

If r is the radius of circular orbit, then the circumference of this orbit is equal to $2\pi r$. Now if λ=wave length and n=total number (which is a whole number like 1, 2, 3......) of the wave lengths associated with the electron wave extending round the nucleus, the circumference is equal to $n\lambda$. Thus :

$$2\pi r = n\lambda$$

or
$$2\pi r = n.\frac{h}{mc} \left(\because \lambda = \frac{h}{mc} \right)$$

or
$$mcr = n.\frac{h}{2\pi}$$

or
$$\text{angular momentum } (mcr) = n.\frac{h}{2\pi}$$

This equation which is based on the wave nature of the electron shows that *the electron can move only in those orbits for which the angular momentum* (mcr) *is an integral multiple of* $h/2\pi$. *In other words the angular momentum is quantised.* Thus we see that wave mechanical picture of the atom presented by de-Broglie leads naturally to Bohr's postulate given above.

Experimental verification of de-Broglie's equation. Verification of the wave nature of the electron has been obtained by Davison and Germer's experiments (1927). They succeeded in diffracting a beam of electrons by means of a nickel surface. The pattern of the electron diffraction obtained by them was found to be similar to that of X-ray diffraction. Not only this, the wavelength of the electrons was also found to be identical with that calculated by de-Broglie with the help of his equation. In this way, the dual nature of the electron and the quantitative nature of de-Broglie's equation was established.

HEISENBERG'S UNCERTAINTY PRINCIPLE

The dual nature of the electron means that any precise measurement of its position would create some uncertainty in the measurement of its momentum and *vice versa*. This was pointed out by Werner Heisenberg in his **Uncertainty Principles**. According to this principle :

> *"It is impossible to determine exactly both the position and the momentum (or velocity) of an electron or of any other moving particle at the same time."*

It means that when an electron behaves as a particle, its position can be determined more or less exactly but at the same time there would be uncertainty about its momentum or velocity. Similarly if the velocity or momentum can be determined precisely there would be uncertainty about its position.

The uncertainty arises from the fact that when a measurement is carried out, the electron under investigation is to be viewed with a sensitive instrument such as a microscope, and in this process the light particles interact with the electron and alter its motion (*i.e*,, velocity). It is not possible, therefore, to say as to what the velocity of this electron is.

Mathematical expression. If Δx and Δp are the uncertainties (*i.e.* errors) in the measurements of position and momentum respectively of a particle, then :

$$\Delta x \times \Delta p > \frac{h}{2\pi}$$

This expression is known as **Uncertainty relation**.

From this relation it is evident that when Δx is small (*i.e.* the position of the electron is measured with accuracy), Δp will be large (*i.e.* the momentum will be measured with less accuracy) and *vice versa*. In other words it means that the certainty of determination of one property introduces uncertainty for the determination of the other.

If ΔE is the uncertainty in energy of the particle and ΔT is the uncertainty in its time of passage past a particular point, then an equivalent relation illustrating the uncertainty principle would be :

$$\Delta E \times \Delta T > \frac{h}{2\pi}$$

UNCERTAINTY PRINCIPLE AND BOHR'S THEORY—PROBABILITY AND CHARGE CLOUD CONCEPT

Bohr had postulated that electrons move in well-defined orbits with fixed velocity (or energy). But, according to uncertainty principle, since an electron also possesses wave-like nature, it is impossible to measure simultaneously its position and momentum with accuracy. On the basis of this principle, therefore, Bohr's picture of an electron in an atom which gives to the electron a fixed position in fixed orbit and fixed velocity is no longer correct, *i.e.* Bohr's model of atom has no meaning, since it is not possible to know simultaneously the exact position and velocity of an electron. The best we can say is that we can only state or predict the **probability of locating** (or finding) an electron with a probable velocity with particular energy in a given region of space at a given time. Thus the uncertainty principle which is based on the wave-nature of the electron only gives the probability of finding an electron in a given space in place of certainty. It is for this reason that the old classical concept of Bohr has now been discarded in favour of the **probability approach.**

The square of Ψ (*i.e.* Ψ^2) gives the probability of finding an electron of given energy in a given region round the nucleus. It is thus possible to identify regions of space round the nucleus where there is higher probability of finding an electron having definite amount of energy. This space is called an **atomic orbital.** Thus :

Atomic orbital is defined as a three-dimensional region (or space) round the nucleus where there is higher probability of finding an electron of specific energy.

Here it should be noted that an orbital is a three-dimensional region within which there is a higher probability that an electron having a certain energy will be found. On the other hand an orbit is two dimension.

There is only one orbital in K shell with $n=1$. This orbital is called $1s$ orbital. In L shell with $n=2$ there are four orbitals *viz.* one $2s$ and three $2p$ (designated as $2p_x$, $2p_y$ and $2p_z$) orbitals. Three $2p$ orbitals represent different orientations in space. Total number of orbitals in main shells are given below :

$K \rightarrow 1s$, $L \rightarrow 2s, 2p_x, 2p_y, 2p_z$; $M \rightarrow 3s, 3p_x, 3p_y, 3p_z, 3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{z^2}, 3d_{x^2-y^2}$; $N \rightarrow$ one $4s$, three $4p$, five $4d$ and seven $4f$ orbitals.

Representation of an orbital. Although it is difficult to give a pictorial representation of an orbital, it is generally represented by a shaded figure in which the intensity of shading (shown by dots) is proportional to the probability of finding the electron at that location. Fig. 1·9 illustrates the probability of finding the electron in $1s$ orbital in hydrogen atom at certain positions near the nucleus. In this figure the density of dots is proportional to the probability of finding the electron at that location. It should be noted that this figure represents a two-dimensional cross-section of three-dimensional distribution of probability about the nucleus.

Diagram such as that shown in Fig. 1·9 is sometimes called an **electron cloud** (or *electronic charge cloud or cloud of negative charge*). This electron cloud is always a diffuse cloud. The dots shown in the figure do not represent the ***number of electrons***, rather they represent a number of probable instantaneous positions of a single electron. In this figure the maximum blackening of the cloud shown in the immediate vicinity of the nucleus indicates that 1*s* electron spends most of its time in this region or in other words the electron probability density is maximum in the region just surrounding the nucleus. In case of hydrogen atom it has been shown that the probability of finding the electron is greatest at a distance of 0·53Å from the nucleus.

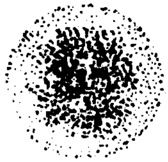


Fig. 1·9. Representation of probability of finding an electron in 1*s* orbital of hydrogen atom near the nucleus–electron cloud representation in hydrogen atom

SCHRODINGER WAVE EQUATION

The fundamental wave equation describing the behaviour of a small particle in terms of wave motion is :

$$\frac{d^2\psi}{dx^2}=-\frac{4\pi^2\psi}{\lambda^2}$$

or
$$\frac{1}{\lambda^2}=-\frac{d^2\psi}{dx^2}\times\frac{1}{4\pi^2\psi}$$

where ψ=amplitude of the wave, x=displacement in a given direction and λ= wavelength.

- On combining this equation with de-Broglie's equation *viz.* $\lambda=h/mc$ or $\frac{1}{\lambda^2}=m^2c^2/h^2$ (m=mass of the particle, c=velocity of the particle and h=Plank's constant), we get

$$m^2c^2=-\frac{h^2}{4\pi^2\psi}\frac{d^2\psi}{dx^2} \qquad ...(i)$$

Now kinetic energy, K.E. of a particle with mass m and moving with velocity c is given by **K.E.**$=mc^2/2$ or K.E.$=m^2c^2/2m$. Eliminating m^2c^2 from this equation and equation (*i*) we get the value of K.E. given by

$$\text{K.E.}=-\frac{h^2}{8\pi^2\psi m}\frac{d^2\psi}{dx^2}$$

Now the total energy, E of the particle is the sum of K.E. and potential energy, P.E., *i.e.* E=K.E.+P.E. Thus

$$\text{E}=-\frac{h^2}{8\pi^2\psi m}\frac{d^2\psi}{dx^2}+\text{P.E.}$$

or
$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2m}{h^2}(\text{E}-\text{P.E})\psi=0$$

This equation is called **Schrödinger** wave equation. This equation is in one dimension, x. If it is written for a particle whose motion is described by three space coordinates x, y and z, then the above equation becomes

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}+\frac{8\pi^2m}{h^2}(\text{E}-\text{P.E.})\psi=0$$

The first three terms on the left hand side of the above equation are represented by $\nabla^2\psi$ (pronounced as *del-square sign*). ∇^2 is known as **Laplacian operator**. Thus the above equation can also be written as :

$$\nabla^2\psi+\frac{8\pi^2m}{h^2}(E-P.E)\,\psi=0$$

where
$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Eigen-values and Eigen-functions. Being a differential equation of second order, Schrödinger equation has several solutions for ψ but many of these are imaginary and hence are not valid. Only those values of ψ are valid which satisfy the following conditions :

(*i*) The wave function must be finite and continuous.

(*ii*) The solution must be single valued *i.e.* at a given point there can never be more than one value for the amplitude, ψ.

(*iii*) $\frac{d\psi}{dx}$, $\frac{d\psi}{dy}$, and $\frac{d\psi}{dz}$ must be continuous functions of x, y, and z respectively.

(*iv*) The solutions must be normalised *i.e.* they must satisfy the relation

$$\int_0^{+\infty}\psi^2\,dr=0$$

where *dr* is a small volume element.

Values of ψ which satisfy the above conditions and hence valid are called **Eigen-functions** and the values of E corresponding to these valid values of ψ (*i.e.* eigen-functions) are called **Eigen-values**. The eigen-function for an electron is called an atomic orbital. As the eigen-values (*i.e.* E values) correspond very nearly to the energy levels associated with different Bohr orbits, the occurrence of definite energy levels in an atom follows directly from the wave-mechanical concepts.

Significance of ψ and ψ^2. The wave function ψ by itself has no physical significance. However, its square (*i.e.* ψ^2) measures the probability of finding an electron of given energy from place to place in a given region round the nucleus, since the probability of finding an electron in a given region is proportional to ψ^2. The probability at any point must be a real quantity. Now, the wave function ψ of an electron is very often an imaginary quantity. Thus if $\psi=a+ib$ (an imaginary quantity) where $i=\sqrt{-1}$ and a and b are real functions of the coordinates, then the probability is equal to $\psi^2=(a+ib)^2$ $=a^2+2iab+b^2$ which is an imaginary quantity. But, since as mentioned above, the probability must be a real quantity, it must more correctly be equal to $\psi\psi^*$ and not ψ^2 where ψ^* is the complex conjugate of ψ (*i.e.*, $\psi^*=a-ib$, since $\psi=a+ib$). Under this condition the product $\psi\psi^*$ will be a real quantity as shown :

$$\psi\psi^*=(a+ib)\,(a-ib)$$
$$=a^2+b^2 \qquad \text{(which is a real quantity)}$$

If ψ turns out to be a real function initially, then its complex conjugation will also be ψ. Thus under this condition the probability will be equal to ψ^2, since $\psi\psi^*=\psi^2$ due to the fact that ψ and its conjugate complex, ψ^*, are the same.

Thus if the probability function is represented by ρ, then

$$\rho=\psi\psi^* \quad \text{(where } \psi \text{ is imaginary)}$$

or $$\rho=\psi^2 \quad \text{(where } \psi \text{ is real)}$$

Wave mechanics of hydrogen-atom (Schrödinger wave equation for hydrogen-atom) and Quantum Numbers. In case of hydrogen-atom, since a single electron of charge $-e$ is revolving round the nucleus of charge $+e$, potential energy, P.E. is equal to $-e^2/r$. Thus on putting P.E.$=-e^2/r$ in Schrödinger wave equation we get

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}+\frac{8\pi^2m}{h^2}\left(E+\frac{e^2}{r}\right)\psi=0 \qquad \ldots(ii)$$

This equation is the **Schrödinger wave equation of hydrogen atom.**

Transformation of equation (*ii*) from the cartesian to spherical coordinates. In equation (*ii*), we have used a cartesian system of coordinates and have taken the nucleus as the origin and thus the position of the electron has been defined by the coordinates *x*, *y*, and *z*. In order to make the mathematical handling of Equation (*ii*) much simpler, the cartesian coordinates *x*, *y*, *z* are replaced by spherical polar coordinates γ, θ, ϕ.

The relation between the two systems is shown in Fig. 1·10.

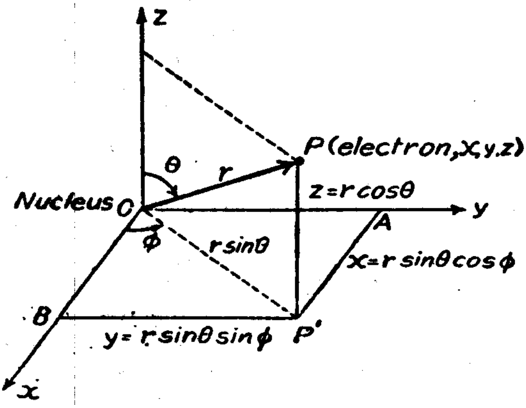


Fig. 1·10. Relation between the cartesian coordinates (*x*, *y*, *z*) and spherical polar coordinates (γ, θ, φ)

The use of polar coordinates is analogous to the method used to specify the position on the earth's surface when the position of a point is defined by the radius of the earth and by two angles : the latitude and longitude.

The value of θ at any point *P* (electron) is, then, described in terms of polar coordinates λ, θ and ϕ. In Fig. 1·10 :

(*i*) *r* is the radial distance (called radius vector or radial line) point *P* (electron) from the origin θ (nucleus),

$$r=\sqrt{x^2+y^2+z^2}$$

(*ii*) θ is the angle between the radius vector, *OP*, and $+z$-axis (*i.e.* *OZ*-axis) which is the axis of the sphere. This angle is called zenith angle and is given by

$$\theta=\cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}}$$

(*iii*) Drop a perpendicular *PP′* from *P* on the *xy*-plane such that *OP′* makes an angle ϕ with $+x$-axis (*i.e.* *OX*-axis), measured in the direction shown. This angle is called azimuthal angle or longitudinal angle and is given by

$$\phi=\tan^{-1}\frac{y}{x}$$

P′A and *P′B* are the normals drawn from *P′* on *OX*- and *OX*-axes respectively.

From Fig. 1·10, it may be seen that :

$$\left.\begin{aligned}x&=r\sin\theta\cos\phi\\y&=r\sin\theta\sin\phi\\z&=r\cos\theta\end{aligned}\right]\qquad\ldots(iii)$$

On the surface of a sphere whose centre is *O*, lines of constant zenith angle θ are like parallels of latitude on a globe (but we note that the value of θ of a point is not the same as its latitude ; $\theta=90°$ at equator, for instance, but the latitude of equator is 0°), and the lines of constant azimuthal angle ϕ are like meridians of longitude (here the definitions coincide if the axis of globe is taken as the $+Z$-axis and the $+X$-axis is at $\phi=0°$)

On transforming Equation (*ii*) with the help of relations (*iii*), we get

$$\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)+\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi}{d\phi}\right)+\frac{1}{\sin^2\theta}\cdot\frac{d^2\psi}{d\phi^2}\right]$$
$$+\frac{8\pi^2m}{h^2}\left(E+\frac{e^2}{r}\right)\psi=0\qquad\ldots(iv)$$

Separation of Variables. In equation (*iv*) the wave function ψ, is a function of three variables, *r*, θ, ϕ and ψ can therefore be separated into the product of three functions *R* (*r*), Θ (θ) and Φ (ϕ). Here by writing $R\ (r)$ we mean that the function R depends on r only and is independent of θ and ϕ. Thus

$$\psi(r, \theta, \phi) = R\ (r)\ .\ \Theta\ (\theta)\ .\ \Phi\ (\phi) \qquad \text{...}(v)$$

Equation (v) can be written in the simplified form as :

$$\psi = R\ .\ \Theta\ .\ \Phi \qquad \text{...}(vi)$$

and correspondingly

$$\left.\begin{aligned} \frac{d\psi}{dr} &= \Theta\ .\ \phi\ .\ \frac{\delta R}{\delta r} \\ \frac{d\psi}{d\theta} &= R\ .\ \Phi\ .\ \frac{\delta\Theta}{\delta\theta} \\ \frac{d\psi}{d\phi} &= R\ .\ \phi\ .\ \frac{\delta\Phi}{\delta\phi} \end{aligned}\right] \qquad \text{...}(vii)$$

Substituting equations (vi) and (vii) in equation (iv) and multiplying throughout by $\frac{r^2 \sin^2 \theta}{R\ .\ \Theta\ .\ \Phi}$, we get

$$\frac{\sin^2\theta}{R} \cdot \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{\sin\theta}{\theta} \cdot \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{1}{\phi} \cdot \frac{d^2\Phi}{d\phi^2}$$
$$+ \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right) r^2 \sin^2\theta = 0 \qquad \text{...}(viii)$$

Now equation ($viii$) can easily be separated into three different equations : One depending on r only, the other depending on θ only and the third depending on ϕ only. The process (which involves advanced mathematics and is, therefore, not being discussed here) of separating equation ($viii$) into three equations involves three constants, n, l and m which are the quantum numbers. The equation depending on r only gives the principal quantum number, n, that depending on θ gives the azimuthal quantum number, l, and that depending on ϕ gives the magnetic quantum number, m. r dependent equation also gives the expression for the energy of different orbitals in H-atom. This expression is

$$E_n = -\frac{2\pi^2 m e^4}{n^2 h^2} \qquad \text{...}(ix)$$

Evidently this expression is identical with Bohr's equation of H-atom which he derived on the basis of classical mechanics. For H-atom the energies calculated by both the methods (*i.e.* classical mechanics method used by Bohr and wave mechanical method used by Schrodinger) agree with experimental values. For more complicated atoms, however, wave mechanical method is superior.

The separation of equation ($viii$) into three equations also shows that the three constants, n, l, m are related in such a way that $(n+l)$ and $(2l+1)$ are both integral ; $l \leq (n-1)$ and m have values $-l$ to $+l$. These considerations immediately show that n and l must be integers (or l may be zero) and that l can have integral values : 0, 1, 2,......$(n-1)$. In other words, the three constants n, l and m are the three quantum numbers and the relation between them arising from the solution of Schrödinger wave equation is also exactly the same which has been deduced by means of spectroscopic measurements.

Here it should be understood clearly that spin quantum number, *s*, does not appear in the solution of wave equation. It has, therefore, to be added.

PROBABILITY DISTRIBUTION CURVES

In an atomic orbital there is a probability of finding the electron in a particular region at a given radial distance and in a particular direction from the nucleus. This gives rise to two types of probability of finding the electrons :

(1) **Radial probability distribution curves** of electrons. These curves give the probability of finding the electron at different *radial*

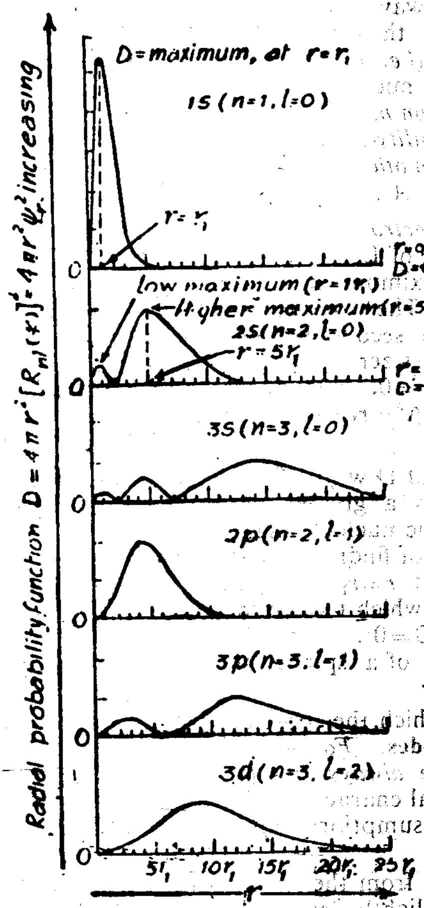


Fig. 1·11. Plots of radial distribution function D against the electron distance r for six states in hydrogen atom.

distances, r from the nucleus and are obtained by plotting the radial distribution function,

$$D=4\pi r^2[R_{nl}(r)]^2=4\pi r^2\psi_r^2$$

against the electron-nuclear distance, r. These curves for $1s$, $2s$, $3s$, $2p$, $3p$, and $3d$-electrons in H-atom are shown in Fig. 1·11.

Curve for 1s-electron. From the curve for $1s$-electron it is evident that the value of D is zero at $r=0$. Now D increases as r increases from zero, passes through a maximum (*i.e.* peak) at $r=0{\cdot}53$ A° which is equal to the radius of Bohr's first orbit, r and finally falls to zero as r tends to infinity. Thus for $1s$-electron $D=0$ at $r=0$ and ∞, and $D=$maximum at $r=0{\cdot}53$A°$=r_1$ (radius of Bohr's first orbit).

That D is maximum at $r=0{\cdot}53$A° makes a difference between Bohr's theory and wave mechanical treatment of hydrogen atom. According to Bohr's theory, in hydrogen atom the electron under ordinary conditions (*i.e.*, in ground state) always stays at a distance of 0·53A° from the nucleus, while according to wave-mechanical treatment, the *electron may exist at any distance from the nucleus but the maximum probability of locating it lies at a distance of 0·53 A° from the nucleus. In other words the radius of maximum probability of 1s-electron is 0·53 A°.*

Curve for 2s-electron. For $2s$-electron the value of D is zero at $r=0$. Now the value of D increases as the value of r increases, passes through a low maximum at $r=0{\cdot}53$A°$=r_1$ and falls to zero at $r=2\times0{\cdot}53$ A°$=2r_1$. The value of D increases as r increases from $2r_1$ and passes through second higher maximum at $r=5\times0{\cdot}53$A°$=5r_1$ and finally approaches zero as r tends to infinity. Thus for $2s$-electron (*i*) D=0 at $r=0$, $2\times0{\cdot}53$ A° ($=2r_1$) and ∞ (*ii*) lower maximum lies at $r=0{\cdot}53$ A°$=r_1$ (*iii*) higher maximum lies at $r=5\times0{\cdot}53$ A° $=5r_1$.

The variation of D with r for $2s$-electron as summarised above shows that there is a greater probability of finding the electron *farther* away from the nucleus (higher maximum at $r=5r_1$) but there is also some chance of finding the electron *very close* to the nucleus (lower maximum at $r=r_1$). At an intermediate distance ($=2r_1$) there is a surface at which the probability of finding the electron is zero (*i.e.* at $r=2r_1$, D=0). Thus the charge-cloud representation of $2s$-electron consists of a sphere surrounded by a second spherical shell.

Surfaces at which the probability of finding the electron goes to zero are called **nodes**. *For any orbital having principal quantum number, n there are always (n−1) nodes* (neglected the node of infinity). This nodal character of probability distributions is consistent with the assumption that the motion of the electron has wave-like character.

It can be seen from the plots that the maximum probability for $2p$-electron is slightly less than that for the $2s$-electron. Also the small additional peak (lower maximum) for $2s$-electron indicates that $2s$-electron penetrates a little closer to the nucleus than a $2p$ electron. Hence a $2s$-electron is attracted more strongly by the nucleus than a 2*p*-electron. This, in other words means that a 2*s*-electron is more stable than a 2*p*-electron, *i.e.*, 2*s*-electron has lower energy than 2*p*-electron ($2s < 2p$), although both the electrons are of the same main energy level.

(2) **Angular probability distribution curves (shapes or boundary surfaces of orbitals).** These curves give the probability of finding an electron in any given *direction* from the nucleus without reference to its distance from the nucleus.

s-orbitals. We have seen that for *s*-orbitals $l=0$. For $l=0$, $m=0$ which indicates that *s*-orbitals have only one orientation. Since for all *s*-orbitals there is only one orientation, these are spherically symmetrical, *i.e.*, electron density in *s*-orbitals is not concentrated along any particular direction. There is an equal chance of finding the electron density in any direction with respect to the nucleus (*see* Fig. 1·12).

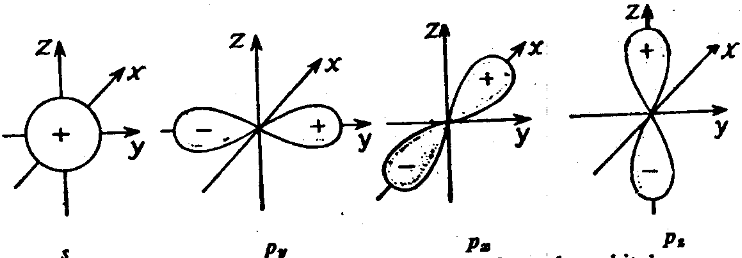


Fig. 1·12. Shapes or boundary surfaces of *s* and *p*-orbitals, *yz*, *xz* and *xy* are the nodal planes of p_x, p_y and p_z orbitals.

p-orbitals. For *p*-orbitals $l=1$. For $l=1$, $m=0, \pm 1$. Three values of *m* for $l=1$ show that *p*-orbitals have three orientations, *i.e.* there are three *p*-orbitals which are named as p_x, p_y and p_z, the subscripts *x*, *y* and *z* referring to the coordinate axes along which their lobes of maximum electron density lie.

In the absence of magnetic field these three *p*-orbitals are equivalent in energy and are, therefore, said to be **three-fold degenerate** or **triply degenerate**. In the presence of an external magnetic field, the relative energies of the three *p* orbitals vary and depend on their orientation or magnetic quantum number. This probably accounts for the splitting of a single spectral line into a number of closely-spaced lines in presence of a magnetic field (*fine structure*).

The *p*-orbitals are of *dumb-bell shape*. Since the three axes *viz.* *x*-, *y*- and *z*-axes are perpendicular to each other, the three *p*-orbitals are also perpendicular to each other. Each of the three *p*-orbitals *has two lobes touching each other at the origin and these lobes are completely symmetrical about one of the three axes, e.g.,* the two lobes of p_x orbital are symmetrical about the *x*-axis. This in other words means that the two lobes of a p_x-orbital extends outwards and away from the nucleus along the *x*-axis. The same case is with p_y and p_z orbitals. Thus the two lobes of a *p* orbital may be separated by a plane that contains the nucleus and is perpendicular to the corresponding axis. Such plane is called a **nodal plane.** There is no likelihood of finding the electron density on this plane.

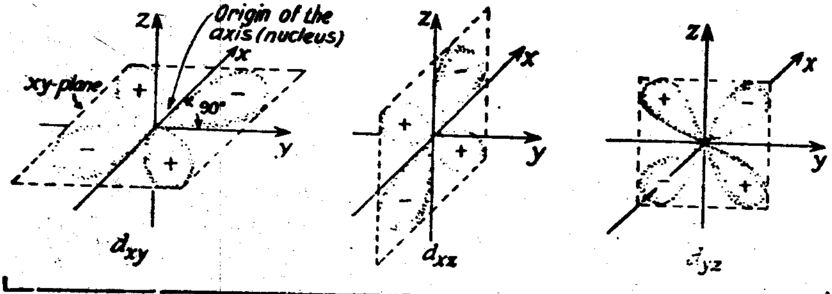
i.e., **such plane has zero electron density.** It can be seen that each of the three *p*-orbitals has **one** such nodal plane, *e.g.*, for p_x-orbital *yz* plane is the nodal plane. In Fig. 1·12 the planes for each orbital are also mentioned.

***d*-orbitals.** These orbitals arise when $n=3$ (M-shell), *i.e.*, these orbitals start with the 3rd main energy level. When $l=2$ (*d*-orbital), $m=0, \pm1, \pm2$ indicating that *d*-orbitals have five orientations, *i.e.*, there are *five* *d*-orbitals which are named as d_{xy}, d_{yz}, d_{zx}, d_{z^2} and $d_{x^2-y^2}$. All these five orbitals, in the absence of magnetic field, are equivalent in energy and are, therefore, said to be **five-fold degenerate.** Each of these appears as a four suasages fastened to a common point in space. The following additional features of these orbitals may be noted :

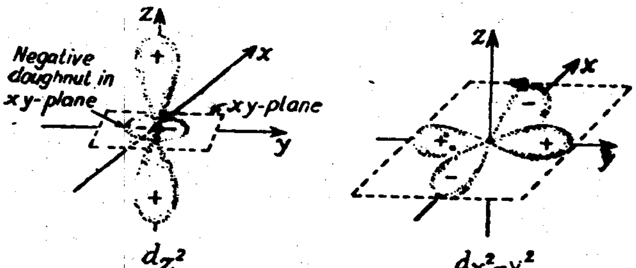
(*i*) The three orbitals namely d_{xy}, d_{yz} and d_{zx} have their *lobes lying symmetrically between the coordinate axes* indicated in the subscript to *d*, *e.g.* the lobes of d_{xy} orbital are lying between the *x*-and *y*-axes. This set of three orbitals is known as d_ε or t_{2g} set.

(*ii*) $d_{x^2-y^2}$ and d_{z^2} orbitals have *their lobes along the axes* (*i.e.* along the axial directions), *e.g.*, the lobes of $d_{x^2-y^2}$ orbital lie along the *x* and *y*-axes, while those of d_{z^2} orbital lie along the *z*-axis. This set is known as d_γ or e_g set.

e_g set is called the *axial set* while the t_{2g} set is the *non-axial set*, since the lobes of the orbitals of e_g set lie along the axes and those of the orbitals of t_{2g} set lie in space between the axes (*see* Fig 1·13).



d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} or d_ε set·non or axia! set)



d_{z^2} and $d_{x^2-y^2}$ orbitals (e_g or d_γ set or axial set)

Fig. 1·13. Shapes or boundary surfaces of *d*-orbitals.

ENERGY LEVEL DIAGRAMS

The energy of an electron is determined by the values of n and l quantum levels. When we discuss the order of energy of orbitals, the following two case arise.

(*a*) **Energy level diagram of one-electron atom.** Hydrogen has only one electron which is present in the lowest energy level for which $n=1$ ($1s^1$ electron). When hydrogen atom absorbs energy, $1s^1$ electron may jump to higher main energy levels (*e.g.* K, L, M...etc.) or to higher orbitals (*e.g.* 2*s*, 2*p*...etc). The spectral study of hydrogen atom has shown that its spectral lines correspond to the major energy levels only. Thus the energy of an electron present in a given principal energy level is the same irrespective of the orbital of the same main energy level to which it may belong. This in other words means that the energies of *s*, *p*, *d*, *f* orbitals of the same main energy level are identical, *e.g.* the order of energy of various orbitals in hydrogen atom is as follows :

$$1s < 2s=2p < 3s=3p=3d < 4s=4p=4d=4f < ......$$

This order has been shown in Fig. 1·14 and is called *energy level diagram for hydrogen atom.*

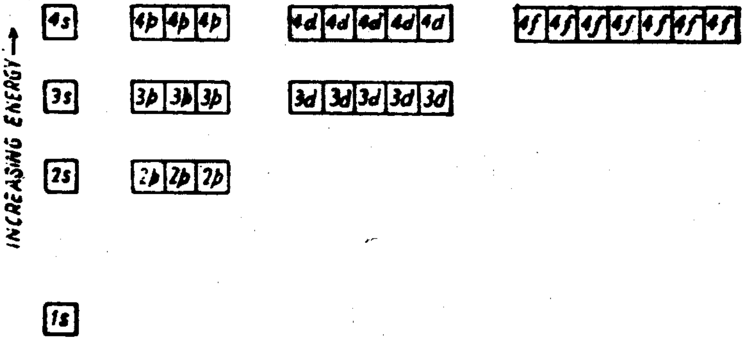


Fig. 1·14. Energy level diagram of hydrogen atom.

This discussion makes it obvious that for an atom having only one electron the energy of a level is determined by the value of n only. The value of l merely determines the shape of the orbital.

(*b*) **Energy level diagram for poly-electron atoms.** In case of a poly-electron atom the energies of various orbitals belonging to different main energy levels have been found in the following increasing order.

$$\xrightarrow{\text{Energy increasing}}$$

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p...$$

This order is shown in energy level diagram given in Fig. 1·15. This order shows that the energies of the orbitals of the same main energy levels (*i.e.* having the same value of n) increase as the values of l increase, *e.g.*

orbitals of *n*th main energy level	:	*ns*	*np*	*nd*	*nf*
Values of *l* for *s*, *p*, *d* and *f* orbitals	:	0	1	2	3
Order of energy	:	$ns < np < nd < nf$			

The order shown above is because of the fact that as the value of *l* increases, the orbital penetration near the nucleus decreases and the shielding due to inner electrons becomes more effective. In other words an electron with larger value of *l* feels less nuclear charge.

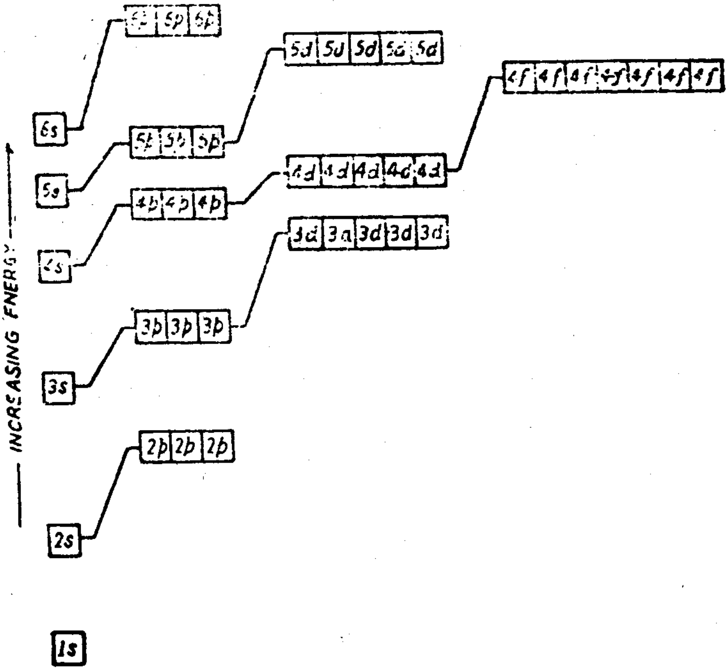


Fig. 1·15. Energy level diagram of poly-electron atoms.

Here it should be noted that the order of energy of orbitals shown above applies well for the elements of low atomic numbers only. With the increase in atomic number the relative energies of many of the levels change slightly.

For the elements with atomic number less than 20, the energy of 3*d*-orbital is higher than that of 4*s*-orbital ($4s < 3d$), but this order for the elements with atomic number greater than 20 is reversed (*i.e.* $3d < 4s$). Similar changes occur in the relative energies of 4*f* and 5*d*-orbitals before and after the atomic number 57.

RULES FOR FILLING THE ORBITALS WITH ELECTRONS AND ELECTRONIC CONFIGURATION OF ELEMENTS.

The filling up of orbitals with electrons takes place according to certain rules which are given below :

(*i*) The maximum number of electrons in a main shell is equal to $2n^2$ where n is the shell number.

(*ii*) The maximum number of electrons in a sub-shell (or an orbital as it is called) like s, p, d or f is equal to $2(2l+1)$ where $l=0$, 1, 2 or 3 for s, p, d and f orbitals respectively. Thus s, p, d and f orbitals can have a maximum of 2, 6, 10 and 14 electrons respectively.

(*iii*) **Aufbau Principle.** Aufbau is a German expression which means *binding up* or *construction.* It is pronounced as *of bow : According to this principle the orbitals are filled up in the order of increasing energy, i.e. the orbital with the lowest energy is filled up first while that with the highest energy is filled up in the end.* The energy of various orbitals increases in the order given below :

$$\xrightarrow{\text{Energy Increases}}$$

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < 8s < \ldots$$

The order shown above is the order in which the orbitals are filled with electrons. This order can also be represented diagrammatically (*See* Fig. 1·15). This diagram is generally called **electron configuration diagram.** In this diagram we find that the order of filling is in vertical manner from top to bottom and then from left to right.

As a working rule a new electron enters the orbital for which $(n+l)$ is minimum, *e.g.* if we consider $3d$ and $4s$ orbitals, the electron will first enter $4s$ orbital in preference to $3d$ orbital. This is because of the fact that the value of $(n+l)$ for $4s$ orbital is less $(=4+0=4)$ than that for $3d$ orbital $(3+2=5)$.

In case of orbitals for which $(n+l)$ values are the same, the new electron enters the orbital for which n is minimum, *e.g.* if there

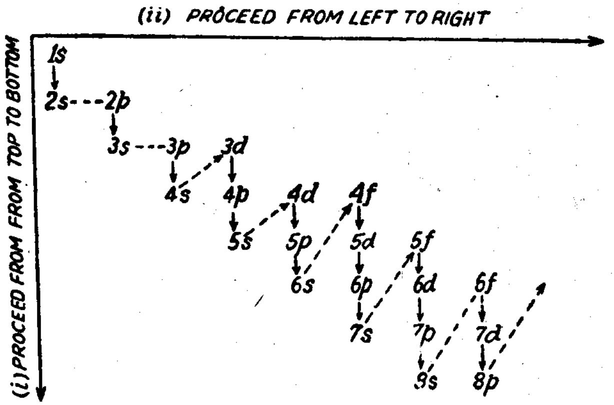


Fig. 1·16. Electron configuration diagram showing Aufbau principle to fill up orbitals with electrons.

is a choice for the electron to enter 3*d* and 4*p* orbital for both of which $(n+l)$ values are the same $(=3+2=5,\ 4+1=5)$, the electron will prefer to go to 3*d*-orbital, since *n* is lower for this orbital.

The order of filling of orbitals with electrons as given above shows that after 6*s* orbital the next electron must enter 4*f* orbitals but actually what happens is that after the completion of 6*s* orbital, one electron goes to 5*d* orbitals (instead of 4*f* orbitals) and after a single electron has been added to 5*d* orbitals, the filling of 4*f* orbitals starts and this filling continues until 4*f* orbitals are completely filled $(4f^{14})$. Now 5*d* orbitals which are already singly filled $(5d^1)$ again start to fill up and are completely filled. *This is because 4f and 5d orbitals have almost the same energy.*

Similarly one or more electrons enter the 6*d* orbitals before any electron occupies 5*f* orbitals. This is also because of the fact that 5*f* and 6*d* orbitals are close to each other in energy. Thus the orbitals must be filled in the following order.

Orbitals being Filled →

$1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^2,\ 3d^{10},\ 4p^6,\ 5s^2,\ 4d^{10},\ 5p^6,\ 6s^2,\ 5d^1,\ 4f^{14},$
$5d^{2\ to\ 10},\ 6p^6,\ 7s^2,\ 6d^{1\ or\ 2},\ 5f^{14},\ 6d^{2\ or\ 3\ to\ 10},\ 7p^6,\ 8s^2.$

(*iv*) **Spins of electrons.** *Each of the sub-orbitals (e.g.* $s, p_x, p_y, p_z, d_{xy}, \ldots$*) can hold only two electrons and these two electrons must have opposite spins in accordance with Pauling's exclusion principle.* Electrons entering singly tend to have the same spins to obey the exclusion principle.

(*v*) The electronic configuration of an atom is written in terms of nl^x notation where *n* is the main energy shell number and has the values 1, 2, 3..., *l* is one of the sub-shells (or orbitals) such as *s, p, d, f* ... and *x* gives the total number of electrons present in sub shell defined by *n* and *l* values.

(*vi*) **Hund's rule of maximum multiplicity.** On the basis of magnetic measurements which are helpful in determining the electronic configuration of elements, Hund's put forward an empirical rule known after this name as **Hund's rule of maximum multiplicity.** According to this rule *electrons enter the sub-orbitals (e.g.,* $s, p_x, p_y, p_z, d_{xy}\ldots$*) in such a way as to give the maximum number of unpaired electrons and these unpaired electrons have the same directions of spins.* Thus, when several sub-orbitals of equal energy (degenerate orbitals) are available, electrons prefer to occupy separate orbitals rather than get paired in the same orbital. This, in other words, means that pairing begins with the introduction of second electron in *s* orbital, the fourth in *p*-orbital, the sixth in *d*-orbital and eighth in the *f*-orbital.

(*vii*) Sub-orbitals (*e.g.* $s, p_x, p_y, p_z, d_{xy}, \ldots$) tend to become completely-filled or half filled, since such orbitals are more stable than any other orbital.

The complete electronic configuration of the elements from hydrogen (atomic number, $Z=1$) to Ku ($Z=104$) have been determined with the help of the above rules and are given in Table 1·6.

A study of the Table shows that the actual (*i.e.* experimental) configurations as given in the Table of some transition elements (*d*-block elements) are different from their expected configurations as shown below :

Series	*Element with atomic number*	*Expected valence shell configuration*	*Actual valence shell configuration*
3*d-series*	Cr_{24}	$3d^4 4s^2$	$3d^5 4s^1$
	Cu_{29}	$3d^9 4s^2$	$3d^{10} 4s^1$
4*d-series*	Nb_{41}	$4d^3 5s^2$	$4d^4 5s^1$
	Mo_{42}	$4d^4 5s^2$	$4d^5 5s^1$
	Ru_{44}	$4d^6 5s^2$	$4d^7 5s^1$
	Rh_{45}	$4d^7 5s^2$	$4d^8 5s^1$
	Pd_{46}	$4d^8 5s^2$	$4d^{10} 5s^0$
	Ag_{47}	$4d^9 5s^2$	$4d^{10} 5s^1$
5*d-series*	Pt_{78}	$4f^{14} 5d^8 6s^2$	$4f^{14} 5d^9 6s^1$
	Au_{79}	$4f^{14} 5d^9 6s^2$	$4f^{14} 5d^{10} 6s^1$

Obviously the actual configurations are obtained by shifting one or two electrons from *ns* to $(n-1)$ *d*-orbitals. Such type of shifting in case of some elements like Cr, Cu, Mo, Pd, Ag and Au can be explained on the basis of the concept that half-filled or completely-filled $(n-1)$ *d*-orbitals are more stable than d^4, d^8 and d^9 orbitals. Anomalous configurations of other elements like Nb, Ru, Rh and Pt are explained on the basis of nuclear-electronic and inter-electronic forces the discussion of which is beyond the scope of this book.

Table 1·6. Ground State Electronic Configurations of the Elements

Period Number	Elements with atomic number	*K* $n=1$	*L* $n=2$		*M* $n=3$			*N* $n=4$				*O* $n=5$				*P* $n=6$				*Q* $n=7$	
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
1	H_1	1																			
	He_2	2																			
2	Li_3	2	1																		
	Be_4	2	2																		
	B_5	2	2	1																	
	C_6	2	2	2																	
	N_7	2	2	3																	
	O_8	2	2	4																	
	F_9	2	2	5																	
	Ne_{10}	2	2	6																	
3	Na_{11}	2	2	6	1																
	Mg_{12}	2	2	6	2																
	Al_{13}	2	2	6	2	1															
	Si_{14}	2	2	6	2	2															
	P_{15}	2	2	6	2	3															
	S_{16}	2	2	6	2	4															
	Cl_{17}	2	2	6	2	5															
	Ar_{18}	2	2	6	2	6															
4	K_{19}	2	2	6	2	6		1													
	Ca_{20}	2	2	6	2	6		2													
	Sc_{21}	2	2	6	2	6	1	2													
	Ti_{22}	2	2	6	2	6	2	2													
	V_{23}	2	2	6	2	6	3	2													
	Cr_{24}	2	2	6	2	6	5	1													
	Mn_{25}	2	2	6	2	6	5	2													
	Fe_{26}	2	2	6	2	6	6	2													
	Co_{27}	2	2	6	2	6	7	2													
	Ni_{28}	2	2	6	2	6	8	2													
	Cu_{29}	2	2	6	2	6	10	1													
	Zn_{30}	2	2	6	2	6	10	2													
	Ga_{31}	2	2	6	2	6	10	2	1												
	Ge_{32}	2	2	6	2	6	10	2	2												
	As_{33}	2	2	6	2	6	10	2	3												
	Se_{34}	2	2	6	2	6	10	2	4												
	Br_{35}	2	2	6	2	6	10	2	5												
	Kr_{36}	2	2	6	2	6	10	2	6												
5	Rb_{37}	2	2	6	2	6	10	2	6			1									
	Sr_{38}	2	2	6	2	6	10	2	6			2									
	Y_{39}	2	2	6	2	6	10	2	6	1		2									
	Zr_{40}	2	2	6	2	6	10	2	6	2		2									
	Nb_{41}	2	2	6	2	6	10	2	6	4		1									
	Mo_{42}	2	2	6	2	6	10	2	6	5		1									
	Te_{43}	2	2	6	2	6	10	2	6	5		2									
	Ru_{44}	2	2	6	2	6	10	2	6	7		1									
	Rh_{45}	2	2	6	2	6	10	2	6	8		1									
	Pd_{46}	2	2	6	2	6	10	2	6	10		0									
	Ag_{47}	2	2	6	2	6	10	2	6	10		1									
	Cd_{48}	2	2	6	2	6	10	2	6	10		2									
	In_{49}	2	2	6	2	6	10	2	6	10		2	1								
	Sn_{50}	2	2	6	2	6	10	2	6	10		2	2								
	Sb_{51}	2	2	6	2	6	10	2	6	10		2	3								
	Tc_{52}	2	2	6	2	6	10	2	6	10		2	4								
	I_{53}	2	2	6	2	6	10	2	6	10		2	5								
	Xe_{54}	2	2	6	2	6	10	2	6	10		2	6								

Period Number	*Elements with atomic number*	*K* $n=1$	*L* $n=2$		*M* $n=3$			*N* $n=4$				*O* $n=5$				*P* $n=6$				*Q* $n=7$	
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	6*f*	7*s*	7*p*
6	Cs$_{55}$	2	2	6	2	6	10	2	6	10		2	6			1					
	Ba$_{56}$	2	2	6	2	6	10	2	6	10		2	6			2					
	La$_{57}$	2	2	6	2	6	10	2	6	10		2	6	1		2					
	Ce$_{58}$	2	2	6	2	6	10	2	6	10	2	2	6	0		2					
	Pr$_{59}$	2	2	6	2	6	10	2	6	10	3	2	6	0		2					
	Nd$_{60}$	2	2	6	2	6	10	2	6	10	4	2	6	0		2					
	Pm$_{61}$	2	2	6	2	6	10	2	6	10	5	2	6	0		2					
	Sm$_{62}$	2	2	6	2	6	10	2	6	10	6	2	6	0		2					
	Eu$_{63}$	2	2	6	2	6	10	2	6	10	7	2	6	0		2					
	Gd$_{64}$	2	2	6	2	6	10	2	6	10	7	2	6	1		2					
	Tb$_{65}$	2	2	6	2	6	10	2	6	10	9	2	6	0		2					
	Dy$_{66}$	2	2	6	2	6	10	2	6	10	10	2	6	0		2					
	Ho$_{67}$	2	2	6	2	6	10	2	6	10	11	2	6	0		2					
	Er$_{68}$	2	2	6	2	6	10	2	6	10	12	2	6	0		2					
	Tm$_{69}$	2	2	6	2	6	10	2	6	10	13	2	6	0		2					
	Yb$_{70}$	2	2	6	2	6	10	2	6	10	14	2	6	0		2					
	Lu$_{71}$	2	2	6	2	6	10	2	6	10	14	2	6	1		2					
	Hf$_{72}$	2	2	6	2	6	10	2	6	10	14	2	6	2		2					
	Ta$_{73}$	2	2	6	2	6	10	2	6	10	14	2	6	3		2					
	W$_{74}$	2	2	6	2	6	10	2	6	10	14	2	6	4		2					
	Re$_{75}$	2	2	6	2	6	10	2	6	10	14	2	6	5		2					
	Os$_{76}$	2	2	6	2	6	10	2	6	10	14	2	6	6		2					
	Ir$_{77}$	2	2	6	2	6	10	2	6	10	14	2	6	7		2					
	Pt$_{78}$	2	2	6	2	6	10	2	6	10	14	2	6	9		1					
	Au$_{79}$	2	2	6	2	6	10	2	6	10	14	2	6	10		1					
	Hg$_{80}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2					
	Tl$_{81}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1				
	Pb$_{82}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2				
	Bi$_{83}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3				
	Po$_{84}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4				
	At$_{85}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5				
	Rn$_{86}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6				
7	Fr$_{87}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			1	
	Ra$_{88}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			2	
	Ac$_{89}$	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1		2	
	Th$_{90}$	2	2	6	2	6	10	2	6	10	14	2	6	10	0	2	6	2		2	
	Pa$_{91}$	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1		2	
	U$_{92}$	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1		2	
	Np$_{93}$	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1		2	
	Pu$_{94}$	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	0		2	
	Am$_{95}$	2	2	6	2	6	10	2	6	10	14	2	6	10	7.	2	6	0		2	
	Cm$_{96}$	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	5	1		2	
	Bk$_{97}$	2	2	5	2	6	10	2	6	10	14	2	6	10	9	2	6	0		2	
	Cf$_{98}$	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	0		2	
	Es$_{99}$	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	0		2	
	Fm$_{100}$	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	0		2	
	Md$_{101}$	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	0		2	
	No$_{102}$	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0		2	
	Lw$_{103}$	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1		2	
	Ku$_{104}$														14						

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2

Extended or Long Form of Periodic Table

MENDELEEF'S PERIODIC LAW AND MENDELEEF'S PERIODIC TABLE

It was in 1861 that Mendeleef for the first time attempted to classify the elements in some order that could explain their properties. He gave a law known as **Mendeleef's Periodic Law** which states that *the physical and chemical properties of the elements are a periodic function of their atomic weights*. He arranged the elements in the increasing order of their atomic weights in the form of a table known as **Mendeleef's Periodic Table** dividing the elements into groups (vertical columns) and periods (horizontal rows).

The post-Mendeleef developments, however, brought out a number of defects and anomalies in this Table. The anomaly was the position of three pairs of elements : *tellurium and iodine, argon and potassium* and *nickel and cobalt* which was not in accordance with their chemical behaviour. The accommodation of rare-earths and isotopes on the basis of their rising atomic weights also posed a problem.

MODERN PERIODIC LAW

The work of Mosley (1911) proved beyond doubt that the properties of the elements are well explained and most of the anomalies and defects of Mendeleef's Periodic Table disappear if the basis of classification of the elements is changed from atomic weights to atomic numbers. This formulates the modern periodic law as : *the physical and chemical properties of elements are a periodic function of their atomic number.*

EXTENDED OR LONG FORM OF PERIODIC TABLE

In order to remove the defects of Mendeleef's periodic table a number of tables have been suggested for the classification of elements. All these tables classify the elements on the basis of modern periodic law, *i.e.* the elements are arranged in the increasing order of their atomic numbers. Out of such various tables the one facing this page is most widely used and is called **Long Form of Periodic Table.** It is also referred to as **Bohr's Table,** since it apparently follows the Bohr scheme of the arrangement of elements into four types based on their electronic configurations. However, the credit cannot be assigned to any single person for the development of this widely used periodic table.

Mechanically this table is derived from the original Mendeleef's table by merely *extending* each of the long periods and separating the sub-groups by breaking its short periods. Hence the name **extended form of periodic table.**

Different Portions of the Long Form of periodic table. The long form of the periodic table has the following portions :

1. **The Left Portion.** This portion has the elements of groups IA and IIA. These elements are extremely electropositive in character.

2. **The Right Portion.** This portion consists of the elements of groups IIIA, IVA, VA, VIA, VIIA and zero. This portion has metals, all metalloids such as Ge, As, Se, Sb, Te, non-metals and noble gases. The noble gases are present to the extreme right and the extremely electronegative elements (*ie.*, VIIA group elements—halogens) are situated on the left of the inert gas group. The typical non-metals lie on the diagonal drawn from C_6 to Rn_{86} through P_{15}, Se_{34} and I_{53}. (The numbers indicate the atomic numbers of the elements).

3. **The Middle Portion.** This portion consists of the elements of groups IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB. Elements present in this portion can be classified into two groups :

(*i*) **Transitional Elements.** These elements are divided into four series :

(*a*) *First transition series.* This series has 10 elements from Sc_{21} to Zn_{30}.

(*b*) *Second transition series.* This series has also 10 elements from Y_{39} to Cd_{48}.

(*c*) *Third transition series.* The total number of elements in this series is also ten. These elements are La_{57} and from Hf_{72} to Hg_{80}.

(*d*) *Fourth transition series.* At present this series has only 3 elements which are Ac_{89}, Ku_{104} and Ha_{105}.

(*ii*) **Inner Transition Elements.** These inner transition elements have been grouped into two groups :—

(*a*) *Lanthanides.* These are 14 in all from Ce_{58} to Lu_{71}. These elements are present in IIIB group of the periodic table. For convenience, all these elements have been placed at a separate place at the bottom of the periodic table.

(*b*) *Actinides.* These are also 14 in all from Th_{90} to Lw_{103} These elements are also the members of IIIB group. For convenience these elements are also given a separate place at the bottom of the periodic table.

Study of Periods and Groups

Periods. These are the horizontal rows. Long form of the periodic table consists of 7 periods :—

(*i*) *First Period* ($n=1$). $n=1$ indicates that there is only one main energy level for the elements of this period. This period has two elements *viz.* H_1 and He_2.

(*ii*) *Second Period* ($n=2$). There are two shells in the elements of this period. It has 8 elements *viz.* Li_3 to Ne_{10}.

(*iii*) *Third period* ($n=3$). This period also has 8 elements : Na_{11} to Ar_{18}. Second and third periods are called *short periods.*

(*iv*) *Fourth Period* ($n=4$). This period has 18 elements (K_{19} to Kr_{36}).

(*v*) *Fifth Period* ($n=5$). This period also has 18 elements (Rb_{37} to Xe_{54}).

(*vi*) *Sixth Period* ($n=6$). This period has 32 elements. Fourth, fifth and sixth periods are called *long periods.*

(*vii*) *Seventh Period.* ($n=7$). This is an incomplete period which at present has 19 elements which are from Fr_{87} to Ha_{105}. All these elements are radioactive. Out of these the elements namely Fr_{87}, Ra_{88}, Ac_{89}, Th_{90}, Pa_{91} and U_{92} are naturally occurring radioactive elements while the remaining elements (*i.e.*, Np_{93} to Ha_{105}) are man-made (*i e.*, artificially prepared) radioactive elements and are called *transuranium elements.*

Groups. The vertical columns are called groups. These are 16 in all as shown below :

(*i*) IA, IIA, IIIA, IVA, VA, VIA and VIIA groups (7 groups). The elements of these 7 groups are called *normal elements.*

(*ii*) IB, IIB, IIIA, IVB, VB, VIB and VIIB groups (7 groups).

(*iii*) VIII group. This group has three columns.

IB, IIB, IVB, VB, VIB, VIIB and VIII groups have *purely transitional elements* while in IIIB group some elements are transition elements and the remaining are *inner transitional elements.*

(*iv*) *Zero Group.* This group has inert gas elements.

In this way, we find that the total number of vertical columns is 18 while the number of groups is only 16.

Why is long form of periodic table more clear than the Mendeleef's periodic table? (*i*) The arrangement of the elements is based on a more fundamental basis, *viz.*, atomic number.

(*ii*) In this periodic table the position of an element is related to the electronic configuration of its atoms.

(*iii*) There is a gradual change in properties of the elements with the increase in their atomic numbers.

(*iv*) *Position of transition elements.* The significance of the transition elements is that these elements have properties intermediate between those of *s*- and *p*-block elements. In this table the transition elements have, therefore, been placed in the middle of the periodic table.

(*v*) *Inner transition elements.* These are the elements that interrupt the transition elements. The interruption by 14 elements (known as *lanthanides*) first occurs in the sixth period between groups IIIB and IVB (between La_{57} and Hf_{72}). Similarly, the interruption of other 14 elements (known as *actinides*) occurs in the seventh period between the same groups (*i.e.* between Ac_{89} and Ku_{104}).

In this table the lanthanides and actinides hove been given a separate place at the bottom of the periodic table.

(*vi*) Due to the separation of the two sub-groups, dissimilar elements (*e.g.*, alkali metals and coinage metals) do not fall together.

(*vii*) *Separation of metals from non-metals.* In this table a complete separation between metals and non-metals has been achieved. The elements on the left hand side of the periodic table *i.e.*, the elements of groups IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB are metals while the elements present on the right hand side of the periodic table *i.e.*, the elements of groups IIIA, IVA, VA, VIA, VIIA are metals, non-metals and metalloids.

The thick line shown in the periodic table approximately separates the metallic from the non-metallic elements.

The metallic properties are most pronounced in those elements which are present in the lower left corner of the periodic table and the non-metallic properties are pronounced in the upper right corner of the table (excepting the noble gases).

(*viii*) This arrangement of the elements is easy to remember and to reproduce.

(*ix*) *The division of the Long Form of periodic table into four block elements.* The greatest advantage of this periodic table is that this can be divided into four block-elements namely *s*-, *p*-, *d*- and *f*-block elements. In *s*-block, *p*-block, *d*-block and *f*- block there are 2, 6, 10 and 14 elements in each period respectively.

The division of the Long Form of periodic table into four blocks is shown in Fig. 2·1.

Defects of Long form of Periodic Table

(*i*) *The Position of Hydrogen.* The problem of the position of the hydrogen in this periodic table has not been solved completely. Although electronic configuration of hydrogen is the same as the valence shell configuration of the alkali metals in the sense that both have only one electron (H ⟶ $1s^1$, alkali metals ⟶ ns^1), their properties are not similar.

(*ii*) *Position of He.* Chemically helium is an inert gas but since the remaining members of the inert gas group possess the electronic configurations ns^2p^6 against that of He ⟶ $1s^2$, a different place should be given to helium.

Also, helium and alkaline earth metals have similar electronic configurations and as such helium should be placed in the group of alkaline earth metals. But this cannot be done because the properties of He are altogether different from those of alkaline earth metals.

Thus it is concluded from (*i*) and (*ii*) that hydrogen and helium should be placed in separate groups in the periodic table.

(*iii*) *Position of Lanthanides and Actinides.* This periodic table is unable to include these groups of elements in its main body.

(*iv*) This periodic table does not reflect the exact distribution of electrons among all the elements.

ELECTRONIC CONFIGURATION OF THE ELEMENTS AND THE BUILD-UP OF THE PERIODIC TABLE

The electronic configurations of the atoms of the elements in the ground state (as given in Table 1·6 page 42) are determined with the help of Aufbau Principle, Hund's rule and Paulie's Exclusion Principle described already in chapter on *Structure of the Atom.* While building up the periodic table from hydrogen onwards it is imagined that the next higher atom has essentially the same inner configuration as the preceding one and thus electronic configuration of the next element is determined by adding one electron to the inner configuration of the preceding atom as shown below. In the following discussion the numbers indicated as the subscript to the symbol of the elements are the atomic numbers of the elements concerned.

Period 1 ($n=1$). The single electron in H_1-atom enters the 1*s*-orbital, giving $1s^1$ electronic configuration to *H*-atom. Second electron in *He*-atom also enters 1*s*-orbital to give $1s^2$ configuration to *He*-atom. Thus at *He*, *K* shell *is completely filled.*

Period 2 ($n=2$). At Li_3 the filling up of 2*s*-orbital starts and is complete at Be_4. Similarly at B_5, 2*p*-orbitals start filling and these are completely filled at Ne_{10} which is the end of second period. The complete configuration of Ne_{10} *viz.* $1s^2$, $2s^2p^6$ or [*He*] $2s^2p^6$ shows that at the end of 2nd period *K* and *L* shells *are completely filled.* Evidently 2*s*- and 2*p*-orbitals are filled at the end of this period. In the configuration *viz.* [*He*] $2s^2p^6$, [*He*] indicates the configuration of *He* atom (*viz.* $1s^2$) and that the configuration of Ne has essentially the inner configuration of He.

Period 3 ($n=3$). In this period 3*s*- and 3*p*-orbitals are being occupied and are completely filled at Ar_{18} whose complete configuration is, therefore, $1s^2$, $2s^2p^6$, $3s^2p^6$ or [Ne]$3s^2p^6$ which shows that at Ar M-shell whose maximum capacity to contain the electrons is 18 *is not completely filled,* since 3*d*-orbitals of M-shell are still vacant. *K* and *L* shells are, however, *complete* at the end of this period.

Period 4 ($n=4$). Since 4*s*-orbital is of lower energy than 3*d*-orbital, it will be filled first. Thus the configurations of K_{19} and Ca_{20} are [Ar] $4s^1$ and [Ar] $4s^2$ respectively.

In the next element, Sc_{21}, the additional electron enters 3*d*-orbital and this process ends at Zn_{30} where 3*d*-orbital is completely filled. Thus the configurations of Sc_{21} and Zn_{30} are [Ar] $3d^14s^2$ and [Ar] $3d^{10}4s^2$ respectively. There are certain irregularities in the filling of 3*d*-level, *e.g.*, Cr_{24} and Cu_{29} have the valence shell configurations, $3d^5$ $4s^1$ and $3d^{10}$ $4s^1$ and not the expected ones $3d^4$ $4s^2$ and $3d^9$ $4s^2$. This is due to the fact that the half-filled in Cr_{24}) and completely-filled (d^{10} in Cu_{29}) electronic configurations appear to have extra stability. The series of ten elements namely Sc_{21} to Zn_{30} is called *first transition series.*

At Ga_{31}, 4*p*-orbital starts to fill up and is completely filled at Kr_{36}. Evidently 4*s*-, 3*d*- and 4*p*-orbitals are completely filled at the end of this period.

Period 5 ($n=5$). We have seen that at Kr_{36}, 4*p*-orbital is complete. The next electron enters 5*s*-orbital in Rb_{37} and this orbital is complete at Sr_{38}. Thus these elements have their valence shell configurations as $5s^1$ and $5s^2$ respectively.

At Y_{39} the 4*d* -orbital starts to fill up and is completely filled at Cd_{48}. Thus the valence shell configurations of Y_{39} and Cd_{48} are $4d^1$ $5s^2$ and $4d^{10}$ $5s^2$ respectively. In this series of 10 elements (Y_{39} to Cd_{48}) also the unpairing of 5*s*-electrons takes place to give the stable half-filled $4d^5$ ($Mo \rightarrow 4d^5$ $5s^1$) and completely filled $4d^{10}$ ($Ag \rightarrow$ $4d^{10}$ $5s^1$) configurations. A series of ten elements (Y_{39} to Cd_{48}) constitutes a *second transition series.*

At In_{49} 5*p*-orbital starts to fill up and is completely filled at Xe_{54}.

Period 6 ($n=6$). The next electron enters 6*s*-orbital at Cs_{55} and at Ba_{56} it is complete. Thus these elements have [Xe]$6s^1$ and and [Xe]$6s^2$ electronic configurations respectively.

Now the order in which different orbitals are filled with electrons suggests that after 6*s*-orbital has been completely filled at Ba_{56}, the additional electron must enter 4*f*-orbital at La_{57}, but what happens is that after the completion of 6*s*-orbital, one electron goes to 5*d*-orbital (instead of 4*f*-orbital) and after a single electron has been added to 5*d*-orbital at La_{57} to get its electronic configuration as [Xe] $5d^1\ 6s^2$, the filling of 4*f*-orbital starts and this filling continues in the series Ce_{58} to Lu_{71}, until 4*f*-orbital has 14 electrons at Lu_{71}. The cause of this abnormal behaviour is that 4*f*- and 5*d*-orbitals are very close to each other in energy. Thus in sixth period we have a series of 14 elements (Ce_{58} to Lu_{71}) in which the additional electron enters 4*f*-orbital. These 14 elements are called *lanthanides*. In this series of 14 elements the filling up of 4*f*-orbital is not entirely regular at certain places, since, for example, $4f^7$ (Gd_{64}) and $4f^{14}$ (Yb_{70}) configurations seem to be of added stability.

Now at Hf_{72}, 4*d*-orbital, which has already been singly occupied at La_{57}, again starts to fill up and is completely filled at Hg_{80}. The elements from La_{57} to Hg_{80} ($10+14 = 24$ elements constitute a *third transition series*.

6*p*-orbital is filled from Tl_{81} to Rn_{86}. Evidently at the end of this period 6*s*-, 4*f*-, 5*d*- and 6*p*-orbitals are completely filled.

Period 7 ($n=7$). After 6*p*-orbital, 7*s*-orbital starts to fill up at Fr_{87} and it is complete at Ra_{88}. In the next element namely Ac_{89}, the additional electron goes to 6*d*-orbital (not in 5*f*-orbital). After Ac_{89} the electrons start to fill up 5*f*-orbital which is complete at Lw_{103}. In this period as well a series of 14 elements (Th_{90} to Lw_{103}) appears. The elements of this series are called *actinides*. The elements from Ac_{89} to Lw_{103} constitute *fourth transition series*.

Valence-shell configurations (ground state configurations) of atoms of all the elements of periodic table are given in Table facing page 50.

TYPES OF ELEMENTS ON THE BASIS OF THEIR ELECTRONIC CONFIGURATIONS

(1) **Differentiating Electron Classification.** This classification divides the elements into *four types viz. s-, p-, d* and *f-* block elements depending on the nature of the atomic orbital into which the last electron (called the *differentiating electron*) enters.

(*i*) *s*-**block Elements**. In these elements the differentiating electron enters the *ns*-orbital which is being progressively filled. The elements of groups IA (H, Li, Na, K, Rb, Cs and Fr) and II A (Be, Mg, Ca, Sr, Ba, Ra) belong to this block. The valence-shell configuration of these elements varies from ns^1 to ns^2 where $n=$ number of the valence-shell or number of the period in which the element is present. The members of this block thus lie on the extreme left of the periodic table.

(*ii*) *p*-**block Elements.** The elements in which *p*-orbitals are being progressively filled are called *p*-block. The elements of the groups : III A (B, Al, Ga, In, Tl), IV A (C, Si, Ge, Sn, Pb), V A (N, P, As, Sb, Bi), VI A (O, S, Se, Te, Po), VII A (F, Cl, Br, I, At) and zero (Ne, Ar, Kr, Xe, Rn. Note the exception of He whose configuration is $1s^2$) are the members of this block. In the atoms of these elements the differentiating electron (also known as *additional* or *extra electron*) enters $2p$-, $3p$-, $4p$-, $5p$- and $6p$- orbitals respectively. Since s-orbitals in these atoms are already filled, the valence-shell configuration of the atoms of these elements vary from ns^2p^1 (III A group) to ns^2p^6 (zero group). These elements lie on the extreme right of the periodic table and consist of some metals, all non-metals, metalloids and noble gases.

(*iii*) ***d*-block Elements (Transition Elements).** The elements in which the differentiating electron enters the $(n-1)$ d-orbital of $(n-1)$th main shell are called d-block elements. These are placed in the middle of the periodic table *i.e.* between s-and p-block elements.

The valence-shell configuration of these elements can be represented as $(n-1)d^{1-10}.n\,s^{0,1,2}$. These elements which are also called *transition elements* are classified into four series corresponding to the filling of $3d$-, $4d$-, $5d$-, and $6d$-orbitals of $(n-1)th$ main shell (*a*) *3d-series*. This series has *ten* elements *viz*. Sc$_{21}$, Ti$_{22}$, V$_{23}$, Cr$_{24}$, Mn$_{25}$, Fe$_{26}$. Co$_{27}$, Ni$_{28}$, Cu$_{29}$ and Zn$_{30}$ (4th period elements). In the atoms of these elements the extra electron enters $3d$ orbitals. (*b*) *4d-series*. It has also *ten* elements *viz*. Y$_{39}$, Zr$_{40}$, Nb$_{41}$, Mo$_{42}$, Tc$_{43}$, Ru$_{44}$, Rh$_{45}$ Pd$_{46}$, Ag$_{47}$ and Cd$_{48}$ (5th period elements). In these elements the additional electron goes to $4d$-orbitals. (*c*) *5d-series*. These are also *ten* elements : La$_{57}$, Hf$_{72}$, Ta$_{73}$, W$_{74}$, Re$_{75}$, Os$_{76}$, Ir$_{77}$, Pt$_{78}$, Au$_{79}$ and Hg$_{80}$ (6th period elements). Here the extra electron enters the $5d$-orbitals. (*d*) *6d-series* (*incomplete series*). . At present this series has three elements *viz*. Ac$_{89}$. Ku$_{104}$ and Ha$_{105}$. These are the elements of 7th period (incomplete period). It is hoped that the elements with atomic numbers from 106 to 112 would be the members of this series. In the above three elements the extra electron occupies $6d$-orbitals.

(*iv*) ***f*-block Elements (Inner-transition elements).** The elements in which the extra electron enters the $(n-2)$ f-orbitals of the $(n-2)$th main shell are called f-block elements. The atoms of these elements have their ground state valence-shell configuration represented as $(n-2)f^{0-14}$. $(n-1)d^{0,1,2}.ns^2$.

f-block elements are of two types : (*a*) *4f-series* (*Lanthanides or Lanthanones*). This series has 14 elements *viz*. Ce$_{58}$, Pr$_{59}$, Nd$_{60}$, Pm$_{61}$, Sm$_{62}$ Eu$_{63}$ Gd$_{64}$, Tb$_{65}$, Dy$_{66}$, Ho$_{67}$, Er$_{68}$, Tm$_{69}$, Yb$_{70}$, Lu$_{71}$. In these elements $4f$-orbitals are being progressively filled. (*b*) *5f-series* (*Actinides or Actinones*). This series also has 14 elements *viz*. Th$_{90}$, Pa$_{91}$, U$_{92}$, Np$_{93}$, Pu$_{94}$, Am$_{95}$, Cm$_{96}$, Bk$_{97}$, Cf$_{98}$, Es$_{99}$, Fm$_{100}$, Md$_{101}$, No$_{102}$ and Lw$_{103}$. In these elements, $5f$-orbitals are being progressively filled.

Classification of elements into s-, p-, d- and f-block elements is shown in Fig. 2·1.

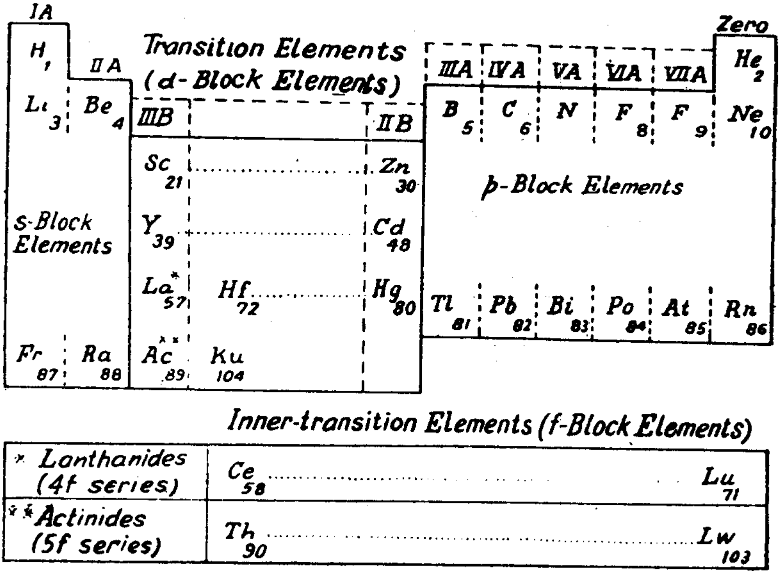

Fig. 2·1. Classification of the elements into *s*-, *p*-, *d*- and *f*-block elements.

(2) **Bohr's Classification.** In this classification proposed by Bohr the elements are grouped into **four classes** depending on the number of incomplete shells of electrons in the atom.

(*i*) **Inert gases.** In the atoms of these elements the *s*- and *p*-*sub-shells of the outermost shell are completely filled.* Thus the valence-shell configuration of these elements is ns^2p^6 with the exception of He which has $1s^2$ configuration.

On account of the highly stable ns^2p^6 configuration in the valence shell these gases have very little tendency to form chemical compounds with other elements.

(*ii*) **Representative or Normal Elements.** In the atoms of these elements the *outermost shell i.e. nth shell only is incompletely filled while all the underlying levels are filled to their capacity.*

These consist of some metals, all non-metals and metalloids and may be divided into two types :

(*a*) *s-block elements.* The outermost shell configurations of these elements vary from ns^1 to ns^2. The members of *s*-block elements lie on the extreme left of the periodic table. These include alkali-metals (group IA) and alkaline earth metals (group IIA). These are 13 in all.

Since the addition of extra electron in the atoms of these elements is taking place in *s*-orbital, these are called *s*-block elements.

(*b*) *p-block elements.* The atoms of these elements have their outermost shell configuration represented by ns^2p^1 to ns^2p^5.

These elements lie between the transitional elements and inert gas elements and are 25 in all.

Since in these elements, the additional electron enters *p*-orbitals, these are called *p*-block elements and on this basis, inert gas elements are also *p*-block elements. Evidently these are present at the extreme right of periodic table, if inert gas elements are also included in these.

(*iii*) **Transition Elements** (*d-block elements*). In these, the *outermost two shells are incomplete.* These are placed in the middle of periodic table, between *s*- and *p*-block elements.

Atoms of these elements have $(n-1)^{1-10}\, ns^{0 \text{ or } 1 \text{ or } 2}$ general configuration. Evidently it is the *d*-orbital of the penultimate shell [*i.e.* $(n-1)$*th* shell] that is partly filled or in which the addition of the extra electrons takes place. It is due to this reason that these are called *d*-block elements.

Four transition series appear among the transition elements corresponding to the filling of 3*d*-, 4*d*-, 5*d*- and 6*d*-orbitals of $(n-1)$*th* shell.

(*a*) *3d-series.* This series has ten elements : Sc_{21} to Zn_{30}. In these extra electron enters 3*d*-orbitals.

(*b*) *4d-series.* These are also ten elements : Y_{39} to Cd_{48}. In these additional electron enters 4*d*-orbitals of $(n-1)$*th* shell.

(*c*) *5d-series.* These are also ten elements : La_{57} , Hf_{72} to Hg_{80}. Here electron enters 5*d*-orbital.

(*d*) *6d-series* (incomplete). It has three members at present. These are Ac_{89}, Ku_{104} and Ha_{105}. It is hoped that the elements with atomic numbers from 106 to 112 would be the members of this series.

(*iv*) **Inner Transition Elements** (*f*-block elements). *The atoms of these elements have outer three shells incomplete.* These three incomplete shells are (*i*) outermost *ns*-orbital (*ii*) $(n-1)$ *d*-orbital and (*iii*) $(n-2)$ *f*-orbital.

The atoms of these elements have their general electronic configurations as $(n-2)f^{1-14} \cdot (n-1)d^{0 \text{ or } 1 \text{ or } 2} \cdot ns^2$.

Strictly speaking, these elements are transition elements, although they may be so distinguished electronically from regular transition elements as to be literally members of transition series within transition series. Hence the term inner transition.

If we accept the valence shell configurations of the inner transition elements as given above La_{57} ($4f^0\, 5d^1\, 6s^2$) would be excluded from this series. However, similarities in chemical and physical characteristics existing between La and the inner transition series commonly justify the inclusion of La in the inner transitional elements.

These are of two types : (*a*) *4f-series.* These are fourteen in all (Ce_{58} to Lu_{71}) and are called Lathanides or Lathanones in which the 4*f*-orbital is being filled. (*b*) *5f-series.* These are also fourteen in all (Th_{90} to Lw_{103}) and are called *Actinides* or *Actinones.* In these the 5*f*-orbital is being filled.

The electronic configuration of elements can be summarised by saying that (*i*) in noble gases the *ns*-, *np*-, $(n-1)d$- and $(n-2)f$-orbitals are filled. (*ii*) in the representative elements (*i.e.* *s*- and *p*-block elements) *ns*- and *np*- orbitals are filled (*iii*) in transition elements the $(n-1)$ *d*-orbitals are filled and (*iv*) in the inner transition elements the $(n-2)$ *f*-orbitals are being filled, in each case *n* being the principal quantum number of the outer electron shell.

Comparison of the two Classifications. In the *Bohr Classification* the properties of an element are assumed to depend on the complete configuration while the *Differentiating Classification* not only emphasises on the role of the entire configuration but also lays stress on the effect of the successive electron additions in modifying the properties. The differentiating electron configuration is certainly most rational and is now commonly in use.

References

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3

Periodic Properties

ATOMIC AND IONIC RADII

The term *atomic* or *ionic radius* is generally used for distance between the nucleus and the outermost shell of electrons of the atomic or ionic particle. Since it is impossible to isolate an individual atom or an ion, it is not possible to measure the atomic or ionic radius. These quantities are, however, generally derived in an indirect manner from the measured distance between the nuclei of two bonded atoms in a gaseous molecule or between the nuclei of two ions in crystals (or solids). In the former case, these distances are called *internuclear distances* (or *bond lengths* or *bond distances*) and in the latter case these are called *interionic distances*.

The internuclear distances (in covalent substances) and interionic distances (in ionic substances) are generally determined by X-ray diffraction, electron diffraction, NMR spectroscopy techniques etc.

Classification of atomic radii. Atomic radii are sub-divided into three classes : (*a*) *Covalent radii* as in non-metals and in covalent molecules in general (*b*) *Metallic* (or *crystal*) *radii* as in metals, alloys or inter-metallic compounds, and (*c*) *Van der Waals radii.*

(*a*) **Covalent Radius.** *It is defined as half of the distance between the nuclei of two like atoms bonded together by a single covalent bond.* Thus covalent radii are essentially single bond covalent radii (SBCR).

Consider a homo-nuclear diatomic molecule A_2 having two like atoms *viz.* A and A bonded together by a covalent bond. If in this molecule the two like atoms are regarded as effective spheres in close contact with each other, then according to the definition of covalent radius as given above, the distance between the nuclei of these two atoms (*i.e.*, bond length or internuclear distance d_{A-A}) should be equal to the sum of single-bond covalent radii of both the atoms.

Thus : Periodic Properties

$$d_{A-A}=r_A+r_A \qquad ...(1)$$

or

$$r_A=\frac{d_{A-A}}{2} \qquad ...(2)$$

where r_A=single-bond covalent radius of atom A.

If in a hetero-nuclear diatomic molecule AB the two atoms A and B are bonded together by purely covalent bond, then the inter-nuclear distance (*i.e.*, bond length) d_{A-B} is equal to the sum of r_A and r_B. In other words, if the electronegativity of atom A (x_A) is equal to that of B (x_B), then d_{A-B} is equal to r_A+r_B, *i.e.*,

$$d_{A-B}=r_A+r_B,$$

when

$$x_A=x_B$$

If x_A is not equal to x_B, experimental value of d_{A-B} is less than that obtained by the sum of r_A and r_B as is evident from the following examples :

(*i*) $(d_{C-I})_{exp}=2{\cdot}14$ A°

$(d_{C-I})_{cal}=r_C+r_I=0{\cdot}77+1{\cdot}33=2{\cdot}10$ A°

(*ii*) $(d_{S-Br})_{exp}=2{\cdot}27$ A°

$(d_{S-Br})_{cal}=r_S+r_{Br}=1{\cdot}02+0{\cdot}14=2{\cdot}16$ Å

The deviation is due to a number of factors such as (*a*) electronegativity difference between the bonded atoms A and B (or in other words due to the increasing ionicity of the A—B bond and (*b*) multiplicity of the bond between A and B.

In order to compensate for the ionic character of A—B bond, Schomaker and Stevenson (1941) have suggested that, in general, the interatomic distance d_{A-B} for a bond A—B, should be taken as the sum of covalent radii, r_A and r_B, for the atoms A and B, coupled with a correction term equal to $-0{\cdot}09\ (x_A-x_B)$, where (x_A-x_B) is the difference in the absolute values of electronegativity of A and B. Thus :

$$d_{A-B}=r_A+r_B-0{\cdot}09(x_A-x_B) \qquad ...(3)$$

In case of some bonds (*e.g.* Si—C bond) the application of Eqn. (3) reduces the discrepancy between $(d_{A-B})_{cal}$ and $(d_{A-B})_{obs}$ while in case of some other bonds (*e.g.*, C—Cl bond), the discrepancy increases.

A more general equation for calculating d_{A-B} has been given by Pauling. This equation is :

$$d_{A-B}=r_A+r_B-C(x_A-x_B) \qquad ...(4)$$

where C is called *Schomaker and Stevenson coefficient* and has different values (in Å) for atoms A and B.

Single-bond covalent radii or simply covalent radii as these are called of *s*- and *p*-block elements are given in Table 3·1.

Table 3·1. *Covalent Radii (single-bond covalent radii) for s- and p-block Elements (Å)*

s-block elements		*p*-bock elements					
I A	*II A*	*III A*	*IV A*	*V A*	*VI A*	*VII A*	*Zero*
H 0·32							He 0.93
Li 1·23	Be 0·90	B 0·82	C 0·77	N 0·75	O 0·73	F 0·72	Ne 0·71
Na 1·54	Mg 1·36	Al 1·18	Si 1·11	P 1·16	S 1·02	Cl 0·99	Ar 0·98
K 2·03	Ca 1·74	Ga 1·26	Ge 1·22	As 1·20	Se 1·16	Br 1·14	Kr 1·12
Rb 2·16	Sr 1·91	In 1·44	Sn 1·41	Sb 1·40	Te 1·36	I 1·33	Xe 1·31
Cs 2·35	Ba 1·98	Tl 1·48	Pb 1·47	Bi 1·46	Po 1·46	At (1·45)	Rn —
Fr —	Ra —						

Types of Covalent radii. Covalent radii may be *single-bond, double-bond* and *triple-bond covalent radii* which involve single, double and triple bond respectively. The double-bond and triple-bond covalent radii are called *mutiple-covalent radii.*

Double and triple bond covalent radii (in Å) of some common elements are given below : B=0·76, 0·68 (Group III A); C=0·67, 0·60 ; Si=1·07, 1·00 ; Ge=1·12 ; Sn=1·30 (Group IV A) ; N=0·60, 0·55 ; P=1·00, 0·93 ; As=1·11 ; Sb=1·31 (Group VA); O=0·57, 0·56(O_2^+) ; S=0·97, 0·94 ; Se=1·07; Te=1·27 (Group VIA). Some elements do not have triple bond covalent radii.

(*b*) **Metallic Radius (Crystal radius).** This is used for metal atoms which are assumed to be closely packed spheres in the metallic crystal. The metal atoms are supposed to touch one another in the crystal and *the crystal radius is defined has one-half of the distance between the nuclei of two adjacent metal atoms in the metallic close-packed crystal lattice in which metal exhibits a coordination number of 12, e.g.*, the inter-nuclear distance between two adjacent sodium atoms in a crystal of sodium metal is 3·80 Å only, the atomic radius (or metallic radius) of Na metal=3·80/2=1·90 Å. *Metallic radii are about* 10 to 15% *higher than the single-bond covalent radii.* Metallic radii of *s*- and *p*-block elements are given in Table 3·2. These values are for coordination number of 12.

Table 3·2. Metallic radii of *s*- and *p*-block elements (in Å). These values are for coordination number of 12.

s-block elements		*p-block elements*			
IA	*II A*	*III A*	*IV A*	*V A*	*VI A*
H —					
Li 1·55	Be 1·12	B 0·98	C 0·91	N 0·92	O —
Na 1·90	Mg 1·60	Al 1·43	Si 1·32	P 1·28	S 1·21
K 2·35	Ca 1·97	Ga 1·41	Ge 1·37	As 1·39	Se 1·40
Rb 2·48	Sr 2·15	In 1·66	Sn 1·62	Sb 1·59	Te 1·60
Cs 2·67	Ba 2·22	Tl 1·71	Pb 1·75	Bi 1·70	Po 1·76

Since the metallic bond which controls the proximity of the metal atoms to one another in the metallic crystal is not localised bond between the bonded atoms, as is covalent bond, the bonded metal atoms in the metallic crystal lattice are not drawn close to each other as they are in a covalent bond.

The metallic radii are smaller than the Van der Waals radii, since the bonding forces in the metallic crystal lattice are much stronger than the Van der Waals forces.

(c) **Van der Waals Radius or Collision Radius.** In the solid state, the non-metallic elements usually exist as aggregations of molecules. The bonding *within* a non-metal molecule is largely covalent in character, and yet the individual molecules are *held to each other by what are usually called Van der Waals forces.* Half the distance between two atoms within two molecules so located may be called Van der Waals radius *i.e., Van der Waals radius is half of the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules.*

Thus radii are *non-bonded.* When two molecules approach each other *without forming a chemical bond,* there will be a slight attraction between them due to a mutual distortion of their electron clouds ; this force is called Van der Waals force. These forces are absent when we have the substance in gaseous condition, but they draw together the molecules of a liquid and hold molecules in their places in a crystal lattice at low temperature.

In the crystalline form of benzene hexachloride ($C_6H_6Cl_6$) the molecules are arranged so that the shortest distance between chlorine nuclei on different molecules is 3·6 Å. Thus in this molecule the Van der Waals radius of chlorine is 3·6/2=1·8Å (half of the inter-atomic distance). In $CdCl_2$ the shortest distance between chlorine atoms not bonded to the same mutual cadmium atom is 3·76 Å. Here the Van der Waals radius of chlorine is 3·76/2=1·88 Å which is one-half of the inter-atomic distance.

Values of Van der Waals radii of some elements are given in Table 3·3.

Table 3·3. Van der Waals radii* of some elements (in Å)

V A	*VI A*	*VII A*	*Zero*
N 1·5	O 1·40	H 1·2 F 1·36	He 1·20 Ne 1·60
P 1·9	S 1·85	Cl 1·80	Ar 1·91
As 2·0	Se 2·0	Br 1·95	Kr 2·0
Sb 2·2	Te 2·20	I 2·15	Xe 2·20

*The values of Van der Waals radii are obtained from X-ray study of the elements in solid state.

Comparison between Van der Waals and Covalent Radii. This comparison can be made by considering chlorine atom. Consider two molecules of chlorine *viz.* $Cl_2(1)$ and $Cl_2(2)$ in close contact with each other (no bond formation) (*see* Fig. 3·1). Let X and Y be the two nuclei of the two chlorine atoms of $Cl_2(2)$ molecule and X′ and Y′ be those of the two chlorine atoms of $Cl_2(1)$ molecule. The half of the distance between the nuclei Y and X′ of the two non-bonded neighbouring chlorine atoms of adjacent molecules $Cl_2(1)$ and $Cl_2(2)$ is Van dar Waals radius of chlorine atom while half of the distance between the two nuclei X and Y in the same molecule $Cl_2(2)$ is the covalent radius of chlorine atom. In case of chlorine Van der Waals radius$=3{\cdot}60/2=1{\cdot}8$Å while covalent radius$=1{\cdot}99/2=0{\cdot}99$Å. *Thus covalent radius is smaller than the Van der Waals radius.*

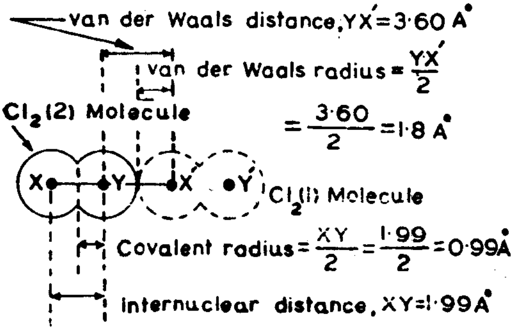

Fig. 3·1. Comparison between covalent and Van der Waals radius in chlorine atom. $Cl_2(1)$ and $Cl_2(2)$ are two chlorine molecules in close contact with each other (no bond formation). X and Y are the two nuclei of the two chlorine atoms of $Cl_2(2)$ molecule while X′ and Y′ are those of $Cl_2(1)$ molecule.

Here it may be noted that noble gases do not form covalent bonds. Thus in crystals of noble gases no chemical forces operate between the atoms. It is only the Van der Waals forces that are attractive forces prevailing in these atoms. Thus *for noble gases in the solid state the crystal radii (i.e. atomic radii) are actually Van der Waals radii.*

Determination ionic of Radii

As already stated covalent radii can be evaluated by an indirect method. The distance between the nuclei of the two bonded atoms (*i.e. inter-nuclear* or *inter-atomic distance* or *bond length* or *bond distance*) in covalent molecule in determined by X-ray, electron and neutron diffraction and spectroscopy. *The half of this inter-nuclear distance gives the value of covalent radius.* Here it has been assumed that both the atoms behave as effective spheres which are in contact with each other in the solid state.

IONIC RADII

Ionic radius may be defined as the distance between the nucleus of an ion and the point upto which the nucleus has influence on its electron cloud. The values of ionic radii of *s*- and *p*-block elements are given in Table 3-4.

Table 3·4. *Ionic (crystal) radii in Å for coordination number six of s- and p-block elements*

s-block elements		*p-block elements*				
IA	IIA	IIIA	IVA	VA	VIA	VIIA
H^+ 0·29						
H^- 1.60						
Li^+ 0·60	Be^{2+} 0·31	B^{3+} 0·20	C^{4-} 2·60	N^{3-} 1·71	O^{2-} 1·40	F^- 1·36
			C^{4+} 0·15	N^{5+} 0·11	O^{6+} 0·09	F^{7+} 0·07
Na^+ 0·95	Mg^{2+} 0·65	Al^{3+} 0·50	Si^- 2·71	P^{3-} 2·12	S^{2-} 1·84	Cl^- 1·81
			Si^{4+} 0·41	P^{5+} 0·34	S^{6+} 0·29	Cl^{7+} 0·26
K^+ 1·33	Ca^{2+} 0·99	Ga^+ 1·13	Ge^{2+} 0·93	As^{3-} 2·22	Se^{2-} 1·98	Br^- 1·95
		Ga^{3+} 0·62	Ge^{4+} 0·53	As^{5+} 0·47	Se^{6+} 0·42	Br^{7+} 0·39
Rb^+ 1·48	Sr^{2+} 1·13	In^+ 1·32	Sn^{2+} 1·12	Sb^{3-} 2·45	Te^{2-} 2·21	I^- 2.16
		In^{3+} 0·81	Sn^{4+} 0·71	Sb^{5+} 0·62	Te^{6+} 0·56	I^{7+} 0·50
Cs^+ 1·69	Ba^{2+} 1·35	Tl^+ 1·40	Pb^{2+} 1·20	Bi^{3+} 1·20	Po —	At —
		Tl^{3+} 0·95	Pb^{4+} 0·84	Bi^{5+} 0·74	—	—
Fr^+ 1·76	Ra^{2+} 1·40					

Determination of Ionic Radii

The determination of ionic radii is more difficult than that of covalent radii, since like atoms do not form ionic bond with each other. The size of an ion (*i.e.* ionic radius) can be determined only when that of some other ion is also known.

The following methods have been used for the determination of ionic radii.

(*i*) **Lande's Method.** If in an ionic crystal the anion is very large compared to the cation, there is anion-anion contact in the crystal lattice, *e.g.* since in Li^+I^- ionic crystal Li^+ ion is very small compared to I^- ion ($Li^+=0{\cdot}60$ Å, $I^-=2{\cdot}16$ Å), I^- ions are in contact with each other (*see* Fig. 3·2). The edge length AB of Li^+I^- unit cell has been found experimentally equal to 6·00Å. The diagonal CB of the square face is thus given by :

$$CB^2=(6)^2+(6)^2=72\text{Å}$$

or $$CB=\sqrt{72}\ \text{Å}$$

Now since the anions are in contact with each other, the diagonal, CB is equal to four times the radius of I^-ion, r_{I^-}. Thus :

$$CB=\sqrt{72}=4\,r_I$$

or $$r_{I^-}=\frac{1}{4}\sqrt{72}=2{\cdot}12\text{Å}$$

In the crystal of K^+I^-, the cations and anions are of comparable size and hence there is cation-anion contact (*see* Fig. 3·3).

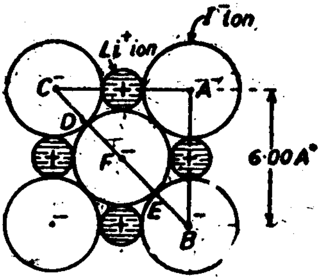

Fig. 3·2. A portion of crystal structure of Li^+I^- showing contact between I^- ions.
Note—
(i) $CD=DF=FE=EB=r_{I^-}$
(ii) Diagonal, $CB=4r_{I^-}$

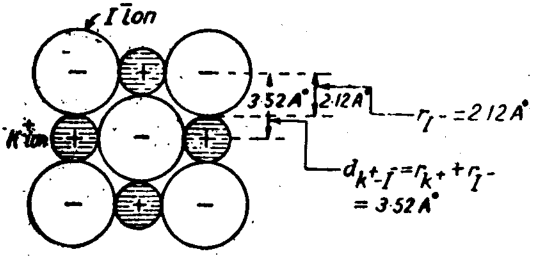

Fig. 3·3. A portion of K^+I^- crystal showing contact between K^+ and I^- ions.

Experimental value of the internuclear distance in K^+I^- crystal, $d_{K^+-I^-}$ is 3·52Å which is equal to the sum of r_{K^+} and r_{I^-} Thus :

(r_{I^-} =2·12A as calculated above)

$$d_{K^+-I^-} = r_{K^+} + r_{I^-}$$

or $$3{\cdot}52 = r_{K^+} + 2{\cdot}12$$

or $$r_{K^+} = 3{\cdot}52 - 2{\cdot}12 = 1{\cdot}40\text{Å}$$

(*ii*) **Pauling's method.** Pauling has calculated the ionic radii of ions of such ionic crystals which have iso-electronic ions. (*The ions which have the same number of electrons are called iso-electronic ions*).

Pauling's method is based on the following assumptions :

(*a*) The cation, c^+ and the anion, a of the ionic crystal, c^+a^- are assumed to be in close contact with each other, *i.e the inter-ionic distance, $d_{c^+-a^-}$ between c^+ and a^- ions in c^+a^- crystal is equal to the sum of their ionic radii. Thus*

$$d_{c^+-a^-} = r_{c^+} + r_{a^-} \qquad \text{...}(i)$$

where r_{c^+} and r_{a^-} are the ionic radii of the cation, c^+ and of anion, a^- respectively.

(*b*) *If the ions viz. c^+ and a^- of the crystal are iso-electronic, their ionic radii are inversely proportional to the effective nuclear charges acting on these ions.* Thus :

$$\frac{r_{c^+}}{r_{a^-}} = \frac{(Z_{eff})_{a^-}}{(Z_{eff})_{c^+}} \qquad \text{...}(ii)$$

where $(Z_{eff})_{c^+}$ and $(Z_{eff})_{a^-}$ are the effective nuclear charges acting on the cation, c^+ and on the anion, a^- respectively.

The effective nuclear charge Z_{eff} acting on an ion is the actual nuclear charge, Z (*i.e.* atomic number) minus a factor, σ. This factor takes into account the screening effects of electrons in the inner energy levels and is called *screening constant*. Thus $(Z_{eff})_{c^+}$ and $(Z_{eff})_{a^-}$ are given by :

$$\left.\begin{array}{l}(Z_{eff})_{c^+} = Z_{c^+} - \sigma_{c^+}\\(Z_{eff})_{a^-} = Z_{a^-} - \sigma_{a^-}\end{array}\right\}$$

With the help of these relations equation (*ii*) reduces to :

$$\frac{r_{c^+}}{r_{a^-}} = \frac{Z_{a^-} - \sigma_{a^-}}{Z_{c^+} - \sigma_{c^+}} \qquad \text{...}(iii)$$

By solving equations (*i*) and (*iii*) the values of r_{c^+} and r_{a^-} can be found, provided that values of Z_{c^+}, Z_{a^-}, σ_{c^+} + σ_{a^-} and $d_{c^+-a^-}$ are known.

Illustration. Let us apply this method for the determination of the radii of Na^+ and F^- ions in Na^+F^- crystal.

With the help of spectral data Slater has shown *that σ for an ion having Ne-type configuration* (i.e. $1s^2$, $2s^2p^6$ configuration) is 4.5. Since both the ions in NA^+F^- crystal have Ne-type configuration, $\sigma_{Na^+} = \sigma_F = 4.5$. for $Na^+ F^-$ ionic crystal, $Z_{Na^+} = 11$ and $Z_{F^-} = 9$.

Thus equation (*iii*) given above can be written as :

$$\frac{r_{c+}}{r_{a^-}} = \frac{9-4{\cdot}5}{11-4{\cdot}5} = \frac{4{\cdot}5}{6{\cdot}5} \quad \ldots(A)$$

Experimentally it has been found that the inter-ionic distance, $d_{Na^+-F^-}$ between Na^+ and F^- ions in Na^+F^- crystal is 2·31A° *i.e.*

$$r_{Na^+} + r_{F^-} = d_{Na^+-F^-} = 2{\cdot}13 \quad \ldots(B)$$

On solving equations (A) and (B) we get

$$r_{Na^+} = 0{\cdot}95 \text{ A}°$$

and $$r_{F^-} = 1{\cdot}36 \text{ A}°.$$

CRYSTAL COORDINATION NUMBER

In ionic crystal positive ions are surrounded by negative ions and *vice versa*. The number of ions of opposite charge surrounding an ion in the crystal lattice is called the **crystal coordination number** or simply **coordination number** and is represented by C.N.

In case of ionic crystals of AB type (*e.g.* NaCl, ZnS) in which the number of each kind of ions is the same, the coordination number of the positive ion is the same as that of the negative ion, *e.g.* in NaCl the C.N. of Na^+ and Cl^- ions is *six*. Thus in NaCl crystal each Na^+ ion is surrounded by equidistant six Cl^- ions and similarly each Cl^- ion is surrounded by equidistant six Na^+ ions. On the other hand in case of ionic crystals of AB_2 or A_2B type (*e.g.* CaF_2, Na_2S) in which the number of each kind is not the same, the coordination number of positive ion is different from that of negative ion, e.g. in CaF_2 the number of F^- ions is double that of Ca^{2+} ions. Thus the coordination number of F^- ion is double that of Ca^{2+} ion. X-ray study has shown that coordination numbers of Ca^{2+} and F^- ions are 8 and 4 respectively.

RADIUS RATIO

Definition. The radius ratio (R_r) is defined as the ratio of the radius of cation (r_{c^+}) to that of anion (r_{a^-}) in an ionic crystal c^+a^-.

Thus :

$$R_r = \frac{r_{c+}}{r_{a^-}}$$

Application. With the help of radius ratio it is possible to predict the cation/anion coordination number in any ionic crystal. Thus radius ratio can be used to predict the shape (*i.e.* the arrangement of different ions) of the ionic crystal. The effect of radius ratio in determining the coordination number and shape of ionic crystals is known as **radius ratio effect**.

Obviously as the cation becomes larger with respect to the anion *i.e.* R_r increases, more number of anions can fit around the cation *i.e.* the C.N. of cation will increase. Thus C.N. of which will give the most stable structure to any pair of ions, c^+ and a is dependent on the radius ratio, $R_r = r_{c^+}/r_{a^-}$ value.

The relationship between the various structures and radius ratio are shown in Table 3·5.

Table 3·5. *The limiting radius ratio ($R_r = r_{c^+}/r_{a^-}$) values for various Coordination numbers (ccp=cubic close packing, hcp=hexagonal close packing)*

Limiting value of $R_r = \frac{r_{c^+}}{r_{a^-}}$	*Coordination number*	*Geometry (i.e. shape) of the ionic crystal (with examples)*
0 to 0·155	2	Linear
0·155 to 0·225	3	Trigonal planar (Boron oxide)
0·255 to 0.414	4	Tetrahedral (ZnS)
0·414 to 0·732	4	Square planar
0·414 to 0·732	6	Octahedral (NaCl)
0·732 to 1·000	8	Body-centred cubic or twisted cubic (CsCl)
1	12	Close packing (metals) (*ccp* and *hcp*)

The following examples of ionic crystals of AB type (*e.g.* NaCl, CsCl etc.) illustrate how the radius ratio concept can be used to predict the shape (*i.e.* the arrangement of different ions) of ionic crystal.

(*i*) *Sodium chloride structure.* The radius ratio for NaCl $= r_{Na^+}/r_{Cl^-} = 0·59/1·81 = 0·524$ which lies between 0·914 and 0·732 (see Table). Thus the co-ordination number should be 4 or 6 and the shape of NaCl ionic crystal should, therefore, be either square planar or octahedral. X-ray study of NaCl crystal has shown that the crystal has octahedral structure, *i.e.* each Na^+ ion is surrounded by six equidistant Cl^- ions placed at the corners of a regular-octahedron and similarly each Cl^- ion is sorrounded by six equidistant Na^+ ions. In other words the stoichiometry of Na^+Cl^- is 1 : 1 and coordination number is 6 : 6.

(*ii*) *Cesium chloride structure.* In this ionic crystal the radius ratio $= 1·69/1·81 = 0·93$ which lies between 0·732 and 1·000. Thus a coordination of 8 and a cubic structure is suggested for this ionic crystal, *i.e.* each Cs^+ ion is surrounded by eight Cl ions as its nearest neighbours and similarly each Cl^- ion is surrounded by eight Cs^+ ions. Thus the stoichiometry of Cs^+Cl^- is 1 : 1 and the coordination number is 8 : 8.

FACTORS INFLUENCING THE MAGNITUDE OF IONIC RADII

The following factors are important :

(i) **Coordination number.** *With the increase of coordination number, the inter-ionic distance and hence the ionic radius also increases, e g.* the radius of Cl^- ion in CsCl crystal (8 : 8 coordination) is somewhat higher than that of Cl^- ion in NaCl crystal (6 : 6 coordination). This is because of the fact that in CsCl crystal each ion is surrounded by a greater number of ions as compared with NaCl crystal and this results in less attraction between different ions of CsCl crystal and consequently greater is the radius of Cl^- ion.

In case of three common structures of AB type ionic crystals (*e.g.* ZnS, NaCl and CsCl), NaCl (6 : 6 coordination number) is generally taken as standard and the values of ionic radii in CsCl (8 : 8 coordination number) and ZnS (4 : 4 coordination number) are expressed with respect to those in NaCl. Thus, if the radii of NaCl are taken equal to 1, the relative radii of ZnS are found to be 0·95 (*i.e.* 5% lower than that in NaCl) and those in CsCl are 1·03 (*i.e.* 3% higher). This is shown below :

Structure type	:	ZnS	NaCl	CsCl
Coordination numbers	:	4 : 4	6 : 6	8 : 8
Relative radii	:	0·95	1·00	1·03

(ii) **Radius Ratio (R_r).** The radius ratio R_r, which is given by : $R_r = r_{c+}/r_{a-}$ also influences the magnitude of ionic radii. As the value of R_r decreases towards limited value for an ion-anion contact, the repulsion between anions will progressively increase and thus tend to distend the structure to increase the apparent radii of the component ions.

(iii) **Covalent character in the ionic bond** Covalent character in the ionic bond existing between the cation and anion forming the ionic crystal decreases the measured inter-ionic distance and hence the ionic radius is decreased.

PERIODIC VARIATIONS OF ATOMIC AND IONIC RADII

Atomic or ionic radius is a periodic function of the atomic number, *i.e.* it changes with the change of atomic number in the periodic table as shown below :

(a) **In a period.** *Atomic and ionic radii both decrease from left to right across a period in the periodic table when we consider only normal elements—e.g.* in the elements of 2nd period the covalent radii decrease as we move from Li to F as shown below :

Elements of 2nd period	:	Li	Be	B	C	N	O	F
Covalent radii (A°)	:	1·23	0·90	0·82	0·77	0·75	0·73	0·72

——————Values decreasing——————→

Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the *largest size* while the halogens (that are present at the extreme right, excluding the zero group elements) have the *smallest size.*

Explanation. We know that as we proceed from left to right in a period, the electrons are added to the orbitals of the same main energy level. Addition of differentiating electrons to the same main energy level puts the electrons, on the average, no farther from the nucleus and hence cannot add to the size. But with the addition of each electron, the nuclear charge (*i.e.* atomic number) increases by one. The increased nuclear charge attracts the electrons more strongly close to the nucleus and thus decreases the size of the atoms.

(*b*) **In a group.** *On moving down a group of regular elements both atomic and ionic radii increase with increasing atomic number, e.g.* in the elements of IIA Group both covalent and ionic radii of M^{2+} ions increase when we pass from Be to Ba.

Elements of IIA Group :	Be	Mg	Ca	Sr	Ba
Covalent radii (Å) :	0·90	1·36	1·74	1·91	1·98
Ionic radii of M^{2+} cations (Å) :	0·31	0·65	0·99	1·13	1·35

——————Values increasing——→

Explanation. When we proceed from top to bottom in a group, the following two opposite forces act simultaneously.

(*i*) On proceeding downwards in a group the electrons are added to higher main energy levels which are, on the average, farther from the nucleus. This effect decreases the electrostatic attraction between the nucleus and the valence-shell electrons and this decreased electrostatic attraction increases the atomic and ionic radii.

(*ii*) The nuclear charge (*i.e.* atomic number) increases as we proceed from top to bottom. This increase in nuclear charge decreases the atomic and ionic radii.

The net effect of these two opposite forces is that the decreased electrostatic attraction which is caused by the effect of extra shell being added in the configuration of the elements outweighs the effect caused by the increase in the nuclear charge, *i.e.* it is only the effect of the decrease in electrostatic attraction that predominates. Thus atomic and ionic radii go on increasing as the nuclear charge increases in proceeding downwards in a group.

Size of iso-electronic species. As already stated *iso-electronic species* (which may be atoms or ions) *are those which have the same number of electrons. For such species, the size decreases with an increase in atomic number.* This fact is evident from Table 3·6 in which the atomic and ionic radii of some iso-electronic species with Ne-type configuration ($1s^2$, $2s^2p^6$) are given.

Explanation. As the atomic number, Z (*i.e.* nuclear charge) increases, the increasing nuclear charge acts on the same number of electrons in each member of the series and consequently the radius decreases.

The successive decrease in the values of radii can also be explained by saying that since on moving from C^{4-} to Cl^{7+} in the series, the value of Z/*e* ratio (Z=Atomic number, *e*=No. of electrons in the atom or ion) increases, the values of radii decrease (*see* Table 3·6).

Table 3·6. *Variation of radii of iso-electronic ions and atoms with Ne-type configuration namely* $1s^2$, $2s^2p^6$

Ion or Atom	*Atomic number Z (nuclear charge)*	*No. of electrons in the ion or atom (e)*	*Z/e ratio*	*Atomic or ionic Radii in Å*
C^{4-}	6	10	6:10=0·6	2·60
N^{3-}	7	10	0·7	1·71
O^{2-}	8	10	0·8	1·40
F^-	9	10	0·9	1·36
Ne^0	10	10	1·0	1·12
Na^+	11 ↓ increasing	10	1·1 ↓ increasing	0·95 ↓ decreasing
Mg^{2+}	12	10	1·2	0·65
Al^{3+}	13	10	1·3	0·50
Si^{4+}	14	10	1·4	0·41
P^{5+}	15	10	1·5	0·34
S^{6+}	16	10	1·6	0·29
Cl^{7+}	17	10	1·7	0·26

Size of cations of the same element but with different oxidation states. *The size of the cations of the same element in different oxidation states decreases with the increase in oxidation state, e.g.* Fe^{2+} ion is larger than Fe^{3+} ion in size (Fe^{2+}=0·76Å, Fe^{3+}=0·64Å).

Explanation. The decrease in size with the increase in oxidation state is explained on the basis of Z/*e* concept. Z/*e* ratio for Fe^{2+} ion is less than that for Fe^{3+} ion. Z/*e* ratio for Fe^{2+} ion=26/24, Z/*e* for Fe^{3+} ion=26/23.

Size of an anion and a cation compared to its parent atom. *The size of an anion is greater while that of the cation is smaller than that* *of its parent atom, e.g.* $F^-(=1{\cdot}36Å) > F(=0{\cdot}72Å)$; $Cl^-(=1{\cdot}81Å) > Cl(=0{\cdot}99Å)$; $Na^+(=0{\cdot}95Å) < Na(=1{\cdot}90Å)$; $Ca^{2+}(=0{\cdot}99Å) < Ca(=1{\cdot}97Å)$.

Explanation. Let us consider the radii of Na, Na^+, Cl and Cl^-. The reason of the fact that Na^+ ion is smaller than Na atom is that Na^+ ion has 10 electrons ($Na^+ \longrightarrow 1s^2, 2s^2p^6$) while Na atom has 11 electrons ($Na \longrightarrow 1s^2, 2s^2p^6, 3s^1$). The nuclear charge (charge on the nucleus) in each case is the same, *i.e.* equal to +11 (atomic number of Na). This nuclear charge of +11 can pull 10 electrons of Na^+ ion inward more effectively than it can pull a greater number of 11 electrons of Na atom. Thus Na^+ ion is smaller than Na atom.

The reason why Cl^- ion is bigger than Cl atom can also be explained on a similar basis. The Cl^- ion has 18 electrons ($Cl^- \longrightarrow 1s^2, 2s^2p^6, 3s^2p^6$) while Cl atom has only 17 electrons ($Cl \longrightarrow 1s^2, 2s^2p^6, 3s^2p^5$). The nuclear charge in each case is +17 which cannot pull 18 electrons of Cl^- ion as effectively as it can pull 17 electrons of Cl atom inward. Thus Cl^- ion is bigger than Cl atom.

The same arguments can be applied for other positively and negatively charged ions.

Why a cation is smaller and an anion is bigger than its parent atom can also be explained on the basis of Z/e ratio concept. Since Na atom has lower Z/e ratio (= 11/11) than Na^+ ion (= 11/10), Na atom is smaller than Na^+ ion. Similarly Cl^- ion (Z/e ratio = 17/18) is bigger than Cl atom (Z/e ratio = 17/17).

IONISATION POTENTIAL OR IONISATION ENERGY

The electrons are raised to higher energy levels by absorption of energy from an external source. If this process is continued, a stage comes when the electron goes completely out of the influence of the nucleus and a positive ion is produced.

The amount of energy required to remove the most loosely bound electron (i.e., the outermost electron) from an isolated gaseous atom of an element in its lowest energy state (i.e., ground state) to produce a cation is known as ionisation potential or ionisation energy of that element. It is generally represented as I or IP and is measured in electron volts (eV) or Kilo calories (K. calories) per gm atom. Thus ionisation potential can be defined by the process.

$$\underset{\text{Isolated gaseous atom}}{M(g)} + \text{Energy supplied (Ionisation energy, I)} \longrightarrow \underset{\text{Cation}}{M^+(g)} + e^-$$

The process by which the element loses an electron (*i.e.*, ionises) to convert itself into a cation is called its **ionisation**. This process is an endo thermic process, since energy is supplied to effect it.

The values of ionisation potential of *s*- and *p*-block elements are given in Table 3·7.

Table 3·7. Ionisation potentials (in *e*V) of *s*-and *p*-block elements.

s-block Elements		*p-block Elements*					
I A	*II A*	*III A*	*IV A*	*V A*	*VI A*	*VII A*	*Zero*
H 13·5							He 24·5
Li 5·4	Be 9·3	Be 8·3	C 11·2	N 14·5	O 13·6	F 17·4	Ne 21·6
Na 5·1	Mg 7·6	Al 6·0	Si 8·1	P 11·0	S 10·4	Cl 13·0	Ar 15·8
K 4·3	Ca 6·1	Ga 6·0	Ge 7·8	As 9·8	Se 9·8	Br 11·8	Kr 14·0
Rb 4·2	Sr 5·7	In 5·7	Sn 7·3	Sb 8·6	Te 9·0	I 10·4	Xe 12·1
Cs 3·9	Ba 5·2	Tl 6·1	Pb 7·4	Bi 7·2	Po 8·4	At —	Rn 10·7

Successive ionisation potentials. The electrons are removed in stages one by one from an atom. The amount of energy required to remove the first electron from a gaseous atom is called its **first ionisation potential**. The energy required to remove the second electron from the cation is called **second ionisation potential**. Similarly we have **third, fourth**...ionisation potentials. Thus :

$$M(g) + I_1 \longrightarrow M^+(g) + e^-$$

$$M^+(g) + I_2 \longrightarrow M^{2+}(g) + e^-$$

$$M^{2+}(g) + I_3 \longrightarrow M^{3+}(g) + e^-$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

The values of eight successive ionisation potentials of some elements are given in Table 3·8. These values show that these increase in the order :

$$I_1 < I_2 < I_3 < I_4 < \ldots\ldots$$

The successive increase in their values is due to the fact that it is relatively more difficult to remove an electron from a cation

Table 3·8. Values of $I_1, I_2 ... I_8$ of some elements (in *eV*)

Elements with atomic numbers	*Electronic Configuration*	*Successive ionisation potentials (eV)*							
		I_1	I_2	I_3	I_4	I_5	I_6	I_7	I_8
H_1	$1s^1$	13·6							
He_2	$1s^2$	24·6	54·4						
Li_3	$1s^2, 2s^1$	5·4	75·6	122·4					
Be_4	$1s^2, 2s^2$	9·3	18·2	153·9	217·7				
B_5	$1s^2, 2s^2p^1$	8·3	25·1	37·9	259·3	340·1			
C_6	$1s^2, 2s^2p^2$	11·3	24·4	47·9	64·5	39·2	489·8		
N_7	$1s^2, 2s^2p^3$	14·5	29·6	47·4	77·5	97·9	551·9	666·8	
O_8	$1s^2, 2s^2p^4$	13·6	35·1	54·9	77·4	113·9	138·1	739·1	871·1
F_9	$1s^2, 2s^2p^5$	17·4	35·0	62·6	87·2	114·2	157·1	185·1	953·6
Ne_{10}	$1s^2, 2s^2p^6$	21·6	41·1	64·0	97·2	126·4	157·9	—	—

having higher positive charge than from a cation having lower positive charge or from a neutral atom.

Factors affecting the magnitude of ionisation potential and its periodic variations. The magnitude of ionisation potential depends on the following factors :

(*i*) **Charge on the nucleus (*i.e.*, nuclear charge) and variation in a period.** The greater the charge on the nucleus of an atom, the more difficult it would be to remove an electron from the atom and hence greater would be the value of ionisation potential.

Thus the value of ionisation potential generally increases in moving from left to right in a period, since the nuclear charge of the elements (*i.e.*, atomic number) also increases in the same direction *e.g.*,

Elements of 2nd period	:	Li	Be	B	C	N	O	F	Ne
Nuclear charge	:	+3	+4	+5	+6	+7	+8	+9	+10
Ionisation potential (eV)	:	5·4	9·3	8·3	11·3	14·5	13·6	17·4	21·6

The increase in the magnitude of ionisation potential is due to the fact that with the increase in nuclear charge the electrostatic attraction between the outermost electrons and the nucleus increases and hence it becomes comparatively more difficult to remove an electron.

(*ii*) **The extent to which the most loosely bound electron penetrates the cloud of electronic charge encompassed by the inner electronic shells.** For a given value of n the degree of penetration of electrons will decrease in the order : $s > p > d > f$, *i.e.* on average an s electron will approach the nucleus more closely than a p-electron, a p-electron more closely than d and d more closely than f. Thus other factors being equal, an s-electron will be harder to remove than a p-electron, a p- electron harder to remove than a d electron and so on. The ionisation potentials will decrease in this order. Let us illustrate this point by considering the following examples :

(*a*) The ionisation potential corresponding to the removal of $2p^1$ electron of boron ($B \rightarrow 2s^2p^1$) is 8·3 *eV* while those corresponding to the removal of two $2s$ electrons are 25·1 and 37·9 *eV*.

(*b*) Let us consider two different elements of the same period for which the value of principal quantum number (n) is the same. Ionisation energy of boron ($B \rightarrow 2s^2p^1$) is lower than that of beryllium ($Be \rightarrow 2s^2$) [B = 8·3 *eV*, Be = 9·3 *eV*], since in case of boron we have to remove a $2p^1$ electron to get $B^+[B(2s^2p^1) \rightarrow B^+(2s^2)+e^-]$ while in case of Be we have to remove a $2s^1$ electron of the same main energy level to have Be^+ ion. $[Be(2s^2) \longrightarrow Be^+(2s^1)+e^-]$.

(*iii*) **Completely-filled and half-filled orbitals.** According to Hund's rule atoms having half-filled or completely-filled orbitals are comparatively more stable and hence more energy is needed to remove an electron from such atoms. *The ionisation potential of such atoms is, therefore, relatively higher than expected normally from their position in the periodic table.*

Example. A few irregularities that are seen in the increasing values of ionisation potential along a period can be explained on the basis of the concept of half-filled and completely filled orbitals, *e.g.* Be and N in the second period and Mg and P in the third period have slightly higher values of ionisation potentials than those normally expected. This is explained on the basis of extra stability of the completely-filled $2s$-orbital in Be($Be \rightarrow 2s^2$) and $3s$-orbital in Mg($Mg \rightarrow 3s^2$) and of half-filled $2p$-orbital in N ($N \rightarrow 2s^2p^3$) and $3p$-orbital in P($P \rightarrow 3s^2p^3$).

(*iv*) **The shielding effect *i.e.*, screening effect of the inner electrons on the valence-electrons and variation in a group,** **A study of Fig. 3·4 shows that a valence-electron in a multi-electron atom is attracted by the nucleus and repelled by the electrons of inner-shells.**

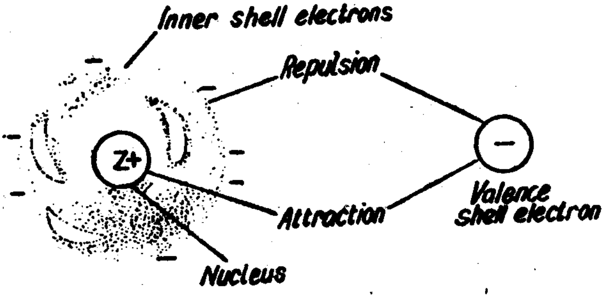

Fig. 3·4. Effect of inner-electron shells on a valence shell electron in a multi-electron atom—shielding effect.

The combined effect of this attractive and repulsive force acting on the valence-electron is that the valence-electron experiences less attraction from the nucleus. This is known as screening effect. Thus larger the number of electrons is the inner-shell, lesser is the attractive force holding the valence-electron tot he nucleus and consequently the lower will be the value of ionisation potential.

As we move down a group, the number of inner-shells increases and hence the ionisation potential tends to decrease, e.g.,

Elements of II A group	:	Be	Mg	Ca	Sr	Ba
No. of inner-shells	:	1	2	3	4	5
Ionisation potential (eV)	:	9·3	7·6	6·1	5·7	5·2

Decreasing ⟶

(v) **Atomic radius and variation in a group.** *With the increase in atomic radius, the ionisation potential decreases.* This is because of the fact that in case of larger atoms the attraction between the nucleus and outer-most electron is less and hence it is easier to remove an electron from a larger atom than from a smaller one. Thus *on moving from top to bottom in a group the ionisation potential of the elements decreases with the increase of their atomic radii, e.g.,*

Elements of IA group	:	Li	Na	K	Rb	Cs
Covalent radii (Å)	:	1·55	1·90	2·35	2·48	2·67
Ionisation potential (eV)	:	5·3	5·1	4·3	4·2	3·9

Decreasing ⟶

(vi) **Principal quantum number (n) and variation in a group.** Principal quantum number (*n*) determines the location of an electron from the nucleus. **Farther away the electron from the nucleus, more** loosely would it be bound to it and more easy it would be to remove it. In other- words *higher the value of n, the lower will be the amount of energy required to remove the electron i.e., its ionisation potential will be lower.*

Thus *on moving from top to bottom in a group, as the value of n for the valence-electron increases, ionisation potential decreases as* is evident from the following examples.

(*a*) Values of first and second ionisation potentials of Li (Li $\longrightarrow$ $1s^2, 2s^1$) are 5·4 e*V* and 75·6 e*V* respectively. 5·3 e*V* is the energy required to remove $2s^1$-electron with $n=2$ and 75·6 e*V* is that needed for the removal of $1s^1$-electron with $n=1$. Quite evidently, since n for $2s^1$-electron is greater than that for $1s^1$-electron, first ionisation potential of Li atom is smaller than the second one.

(*b*) First ionisation potentials for Ne (Ne $\longrightarrow$ $2s^2p^6$) and Ar (Ar $\longrightarrow$ $3s^2p^6$) are 21·6 e*V* and 15·8 e*V* respectively. These values correspond to the removal of $2p^1$-electron in Ne atom and $3p^1$-electron in Ar atom. Obviously, since n for Ne(=2) is smaller than that for Ar(=3), ionisation potential of Ne(=21·6 e*V*) is higher than that of Ar (=5·8 e*V*).

Exception to the vertical trend of ionisation potential.

There is an exception to the vertical trend of ionisation potential. This exception occurs in case of those elements whose atomic numbers are greater than 72. Thus the ionisation potentials of the elements from Ta_{73} to Pb_{82} are greater than those of the elements of the same sub-group above them as shown below : (First ionisation potential values are given in electron volts, eV).

VB	*VI B*	*VII B*	*VIII*			*I B*	*II B*	*III A*	*IVA*
Nb_{41}	Mo_{42}	Tc_{43}	Ru_{44}	Rh_{45}	Pd_{46}	Ag_{47}	Cd_{48}	In_{49}	Sn_{50}
6·8	7·1	7·2	7·3	7·4	8·3	7·5	8·9	5·7	7·3
Ta_{73}	W_{74}	Re_{75}	Os_{76}	Ir_{77}	Pt_{78}	Au_{79}	Hg_{80}	Tl_{81}	Pb_{82}
7·7	7·8	7·8	8·7	9·2	9·0	9·2	10·4	6·1	7·4

The reason for the abnormal behaviour (*i.e.* an increase in the value of I_1 from Nb $\rightarrow$ Ta, Mo $\rightarrow$ W,......, Sn $\rightarrow$ Pb) shown by the elements from Ta_{73} to Pb_{82} is due to the *lanthanide contraction* as a result of which there occurs an increase in the nuclear charge without a corresponding increase in size through the rare earths. In fact, the size actually decreases in this region.

APPLICATIONS OF THE CONCEPT OF IONISATION POTENTIAL

The concept of ionisation potential can be used to draw a number of important conclusions. Some of the applications of the concept of ionisation potential are given below :

(*i*) **To explain the trend from metallic to non-metallic character of elements from left to right in a period.** At the left of a period in periodic table (P.T.), we have the elements with low ionisation potential values. These elements, therefore, react by losing electrons and thus form ionic bonds. These elements are, therefore, **typical metals.**

As we proceed to the right of P. T., the ionisation potential values increase and consequently the tendency of the elements to lose the electrons decreases *i.e.* the tendency to form the ionic bonds decreases, but at the same time, the tendency to form the covalent bonds increases. Near the end of a period, since the elements have high values of ionisation potential, these tend to take up electrons and thus form negative ions. Thus these elements are **typical non-metals.**

Similarly, the trend from non-metallic to metallic character of elements in a group of *p*-block elements can well be explained on the basis of ionisation potential data.

(*ii*) **To determine the number of Valence Electrons in an atom.** The knowledge of ionisation potentials can also be used to find out the number of valence electrons in an atom. For example in case of Li the values of I_1 and I_2 are 5·4 eV and 75·6.eV. These values show that one electron can much more readily be removed than the other. Thus there is only one-electron in the valence shell of Li atom.

Similarly, since there is a marked increase in the (*i*) I_2 and I_3 values of Be (*ii*) I_3 and I_4 values of B (*iii*) I_4 and I_5 values of C (*iv*) I_5 and I_6 values of N (*v*) I_6 and I_7 values of O and (*vi*) I_7 and I_8 values of F, there are (*i*) 2 valence electrons in Be atom, (*ii*) 3 valence electrons in B atom, (*iii*) 4 valence electrons in C atom, (*iv*) 5 valence electrons in N atom, (*v*) 6 valence electrons in O atom, and (*vi*) 7 valence electrons in F atom.

(*iii*) **Relative Reactivity of Elements.** Elements having high values of ionisation potentials are less reactive (*e.g.* inert gases), while those having low values are very reactive (*e.g.* Alkali metals and Alkaline earth metals).

Exceptions. This rule is applicable only to those elements which have dominant electro-positive character (*i.e.* alkali metals and alkaline earth metals) and not to those which are highly electro-negative, *e.g.*, ionisation potential of F is 17·42 eV, which is very high and, therefore, shows that F should be inert, but F is actually very reactive.

(*iv*) **Reducing power of an element.** Lower the value of ionisation potential of an element, the greater is its reducing power, since easily removed electron from the element would be accepted by the oxidising agent thereby, lowering its oxidation state.

$$\underset{\substack{\text{(reducing}\\ \text{agent)}}}{A^{\circ}} \xrightarrow[\text{(oxidation of } A^{\circ})]{-e} A^{+} \qquad \ldots(1)$$

$$\underset{\substack{\text{(oxidising}\\ \text{agent)}}}{B^{\circ}} \xrightarrow[\text{(reduction of } B^{\circ})]{+e^- \text{ obtained from (1)}} B^{-} \qquad \ldots(2)$$

(*v*) **Basic character of elements.** Lower the value of ionisation potential of an element, the greater will be the basic character of the element concerned.

ELECTRON AFFINITY OR AFFINITY ENERGY

In ionisation potential we express the energy supplied to the atom to remove successively one, two or more electrons, and thereby produce cations. In the concept of electron affinity we refer to a reverse process. Thus we have an energy associated with the addition of an electron (or even more electrons in succession) to a neutral atom.

The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state (i.e. ground state) to produce an anion is called its electron affinity or affinity energy. It is generally represented as EA or E and is measured in electron volts (eV) or Kilocalories (Kcalories) per gm atom. Thus electron affinity can be defined by the equation :

$$\underset{\substack{\text{Neutral gaseous}\\ \text{atom}}}{A(g)} + e^-(g) \longrightarrow \underset{\text{Anion}}{A^-(g)} + \text{Energy released (Electron affinity E)}$$

The above process by which the neutral gaseous atom adds an electron is an exo-thermic process, since energy is released in it. Since electron affinity represents the energy released, it is represented with a negative sign placed before it. Electron affinity just defined is actually **first electron affinity** (E_1), since it corresponds to the addition of one electron only. In the process of adding an electron to an anion, $A^-(g)$ against the electrostatic repulsion between the electron being added and the negative charge on $A^-(g)$ ion, energy instead of being released is supplied to $A^-(g)$ to form $A^{2-}(g)$.

$$A(g) + e^-(g) \longrightarrow A^-(g) + \text{Energy released } (E_1)$$

$$A^-(g) + e^-(g) + \text{Energy supplied} \longrightarrow A^{2-}(g)$$

Energy supplied in the process to convert $A^-(g)$ to $A^{2-}(g)$ is called **second electron affinity**, E_2 of A. Since E_2 is the energy absorbed, it is given a positive sign.

Values of E_1 of many elements and E_2 of some elements are given in Table 3.9.

Table 3·9. Electron affinities (in eV) of some elements. Values given in brackets are second electron affinity values.

IA	*II A*	*III A*	*IV A*	*V A*	*VI A*	*VII A*	*Zero*
H —0·75							He 0·0
Li —0·61	Be 0·0	B —0·30	C —1·25	N —1·20	O —1·48 (+7·3)	F —3·6	Ne 0·0
Na —0·82	Mg 0·0	Al —0·52	Si —1·39	P —0·80	S —2·0 (+3·4)	Cl —3·8	Ar 0·0
K —0·69						Br —3·5	Kr 0·0
						I —3·2	Xe 0·0

Factors influencing the magnitude of electron Affinity. The magnitude of E is influenced by a number of factors such as (*i*) *Atomic size* ; (*ii*) *Effective nuclear charge* ; and (*iii*) *Screening effect by inner electrons.*

In general E value decreases with the increasing atomic radius and increases with the decreased screening effect by the inner electrons.

Besides these factors E value also depends on the type of orbital into which the electron is added. Other factors remaining constant, E value is the greatest for an electron entering an *s*-orbital and decreases for *p*-, *d*-, and *f*-orbitals.

PERIODIC VARIATIONS

(*a*) **In a group.** *In moving down a group electron affinity values generally decrease, e.g.* $E_{Cl} > E_{Br} > E_{I}$. This is due to the *steady increase in the atomic radius of the elements.*

Exceptions. There are, however, some exceptions to this general rule as is evident from the following examples :

(*i*) Although the elements of second period of the periodic table are relatively smaller in size than those of the third period, yet *E* values of elements of second period are smaller than the *E* values of third period elements. This unexpected behaviour is explained by saying that the much smaller sizes of the second period elements give a very much higher value of charge densities (which is equal to $1e^-/\frac{4}{3}\pi r^3$) for the respective negative ions. A high value of electron density is opposed by the inter-electronic repulsion forces.

(*ii*) Table 3.9 clearly shows that $E_F > E_{Cl}$ ($E_F = -3.7$ eV, $E_{Cl} = -3.8$ eV). The lower value of E for F is probably due to the electron-electron repulsion in relatively compact 2*p*-orbital of F-atom.

Table 3.9 also shows that since the halogens have relatively higher E values, these have greater tendency to pick up electrons *i.e.* these act as powerful oxidising agents. Now the highest value of E for Cl indicates that chlorine should be the strongest oxidising agent. In fact fluorine has been found to be the strongest oxidising agent and the oxidising power of halogens is in the order : $F>Cl>Br>I$. The higher oxidising power of F is explained by saying that actually it is the oxidation potential, E_0, defined as $X(g)+e^- \longrightarrow X^-$ (hydrated ion)$+E_0$, and not the E value alone which determines the strength of an oxidising agent. As the value of E_0 increases, the oxidising power also increases. Values of E_0 for the halogen molecules are : $F_2=-186{\cdot}6$ kcal/mole, $Cl_2=-147{\cdot}5$, $Br_2=-136{\cdot}5$ and $I_2=122{\cdot}6$. These values clearly show that since E_0 for fluorine molecule is the highest, F is the strongest oxidising agent.

The stronger oxidising property of fluorine is also assumed due to smaller value of dissociation energy of F_2 molecule as compared to other halogen molecules. Their dissociation energies (*i.e.* bond energies) are as $(H_d)_{F_2}=1{\cdot}64$ eV/mole, $(H_d)_{Cl_2}=2{\cdot}48$ eV, $(H_d)_{Br_2}=2{\cdot}00$ eV, $(H_d)_{I_2}=1{\cdot}56$ eV.

The low value of H_d for F_2 molecules is presumably due to the repulsion operating between the non-bonding 2*p*-electrons on the bonded F-atoms. Comparatively large values of H_d of Cl_2, Br_2 and I_2 molecules are probably due to the possibility of π-bonding involving *d*-orbitals and/or due to the hybridisation of *p*- and *d*-orbitals of Cl_2, Br_2 and I_2 which makes the bonds Cl—Cl and Br—Br stronger.

(*b*) **In a period.** *Electron affinity values generally increase on moving from left to right in a* period in the periodic table.

Exceptions. There are, however, exceptions also to this general rule ; *e.g.*

(*i*) Be and Mg have their E values equal to zero. Since Be and Mg have completely filled *s*-orbitals (Be $\longrightarrow 2s^2$, Mg $\longrightarrow 3s^2$), the additional electron will be entering the 2*p*-orbital in case of Be and 3*p*-orbital in case of Mg which are of considerably higher energy than the 2*s*-orbitals respectively. Similarly in case of inert gases in which the *ns*- and *np*-orbitals are completely filled (ns^2p^6 configuration) the incoming electron must go into an electron shell having a larger value for the principal quantum number, *n*. Thus inert gases also have their E values equal to zero.

Nitrogen and phosphorus have unexpected lower values of electron affinities. This is because of the presence of half-filled 2*p*-orbitals which are relatively more stable and hence to which it is difficult to add an additional electron.

EXPERIMENTAL DETERMINATION OF ELECTRON AFFINITY

The evaluation of electron affinity of an element is made by Born-Haber cycle which has been described under *Lattice Energy of Ionic Crystals.*

IMPACT OF ELECTRON AFFINITY CONCEPT ON CHEMICAL BEHAVIOUR

(*i*) *The higher the value of E of an element, the greater would be its capacity to accept an electron, i.e.* the element will behave as a *strong oxidising agent.*

(*ii*) The relative values of ionisation potential and electron affinity of two elements decide the nature of bond between the atoms. In general, *with the increase of the difference, the amount of ionic character decreases* or *covalent character increases.*

ELECTRONEGATIVITY

Definition. Consider the formation of a covalent bond between two similar atoms of a molecule like H_2. In this molecule the electron pair participating in the formation of covalent bond *is shared equally* by both hydrogen atoms *i.e.* the electron pair lies exactly in the centre of the molecule.

On the other hand consider the formation of a covalent bond between two dissimilar atoms of a molecule like HCl. In this molecule the electron pair participating in the formation of covalent bond is not shared equally by the two atoms *viz.* H and Cl, *i.e.* the electron pair lies near to Cl atom than to H atom. The reason for this unequal sharing of electron pair is given by saying that Cl atom has a greater tendency than H atom to attract the electron pair shared between them towards itself. In other words Cl atom has greater electronegativity than H atom. Thus *the electronegativity of a bonded atom is defined as its relative tendency* (*or ability*) *to attract the shared electron pair towards itself.*

Electronegativity of an atom A is generally represented as x_A.

SCALES OF ELECTRONEGATIVITY

The electronegativity scales that have been constructed from various types of experimental data are completely arbitrary as also the units employed. Some of the scales suggested for measuring electronegativity of an atom are described below :

(1) **Pauling's Bond Energy Scale (1932).** Pauling's method makes a use of bond energies *i.e.* the energy required to break a bond to get neutral atoms. Consider a bond A—B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A—A, B—B and A—B bonds be represented as E_{A-A}, E_{B-B} and E_{A-B} respectively.

It may be seen that the energy of A—B bond is almost always greater than the geometric mean of the energies of A—A and B—B bonds, *i.e.*

$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

The difference between E_{A-B} and $\sqrt{E_{A-A} \times E_{B-B}}$ is called *ionic-resonance energy* of A—B bond and is denoted by Δ_{A-B}. It is thus given by

$$\Delta_{A-B} = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

Δ_{A-B} values do not possess additive property, *i.e.* if we consider three covalent bonds *viz.* A—B, B—C and C—A, then

$$\Delta_{A-B} + \Delta_{B-C} \neq \Delta_{C-A} \qquad ...(i)$$

Here the electronegativities of A, B and C should be in the order $x_A > x_B > x_C$.

The validity of the above relation (*i*) can be shown as follows. Given that $E_{Si-Si} = 43$ kcal/mole, $E_{O-O} = 33$ kcal/mole, $E_{F-F} = 37$ kcal/mole, $E_{F-Si} = 128$ kcal/mole, $E_{F-O} = 44$ kcal/mole, $E_{O-Si} = 89$ kcal/mole, we can calculate the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} as follows :

$$\Delta_{F-O} = E_{F-O} - \sqrt{E_{F-F} \times E_{O-O}}$$
$$= 44 - \sqrt{37 \times 33}$$
$$= 44 - 35 = 9 \text{ kcal/mole}$$

$$\Delta_{O-Si} = E_{O-Si} - \sqrt{E_{O-O} \times E_{Si-Si}}$$
$$= 89 - \sqrt{33 \times 43}$$
$$= 89 - 38 = 51 \text{ kcal/mole}$$

$$\Delta_{F-Si} = E_{F-Si} - \sqrt{E_{F-F} \times E_{Si-Si}}$$
$$= 128 - \sqrt{37 \times 43}$$
$$= 128 - 40 = 88 \text{ kcal/mole}$$

With the help of the values of Δ_{F-O}, Δ_{O-Si} and Δ_{F-Si} as calculated above it can be shown that

$$\Delta_{F-O}+\Delta_{O-Si}\neq\Delta_{F-Si}$$

or
$$9+51\neq 88$$

or
$$60\neq 88$$

However the square roots of the values of ionic-resonance energies show nearly the additive property, *i.e.* the sum of $\sqrt{\Delta_{F-O}}$ and $\sqrt{\Delta_{O-Si}}$ is almost equal to $\sqrt{\Delta_{F-Si}}$ as shown below:

$$\sqrt{\Delta_{F-O}}+\sqrt{\Delta_{O-Si}}\approx\sqrt{\Delta_{F-Si}}$$

or
$$\sqrt{9}+\sqrt{51}\approx\sqrt{88}$$

or
$$3+7{\cdot}2\approx 9{\cdot}4$$

or
$$10{\cdot}2\approx 9{\cdot}4$$

$\sqrt{\Delta_{A-B}}$ is a measure of the partial ionic character of A—B covalent bond, *i.e.* $\sqrt{\Delta_{A-B}}$ increases with the increase of ionic character of A—B covalent bond. $\sqrt{\Delta_{A-B}}$ values also increase with the increase in electronegativity difference (x_A-x_B) between the two bonded atoms A and B. Thus

$$x_A-x_B\propto\sqrt{\Delta_{A-B}}$$

or
$$x_A-x_B=K\left[E_{A-B}-\sqrt{E_{A-A}\times E_{B-B}}\right]^{\frac{1}{2}}$$

The value of the constant, K has been found to be equal to 0·208 which comes from the conversion of experimental values of E_{A-B} measured in kcals/mole into e*V*. Thus:

$$x_A-x_B=0{\cdot}208\left[E_{A-B}-\sqrt{E_{A-A}\times E_{B-B}}\right]^{\frac{1}{2}}$$

This equation gives only the differences in electronegativity values. This equation can be used to calculate *x* values of an atom provided that *x*-value of the other element is known. Pauling assigned an arbitrary value of 4·0 for the electronegativity of fluorine and calculated that of other elements with the help of this equation. It must be remembered that in the calculation of electronegativity values Pauling has expressed ionic-resonance energies not in kcal, but in electron-volts (1 e*V* per bond = 23 kcal per gram bond).

In Table 3·10 the electronegativity values of *s*- and *p*-block elements as determined by Pauling are given (scale F=4·0).

Table 3·10. *Electronegativity values of s- and p-block elements as determined by Pauling (Scale F=4·0).*

s-block elements		*p-block elements*				
IA	*IIA*	*IIIA*	*IVA*	*VA*	*VIA*	*VIIA*
H 2·1						
Li 1·0	Be 1·5	B 2·0	C 2·5	N 3·0	O 3·5	F 4·0
Na 0·9	Mg 1·2	Al 1·5	Si 1·8	P 2·1	S 2·5	Cl 3·0
K 0·8	Ca 1·0	Ga 1·6	Ge 1·8	As 2·0	Se 2·4	Br 2·8
Rb 0·8	Sr 1·0	In 1·7	Sn 1·8	Sb 1·9	Te 2·1	I 2·5
Cs 0·7	Be 0·9	Tl 1·8	Pb 1·8	Bi 1·9	Po 2·0	At 2·2
Fr 0·7	Ra 0·9					

(2) **Mulliken's Scale (1934).** Mulliken suggested that electronegativity is some type of mean of the difference of ionisation potential (IP) and electron affinity (EA) of an atom. To approximate his values to Pauling's electronegativity values, he defined the electronegativity of an atom A by the relation

$$(x_A)_M = \frac{(IP)_A-(EA)_A}{5\cdot6}$$

where $(x_A)_M$ is the electronegativity of atom A on Mulliken's scale and 1/5·6 is a constant of proportionality which has been introduced as a *scale-adjustment factor* so that the electronegativity of the atom on Mulliken's scale may approximate that on Pauling's scale.

Here it should be noted *that in the above relation the factor 1/5·6 is used when IP and EA values are expressed in electron volts.* If these values are taken in kcal/mole, the above relation becomes :

$$(x_A)_M = \frac{(IP)_A-(EA)_A}{2\times62\cdot5}$$

Quite obviously on the basis of Mulliken's scale the conditions for the formation of purely covalent A—B bond and ionic A^-—B^+ or A^+—B^- bonds may be given as follows :

(*i*) For the formation of purely covalent A—B bond,

$$\frac{(IP)_A-(EA)_A}{5\cdot6}=\frac{(IP)_B-(EA)_B}{5.6} \text{ and}$$

hence $$x_A=x_B$$

(*ii*) For the formation of A⁻—B⁺ bond,

$$\frac{(IP)_A-(EA)_A}{5\cdot6}>\frac{(IP)_B-(EA)_B}{5\cdot6}, \text{ and}$$

hence $$x_A>x_B$$

(*iii*) For the formation of A⁺—B⁻ bond,

$$\frac{(IP)_A-(EA)_A}{5\cdot6}<\frac{(IP)_B-(EA)_B}{5\cdot6}, \text{ and}$$

hence $$x_A<x_B$$

Example. *Calculate the electronegativity of chlorine atom on Mulliken's scale.*

Solution. We know that $(IP)_{Cl}=13\cdot0$ *eV* and $(EA)_{Cl}=-4\cdot0$ *eV*

Thus $$(x_{Cl})_M=\frac{(IP)_{Cl}-(EA)_{Cl}}{5\cdot6}=\frac{13\cdot0-(-4\cdot0)}{5\cdot6}=3\cdot03$$

Practical disadvantages of Mulliken's Scale. This scale which is based on a firm theoretical basis suffers from two main practical disadvantages.

(*i*) The values of E's are not readily available.

(*ii*) The quantities I and E refer to the transference of electrons between the atomic orbitals whose exact constitution is not always known.

(3) **The Allred-Rochow Electrostatic Approach (1958).** According to this approach, the electrostatic force of attraction F_{ES} (in dynes), between an atom A and a bonding electron separated from its nucleus by its covalent radius, $(r_A)_{cov}$ in Å, is the measure of electronegativity of atom A. It is assumed that an electron in a bond is attracted by one of the two nuclei according to Coulomb's law *i.e.*,

$$(x_A)_{A-R}=F_{ES}$$

$$=\frac{e^2(Z_{eff})_A}{(r_A)^2_{cov}} \qquad ...(i)$$

where $(x_A)_{A-R}$ = electronegativity value of atom A on Allred-Rochow's scale, e = charge on the electron ($=4\cdot8\times10^{-10}$ esu), and Z_{eff} = effective nuclear charge on atom A which is equal to $Z_A-\sigma_A$, Z_A being the actual nuclear charge of atom A (*i.e.*, Atomic No. of atom A) and σ_A, the screening constant for atom A.

On substituting the value of $e = 4{\cdot}8 \times 10^{-10}$ esu in Equation (*i*), we get

$$(x_A)_{A-R} = F_{ES}$$
$$= \frac{0{\cdot}359 (Z_{eff})_A}{(r_A)^2_{cov}}$$
$$= \frac{0{\cdot}359 (Z_A - \sigma_A)}{(r_A)^2_{cov}} \qquad \ldots(ii)$$

Values of F_{ES} obtained from Eqn. (*ii*) were plotted against the corresponding electronegativity values on Pauling's scale and a straight line was obtained. From the respective slope and intercept of this straight line, Eqn. (*iii*) was obtained for Allred-Rochow's electronegativity $(x_A)_{A-R}$.

$(x_A)_{A-R} = a \,.\, F_{ES} + b$ (compare it with $y = mx + c$) ...(*iii*)

where *a* and *b* are the slope and intercept of the straight line represented by equation (*iii*) respectively. For most atoms $a = 1{\cdot}0$, and $b = 0{\cdot}744$. Substituting these values of *a* and *b* in equation (*iii*) we get

$$(x_A)_{A-R} = 1{\cdot}0 \times \frac{0{\cdot}359 (Z_A - \sigma_A)}{(r_A)^2_{cov}} + 0{\cdot}744$$

or
$$(x_A)_{A-R} = \frac{0{\cdot}359 (Z_A - \sigma_A)}{(r_A)^2_{cov}} + 0{\cdot}744 \qquad \ldots(iv)$$

Values of σ_A can be determined by Slatter's rules.

E. Little Jr. and M. Jones have determined the value of $\left(x_{Pb}\right)_{A-R}$ as follows :

$$\sigma_{Pb} = 76{\cdot}70, \; Z_{Pb} = 82, \; r\left(Pb\right)_{cov} = 5{\cdot}3 \text{ Å}$$

Putting these values of Z_{Pb}, σ_{Pb}, and $\left(r_{Pb}\right)_{cov}$ in equation (*iv*) we get

$$\left(x_{Pb}\right)_{A-R} = \frac{0{\cdot}359 \times (82 - 76{\cdot}70)}{(5{\cdot}3)^2} + 0{\cdot}744 = 1{\cdot}55$$

PERIODIC VARIATIONS

(*a*) **In a period.** Electronegativity increases on moving in a period of the periodic table from left to right. This is due to the increase in nuclear charge as a result of which the added electrons can be held more tightly. Thus the C—N bond should be shown as $C^{\delta +} - N^{\delta -}$ or C→N, the arrow head being towards the more electronegative element N. (Since $x_N > x_C$).

In the same period on moving from left to right the electronegativities increase with the increase in the number of outer-electrons, *e.g.*

Elements of 2nd period	:	Li	Be	B	C	N	O	F
Valence-shell configuration	:	$1s^1$	$2s^2$	$2s^2p^1$	$2s^2p^2$	$2s^2p^3$	$2s^2p^4$	$2s^2p^5$
No. of valence-shell electrons	:	1	2	3	4	5	6	7
Electronegativity values	:	1·0	1·5	2·0	2·5	3·0	3·5	4·0

——————Increasing——————→

(*b*) **In a group.** In moving down through a group of the periodic table since the nuclear charge again increases, the electronegativity of a lower element should be more than that of upper element. Actually it is not so because the disadvantages of increase in atomic radii and the electron shielding effects more than compensate for the advantage gained through increase in the nuclear charge. Consequently a lower element of a group is less electronegative than the upper element of the same group. In general, therefore, *small atoms attract electrons more strongly than large ones and are, therefore, more electronegative.*

Thus the most electronegative elements (*e.g.* F) are present at top right hand corner of the periodic table, while the most electropositive elements (*i.e.* the elements having least value of x such as Cs) are at the bottom left hand corner.

CORRELATION OF IONISATION POTENTIAL AND ELECTRON AFFINITY WITH ELECTRONEGATIVITY

Higher values of ionisation potential indicate that it is difficult to remove an electron from an atom or in other words the atom has greater attraction for electrons, *i.e.*, greater electron affinity. Thus greater value of ionisation potential and greater electron affinity both indicate greater electronegativity.

Non-metals such as halogens, which have high values of ionisation potential and electron affinity, show little tendency to lose electrons. Instead these show a strong tendency to accept electrons, *i.e.* these elements are strongly electronegative. On the other hand the metals such as alkali metals which have small values of ionisation potential and electron affinity, show a strong tendency to lose electrons and as such are strongly electropositive.

Relation between the oxidation state of the element and its electronegativity. It must be remembered that electronegativity is a variable quantity. It varies with the change in the oxidation state of the element. The element in higher oxidation state has more value of electronegativity than in the lower oxidation state. Thus $x_{Fe^{3+}} > x_{Fe^{2+}}$. This is due to the fact that the atom in a higher oxidation state has greater attraction for electrons than when it is in the lower oxidation state. This can also be explained on the basis of their relative magnitude of ionic radii. Since $r_{Fe^{3+}} < r_{Fe^{2+}}$,

$x_{Fe^{3+}} > x_{Fe^{2+}}$

Here $r_{Fe^{3+}}$ and $x_{Fe^{2+}}$ are the ionic radii of Fe^{3+} and Fe^{2+} cations and $x_{Fe^{3+}}$ and $x_{Fe^{2+}}$ are the electronegativity values for the cations Fe^{3+} and Fe^{2+} respectively.

APPLICATIONS OF ELECTRONEGATIVITY CONCEPT

1. Electronegativity difference, $(x_A - x_B)$ and partial ionic character in A—B bond. We have already seen that when $x_A = x_B$, the bond A—B is covalent and when $x_A \neq x_B$, the bond has some ionic character *i.e.*, the bond A—B will be polar-covalent bond and the molecule AB will be a polar molecule.

When $x_A > x_B$, the ionic form A^-B^+ will be more stable than the covalent form A $\overset{\circ}{\times}$ B or A—B and when $x_B > x_A$, the ionic form A^+B^- will be more stable than A—B. The amount of ionic character created in the A—B bond due to the difference in the electronegativity values x_A and x_B depends on $(x_A - x_B)$. Greater the value of $(x_A - x_B)$, the greater the amount of ionic character in the bond.

By plotting percentage ionic character (calculated from obtained dipole moments) for halogen acids against $(x_X - x_H)$, Pauling observed a curve which fitted the expression :

$$\text{Percentage ionic character} = 100[1 - \exp\{1 - \tfrac{1}{4}(x_H - x_X)^2\}] \quad ...(i)$$

With the help of this equation Pauling was able to estimate, although approximately, the per cent ionic character of other A—B bonds from known $(x_A - x_B)$ data. Pauling gave a chart showing the $(x_A - x_B)$ values and their corresponding per cent ionic character of a A—B bond. (*see* Table 3·11).

It will be seen from the Table that when $(x_A - x_B) = 1{\cdot}7$, the bond A—B is approximately 50% ionic and 50% covalent. When $(x_A - x_B) < 1{\cdot}7$, the bond A—B will have more covalent character than 50%. On the other hand when $(x_A - x_B) > 1{\cdot}7$, the A—B bond will show less covalent character than 50% and ionic character will be more than 50%. *Bonds which are more than 50% ionic are commonly termed as* **ionic bonds** *and those which are more than 50% covalent are termed as* **covalent bonds.**

Limitations of Pauling's Equation and Revision made by the Hanny and Smyth.

(*i*) It is found that Pauling's Equation (*i*) gives poor results when $(x_A - x_B)$ values are too large.

(*ii*) Alkali metal hydrides and those of Ca, Sr and Ba are ionic compounds, although the value of $(x_M - x_H)$ is less than 1·7.

(*iii*) At the time Eqn. (*i*) was formulated, the value of the dipole moment of HF was not known. For HF having $(x_F - x_H) = 1{\cdot}9$, Eqn. (*i*) leads to an estimate of 60% ionic character in H—F bond in HF molecule. Later on when the value of dipole moment of HF was known and used to estimate the per cent ionic character, it was found to be having only 45% ionic character.

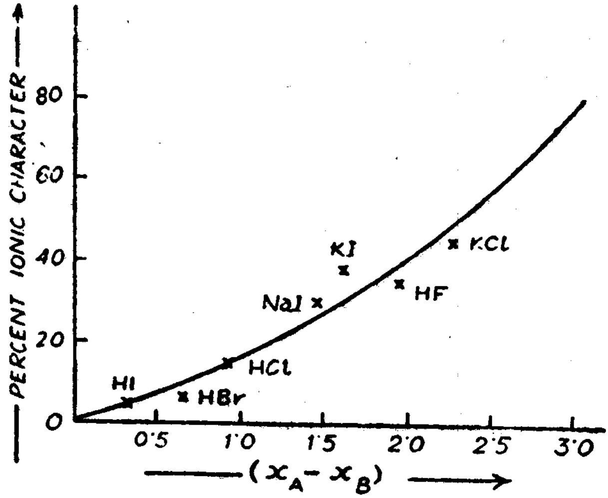

Fig. 3·5. Graph of per cent ionic character in a bond A—B against the electronegativity difference ($x_A - x_B$). Experimental values of ionic character shown by crosses, ×.

Table 3·11. *Relation between* ($x_A - x_B$) *and the percentage of ionic character in A—B bond* ($x_A > x_B$).

($x_A - x_B$) *values*	% *ionic character*	($x_A - x_B$) *values*	% *ionic character*
0·1	0·5	1·7	51
0·2	1	1·8	55
0·3	2	1·9	59
0·4	4	2·0	63
0·5	6	2·1	67
0·6	9	2·2	70
0·7	12	2·3	74
0·8	15	2·4	76
0·9	19	2·5	79
1·0	22	2·6	82
1·1	26	2·7	84
1·2	30	2·8	86
1·3	34	2·9	88
1·4	39	3·0	89
1·5	43	3·1	91
1·6	47	3·2	92

For more exact calculations of ionic character, therefore, the Equation (*i*) was revised by Hanny and Smyth. They obtained a graph (Fig. 3.5) by plotting per cent ionic character against the value of $(x_A - x_B)$, where A = halogen and B = H or an alkali metal.

With the help of this graph they revised Pauling's Equation and gave Eqn. (*ii*) as given below :

$$\% \text{ ionic character} = 100 \times [0{\cdot}16(x_A - x_B) + 0{\cdot}035\ (x_A - x_B)^2]$$
$$= 16(x_A - x_B) + 3{\cdot}5(x_A - x_B)^2 \qquad \ldots(ii)$$

Eqn. (*ii*) clearly shows that when $(x_A - x_B) = 2{\cdot}1$, the bond A—B is 50% ionic (and also 50% covalent). Thus,

$$\approx 50\% \text{ ionic character} = 16(2{\cdot}1) + 3{\cdot}5(2{\cdot}1)^2$$

Bonds with a larger value of $(x_A - x_B)$ will essentially be ionic, having more than 50% ionic character while those with a smaller value of $(x_A - x_B)$ are essentially covalent.

If we substitute the electronegativity values of H, F, Cl, Br and I in Hanny and Smyth's equation *viz.* equation (*ii*), it can be shown that the percentage of ionic and covalent character in H—X bond (X = F, Cl, Br and I) in HF, HBr, HCl and HI molecules is HF = 43% ionic and 57% covalent; HCl = 17% ionic and 83% covalent; HBr = 13% and 87% covalent and HI = 7% ionic and 93% covalent. Thus we see that the percentage of ionic character in the H—X bonds in the above molecules decreases in the order : H—F > H—Cl > H—Br > H—I.

In case of gaseous molecules in which atoms of high electron affinity are associated with atoms of low ionization potential (*i.e.* strongly electropositive elements such as alkali metals and alkaline earth metals), we should expect that the bond would be on the verge of complete ionic character, regardless of the specific chemical identities of the pertinent atoms involved. Thus, since *s*-block elements (alkali metals and alkaline earth metals) have rather small ionisation potentials, they establish ionic bonds.

2. Electronegativity difference, $(x_A - x_B)$ and strength (*i.e.* stability) of A—B bond in AB molecule. Greater is the value of $(x_A - x_B)$, more stable will be the bond, A—B *e.g.* we can explain that the stability of H – X bond in HF, HCl, HBr and HI molecules decreases in the order : H – F > H—Cl > H—Br > H—I as shown below:
$(x_F = 4.0,\ x_{Cl} = 3.0,\ x_{Br}, = 2.1.\ x_I = 2.1$ and $x_H = 2.1)$

H−X bond	:	H−F	H—Cl	H—Br	H—I
$(x_X - x_H)$ (X=F, Cl, Br and I	} :	1·9 >	0·9 >	0·7 >	0·4
Stability of H−X bond	} :	H—F >	H—Cl >	H—Br >	H—I
Heat of formation of H—X bond (kcal/mole)	} :	−64·5 >	—22·0 >	—12·5 >	—1·5

The decrease in the stability of H—X bonds from H—F to H—I is due to the steady decrease in ($x_X - x_H$) values from $x_F - x_H$ to $x_I - x_H$. The decrease in the bond stability is also confirmed by a steady decrease in their heats of formation as shown above.

Stability of compounds in which $x_A - x_B$ is very small. The compounds for which $x_A - x_B$ is very small (*i.e.*, for which x_A and x_B are almost equal), tend to be unstable and hence the heat of formation of such compounds is very small. Examples of such compounds are : Cl_4 (0·0), SiH_4 (0·3), NCl_3 (0·0), PH_3 (0·0), AsH_3 (0·1), SbH_3 (0·2), BiH_3 (0·2). In brackets are given the values of ($x_A - x_B$).

Stability of compounds in which $x_A - x_B$ is very large. Evidently such compounds will be those that are formed by the combination of metals (whose x-values are very low) and non-metals (whose x-values are very large). In this $x_A - x_B$ is very high and hence these compounds are very stable and are with large heats of formation, high melting points and boiling points.

3. **Trends in the acid-base character of the normal oxides of the elements of the same period.** It may be seen that on passing from left to right in a period of periodic table the acidic character of the normal oxides of the elements goes on increasing. The change from strongly basic character to strongly acidic character is because of the increase in the electronegativity value of the element, x_E and the consequent decrease in ($x_O - x_E$) value where x_E and x_O are the electronegativity values of the elements *E* and *O*. The element *E* is the one whose normal oxide is being considered. The trends in acid-base character for the oxides of the elements of third period of periodic table are shown below :

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
x_E :	1·0	< 1·2	< 1·4	< 1·7	< 2·0	< 2·4	> 2·8
($x_O - x_E$) values (x_O = 3·5) =	2·5	> 2·3	> 2.1	> 1·8	> 1·5	> 1·1	< 0·7
Acid-base character	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

4. **Metallic and Non Metallic character of elements.** The element having a higher value of electronegativity will be essentially a non-metal while that with a lower value will be a metal. We have seen that x-values in a periodincrease on proceeding from left to right and those in a group decrease on moving from top to bottom. Consequently, in period the metallic character of the elements decreases and their oxides become less and less basic as we move from left to right. Similarly, on descending a group the metallic character increases. This situation is very much pronounced in case of the elements of IVA and VA group elements. Thus the elements of

these groups begin with non-metals (C and N) and end with metals (Pb and Bi) respectively. Their oxides become increasingly basic.

By now it should not be difficult to understand why Fr which is situated at the bottom left hand corner of the periodic table is the most reactive metal while F which is situated at the top right hand corner of the periodic table is the most reactive non-metal.

5. Colour of the salts. There is a close relationship between the percentage of ionic character and the colour of the salt. The following rules hold good (*i*) if the ionic character of the bond is less than 20%, the compound is coloured (*ii*) if it is more than 20%, the compound is colourless, and (*iii*) if ionic character becomes lesser and lesser than 20%, the compound takes on colour passing through yellow and orange to red and black, *i.e.*, the colour goes on deepening, *e.g.* AgCl (ionic character = 80%)—white, AgBr (24%)—pale-yellow, AgI (15%)—yellow, Ag_2S(4%)—black.

6. Acidic and basic character of XOH molecule. When we consider the ionisation reaction of XOH molecule (where X may be metal or a non-metal) in aqueous solution, the following two cases arise :

(*i*) When $x_O - x_X < x_O - x_H$, O—H bond will be more polar than X—O bond and hence the ionisation of XOH molecule in aqueous solution will take place at O—H bond as shown below :

$$X-O\vdots H + H_2O \longrightarrow XO^- + H_3O^+$$

Since in this ionisation reaction H_3O^+ ions are produced, XOH molecule behaves as an acid.

(*ii*) When $x_O - x_X > x_O - x_H$, X—O bond is more polar than O—H bond and as such the ionisation occurs at X—O bond as shown below :

$$X\vdots O-H + H_2O \longrightarrow [H-OH_2]^+ + OH^-$$

Thus XOH molecule gives OH^- ions and, therefore, behaves as a base

Thus we find that on the basis of the concept of electronegativity it is possible for us to predict whether the compounds of XOH type are acid or basic in aqueous solution.

Gallais has suggested that XOH molecule shows acidic character when x_X is greater than 1·7 and it shows basic character when x_X is less than 1·7.

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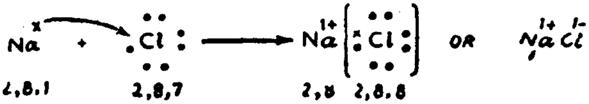
4

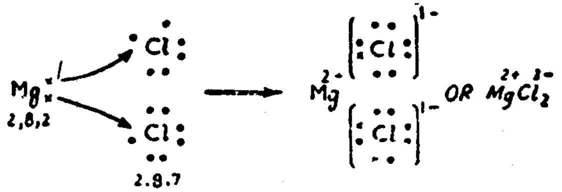
Chemical Bonding

IONIC OR ELECTROVALENT BOND

An ionic bond is established as a result of the *transference of electrons froms one atom to the other.* Elements which have a tendency to lose one or more electrons are called *electropositive* (*e.g.* alkali metals) whilst those which have a tendency to gain electrons are called *electronegative* (*e.g.* halogens). It was suggested by Kossel that when atoms of electropositive and electronegative elements combine together, one or more electrons are transferred from the former to the latter and the atoms are covered into cations and anions. As a result of the mutual electrostatic attraction between the ions so formed, an ionic or electrovalent bond is established.

Examples :





The anions formed always achieve an inert gas configuration when forming ionic bond, while the cations formed may achieve any of the following configurations : (*i*) *Inert gas configuration* (ns^2 or ns^2p^6 configuration). (*ii*) *Pseudo-inert gas configuration* ($ns^2p^6d^{10}$). (*iii*) *The inert pair configuration i.e. 18-plus-2-electrons configuration* $[(n-1)s^2p^6d^{10}.ns^2]$. (*iv*) $ns^2p^6d^x$ type configuration where the sum $(2+6+x)$ should be nine to seventeen. Such type of configuration is very much found in transitional metal cations (*v*) *Irregular configurations.* Cations having such type of configurations can be exemplified by $Ga_2^{4+}(Ga^{2+}-Ga^{2+})$, $Hg_2^{2+}(Hg^{+}-Hg^{+})$ etc.

Characteristics of Ionic Compounds

(*i*) The cations and anions in these compounds are held together by electrostatic lines of forces.

(*ii*) These compounds are polar, soluble in polar solvent such as H_2O, NH_3 etc., but insoluble in non-polar solevents such as CCl_4, C_6H_6 etc.

(*iii*) These compounds are ionisable in solution or in fused state.

(*iv*) Solutions of these compounds are good conductors of electricity.

(*v*) They possess high melting points and boiling points.

(*vi*) The polar linkages present in ionic compounds are non-directional.

Conditions for the formation of an ionic compound. The formation of ionic molecule c^+a^- can be thought to occur through the following steps :

(*i*) Atom *c* gives up an electron by absorbing energy equal to its ionisation energy (or ionisation potential) $(IP)_c$ and is converted into cation, c^+. Thus :

$$c+\text{Energy absorbed }[=(IP)_c]\xrightarrow{-e^-}c^{+}+e^{-}$$

(*ii*) In this step the atom *a* picks up the electron released by *c* and is converted into anion, a^-. In this process, energy equal to affinity energy (or electron affinity) of *a*, $(EA)_a$ is released. Thus :

$$a+e^{-}\longrightarrow a^{-}+\text{Energy released }[=-(EA)_a]$$

(*iii*) This is the final step in which cation, c^+ and anion a^-, due to the electrostatic attraction, combine together to give a stable ionic crystal, c^+a^-. In this process energy equal to heat of formation of the ionic compound, c^+a^-, is released. Heat of formation is equal to $-e^2/r_c{}^{+}+r_a$, where negative sign indicates the release of energy. Here *e* is the ionic charge on c^+ and a^- and $r_c{}^{+}$ and $r_a{}^{-}$ are the ionic radii of c^+ and *a* respectively. Thus :

$$c^{+}+a^{-}\longrightarrow c^{+}a^{-}+\text{Energy released}\left(=-\frac{e^2}{r_{c^+}+r_{a^-}}\right)$$

Thus the overall energy change, E_{ionic}, in the formation of the ionic crystal, c^+a^- is given by

$$E_{ionic}=+(IP)_c-(EA)_a-\frac{e^2}{r_{c^+}+r_{a^-}}$$

Now, if the bonded ions, c^+ and a^-, are more stable than the free atoms, c and a, value of E_{ionic} must be negative. To fulfil this condition $\frac{e^2}{r_{c^+}+r_{a^-}}$ should have a higher value than $[(IP)_c-(EA)_a]$

i.e.
$$\frac{e^2}{r_{c^+}+r_{a^-}} > [(IP)_c-(EA)_a]$$

When this condition is fulfilled, we shall get a larger negative value of $-\frac{e^2}{r_{c^+}+r_{a^-}}$.

Thus for the formation of a stable ionic compound c^+a^- (or a stable ionic bond) the following conditions must be satisfied :

(*a*) Atom c should have a tendency to lose electrons readily *i.e.* $(IP)_c$ *should be low.* Thus atom c should be an electropositive element such as an alkali metal or an alkaline earth metal.

(*b*) Atom a should have a tendency to accept the electron readily given out by atom c *i.e.* $(EA)_a$ *should be large.* Thus atom a should be an electronegative element such as one of the halogens or an element of VI A group elements.

(*c*) Since each ion pair, c^+a^-, resulting from one free atom c and one free atom a has a strong residual electric field, it will attract other ion pairs and thus a large number of such ion pairs will arrange themselves in the most stable way within an ionic crystal *i.e.* a cluster will be formed. In this process further energy will be released and the total energy released in the process of the formation of ionic crystal is known as *crystal* or *lattice energy, U.*

Thus higher the value of lattice energy of the resulting ionic compound, the greater is the ease of its formation.

VARIABLE ELECTROVALENCY

There are many transitional and non-transitional metals which show variable electrovalency. This is due to the *presence of unstable configuration of the core in them* (transitional metals) and *inert pair effect* (heavier *p*-block elements).

(*i*) **Unstable configuration of the core.** If all the valence electrons from an atom are removed, the residue obtained is called the core or **kernel**. The core obtained from a normal element is stable, since it has 2 or 8 electrons (inert-gas configuration), while that obtained from a transitional metal is unstable and one or more electrons may, therefore, be removed from such configuration of the core to get ions with variable oxidation states.

The following are the important *unstable* configurations of a core of a transitional metal.

(*a*) **Configuration varying from** $(n-1)\ s^2p^6d^1$ **to** $(n-1)\ s^2p^6d^9$. The configurations of Fe^{2+} and Co^{2+} ions *viz.* $3s^2p^6d^6$ and $3s^2p^6d^7$

respectively are unstable as compared to ns^2p^6 configuration (inert-gas configuration), since nuclear charge in these ions is not sufficiently strong to keep the electrons of these configurations intact in their position. Thus these ions can easily lose one of the 3*d*-electrons to give Fe^{3+} and Co^{3+} ions respectively.

$$[Fe^{2+}(3s^2p^6d^6) \xrightarrow{-e^-} Fe^{3+}\ (3s^2p^6d^5),$$

$$Co^{2+}(3s^2p^6d^7 \xrightarrow{-e^-} Co^{3+}(3s^2p^6d^6)].$$

Co^{3+} ion is less stable than Fe^{3+} ion.

Ni^{3+} ion is practically non-existent, since in this case the nuclear charge is higher which makes the removal of an electron from $3s^2p^6d^8$ configuration of Ni^{2+} ion more difficult to form Ni^{3+} ion.

(*b*) **Pseudo-inert gas configuration, *i.e.*, 18 electron configuration [$(n-1)\ s^2p^6d^{10}$ configuration].** This type of configuration is found in the cations formed from the elements of IB and IIB groups. For example :

Group I B

$Cu(3s^2p^6d^{10}, 4s^1)$, $Cu^+\ (3s^2p^6d^{10})$, $Cu^{2+}\ (3s^2p^6d^9)$

$Ag(4s^2p^6d^{10}, 5s^1)$, $Ag^+(4s^2p^6d^{10})$, $Ag^{2+}(4s^2p^6d^9$,

$Au(5s^2p^6d^{10}, 6s^1)$, $Au^+(5s^2p^6d^{10})$, $Au^{3+}(5s^2p^6d^8)$

The mono-valent cations *viz.* Cu^+ and Au^+ are unstable due to the presence of unstable $(n-1)\ s^2p^6d^{10}$ configuration in them. Consequently these ions are readily converted into Cu^{2+} and Au^{3+} ions which are relatively more stable. The unstability of Cu^+ and Au^+ ions is due to the fact that the nuclear charge in these ions is not enough to hold the 18 electrons of $(n-1)\ s^2p^6d^{10}$ configuration firmly in these mono-valent cations.

It is only under certain special conditions that Ag^{2+} ion is formed.

The configurations $3s^2p^6d^9$, $4s^2p^6d^9$, $5s^2p^6d^8$, in Cu^{2+}, Ag^{2+}, and Au^{3+} ions respectively are quite stable and hence do not lose other electrons to give cations of still higher valency.

Group II B

$Zn\ (3s^2p^6d^{10}, 4s^2)$, $Zn^{2+}(3s^2p^6d^{10})$

$Cd\ (4s^2p^6d^{10}, 5s^2)$, $Cd^{2+}(4s^2p^6d^{10})$

$Hg\ (5s^2p^6d^{10}, 6s^2)$, $Hg^{2+}(5s^2p^6d^{10})$

Although Zn^{2+}, Cd^{2+}, Hg^{2+} also have the same valence shell configuration as Cu^+, Ag^+, Au^+ have, Zn^{2+}, Cd^{2+} and Hg^{2+} do not give cations of higher oxidation state. This is explained as follows : Since the nuclear charge in Zn^{2+}, Cd^{2+}, Hg^{2+} ions is one unit higher than that in Cu^+, Ag^+, and Au^+ respectively (Atomic nos. of Zn, Cd and Hg are 30, 48, 80 respectively and those of Cu, Ag and Au, are 29, 47, and 79 respectively), all the 18 electrons in Zn^{+2} Cd^{2+} and Hg^{2+} ions are more strongly held with the nucleus than those in Cu^+, Ag^+, Au^+. Thus in case of Zn^{2+}, Cd^{2+}, and Hg^{2+} there can be no loss of any further electron from the $(n-1)s^2p^6d^{10}$ configuration and so it is not possible for these cations to give the cations of higher oxidation state.

(*ii*) **Inert Pair Effect.** In order to understand the concept of inert pair effect let us see how Sn atom, for example, shows +2 and +4 oxidation states. Since Sn atom is a member of IVA group, +4 oxidation state is called its *group number oxidation state*, G. +2 oxidation state is a lower oxidation state and is equal to (G—2).

There are many heavier *p*-block elements which, like Sn, in addition to their group number oxidation state, G also exhibit lower oxidation states equal to (G—2). Examples of such elements are given in Table 4·1.

Group number oxidation state, G is obtained when all the *ns* and *np* electrons from ns^2p^x configuration of *p*-block elements (x=1, 2, 3 and 4 for the elements of groups IIIA, IVA, VA and VIA respectively) are lost, while the lower oxidation state equal to (G—2) is obtained when only *np*-electrons are lost and the *ns*-electron pair, due to its extra stability, remains inert, *i.e.*, it is not lost. Such a pair of *ns*-electrons is called **inert pair** and the effect caused by it is known as **inert pair effect.**

Table 4·1. Heavier *p*-block elements which, in addition to their group number oxidation state, G also show lower oxidation states (given in brackets) equal to (G—2).

III A ns^2p^1	*IV A* ns^2p^2	*V A* ns^2p^3	*VI A* ns^2p^4
—	—	—	—
—	—	—	—
Ga (+1), +3	Ge (+2), +4	—	—
In (+1), +3	Sn (+2), +4	Sb (+3), +5	Te (+4), +6
Tl (+1), +3	Pb (+2), +4	Bi (+3), +5	Po (+2), +4

VARIATION OF INERT-PAIR EFFECT, IN A GROUP AND ITS EFFECT ON THE PROPERTIES OF THE ELEMENTS

The following examples will help us to understand this point.

(*a*) **Group III A Elements.** +3 oxidation state which is the group number oxidation state is common for these elements, but +1 state *becomes more and more stable as we move down the group. This is* *due to the successive increase in inert pair effect from* B to Tl. Thus Tl^+ ion is much more stable than either Ga^+ or In^+ and also the compounds of Tl (I) are more stable than those of Tl (III).

(*b*) **Group IV A elements.** In this group carbon and silicon uniformly show +4 oxidation state ; Ge, Sn and Pb show both +2 and +4 states. The stability of +4 state decreases and that of +2 increases from Ge → Sn → Pb. This is due to the fact that *the inert pair effect increases as we move down the group.* Consequently the stability of the divalent cations is in the order : $Ge^{2+} < Sn^{2+} < Pb^{2+}$.

Since the inert pair effect increases when one moves from Ge to Pb through Sn, this effect is not much marked in germanium compounds. *The compounds of* Ge (II) *are, therefore, unstable and hence get oxidised to* Ge (IV) *compounds easily, i.e.*, the oxidation *viz.*

$$\text{Ge (II)} \;+\; 2e^- \xrightarrow{\text{Oxidation}} \text{Ge (IV)}$$

Unstable (Reduced form, *i.e.*, reducing agent)

Stable (Oxidised form, *i.e.* oxidising agent)

takes place readily. The tendency of Ge(II) compounds to get oxidised to Ge(IV) compounds shows that Ge(II) compounds are *strong reducing agents* and also Ge^{2+} ion is *less stable* than Ge^{4+} ion.

The inert pair effect is much more greater in Sn and this explains the fact that Sn^{2+} ion is *less stable* than Sn^{4+} ion, *i.e.*, Sn (II) *compounds can easily be oxidised* to Sn (IV) compounds.

$$\text{Sn (II)} \;-2e \xrightarrow{\text{Oxidation}} \text{Sn (IV)}$$

Less stable (Reduced form, *i.e.*, reducing agent)

More stable (Oxidised form, *i.e.*, oxidising agent

This in other words means that Sn (II) compounds (*e.g.*, SnO_2, $SnCl_2$) are reducing agents.

In Pb the inert pair effect is greatest with the result that Pb^{2+} state *is much more stable than* Pb^{4+} state. This means that Pb(IV) compounds can easily be reduced to Pb(II) compounds, *i.e.* the reaction *viz.*

$$\text{Pb (IV)} \;+\; 2e^- \xrightarrow{\text{reduction}} \text{Pb (II)}$$

Unstable (Oxidised form *i.e.* oxidising agent)

Stable (Reduced form, *i.e.*, reducing agent)

takes place easily.

The greater tendency of Pb (IV) compounds to be reduced to Pb(II) compounds shows that Pb (IV) compounds (*e.g.*, PbO_2, $PbCl_4$) are powerful oxidising agents.

(*c*) **Group VA elements.** *The +3 state for the elements from* P to Bi which is caused by the loss of three *np*-electrons from ns^2p^3

configuration *becomes more and more common while +5 state becomes less and less so as we move from* N to Bi. *This is due to the greater and greater stability of* ns^2 *electron pair of the valence-shell with increasing atomic size.*

Since the inert pair effect is greatest in the heaviest element *viz.* bismuth, Bi^{3+} ion is more stable than Sb^{3+}. Antimony forms Sb^{5+} ion while bismuth gives an unstable Bi^{5+} ion since it gets reduced into Bi^{3+} ion. Thus Bi (V) compounds are strong oxidising agents.

$$\underset{\substack{\text{Oxidised form}\\ \text{(oxidising agent)}}}{Bi^{5+}} + 2e^- \xrightarrow{\text{reduction}} \underset{\substack{\text{Reduced form}\\ \text{(Reducing agent)}}}{Bi^{3+}}$$

LATTICE ENERGY OF IONIC CRYSTALS

Definition. In an ionic crystal at least two forces are operating. These are : (*i*) the electrostatic attractive force (or attractive potential energy) acting between the oppositely charged ions and (*ii*) inter-atomic repulsive force (or repulsive potential energy). The variation of potential energy (PE) of oppositely charged ions *viz* M^+ and X^- with their inter-nuclear separation (*r*) in the ionic crystal, M^+X^- is shown in Fig. 4·1.

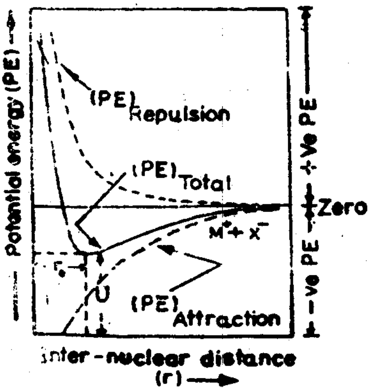


Fig. 4·1. Variation of potential energy (PE) of oppositely charged ions M^+ and X^- with their inter-nuclear separation (*r*) in the ionic crystal, M^+X^-.

The resultant (or total) potential energyis also shown in the same figure. r_0 is the equilibrium distance at which the potential energy is minimum. Thus, if we assume that the potential energy of the ions that are separated by an infinite distance, is zero, the minimum potential energy at r_0 becomes numerically equal to the lattice energy, U of the crystal. Thus *the lattice energy of an ionic crystal may be defined as the decrease in energy that takes place in the process of bringing the ions from an infinite distance to their equilibrium position in the stable lattice.* In other words the lattice energy of an ionic crystal M^+X^- may be defined as the *energy released when the correct number of gaseous cations M^+ and anions X^- are brought together from an infinite distance to form one gram mole of the solid crystal.*

$$M^+(g) + X^-(g) \longrightarrow \underset{\text{(Ionic crystal)}}{M^+X^-(s)} + \text{Energy released (Lattice energy, U)}$$

Lattice energy is also defined as *the energy required to remove ions of one gm mole of a solid ionic crystal from their equilibrium position in the crystal to infinity.*

$$M^+X^-(s) \text{ (ionic crystal)} + \text{Energy required} \longrightarrow M^+(g) + X^-(g)$$

Hence the lattice energy is the same in magnitude but opposite in sign to the energy of dissociation of the crystal. It follows, therefore, that greater the value of lattice energy, numerically, the greater is the energy required to decompose the ionic crystal M^+X^- into its constituent ions, M^+ and X^-.

Theoretical calculation of lattice energy. The lattice energy of an ionic crystal is determined by coulombic interaction between all its ions *viz.* attractive forces acting between the ions of opposite charges and repulsive forces which result from the interpenetration of their outermost electron clouds.

When the coins approach each other, the only force acting at first between them is the attractive force which is directly proportional to the product of the charges carried by the cation and anion and inversely proportional to the distance of their separation. Thus the attractive force [or potential energy, $(PE)_{attraction}$] is given by :

$$(PE)_{attraction} = \frac{(z_+e)(-z^-e)}{r} = -\frac{z_+z^-e^2}{r}$$

Here z_+e and z_-e=charges on the cation and anion, e=charge on the electron, z_+ and z_-=positive integers, and r=distance between the cation and the anion.

As the ions come very close to each other, they repel one another because of interpenetration of their electron clouds. The repulsive force [or repulsion energy, $(PE)_{repulsion}$] is given by :

$$(PE)_{repulsion} = \frac{be^2}{r^n}$$

where n and b are called **Born exponent** and **repulsion coefficient** respectively.

When the ions are brought together from an infinite distance, the total potential energy, $(PE)_{total}$ is given by :

$$(PE)_{total} = (PE)_{attraction} + (PE)_{repulsion}$$

$$= -\frac{z_+z_-e^2}{r} + \frac{be^2}{r^n} \qquad \ldots(i)$$

In an ionic crystal the force on any one ion will be determined not only by the oppositely charged ions which are directly surrounding it but also by the other ions (both positive and negative) at greater distance. Thus in an ionic crystal not only two separate ions are to be considered but the whole crystal must be considered. In order to consider the forces due to all ions imagine an ionic crystal, $M^{z+}X^{z-}$ having NaCl structure in which the ions have net charges equal to z_+e and $-z_-e$ where e is the charge on the electron and z_+ and z_- are positive integers. Let us calculate the potential energy at the site of M^{z+} ion due to all other ions surrounding it. Each M^{z+} ion is surrounded by

six X^{z-} ions (nearest neighbours) at a distance r or $\sqrt{1}\, r$
twelve M^{z+} ions (second nearest neighbours) at a distance $\sqrt{2}\, r$
eight X^{z-} ions at a distance $\sqrt{3}\, r$
six M^{z+} ions at a distance $\sqrt{4}\, r$
twenty four X^{z} ions at a distance $\sqrt{5}\, r$, and so on.

The electrostatic potential energy change when a M^{z+} ion is brought from infinity to its stable position in a NaCl type lattice is equal to the product of z_+e and $-z_-e$ divided by the distance r. Hence the total electrostatic energy of interaction of M^{z+} with all other ions is given by summing up all these terms :

$$(PE)_{M^{z+}} = \Big[\frac{6(z_+e)(-z_-e)}{\sqrt{1}\,r} + \frac{12(z_+e)(z_+e)}{\sqrt{2}\,r} + \frac{8(z_+e)(-z_-e)}{\sqrt{3}\,r} + \frac{6(z_+e)(z_+e)}{\sqrt{4}\,r} + \dots\dots\Big]$$

$$= \Big[-\frac{6e^2}{\sqrt{1}r} z_+z_- + \frac{12e^2}{\sqrt{2}r}(z_+)^2 - \frac{8e^2}{\sqrt{3}r} z_+z_- + \frac{6e^2}{\sqrt{4}\,r}(z_+)^2 - \dots\dots\Big]$$

$$= -\frac{z_+z_-e^2}{r}\Big[\frac{6}{\sqrt{1}} - \frac{12\, z_+}{\sqrt{2}\, z_-} + \frac{8}{\sqrt{3}} - \frac{6z_+}{\sqrt{4}\, z_-} + \dots\dots\Big]$$

Since the ratio of the charges on the ion (z_+/z_-) is constant for a particular type of structure (*e.g.* 1 for NaCl, 2 for CaF_2 etc.), the sum of all the terms of the infinite series given in bracket is constant for an ionic crystal of given geometry. The value of this constant depends on the geometry of the crystal and remains independent of the values of z_+, z_- and r. It is called **Madelung constant** and is generally represented by A. Thus :

$$(PE)_{M^{z+}} = -\frac{z_+z_-e^2A}{r}$$

The same procedure may be used to calculate the electrostatic potential energy of X^{z-} anion, $(PE)_{X^{z-}}$ with all other ions surrounding it. Since the environments of both the ions in NaCl structure is identical, the same expression gives the value of $(PE)_{X^{z-}}$. Thus :

$$(PE)_{X^{z+}} = -\frac{z_+z_-e^2A}{r}$$

The total attractive or electrostatic interaction potential energy, $(PE)_{attraction}$ is then given by half the sum of $(PE)_{M^{z+}}$ and $(PE)_{X^{z-}}$, since the addition of the two would take interaction into account twice. Thus :

$$(\text{PE})_{attraction} = \tfrac{1}{2}\left[(\text{PE})_{M^{z+}} \quad (\text{PE})_{X^{z-}} \right]$$

$$= \tfrac{1}{2}\left[-\frac{z_+z_-e^2A}{r} - \frac{z_+z_-e^2A}{r} \right]$$

$$= -\frac{z_+z_-e^2A}{r}$$

The second term in the total potential energy expression given by equation (*i*) involves the repulsive forces which arise due to the overlapping of the electron clouds of M^{z+} and X^{z-} ions. Born suggested that the repulsive force varies inversely with r^n and hence only nearest neighbours are to be considered in the calculation of repulsive force. According to him, since each M^{z+} ion is surrounded immediately by six X^{z-} ions, the repulsive force, $(\text{PE})_{repulsion}$ is given by :

$$(\text{PE})_{repulsion} = \frac{6\,b\,e^2}{r^n}$$

This expression in a more general form is given as :

$$(\text{PE})_{repulsion} = \frac{Be^2}{r^n}$$

where B and *n* both are constants and are called repulsion coefficient and Born exponent. B is equal to 6 *b* and measures the strength of the repulsive force and depends on the particular ions present in the ionic crystal. The value of *n* depends on the electronic configuration of the ions of the crystal. It generally has a value between 8 to 10 but its value is lower when both ions of the crystal have helium electronic configuration and is higher when both the ions have xenon electronic configuration.

Thus the total potential energy of an ion in a crystal, considering the forces of all neighbouring ions, becomes

$$(\text{PE})_{total} = (\text{PE})_{attraction} + (\text{PE})_{repulsion}$$

$$= -\frac{z_+z_-e^2A}{r} + \frac{Be^2}{r^n} \qquad \ldots(ii)$$

The most stable equilibrium position of an ion will be achieved when attractive and repulsive forces balance each other. In other words the potential energy (PE) is minimum, when $r = r_0$ where r_0 is the equilibrium distance. By differentiating PE with respect to r and equating $\frac{d(\text{PE})}{dr}$ equal to zero, we get

$$\left(\frac{d(\text{PE})}{dr}\right)_{r=r_0} = \frac{z_+z_-e^2A}{r_0^2} - \frac{nBe^2}{r_0^{n+1}} = 0$$

or

$$B = \frac{z_+z_-Ar_0^{n-1}}{n}$$

By substituting the value of B in equation (*ii*) we get $(PE)_0$ given by the expression

$$(PE)_0 = -\frac{z_+ z_- e^2 A}{r_0} + \frac{z_+ z_- A r_0^{n-1}}{n r_0^n} e^2$$

$$= \frac{Ae^2 z_+ z_-}{r_0}\left(\frac{1}{n} - 1\right)$$

The lattice energy, U, is defined as the energy released in the formation of a mole of an ionic crystal from the gaseous ions which are at an infinite distance from each other. Thus if N is the Avogadro's number, then by definition

$$U = -(PE)_0 \times N$$

$$= -\frac{NAe^2 z_+ z_-}{r_0}\left(\frac{1}{n} - 1\right)$$

or

$$U = \frac{NAe^2 z_+ z_-}{r_0}\left(1 - \frac{1}{n}\right) \qquad ...(iii)$$

This equation is called **Born-Lande** equation.

Conclusions drawn from Born-Lande equation (iii). It can be seen from Born-Lande equation given above :

(*i*) that the *lattice energy varies directly as the product of the charges on the ions of the ionic crystal.* Thus the lattice energies of ionic crystals containing uni-univalent (*e.g.* Li^+F^-), uni-bivalent (*e.g.* $Ca^{2+}F_2^-$) and bi-bivalent (*e.g.* $Mg^{2+}S^{2-}$) ions are in the decreasing order : Li^+F^-(U = −240 kcal/mole) < $Ca^{2+}F_2^-$(= −623)
< $Mg^{2+}S^{2-}$(= −777)

(*ii*) that the *lattice energy varies inversely as the inter-nuclear distance, r_0 between the oppositely charged ions in an ionic crystal.* Thus the lattice energies of LiF, LiCl, LiBr and LiI ionic crystals are in the decreasing order. ($X^- = F^-, Cl^-, Br^-, I^-$)

Ionic crystals :	LiF	LiCl	LiBr	LiI
$r_0 = r_{Li^+} + r_{X^-}$(A)	= 0·60 + 1·36 = 1·96	< 2·41	< 2·55	< 2·76
U (kcal/mole)	= −247	> −203	> −193	> −180

Applications of lattice energy With the help of lattice energy we can estimate electron affinities, proton affinities and heats of formation. Further applications are found :

(*a*) in the discussion of the special properties of fluorine in relation to other halogens ;

(*b*) in the account of stabilities of metal hydrides, polyhalides and peroxides and superoxides :

(*c*) in the derivation of crystal field stabilisation energies ;

(*d*) in the discussion of the characterisation of high oxidation states of metals as fluorides and of their low oxidation states as iodides.

Relation between lattice energy and solubility of ionic solids. The magnitude of lattice energy of an ionic solid gives us an idea about its solubility in different solvents. For a solid to dissolve in a solvent the strong forces of attraction between its ions (lattice energy) must be overcome by the ion-solvent interactions. The solvation of ions is referred to in terms of solvation which is always *negative i.e. in the process of solvation, energy is released.* The amount of solvation energy depends on the nature of the solvent. In case of non-polar (covalent) solvents, the solvation energy is small and hence is not sufficient to overcome the lattice energy of the solid. *Consequently the solid does not dissolve in non-polar solvents.* The solvation energy increases, if the solvent has high dipole moment/or high polariability. *As a general rule for a solid to be able to dissolve in a particular solvent its solvation energy must be greater than its lattice energy so that the latter may be overcome by the former.*

Experimental determination of lattice energy of an ionic solid—Born-Haber Cycle. Suppose we have to determine the lattice energy of an ionic solid, MX. Its lattice energy can be determined by a process known as **Born-Haber** cycle devised by Born-Haber in 1919. The various steps of this process can be shown graphically as a cycle, hence the name Born-Haber cycle. This method is based on the assumption that the formation of one mole of crystalline MX can occur either by the direct combination of $M(s)$ and $\frac{1}{2}X_2(g)$ or by an alternative process which consists of five steps.

(1) **Direct combination of $M(s)$ and $\frac{1}{2}X_2(g)$.** It is a single-step reaction and energy equal to the heat of formation of MX, $(\triangle H_{for})_{MX}$ is *released* in it. Thus it is an *exothermic process. The release of energy has been shown by putting negative sign before it,*

$$M(s)+\frac{1}{2}X_2(g) \xrightarrow{\text{Direct combination}} MX(crystal)-(\triangle H_{for})_{MX}$$

(2) **An alternative process.** This process consists of the following five steps :

(*i*) *Sublimation of $M(s)$ to $M(g)$.* In this step one mole of solid M *absorbs* energy equal to its sublimation energy, $(\triangle H_{sub})_M$ and is thus sublimed to gaseous state, $M(s)$. It is thus an *endothermic process. The absorption of energy has been shown by putting positive sign before* $(\triangle H_{sub})_M$

$$M(s)+(\triangle H_{sub})_M \xrightarrow{\text{Sublimation}} M(g)$$

(*ii*) *Dissociation of $\frac{1}{2}X_2(g)$ to $X(g)$.* In this step half a mole of $X_2(g)$ *absorbs* energy equal to half of the dissociation-energy of $X_2(g)$, $\frac{1}{2}(\triangle H_{diss})_{X_2}$ and is converted into $X(g)$. It is thus an *endothermic process. The absorption of energy is shown by positive sign.*

$$\frac{1}{2}X_2(g)+\frac{1}{2}(\Delta H_{diss})_{X_2} \xrightarrow{\text{Dissociation}} X(g)$$

(*iii*) *Ionisation of* $M(g)$ *to* $M^+(g)$. Each $M(g)$ atom *absorbs* energy equal to its ionisation energy (or ionisation potential), $(IP)_M$ and loses its outer-most electron to form $M^+(g)$. It is an *endothermic process. Positive sign associated with* $(IP)_M$ *indicates absorption of energy in the process.*

$$M(g)+(IP)_M \xrightarrow[(-e^-)]{\text{Loss of electron (Ionisation)}} M^+(g)+e^-$$

(*iv*) *Conversion of* $X(g)$ *into* $X^-(g)$. $X(g)$ atom adds the electron given out by $M(g)$ in step (*iii*) to form $X^-(g)$. In this process $X(g)$ *releases* energy equal to its electron affinity (or affinity energy), $(EA)_X$. *Hence negative sign before* $(EA)_X$. *It is thus an exothermic process*

$$X(g) \xrightarrow{\text{Gain of electron}} X^-(g)-(EA)_X$$

(*v*) *Combination of* $M^+(g)$ *and* $X^-(g)$ *to form MX* (*solid*). This is the final step in which $M^+(g)$ formed in step (*iii*) and $X^-(g)$ obtained in step (*iv*) combine together to form one mole of MX (*solid*). In this process energy equal to the lattice energy (or crystal energy) of MX, $(U)_{MX}$ is *released. Hence negative sign before* $(U)_{MX}$. *Thus it is also an exothermic process.*

$$M^+(g)+X^-(g) \xrightarrow{\text{Combination}} MX\ (\text{solid})-(U)_{MX}$$

Diagrammatically the formation of one gm. molecule of solid MX by the direct combination of $M(s)$ and $\frac{1}{2}X_2(g)$ and by an alternative process consisting of five steps mentioned above is shown in Fig. 4·2.

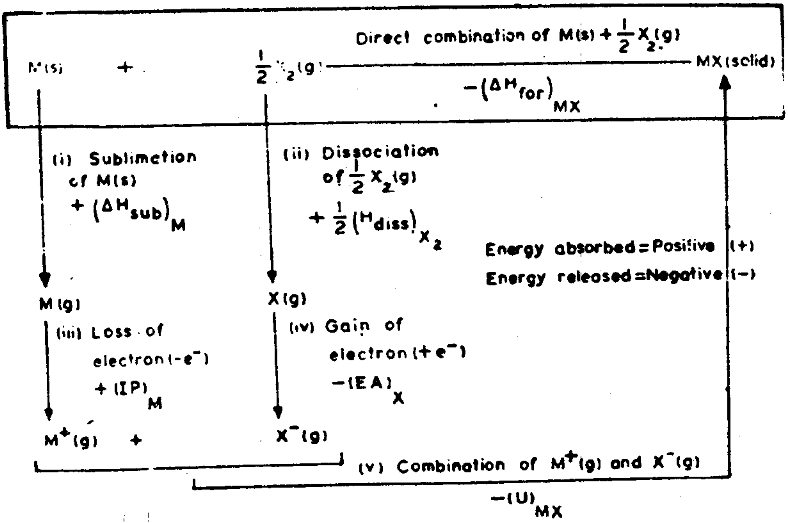


Fig. 4·2. Born-Haber cycle for the formation of an ionic solid, MX by direct combination of $M(s)$ and $\frac{1}{2}X_2(g)$ shown in a rectangle and by an alternative process consisting of five steps : (*i*) to (*v*). Positive sign associated with energy quantities indicates absorption of energy and negative sign indicates release of energy. In brackets are given the values of energy terms determined experimentally.

Since the two processes are independent of each other, by Hess's law the heat of formation of MX, $(\Delta H_{for})_{MX}$ must be equal to the summation of all other energy terms. Thus :

$$(\Delta H_{for})_{MX}=(\Delta H_{sub})_{M}+\tfrac{1}{2}(\Delta H_{diss})_{X_2}+(IP)_M+(EA)_X+(U)_{MX}$$

With the help of this equation we can determine the value of $(U)_{MX}$, if the quantitative values of other energy terms are known. *The quantitative value of each term is substituted in the above equation along with its sign.*

Example. Calculate the lattice energy of NaCl crystal from the following date by the use of Born-Haber cycle. Sublimation energy of Na=26 kcal/g. atom, dissociation energy of $Cl_2=54$ kcal/mole, potential energy for $Na(s)=117$ kcal/atom, electron affinity for $Cl(g)=84$ kcal/g-atom, heat of formation of NaCl=99 kcal/mole.

Solution. Substituting these values in the above equation, we get

$$-99=26+\tfrac{1}{2}\times 54+117+(-84)+(U)_{NaCl}$$

or $\quad (U)_{NaCl}=-99-26-27-117+84=-185$ kcal/mole.

Here we see that in the value of the lattice energy of NaCl, $(U)_{NaCl}$ negative sign appears automatically which shows that energy is released in the formation of NaCl (*solid*) by the combination of $Na^+(g)$ and $Cl^-(g)$.

Deviation. For a large number of ionic solids the values of lattice energy calculated from Eqn. (*iii*) agree fairly with those determined experimentally by using Born-Haber cycle.

There are, however, many ionic solids for which the calculated and experimental values are much different from each other.

Explanation of Deviation. Fajans (1924) explained these deviations on the basis that ideal ionic bond is found in a very few compounds. Most of the ionic compounds possess some covalent character. This transition from ionic character to covalent character has been explained on the basis of polarisation of ions. Thus according to him the difference between the value of lattice energy calculated from equation (*iii*) and that found experimentally by using Born-Haber cycle is due to some amount of covalent character in the ionic solids which arises due to the polarisation of ions.

Uses of Born-Haber Cycle. (*i*) Born-Haber can be used for the determination of electron affinities of elements which are difficult to determine by other methods.

Example. Calculate the electron affinity of iodine with the help of the following data (given in Kcal/mole). $(\Delta H_{for})_{NaI}=-68{\cdot}8$, $(\Delta H_{sub})_{Na}=25{\cdot}9$, $\tfrac{1}{2}(\Delta H_{diss})_{I_2}=25{\cdot}5$, $(IP)_{Na}=118{\cdot}4$, $(U)_{NaI}=-165{\cdot}4$.

Solution. Put these values in the following equation :

$$(\Delta H_{for})_{NaI} = (\Delta H_{sub}) + \tfrac{1}{2}(\Delta H_{diss})_{I_2} + (IP)_{Na} + (EA)_I + (U)_{NaI}$$

or

$$-68{\cdot}8 = 25{\cdot}9 + 25{\cdot}5 + 118{\cdot}4 + (EA)_I + (-165{\cdot}4)$$

or

$$(EA)_I = -68{\cdot}8 - 25{\cdot}9 - 25{\cdot}5 - 118{\cdot}4 + 165{\cdot}4 = -73{\cdot}2 \text{ kcal/mole}$$

(*ii*) Born-Haber cycle is useful in analysing and correcting the stability of various ionic compounds, *e.g.* it explains why MgO is a stable ionic compound, in spite of the fact that very large amount of energies are required to vaporise MgO to Mg^{2+} ion, to dissociate O_2 into atomic oxygen and finally to form O^{2-} ion. Both of these processes are highly endothermic. The heat of formation for MgO is highly negative [$(\Delta H_{for})_{MgO} = -143{\cdot}8$ kcal/mole] in spite of the unfavourable factors mentioned above. This high negative value is due to the very high lattice energy of MgO [$(U)_{MgO} = -935$ kcal/mole] which more than compensates the energy expenditure.

(*iii*) The Born-Haber cycle also helps to understand why most metals fail to form stable ionic compounds in low oxidation states such as MnCl, CaCl, AlO. By comparing the Born-Haber cycle for MCl and MCl_2 (M = Ca or Mg) it can be shown that the formation of MCl_2 is favoured over that of MCl although the energy needed for the formation of $M^+(g)$ and $Cl^-(g)$ ions is lower than that needed for the formation of $M^{2+}(g)$ and $2Cl^-(g)$ from $M(s)$ and $Cl_2(g)$. The much higher lattice energy of MCl_2 over that of MCl more than balances the advantage which MCl had over MCl_2.

ION DEFORMATION OR POLARISATION OF IONS

When a cation approaches an anion closely, the net positive charge on the cation tends to attract the electron cloud of the anion towards itself due to the electrostatic force of attraction existing between them. At the same time the cation also tends to repel the positively charged nucleus of the anion. The combined effect of these two forces is that the *electron cloud of the anion no longer remains symmetrical but is bulged or elongated towards the cation* (*see* Fig. 4·3). This is called **distortion**, **deformation** or **polarisation** of the anion by the cation and the anion is said to be **polarised**. The ability of a cation to polarise (or distort) a nearby anion is called its **polarisation ability or polarisation power.**

(a) No polarisation (b) Polarised anion

Fig. 4·3. Polarisation of an anion (A^-) by a cation (C^+)

The anion also has a similar effect on the cation *i.e.*, the cation is also polarised by the anion, but because the size of a cation is generally smaller, the cation is polarised by the anion to a lesser extent *i.e.*, the polarisation of a cation by an anion is considered almost negligible in most cases. We say, therefore, that the cations have a strong polarisation power and the anions are more susceptible to polarisation, *i.e.*, the anions have more polarisability.

Thus we see that when a cation and an anion come closer to each other, both ions are polarised, but the polarisation produced in anion by cation is appreciable while that produced in cation by anion is negligible.

FACTORS AFFECTING THE POLARISATION OF AN ION—FAJANS'S RULES

The factors which affect the amount of polarisation of an ion have been given by Fajans in his rules known as **Fajans's rules.** These rules are :

(*i*) **Charge on the cation or anion.** Generally speaking *the polarising power of a cation to polarise an anion increases with the increase in its positive charge*. The reason is that a cation having higher charge can attract electrons more effectively. Thus in the anhydrous chlorides *viz.* $NaCl, MgCl_2$ and $AlCl_3$ the polarising power of the cations : Na^+, Mg^{2+} and Al^{3+} increases in the order : $Na^+ < Mg^{2+} < Al^{3+}$, since the positive charges on these cations also increase in the same order.

With the increase of polarisation of Cl^- anion by the cation (Na^+, Mg^{2+}, or Al^{3+}) the covalent character between the cation and anion of these chlorides also increases as we pass from NaCl to $AlCl_3$. The increase in covalent character on moving from NaCl to $AlCl_3$ is confirmed by a gradual decrease in the melting points of these chlorides as shown : $NaCl\ (=800°C) > MgCl_2\ (=712°C) > AlCl_3\ (=575°C)$.

Similarly *the polarisability of an anion also increases with the increase in its negative charge*. This is because of the fact that with an increase in the negative charge, the anion will be able to repel its outermost electrons more effectively. Thus in fluorides and oxides of a metal cation O^{2-} ion is more polarised than F^- ion because F^- has only one negative charge while O^{-2} has two negative charges. This means that oxide is more covalent than the fluoride.

(*ii*) **Size of the cation or anion.** *The polarising power of a cation to polarise an anion increases with the decrease of its size.* Thus the polarising power of the cations like Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+} having the same charge is in the order : $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$ because their cationic radii are in the order : $Be^{2+} (=0{\cdot}31\text{Å}) < Mg^{2+} (=0{\cdot}65\text{Å}) < Ca^{2+} (=0{\cdot}99\text{Å}) < Sr^{2+} (=1{\cdot}13\text{Å}) < Ba^{2+} (=1{\cdot}35\text{Å}) < Ra^{2+} (=1{\cdot}40\text{Å})$. The greatest magnitude of polarising power of Be^{2+} cation makes its salts to show maximum covalent character which is indicated by the minimum melting point of its anhydrous chloride ($BeCl_2 = 405°C$, $MgCl_2 = 712°C$, $CaCl_2 = 772°C$, $SrCl_2 = 872°C$, $BaCl_2 = 960°C$).

The polarisability of an anion increases with the increase in its size. Thus a larger anion is more easily polarised by a cation because the outermost electrons of the larger anion are farther from the positive charge on the nucleus of the anion and are thus more loosely held with the nucleus. Consequently the polarisability of the halide ions in the salts CaX_2 is in the order : $F^- < Cl^- < Br^- < I^-$. This is because of the fact that the radii of these anions also increase in the same order. This makes CaF_2 to show *minimum* and CaI_2 to show *maximum* covalent character. This fact is quite evident by the *maximum melting point* of CaF_2 and *minimum melting point* of CaI_2. (CaF_2=1392°C, $CaCl_2$=772°C, $CaBr_2$=730°C, CaI_2=575°C).

(*iii*) **Electronic Configuration of the Cation.** *A cation with 18 electrons in its outermost shell (non-inert gas* or pseudo inert gas *configuration, $ns^2p^6d^{10}$) has greater polarising power to polarise an anion than a cation with 8- electrons in its outermost shell (inert-gas configuration, ns^2p^6), even if both the cations have the same size and charge.* This is because of the fact that the ten *d*-electrons of $ns^2p^6d^{10}$ shell shield the nuclear charge of the cation less effectively than *s*- and *p*-electrons of ns^2p^6 shell. Thus Cu^+ cation which is with 18-electrons configuration ($Cu^+ \longrightarrow 3s^2p^6d^{10}$) has greater polarising power to polarise Cl^- anion in its anhydrous chloride than Na^+ cation, which is with 8-electrons configuration ($Na^+ \longrightarrow 2s^2p^6$), in NaCl although both the cations have the same charge and size (Cu^+=0·96Å, Na^+=0·95Å). It is for this reason that the anhydrous chlorides of Cu^+, Ag^+ and Au^+ (18-electron configuration) are more covalent than those of Na^+, K^+ and Rb^+ (8-electron configuration) respectively. The decrease in covalent character of the anhydrous chlorides of Na^+, K^+ and Rb^+ is evident from the increase in their melting points as shown :

CuCl=442°C, NaCl=800°C; AgCl=455°C, KCl=776°C ;

AuCl=170°C (decomposes), RbCl=715°C.

Fajans's rules given above can be summarised by saying that *the molecules containing high positive charge on the cation, high negative charge on the anion, small cation or large anion are covalent in character while those containing low positive charge on the cation, low negative charge on the anion, large cation or small anion show ionic character.*

The molecules having cations with 18-electron valence-shell configuration are more covalent than those having 8-electron valence-shell configuration.

APPLICATIONS OF THE CONCEPT OF POLARISATION

Polarisation power of a cation is usually called **ionic potential** or **charge density** and is represented by ϕ(*phi*). It is expressed mathematically as :

$$\phi=\frac{\text{charge on cation}}{\text{radius of cation}}$$

Following are the important applications of the concept of polarisation of ions :

(*i*) **The degree of covalent character in an ionic compound.** *The larger the value of ϕ for a cation, the greater is its polarisation power to polarise the electron cloud of an anion and hence greater is the degree of covalent character in its ionic compound.*

(*ii*) **The tendency of a cation to form complexes.** *The larger the value of ϕ for a cation, the greater is its tendency to form complexes.*

(*iii*) **The tendency of a cation towards solvation.** *The larger the value of ϕ for a cation, the greater is its tendency towards solvation, e.g.* because of the maximum value of ϕ for Li^+ ion, it has the highest tendency towards solvation (*i.e.* hydration energy). It is for this reason that several lithium salts are hydrated (*e.g.* $LiCl \cdot 2H_2O$, $LiClO_4 \cdot 3H_2O$) whereas the salts of other alkali metals are not hydrated. The degree of hydration decreases from Li^+ to Cs^+.

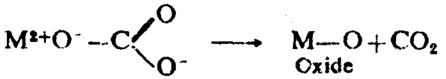
(*iv*) **Nature of oxides.** Larger the value of ϕ for a cation of an oxide, greater is the polarisation power of the cation and greater will be the covalent character of the metal-to-oxygen bond. Also at the same time the cation will show greater tendency to form acidic oxide. For example, Na_2O is more ionic than its neighbour, MgO, since ϕ value for Na^+ ion is less than that for Mg^{2+} ion *i.e.*

$$\phi_{Na^+} < \phi_{Mg^{2+}} \left(\phi_{Na^+} = \frac{1}{0.95} = 1.05,\ \phi_{Mg^{2+}} = \frac{2}{0.65} = 3.08 \right)$$

Cartlidge has examined the nature of oxides of several metals and has suggested that the oxide of a metal, $M_2^{n+}O_n$ is basic when $\sqrt{\phi_{M^{n+}}} < 2.2$, is amphoteric when $\sqrt{\phi_{M^{n+}}} = 2.2$ to 3.2 and is acidic when $\sqrt{\phi_{M^{n+}}} > 3.2$.

Thus, as the value of $\sqrt{\phi_{M^{n+}}}$ increases, the acidic character of the oxide, $M_2^{n+}O_n$ also increases. This increase in the acidic nature is due to the increase in the covalent character of the metal-to-oxygen bond and as such there would be difficulty in breaking this bond on reaction with water.

(*v*) **Thermal stability of carbonates.** Consider a carbonate, $M^{2+}CO_3$. The greater the value of $\phi_{M^{2+}}$ for the cation M^{2+}, greater will be its polarisation power. Thus a cation with a greater value of $\phi_{M^{2+}}$ exercises a strong pull on the electron cloud of the neighbouring O-atom of the CO_3^{2-} ion and as such the metal carbonate gets readily decomposed into CO_2 and the oxide of the metal, MO. Greater the value of $\phi_{M^{2+}}$ for a cation, M^{2+} in a carbonate, $M^{2+}CO_3$, the lesser is the thermal stability of the carbonate. The decomposition of a carbonate $M^{2+}CO_3$ having a metal, M, with greater value of $\phi_{M^{2+}}$ is shown below :



(Metal carbonate)

Since the values of $\phi_{M^{2+}}$ for the alkaline earth metal cation, M^{2+} decreases from Be^{2+} to Ba^{2+}, the thermal stability of their carbonates, $M^{2+}CO_3^{2+}$ increases in the order : $BeCO_3 < MgCO_3 < CaCO_3$ $SrCO_3 < BaCO_3$ as is evident from the gradual increase in the temperature at which their decomposition into oxide (MO) and CO_2 occurs ($BeCO_3 < 100$°C, $MgCO_3 = 350$°C, $CaCO_3 = 547$°C, $SrCO_3 = 778$°C, $BaCO_3 = 998$°C).

A similar reason may also be applied to a number of other decomposition reactions such as :

$$\overset{II}{M}SO_4(s) \longrightarrow \overset{II}{M}O(s) + SO_3(g)$$

$$\overset{II}{M}(OH)_2(s) \longrightarrow \overset{II}{M}O(s) + H_2O(g)$$

$$\overset{I}{M}BF_4(s) \longrightarrow \overset{I}{M}F + BF_3(g)$$

In all the cases cited above the salt having the smallest cation shows the lowest thermal stability *i.e*, the temperature at which the decomposition occurs is the lowest.

(*vi*) **Nature of anhydrous halides.** It has been shown that if the value of $\sqrt{\phi}$ for the cation in the anhydrous halide is less than 2·2, the halide will be ionic and good conductor of electricity. On the other hand, if the value of $\sqrt{\phi}$ is more than 2·2, the halide will be covalent and a non-conductor of electricity.

(*vii*) **Diagonal relationship.** Since the value of ϕ for Be^{2+} (=2/0·31=6·4) is almost of the same order as that of the diagonally situated Al^{3+} (=3/0·50=6.0), these elements have almost many similar properties. However this type of explanation of diagonal relationship should not be over-emphasized, *e.g.* ϕ for Li^+ (=1/0·60=1·6) differs less from that of Na^+ (=1/0·95=1·05) than from that Mg^{2+} (=2/0·65=3·07).

(*viii*) **Melting points of compounds.** As already stated, *with the increase of polarisation, the degree of covalent character in an ionic compound also increases and this increased covalent character decreases the melting points of the compounds.*

(*ix*) **Solubility of salts.** *With the increase of polarisation, the bility of the compound decreases, e.g.* in the sulphides and oxides of a metallic cation, S^{2-} ion is more polarised by the metallic cation than the O^{2-} ion, since S^{2-} ion is bigger than O^{2-} ion in size and it is for this reason that the sulphides are less soluble than the oxides of the same metal.

(*x*) **Bond energy.** *olarisation tends to increase the bond energy.*

COVALENT BOND

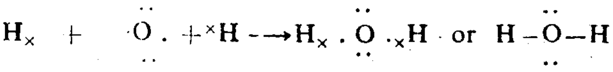
Lewis-Langmuir concept. Lewis suggested in 1919 that there are atoms which attain inert gas configuration (*i.e.* $1s^2$ or ns^2p^6 configuration) by sharing one or more electron pairs with similar or dissimilar atoms. Each atom contributes one electron to the electron pair and has equal claim on the shared electron pair. Langmuir called the Lewis electron pair bond a **covalent bond**. Thus the concept of covalent bond is known as Lewis Langmuir concept.

A covalent bond is expressed in the formula by placing a bar (—) between the atoms bonded together. A covalent bond is *non-polar* and *non-ionised* because in its formation electrons are not transferred from one atom to the other and thus the molecule having the covalent bond *does not acquire polarity* and no ions are formed. It is for this reason that covalent bond is also called *non-polar bond.*

Types of Covalent bond. Covalent bond may *be single covalent bond, double covalent bond* or *triple covalent bond.* Double and triple covalent bonds are called **multiple covalent bonds**.

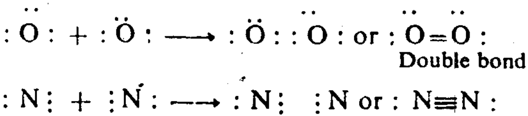
Single covalent bonds are formed *by the sharing of only one electron pair between the bonded atoms, e.g.*

$$H_{\times} + .H \longrightarrow H\overset{\times}{\underset{\cdot}{}}H \text{ or } H-H$$



$$H_{\times} + \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot + {}^{\times}H \longrightarrow H_{\times}\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot{}_{\times}H \text{ or } H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$$

Double and triple covalent bonds are formed when the atoms bonded together share two or three electron pairs respectively, e.g.



$$:\overset{\cdot\cdot}{O}: + :\overset{\cdot\cdot}{O}: \longrightarrow :\overset{\cdot\cdot}{O}::\overset{\cdot\cdot}{O}: \text{ or } :\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{O}:$$

Double bond

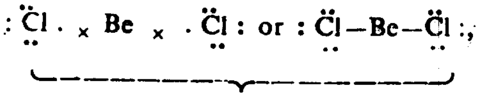
$$:\dot{N}: + :\dot{N}: \longrightarrow :N\vdots\,\vdots N: \text{ or } :N\equiv N:$$

Triple bond

The Octet Rule. We find that when two atoms form covalent bonds, they attain an inert gas configuration with an octet of electrons *i.e.* ns^2p^6-configuration is attained. This is known as *octet rule.* In H_2 molecule each of the two H-atoms, however, attains $1s^2$-configuration.

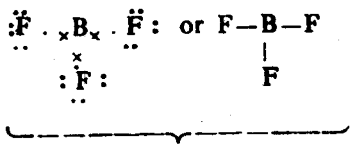
Deviation of octet rule. There are examples of molecules in which the octet rule breaks down *i.e.* the atoms have electrons either less than eight (*i.e.* incomplete octet) or more than eight (*i.e.* expansion of octet). This fact can be illustrated by considering the following molecules.

(*a*) **Incomplete octet.** The structures of $BeCl_2$, BF_3 and NO molecules as shown below indicate that the central atoms *viz.* Be (in $BeCl_2$), B (in BF_3) and N (in NO) are surrounded by four, six and seven electrons in their valence-shell respectively, while other atoms of these molecules obey the octet rule.

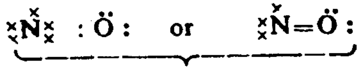


$$\underbrace{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot{}_{\times}Be{}_{\times}\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \text{ or } :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}-Be-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:}_{}$$

$BeCl_2$ molecule



BF_3 molecule



NO molecule

The central atoms (shown in thick type) in the molecules $\mathbf{Be}(C_2H_5)_2$, $\mathbf{B}Cl_3$, $\mathbf{Ga}(CH_3)_3$ etc. also have incomplete octet.

(*b*) **Expansion of octet.** No stable molecules are known in which the atoms of the second period have more than eight electrons in their valence-shell. Elements of third and subsequent periods, however, form molecules wherein the atoms have more than 8 electrons, *e.g.*

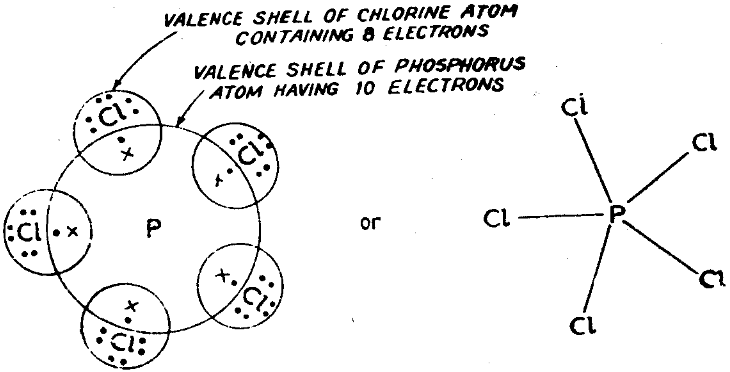
(*i*) **PCl_5, ClF_3 and ICl_3 molecules.** In PCl_5 molecule phosphorus atom is linked with five chlorine atoms by five covalent bonds, showing that phosphorus atom (central atom) is surrounded by $5+5=10$ electrons, *i.e.* the octet is expanded. Similarly it may be seen that in ClF_3 (No. of covalent bonds$=3$) and ICl_3 (No. of covalent bonds $=3$) molecules the central atoms *viz.* Cl and I respectively are surrounded by $6+4=10$ electrons (expansion of octet).

SF_6 (No. of covalent bonds$=6$ and hence total number of electrons in the valence-shell of sulphur atom$=6+6=12$) is another example in which the octet is expanded. Similarly in OsF_8 and O_5O_4 molecules the central atom *viz.* Os(O_6 $\longrightarrow$ $5d^6\ 6s^2$) is surrounded by $6+2+8=16$ electrons. Again the octet is expanded.

Explanation of the failure of Octet rule. The failure of the octet rule in the formation of the molecules mentioned above can be explained with the help of the following concepts.

(1) *Sidgwick' rule of maximum covalency.* This rule states that it is not essential for an element to have a maximum covalency of four *i.e.*, it is not essential for an element to have $4\times2=8$ electrons in its valence shell for its stability. The covalency of an element may exceed four and the octet may be expanded. The maximum covalency of an element actually depends on the period in which the element concerned is present. For hydrogen (first period with $n=1$) it is 2, for the elements of 2nd period with $n=2$ (Li to F) it is 4, for the elements of 3rd ($n=3$) and 4th ($n=4$) period it is equal to 6 and for those in higher periods ($n>4$) it is equal to 8 Consequently the maximum capacity of the valence-shell of an atom to contain electrons (or maximum number of electrons being shared) for the elements mentioned above is equal to $2\times2=4$, $4\times2=8$, $6\times2=12$ and $8\times2=16$ respectively.

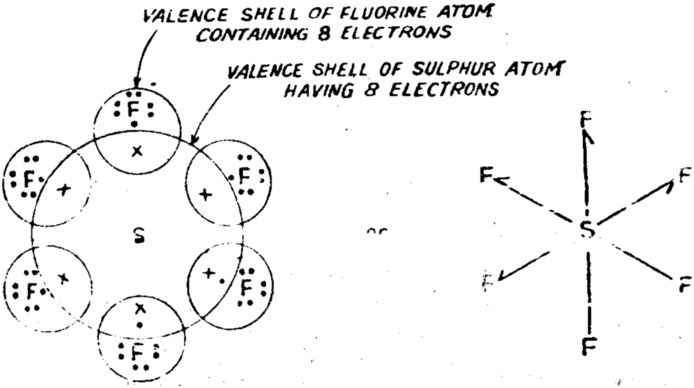
On the basis of Sidwick's rule the structure of PCl_5 can be shown as given in Fig. 4·4.



(a) (b)

Fig. 4·4. Formula of PCl_5 on the basis of Sidgwick's view
(a) Electronic formula (b) Structural formula.

(2) *Sugden's view of Singlet Linkages*. Sugden, however, believes that the octet rule is never violated and in PCl_5, the three chlorine atoms are linked with P-atom by three covalent bonds (*i.e.* 3 electron pairs are being shared between P and Cl atoms) and each of the remaining two Cl-atoms is linked to P-atom by a bond formed by *the sharing of only one electron* between P- and Cl-atoms. This special type of bond which is established by the one sided sharing of only one electron between two atoms is called **singlet linkage** (also called *single electron linkage*, *half-bond* or simply *singlet*). It is a special type of co-ordinate bond, since a single electron being shared is from one of the two bonded atoms. This atom is the central atom *e.g.*, in PCl_5 molecule the two electrons being used in the formation of two singlets are from P-atom. A singlet linkage is represented by a half-arrow (⇀) with head pointing from the donor towards the acceptor. On this basis the structure of SF_6 can be shown as given in Fig 4·5.



(a) (b)

Fig. 4·5 Structure of SF_6 on the basis of Sugden's view of singlet linkages concept
(a) Electronic formula (b) Structural formula.

POLAR AND NON-POLAR COVALENT BONDS

In a covalent bond between two like atoms A and A the shared electron pair between the atoms will necessarily be shared equally by both the atoms and hence the covalent bond will have no ionic character. Such type of bond may be regarded as true covalent bond. But in a covalent bond either between two unlike atoms A and B or between two like atoms having different neighbours (*e.g.* C-atoms in H_3C-CCl_3 molecule), the shared electron pair will not be equally shared by both the atoms, since, if A atom has a stronger attraction for electron pair (*i.e.* has greater electron affinity) than B, the shared electron pair will be attracted towards A and away from B. This type of permanent displacement of electron pair towards A in the covalent bond will develop a fraction of negative charge, δ^-, on atom A and a fraction of positive charge, δ^+, on atom B. These fractional charges should not be confused with unit charges. Under these circumstances the molecule AB will be depicted is $\overset{\delta^-}{A}-\overset{\delta^+}{B}$ and the bond between A and B which has some ionic character is called **polar covalent bond**. The bond between the two like atoms (*e.g.* in H_2, Cl_2 etc. molecules) is called a **non-polar or homo-polar covalent bond**, or simply **covalent bond**. Actually covalent bonds also have slight ionic character *e.g.* the bond H—H in H_2 molecule also has about 2% ionic character which arises from the small contributions of the ionic resonance structures to the total structure of H_2 molecule. The extreme case of unequal sharing of an electron pair between the two atoms gives ionic bond in compounds such as CsF, NaCl or CaF_2 in which one atom (*e.g.* Cs, Na, Ca) is electro-positive and the other atom (*e.g.* F, Cl) is electro-negative in character.

Thus the non-polar covalent bond and ionic bond are extremes for the sharing of an electron pair between the two nuclei. Between these extremes are many polar covalent bonds (*i.e.* covalent bonds having some ionic character).

When in a molecule AB the electronegativity of atom A ($=x_A$) is equal to that of B ($=x_B$) [*i.e.* when we consider a molecule having two identical atoms *e.g.* H_2, Cl_2, molecules], the bond A—B will be covalent. When $x_A \neq x_B$, the bond will have some ionic character. The amount of ionic character will primarily depend on the value of $(x_A \sim x_B)$. Thus if $x_A > x_B$, the bond will be ionic represented as $A^- - B^+$, and, if $x_A < x_B$, then it will again be ionic represented as $A^+ - B^-$ but when $x_A = x_B$, it is represented as $A \times B$ or A—B and the bond is purely covalent bond.

Variable Covalency—Maximum Covalency. *Covalency of an element is defined as the number of electrons contributed by it for sharing purpose.* Generally the covalency of an element which has only *s*- and *p*-orbitals in its valence-shell (*e.g.*, H, O, N etc.) is a fixed quantity (*not always*) and is equal to the total number of unpaired electrons in *s*- and *p*-orbitals, *e.g.*, the covalency of the elements *viz.* $H(1s^1)$, $F(2s^2, 2p_x^2\ 2p_y^2\ 2p_z^1)$, $O(2s^2, 2p_x^2, 2p^1_y\ 2p_z^1)$ and $N(2s^2, 2p_x$

$2p_y^1\ 2p_z^1$) is equal to 1, 1, 2 and 3, since these elements have 1, 1, 2 and 3 unpaired electrons respectively.

On the other hand the elements having *d*-orbitals in their valence-shell configuration (*e.g.*, S, P, Cl etc.) show variable covalency. For example

(1) **Sulphur atom.** (*i*) Sulphur atom in its ground state has two unpaired electrons (S $\rightarrow$ $3s^2,\ 3p_x^2\ 3p_y^1\ 3p_z^1$) and, therefore, shows a covalency of two.

(*ii*) The valence-shell configuration of sulphur atom in the first excitation state is obtained by promoting one of the paired $2p_x$ electrons to the vacant $3d$-orbital to get four unpaired electrons which result in a covalency of four of sulphur atom as shown below :

S-atom in first excitation state : $3s^2,\ \underbrace{3p^1_x\ 3p_y^1\ 3p_z^1\ 3d_{z^2}^1}_{\text{For unpaired electrons result in a covalency of four}}$

(*iii*) On the same basis the covalency of six of sulphur atom can also be explained.

S-atom in the second excitation state :

$$\underbrace{3s^1,\ 3p_x^1\ 3p_y^1\ 3p_z^1,\ 3d^1_{z^2}\ 3d^1_{x^2-y^2}}_{\text{Six unpaired electrons explain the covalency of six}}$$

(2) The covalencies equal to 3 and 5 for phosphorus atom and higher covalencies equal to 3, 5 and 7 for the halogen atoms other than fluorine can also be explained on the basis of the same arguments. It may be noted that *the maximum covalency exhibited by an element is equal to the number of unpaired electrons obtained after unpairing all the s- and p-electrons.* It may also be seen that *the variable covalency is shown only by those elements whose atoms have vacant d-orbitals in their valence-shell configuration so that unpairing of s- and p-electrons by promoting them to vacant d-orbitals may be possible. The elements having no d-orbitals* (*e.g.*, elements of 2nd period) *do not exhibit variable covalency.* Thus we can explain why the molecules like NCl_5 and OF_6 do not exist

CHARACTERISTICS OF COVALENT COMPOUNDS

(*i*) Covalent compounds are formed by the sharing of electrons between the atoms and as such there is no ion formation. Parts of their crystal lattice are molecules which are held by weak Van der Waals forces.

(*ii*) These are generally soluble in organic solvents.

(*iii*) Unlike electrovalent compounds which are solids, these may be solids, liquids or gases. Their melting and boiling points are low.

(*iv*) These are generally soft, easily fusible and volatile.

(*v*) The covalent bond is directional and as such there is a possibility of position isomerism and stereo-isomerism amongst these compounds.

CO-ORDINATE OR DATIVE BOND

In a purely covalent bond each of the electrons in a shared duplet is contributed by each of the two combining atoms ; or in other words we have a sharing of a give-and-take character. There is another—a less equitable mode of partnership, in which one of the atoms allows the other to provide both the electrons which are to be shared. The rich latter partner is called the **donor** and the former the **acceptor** and the name 'dative covalency' (Menzies) or 'co-ordinate covalency' (Sidgwick) is given to the combination. The donation of the pair is made out of a '*lone*' pair of electrons to the acceptor which is in need of the pair to complete its octet. In this mechanism, although the sharing is equitable, the contribution is one-sided, and therefore, a slight polarity develops in the molecule. For this reason it is also called a *semi-polar* bond by Sugden.

The normal covalency can be distinguished from co-ordinate covalency as follows :

(*i*) *Normal covalency*—

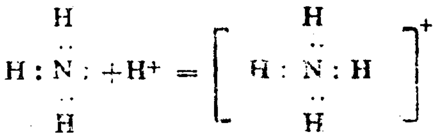
$$A\cdot + B^{\times} \longrightarrow A \overset{\cdot}{\times} B \text{ or } A—B$$

(*ii*) *Co-ordinate covalency*—

$$A : B \longrightarrow A : B \text{ or } A \longrightarrow B \text{ or } \overset{+}{A}—\overset{-}{B}$$

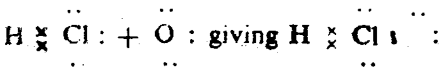
(In this case both the electrons are provided by A. One can assume that in the first step A denotes one electron to B and thus A becomes A^+ [somewhat positive] and B becomes B^- [somewhat negative], and then the sharing takes place. A is the donor and B is the acceptor as indicated by the arrow.)

(*i*) On this basis, the formation of NH_4^+ ion from NH_3 can be explained thus :

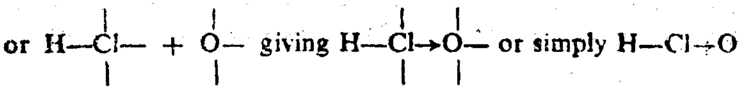


$$H : \overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : + H^+ = \left[H : \overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : H \right]^+$$

(*ii*) One can also explain the formation of HClO from HCl :



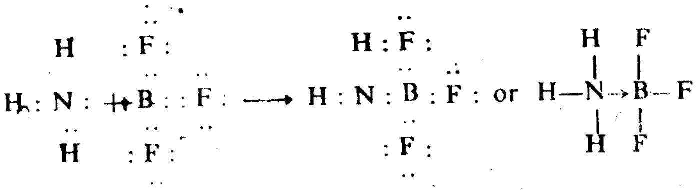
$$H \overset{\times}{\underset{\times}{}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : + \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : \text{ giving } H \overset{\times}{\underset{\times}{}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \; \overset{\cdot\cdot}{} : \quad ...(1)$$



$$\text{or } H—\overset{|}{\underset{|}{Cl}}— + \overset{|}{\underset{|}{O}}— \text{ giving } H—\overset{|}{\underset{|}{Cl}}\rightarrow\overset{|}{\underset{|}{O}}— \text{ or simply } H—Cl\rightarrow O \quad ...(2)$$

A single line including the arrow-line in equation (2) corresponds to a pair of electrons, and the arrow-head indicates the direction in which donation is made.

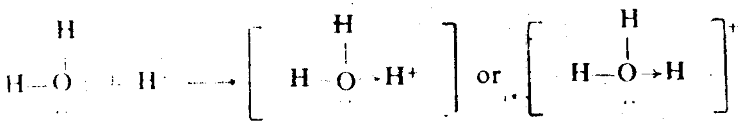
(*iii*) The combination of ammonia with boron trifluoride, is also through a coordinate linkage as shown below :



$$\begin{array}{c} H \\ H:\underset{..}{N}: \\ H \end{array} + \begin{array}{c} :\overset{..}{F}: \\ B:\overset{..}{\underset{..}{F}}: \\ :\underset{..}{F}: \end{array} \longrightarrow \begin{array}{c} H:\overset{..}{F}: \\ H:N:B:\overset{..}{F}: \\ :\underset{..}{F}: \end{array} \text{ or } \begin{array}{c} H\quad\; F \\ H-N\rightarrow B-F \\ H\quad\; F \end{array}$$

Since the 2*s* electron pair in NH_3 is not used in bonding it can be spared for donation to boron to form a coordinate bond.

(*iv*) The formation of H_3O^+ ion (hydronium ion) can be explained as follows :



$$\begin{array}{c} H \\ H-\underset{..}{\overset{..}{O}} \end{array} + H^+ \longrightarrow \left[\begin{array}{c} H \\ H-\underset{..}{O}-H^+ \end{array}\right] \text{ or } \left[\begin{array}{c} H \\ H-\underset{..}{O}\rightarrow H \end{array}\right]^+$$

Characteristics of Coordinate Compounds. Coordinate compounds exhibit characteristics similar to covalent compounds :

(*i*) They do not ionise in water and are poor conductors of electricity.

(*ii*) They are very sparingly soluble in water but dissolve in organic solvents.

(*iii*) Since a coordinate linkage is *semi-polar*, the coordinate compounds possess melting and boiling points which are higher than those of purely covalent compounds but lower than ionic compounds.

(*iv*) The coordinate linkage is also rigid and directional and therefore, such compounds can also exhibit space isomerism.

(*v*) The coordinate linkage is easily broken when the donor and acceptor are molecules which are capable of independent existence.

HYDROGEN BOND

In order to understand the concept of hydrogen bond let us consider a molecule, say, HA in which H atom is linked with a *strongly electronegative atom* A (A may be N, O or F) by a normal covalent bond. The electron pair being shared between H and the strongly electronegative atom A will evidently lie far away from H atom and thus partial positive and negative charges will be developed on H and A atoms respectively. Consequently HA molecule will behave as a dipole represented as $\overset{\delta+}{H}-\overset{\delta-}{A}$ with A as its negative end and H as its positive end. If another molecule H—B which also forms a dipole $\overset{\delta+}{H}-\overset{\delta-}{B}$ (B is a strongly electronegative atom like N, O and F) is brought near $\overset{\delta+}{H}-\overset{\delta-}{A}$ dipole, these two dipoles will be linked together by a special type of bond which is called **hydrogen bond** and is *represented by dotted lines.* Thus the existence of hydrogen bond between A—H and B—H molecules can be shown as:

$$\overset{\delta-}{A}-\overset{\delta+}{H}\ldots\ldots\ldots\overset{\delta-}{B}-\overset{\delta+}{H}$$

H-atom acts as a bridge between the electronegative atoms, A and B. Thus hydrogen bond can be defined as follows :

The attractive force that binds a hydrogen atom, which is already covalently attached with a strongly electronegative atom of a molecule (here it is HA molecule) *with another electronegative atom of some other molecule* (here it is BH molecule) *is known as hydrogen bond.* The atoms A and B may be the same or different, *i.e.*, the molecules AH and BH may be the same or different

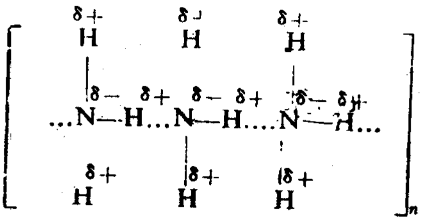
Types of Hydrogen Bonding. Hydrogen bonds have been classified into two major classes :

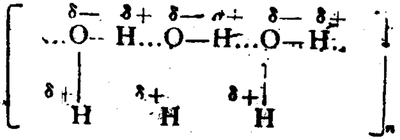
(*a*) **Inter-molecular H-Bonding (Association).** *The hydrogen occurring between two a more similar or different molecules is called inter-molecular hydrogen bonding.*

Examples : (*i*) H_2O, NH_3 and HF molecules. When a number of HF molecules are brought together, the positive end of one dipole, $\overset{\delta+}{H}-\overset{\delta-}{F}$ attracts the negative end of the other similar dipole, H—F and these molecules are *associated* together to form a clustre, $(HF)_n$ shown as :

$$\left[\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\overset{\delta+}{H}-\overset{\delta+}{F}\ldots\overset{\delta+}{H}-\overset{\delta+}{F}\ldots\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\right]_n$$

The formation of the associated molecules of the hydrides of N and O *viz.* $(NH_3)_n$ and $(H_2O)_n$ is due to the existence of inter-molecular hydrogen bonding in NH_3 and H_2O molecules. Their formation can be shown as follows :





(*ii*) **KX.HX or KHX$_2$ molecules.** Cl, Br and I are not so strongly electronegative as F and, therefore, the molecules HCl, HBr and HI do not behave as dipole and also the shared pair of electrons do not lie so far away from H atom that it may attract Cl, Br or I atoms of the neighbouring HCl, HBr and HI molecules. Thus in case of these molecules no significant H-bonding is possible. The non-existence of H-bonding in these molecules explains the non-existence of the molecules like KCl.HCl (or KHCl$_2$), KBr.HBr (or KHBr$_2$) and KI.HI(KHI$_2$), although KF.HF (or KHF$_2$) has been isolated. The anion HF_2^- present in KHF$_2$ salt has the structure : $[F \; H—F]^-$. This anion has the strongest known hydrogen bond (bond energy = 27 kcal/mole). It has been shown experimentally that hydrogen is midway between the two fluorine atoms. Thus HF_2^- anion consists of two F^- ions shielded from each other by a proton (H^+) as shown : [F...H—F] or [F^- H^+ F^-]

(*iii*) **Cupric Sulphate pentahydrate** ($CuSO_4 \cdot 5H_2O$). In $CuSO_4 \cdot 5H_2O$, one of the molecules of water of crystallisation is different from the other four molecules and this suggests us to write the formula as $Cu(H_2O)_4 SO_4 . H_2O$. In the crystal structure of this compound (shown in Fig. 4·6) each Cu^{2+} ion is surrounded octahedrally by six O-atoms four of which are of four water molecules and the two are of SO_4^{2-} ion. Thus four water molecules are associated with Cu^{2+} ion as co-ordinated water and the remaining fifth water molecule is held to SO_4^{2-} ion and to two of the four co-ordinated water molecules by H-bonds to give an overall structure to $Cu(H_2O)_4 SO_4 . H_2O$ as shown in Fig. 4·6

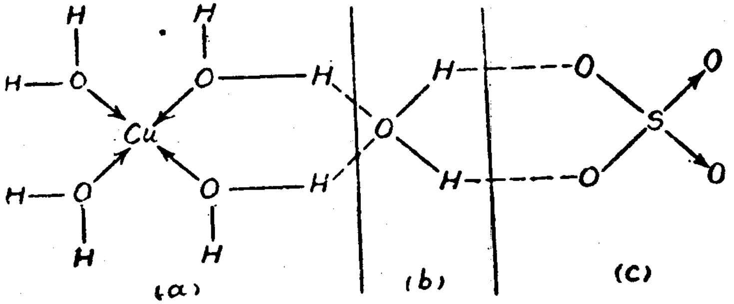


Fig. 4·6. Crystal structure of $CuSO_4 \cdot 5H_2O$.

(*a*) Four water molecules coordinated to Cu^{2+} ion

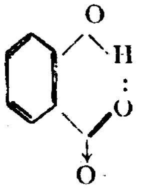
(*b*) Fifth water molecule held to SO_4^{2-} ion shown at (*c*) and two of the four water molecules by hydrogen bonds

(*c*) SO_4^{2-} ion held with fifth water molecule shown at (*b*) by hydrogen bonds.

(*iv*) **Ice.** *See "properties explained by hydrogen bonding".*

(*b*) **Intra-molecular H-bonding (Chelation).** *H-bonding occurring within a single molecule is called intra-molecular H-bonding.* In intra-molecular H-bonding, the H-atom is bonded to two atoms of the same molecule. This type of H-bonding may lead to the linking of two groups to form a ring structure and such an effect is one kind of *chelation.*

An important example of a molecule having intra-molecular H-bonding is furnished by *o*-nitro phenol. *o*-nitro phenol boils at 214°C, while the *m*- and *p*-isomers boil at 290°C and 270°C respectively. Thus we see that *o*-form has the minimum boiling point which is accounted for on the assumption that *o*-form contains an intra-molecular (*i.e.*, internal) H-bonding which can be represented as



This type of intra-molecular H-bonding is not possible in *m*- and *p*-isomers because of the size of the ring that would result. Thus in *m*- and *p*-forms inter-molecular H-bonding takes place and this results in some degree of association among a number of *m*- and *p*-forms. It is this association which accounts for the higher boiling points of *m*- and *p*-isomers.

Properties of Hydrogen Bond. (*i*) A H-bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms (excluding H-atoms).

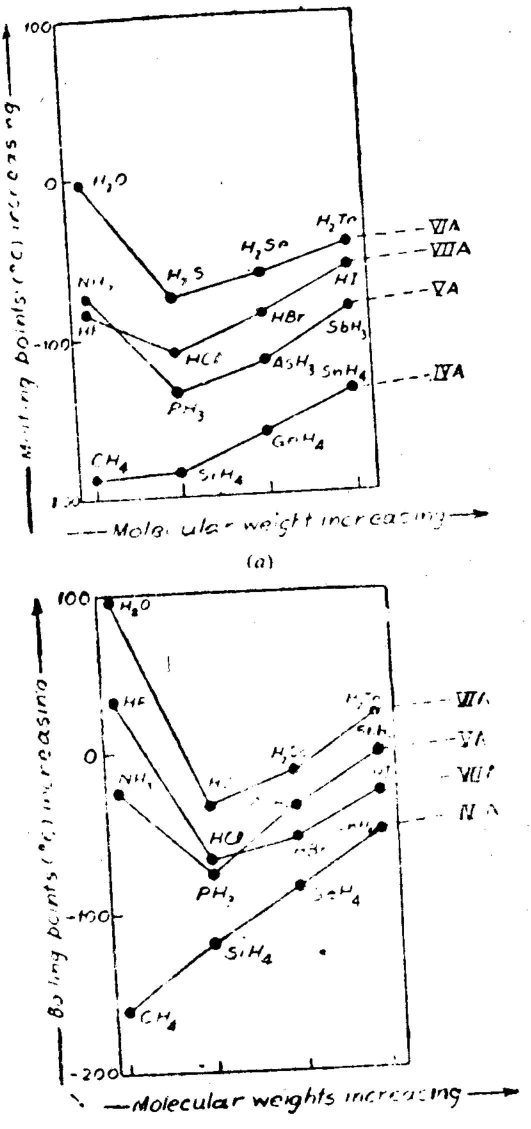
(*ii*) Bond energy of a H bond is in the range of 3—10 kcal/mole while that of a normal covalent bond is in the range of 50—100 kcal/mole. Thus a H-bond (*i.e.*, H... B bond) is much weaker than a covalent bond, A—H. The difference in energy between A—H and H....B bond indicates that these have different bond lengths which in turn shows that H-atom in A—H...B is never midway between the two atoms A and B ; it is rather always nearer to atom A which is covalently bonded to H-atom. H-bond has more energy (=3—10 kcal/mole) than van der Waals forces (=1 kcal/mole).

(*iii*) The formation of a H-bond does not involve any sharing of electron pairs. It is, therefore, quite different from a covalent bond.

(*iv*) A H-bond in A—H...B is formed most easily when both the atoms, namely, A and B are highly electronegative. Thus the ease of formation of a H-bond in A—H...B increases with the increase in the electronegativity value of atom A represented as x_A. This tendency clearly explains that the tendency of A—H bond to form a H-bond increases from N—H through O—H to F—H, since $x_N < x_O < x_F$. This tendency decreases in passing from O—H to S—H or from F—H to Cl—H, since $x_O > x_S$ and $x_F > x_{Cl}$. It clearly shows that F-atom, which has the highest electronegativity value (x_F value) forms the strongest H-bonds.

Properties explained by hydrogen bonding.

(*i*) **State of H_2O and H_2S.** We have already stated that the ease of formation of a hydrogen bond in A—H...B decreases with the



(*a*)

(*b*)

Fig. 4·7. Plots of the melting points [Fig. (*a*)] and boiling points [Fig (*b*)] of the hydrides of the elements of IVA, VA, VIA and VIIA groups against their molecular weights.

decrease of the electronegativity of atom B. Thus, since $x_O > x_S$, there is a considerable hydrogen bonding in H_2O while in H_2S the same is absent. In other words H_2O molecules can associate together to form a *polymerised molecule*, $(H_2O)_n$ (called *clustre*) in which hydrogen atom acts as a bridge between the two oxygen atoms which are highly electronegative atoms. It is due to the formation of polymerised $(H_2O)_n$ molecule containing hydrogen bonds *that water exists as a liquid* while H_2S in which there is no hydrogen bond formation cannot form clusture and *hence exists as a gas*.

(*ii*) **Melting and boiling points (mp's and bp's) of hydrides of N, O and F.** If the melting points and boiling points of the hydrides of the elements of IV A, V A. VI A and VII A groups are plotted against the molecular weights of these hydrides, we shall get the plots as shown in Fig. 4·7 (*a*), (*b*)

From these plots it may be seen that although in case of SbH_3, AsH_3, PH_3 (V A group elements hydrides), H_2Te, H_2Se, H_2S (VI A group elements hydrides) and HI, HBr, HCl (VIII group elements hydrides) there is a progressive decrease in their mp's and bp's, with the decrease in their molecular weights. the mp's and b.p's of NH_3, H_2O and HF hydrides suddenly increase with a further decrease of their molecular weights. The sudden increase in mp's and bp's in these hydrides is due to the inter-molecular H-bonding in between H and F in case of HF, in between H and O in case of H_2O and in between H and N in case of NH_3 respectively. The existence of H-bonding in these molecules gives *polymerised molecules*. $(NH_3)_n$, $(H_2O)_n$ and $(HF)_n$ having H-bonds. In order to break the H-bonds existing in these polymerised molecules more energy is required. Thus mp's and bp's of these molecules are suddenly raised.

Having no power to form H-bonds the simple carbon family hydrides (SnH_4, GeH_4, SiH_4 and CH_4) show a decrease in their bp's and mp's with the decrease in their molecular weights.

(*iii*) **Ice has less density than water.** The explanation of this fact is as follows :

In the crystal structure of ice, the O-atom is surrounded by four H-atoms. Two H-atoms are linked to O-atom by covalent bonds shown as '*a*' and the remaining two H-atoms are linked to O-atom by two H-bonds shown by dotted lines (Fig. 4·8). Thus in ice every water molecule is associated with four other water molecules by H-bonding in a tetrahedral fashion. Ice has an open structure with a large empty space due to the existence of H-bonds. As ice melts at 0°C a number of H-bonds are broken down and the space between water molecules decreases so that water molecules move closer together. The density of water increases, therefore, from 0° to 4°C at which it is at maximum. Above 4°C the increase in kinetic energy of the molecules is sufficient to cause the molecules to begin to disperse and the result is that the density steadily decreases with increasing temperature. Crystal structure of ice is shown in Fig. 4·8.

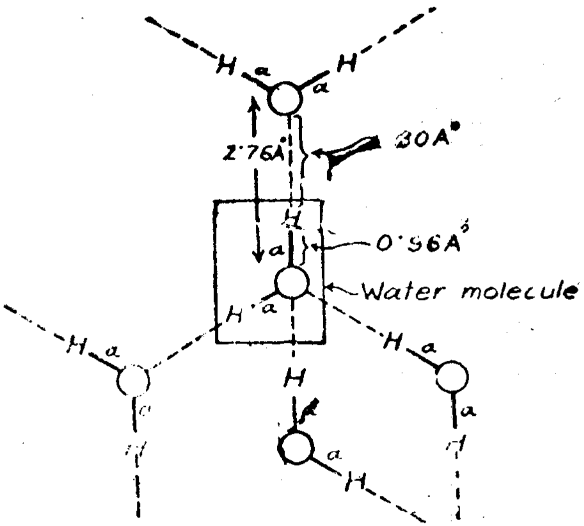


Fig. 4·8 Open cage-like tetrahedral crystal structure of ice. Circles indicate oxygen atoms. Bonds represented by '*a*' are normal covalent bonds, while those represented by dotted lines are hydrogen bonds.

(*iv*) **There is a contraction in water when it is warmed upto 4°C.** How to explain it? As water is warmed from 0°C onwards, more and more hydrogen bonds break down so that water molecules come closer and closer to one another. The moving of water molecules closer together results in *contraction*. However, there is also an *expansion* in the volume of water. It appears that upto 4°C the effect of contraction predominates and hence there is contraction in the volume of water when it is warmed upto 4°C. Above 4°C the effect of expansion predominates and hence there is an expansion in the volume of water when it is heated at a temperature more than 4°C.

Detection of hydrogen bond. The following methods have been used for the detection of hydrogen bond in different compounds.

(*i*) **Infra-red spectroscopy.** When a complex of the type A—H... ..B containing hydrogen bond is formed, several changes like those mentioned below are observed in the infra-red region.

(*a*) The absorption band due to the A—H stretching vibrations (fundamental and overtones) are shifted to lower frequencies. These shifts range from about 30 cm⁻¹ to several hundred cm⁻¹ or more. This shifting is due to the weakening of the force constant for A—H stretching mode which is caused by the formation of hydrogen bond.

(*b*) New vibrational modes which correspond to H......B stretching and deformation are observed at low frequencies in the far infra-red region.

The fundamental frequency which is associated with OH stretching is found at 3600 cm^{-1}. If the OH group forms *inter-molecular hydrogen bonds*, an additional band appears at 3300 cm^{-1}. Increase in temperature or in dilution of the solution weakens the intensity near 3300 cm^{-1} and increases the same near 3600 cm^{-1}. This shows that hydrogen bond formation is diminished with the increase of temperature and dilution of the solution (*i.e.*, decrease in concentration).

If an intra-molecular hydrogen bond is formed, as in salicylaldehyde, suppression of *free* OH group is so complete that the band at 3600 cm^{-1} is absent, the only band which is observed is at 3300 cm^{-1}

(*ii*) **Proton Magnetic Resonance (PMR) method** The formation of a hydrogen bond A—H......B in liquids and solutions modifies electron density round the proton of A—H group and hence its shielding. In most cases PMR absorption is displaced down field (*i.e.* towards lower magnetic field), causing a hydrogen bonding shift which is added to the existing chemical shift. Therefore, with the exception of some cases involving aromatic molecules, the hydrogen bonding shift is usually negative.

PMR method is useful for the cases with small shifts and overlapping bands in their infra-red spectra.

(*iii*) **Electronic absorption spectroscopy**. Visibleand ultra-violet spectroscopy in the visible region from 6000—2000 A° involves excitation of electronic energy levels. Experimentally it has been observed that electronic transitions are shifted to the blue (*hypso-chromic shifts*) when the chromophore is involved in hydrogen bonding as an *acceptor* and are shifted to red (*betho-chromic shifts*) when the chromophore serves as *donor*.

(*iv*) **X-ray method**. When the distances between certain pairs of atoms are usually short and the number of these short distances corresponds to the number of hydrogen bonds required by the formula. the short distances may be considered to indicate the positions of the hydrogen bonds, *e.g.* in the crystal of sodium hydrogen carbonate, two of the oxygens of each planar carbonate group are only 2·55 Å from the nearest oxygens of adjacent groups, while the third is separated from its nearest neighbours. It is thus assumed that the short distances indicate the positions of the hydrogen atoms and the resulting structure is an infinite chain ion in which discrete carbonate ions are linked through hydrogen bonds.

Theories (or Nature) of hydrogen bond. In order to explain the nature of hydrogen bond the following theories have been suggested :

(*i*) **Electrostatic Approach**. The covalency of H-atom is limited to one, *i.e.*, H-atom can be linked to only one atom, say A. This is because of the fact that 1*s*- atomic orbital of H-atom becomes completely filled after it has formed a covalent bond, A–H. Thus H-atom already covalently bonded to atom A in A—H bond cannot form a second covalent bond with another atom, say B. This shows that A–H–B in which H-atom shows bivalency is unlikely, because, if it is likely at all, it would require the use of 2*s*- or 2*p*- orbitals of H-atom which are of much higher energies and consequently are useless for bonding. Further if A—H—B is supposed to be correct, we should expect H-atom to be equidistant from A and B, if $x_A = x_B$, but this is not confirmed by experiments. It shows that attraction of H-atom in A—H bond towards atom B must be largely due to ionic or electrostatic forces, *i.e.*, H-atom *must be regarded predominantly electrostatic in nature.*

We have seen that in A—H, H-atom can form a H-bond with atom B when atom A is highly electronegative. This situation produces a bond dipole $A^{\delta-}$—$H^{\delta+}$ with A as its negative end. A second electronegative atom B, attached to some other atom (say E) or molecule, will also form the negative end of the dipole $B^{\delta-}$—$E^{\delta+}$. Now since the electrostatic attraction between $H^{\delta+}$ (positive end of $A^{\delta-}$—$H^{\delta+}$ dipole) and B^{δ} (negative end of B^{δ}—$E^{\delta+}$ dipole) is greater than the repulsion between the like charges, the two dipoles come closer and H-bond is established between $H^{\delta+}$ and $B^{\delta-}$ due to the electrostatic attraction as shown A^{δ}—$H^{\delta+}$...B^{δ}—$E^{\delta+}$. This situation in HF_2^- ion is represented as $(F-H...F^-)$ where A and B atoms are two F-atoms. The electrostatic attraction occurs between $H^{\delta+}$ and the lone pair of electrons on the electronegative atom B.

The H-bond may thus be regarded predominantly electrostatic in nature. However, it also possesses a small amount of covalent character and is mainly a case of simple dipole-dipole or ion-dipole attraction.

(*ii*) **Valence Bond Theory (VBT) treatment.** According to VBT hydrogen bond is not electrostatic in nature, but it involves the following resonance structures :

$$\underset{\text{(I)}}{A^{\delta-}—H^{\delta+}...B^{\delta-}} \leftrightarrow \underset{\text{(II)}}{A—H : B} \leftrightarrow \underset{\text{(III)}}{A—H \leftarrow B}$$

Structure (III) shows that hydrogen atom is covalently linked with A and B. Thus in this structure hydrogen atom is bicovalently linked. Structure (I) results from dipole interaction while structure (II) arises due to induced dipole interaction. Structure (III) does not make contribution to the overall energy of hydrogen bond while structures (I) and (II) make major contributions to the overall energy of the bond. There are cases in which all the three forms make equal contributions. HF_2^- ion is an example in which all three forms shown below make equal contribution :

$$\underset{(I)}{F^- - H^+ - F^-} \leftrightarrow \underset{(II)}{F^- - H - F} \leftrightarrow \underset{(III)}{F - H - F^-}$$

(*iii*) **Molecular Orbital theory (MOT) treatment.** Pimentel has used MOT to explain the hydrogen bonding in HF_2^- ion. According to him 1s-orbital of hydrogen atom combines with two $2p_z$ atomic orbitals of two fluorine atoms along the bond formation axis. Thus, if two $2p_z$ atomic orbitals of two fluorine atoms are represented as $2p_F$, the various MO's formed in the symmetrical F—H...F bond may be described as :

$$\psi^b \text{ (bonding MO)} = 2p_z + 2p_F + a_1 s$$
$$\psi^{nb} \text{ (non-bonding MO)} = 2p_F + 2p_F$$
$$\psi^* \text{ (anti-bonding MO)} = 2p_F + 2p_F - a_2 s$$

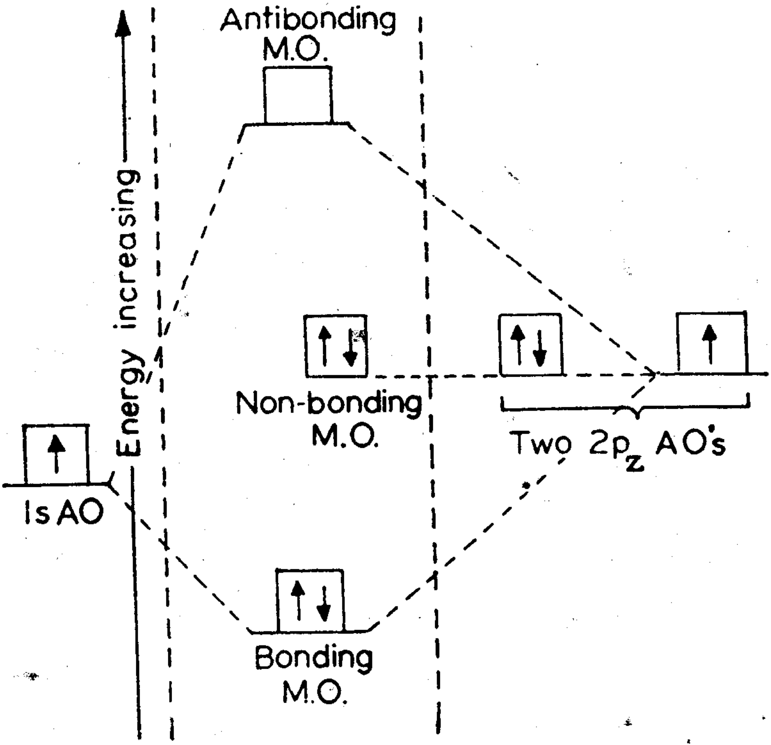


Fig. 4·9. Molecular orbital diagram of HF_2^- ion.

where a_1 and a_2 are the mixing coefficients. The two electrons involved in the bond formation occupy the bonding MO (*see* Fig. 4·9) which spreads out axially on either side of hydrogen atom and thus forms two equivalent weak bonds. Two electrons are concentrated mainly on fluorine atoms in the non-bonding MO. The molecular orbital diagram of HF_2^- ion is shown in Fig. 4·9.

ODD ELECTRON BONDS

It was shown by Lewis in 1916 that there were a number of stable molecules in which a bond is formed by the sharing of one electron or three electrons, *i.e.*, there existed an odd number of electrons between the two bonded atoms. *The bonds of this type which are formed by an odd number of electrons are called odd electron bonds and the molecules having such bonds are called odd molecules or odd electron molecules.*

Odd electron bonds may be one electron-, three electron-, five electron-, etc., bonds. In our discussion we shall, however, take about the former two types of bonds only.

Molecules and ions having odd-electron bonds. According to VBT, the odd electron species have been classified into two categories :

(*a*) **One electron bond molecules and ions.** H_2^+ ion is an example in which one electron bond is formed. This ion has been detected spectroscopically. According to VBT, H_2^+ ion is considered to be a resonance hybrid of the two resonating structures (*a*) and (*b*) given below :

$$(a)\ {}^{+}\mathrm{H} \bullet \mathrm{H} \qquad\qquad (b)\ \mathrm{H} \bullet \mathrm{H}^{+}$$

H_2^+ ion has its bond energy equal to 61 kcal/mole. These two forms are of equal stability (*i.e.*, equal energy). H_2 molecule has its bond energy equal to 109 kcal/mole. Internuclear distance between the H-atoms in H_2^+ ion is 1·06Å and in H_2 molecule it is 0·74 Å. Thus :

$$\mathrm{H}\!-\!\!-\!\bullet\!-\!\!-\!\mathrm{H}^{+} \qquad\qquad \mathrm{H}\!-\!\!-\!\bullet\!-\!\!-\!\bullet\!-\!\!-\!\mathrm{H}$$

$$\longleftarrow 1{\cdot}06 \qquad\qquad \longleftarrow 0\ 74\ \text{Å} \longrightarrow$$

Other examples having 1-electron bond are Li_2^+, Na_2^+, K_2^+ ions and B_2H_6 (di-borane) molecule.

(*b*) **Three electron bond molecules and ions.** Examples of some molecules and ions having 3-electron bond are given below :

(*i*) *He_2^+ ion.* This ion is represented as a resonance hybrid of (*a*) and (*b*).

$$\underset{(a)}{\mathrm{He}\overset{\times}{\underset{\times}{}} \bullet \mathrm{He}^{+}} \longleftrightarrow \underset{(b)}{{}^{+}\mathrm{He} \bullet \overset{\times}{\underset{\times}{}}\mathrm{He}}$$

Resonance between the two forms (*a*) and (*b*) leads to the formation of a three-electron bond between He and He^+. Thus He_2^+ ion is $[\mathrm{He}\,..\,\mathrm{He}]^+$. It is only one electron that plays part in the resonance phenomenon. It is, therefore, not surprising that 1- and 3 electron bonds have approximately the same energy. The binding energy in He_2^+ ion is 58 kcal/mole. The three electrons involved in the 3-

electron bond in He_2^+ ion arise from similar AO's (here these AO's are 1*s*- orbitals) in the isolated atoms.

(*ii*) *O_2 Molecule*. Normal VBT structure for O_2 molecule is

$$:\underset{\cdot\cdot}{\mathrm{O}} = \underset{\times\times}{\mathrm{O}}{}^{\times}_{\times}$$

This structure, however, does not represent the paramagnetic property of O_2 molecule. It is, therefore, assumed that two O-atoms in O_2 molecule are linked by a normal covalent bond (*i.e.*, 2-electron bond) and two 3-electron bonds. Thus O_2 molecule is

$$:\mathrm{O}\overset{\cdots}{\underset{\cdots}{-}}\mathrm{O}:$$

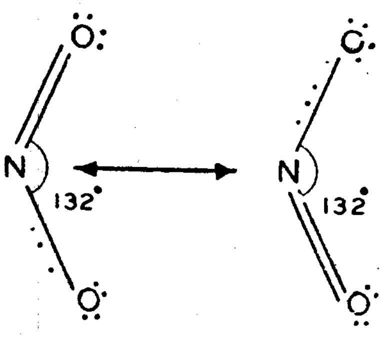
Evidently this structure explains the paramagnetic property of O_2 molecule due to the presence of two unpaired electrons in the molecule. Such a molecule is known as **"double-odd molecule"**.

(*iii*). *Nitric Oxide Molecule* (*NO*). This molecule has two 2-electron bonds and one 3-electron bond. Thus it can be represented as

$$:\mathrm{N}\overset{\bullet\times\times}{=\!=\!=}\mathrm{O}^{\times}_{\times}$$

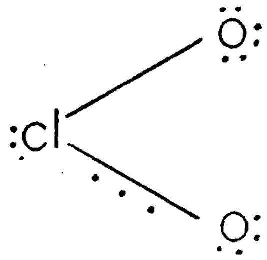
Of the four valence orbitals of each atom, namely, 2*s*, $2p_x$, $2p_y$ and $2p_z$, one is used for the lone pair of electrons, two for the double bond electrons and the fourth is used for the 3-electron bond. The molecule has almost no tendency to dimerise.

(*iv*) *Nitrogen dioxide* (*NO_2*). The real structure of this molecule is a resonance hybrid of the structures shown in Fig. 4·10. The molecule has a strong tendency to dimerise.

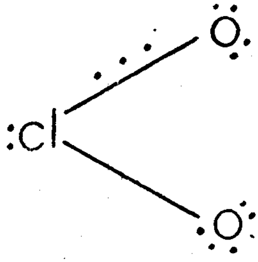


(a) (b)

Fig. 4·10. Resonance forms of NO_2 molecule (*v*) *Chlorine dioxide molecule* (ClO_2). The structure of this molecule is considered to be resonating between the following two 3-electron bond forms :



(a)



(b)

Properties of odd electron Bonds

(*i*) One- and three-electron bonds are approximately half as strong as an ordinary electron-pair bond (*i.e.*, normal covalent bond). This point can be illustrated by considering the internuclear distances in H_2 molecule and H_2^+ ion. We have seen that in H_2 molecule and H_2^+ ion the internuclear distances are respectively 0·74 Å and 1·06 Å. These values indicate that one-electron bond in H_2^+ ion is weaker than a normal covalent bond (*i.e.* 2 electron bond) in H_2 molecule.

Linnett has shown that since N—Cl bond length in nitrosyl chloride (NOCl) is greater than that in $NHCl_2$ molecule (N—Cl distance in NOCl = 1·95 Å and N—Cl distance in $NHCl_2$ = 1·76 Å), it is assumed that nitrogen-chlorine bond in NOCl is a 1-electron bond that in $NHCl_2$ is a normal covalent bond.

(*ii*) One-electron bond between two atoms A and B is considered to be a resonance hybrid between the following two extreme structures :

$$A\bullet\ B \longleftrightarrow A\ \bullet B$$

Similarly a three-electron bond is also considered to be a resonance hybrid of the following two structures :

$$A\bullet : B \longleftrightarrow A : \bullet B$$

(*iii*) Such bonds are not stable, if the electronegativity difference between the atoms involved is large. It has been found that 1-electron and 3-electron bonds are generally established either between like atoms or between those atoms differing by not more than 0·5 in electronegativity values, since only then the resonance structures of approximately equal stabilities would be obtained. Formation of 1-electron bond generally occurs between like atoms while its formation between unlike atoms is extremely rare.

(*iv*) Molecules containing a three-electron bond in addition to an electron pair bond sometimes show a tendency to dimerise. Since the three electron bond is half as strong as an electron pair bond, the energy of dimer will be close to that of two monomeric molecules.

$$A \overset{\cdots}{-} B + A \overset{\cdots}{-} B \xrightarrow{\text{Dimerisation}} :A \cdots B - B \cdots A:$$

(*v*) Bond length of a 1-electron bond is greater than that of a 2-electron bond, *e.g.*, in H_2^+ ion bond length is 1·06 Å while that in H_2 molecule is 0·74 Å. This clearly explains why a 1-electron bond is weaker than a normal covalent bond. Similarly the bond length of a three-electron bond is intermediate between those of a double and a triple bond, *e.g.*, the bond length in NO molecule which is considered to possess 2½ normal bonds has been found experimentally equal to 1·15 Å, a value which is intermediate between the expected bond length for a double bond (=1·20 Å) and for a triple bond (=1·06 Å).

MOLECULAR ORBITAL THEORY (MOT) TREATMENT OF ODD ELECTRON BONDS

MOT treatment of odd electron bonds can be explained by considering H_2^+ ion (one-electron bond ion) and NO molecule (three-electron bond molecule) as follows :

(*i*) **H_2^+ ion.** According to MOT the configuration of H_2^+ ion is $(\sigma^b_{1s})^1$ showing that one of the bonding molecular orbitals is half-filled.

(*ii*) **NO molecule.** According to MOT this molecule (5+6=11 electron species) has the following configuration :

$$(\sigma_{2s}{}^b)^2, (\sigma_{2s}{}^*)^2, (\pi_x{}^b)^2 = (\pi_y{}^b)^2, (\sigma_z{}^b)^2, (\pi_x{}^*)^1 = (\pi_y{}^*)^0$$

In this configuration $(\pi_x{}^b)$ $(\pi_x{}^*)^1$ represents a three-electron bond in the molecule.

BONDING IN METALS—METALLIC BOND

Metals are good electrical and thermal conductors, they are opaque and have high refracting power, they have high melting and boiling points, they crystallise with high co-ordination numbers of 12 or 14. Such properties of metals cannot be explained on the basis of normal ionic or covalent bonding.

Since all the atoms of a metal crystal are *identical*, these cannot be bound together by ionic bonds as cations and anions are bound together in an ionic crystal Ionic bond is formed between atoms of different electronegativity. Van der Waals forces are much too weak to account for high melting points of metals. Also each atom in a metal crystal cannot be bonded to each of its 8 or 14 neghbours by ordinary covalent bonds, since in metals the number of valence-electrons is insufficient for the formation of covalent bonds with all the close or closest neighbours ; *e.g.* Li has only one valence electron (Li ⟶ $1s^2, 2s^1$) per atom which is insufficient to form covalent bonds with 8 or 14 near neighbours in its crystal. There is certainly no obvious way by which Li atom can form 8 or 14 bonds.

Obviously there is a new type of cohesive force in metals which is called *metallic bond.*

How the metal atoms in a metal crystal are bonded together has been answered by the following theories :

(1) **Electron-pool or electron-gas theory.** This theory was first proposed by Drude in 1900 and was later on developed by Lorentz (1916). This theory is also, therefore, called *Drude-Lorentz theory.*

According to this theory each atom in a metal crystal loses all its valence-electrons. The electrons thus obtained form an *electron pool* or *gas* and the resulting positively charged metal ions are believed to be held together by this electron pool or gas. The positively charged metal ions do not float randomly in the sea of electrons but have definite position at measurable distances from each other in the crystal lattice. Since the valence-electrons are not attached to any individual ions or pairs of ions but belong to the crystal as a whole, they are free to move throughout the lattice from one part of the crystal to the other as gas molecules move freely throughout their container. The number of such free electrons is not certain. Thus, *according to this theory, metallic solids may be supposed as a collection of positive atomic cores immersed in a fluid of mobile electrons or sea of mobile electrons* (*see* Fig. 4·11). *The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond.*

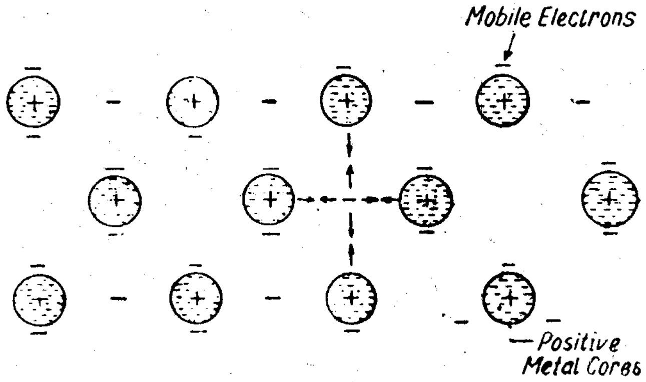


Fig. 4·11. A schematic representation of sea of mobile electrons and positive metal cores. The attraction between positive metal cores and mobile electrons constitute the metallic bond (Attraction has been shown by arrows)

Electron-pool theory and metallic properties. The electron-pool theory of metallic bonding can well explain, qualitatively at least, a number of metallic properties.

(*i*) **Metallic lustre.** As a beam of light falls on the surface of a metal, the mobile electrons move to some excited state. On coming back from the excited state to the ground state in one or more jumps, light of all wavelengths in the visible region is emitted.

Thus when light falls on a metal surface, it appears as if light is being reflected. The surface, therefore, emits the typical metallic lustre.

(*ii*) **Electrical Conductivity.** This property of metals is due to the presence of mobile valence-electrons. These electrons being free to move, are in a position to move in an electric field and thus conduct electricity through the metal (*see* Fig. 4·12).

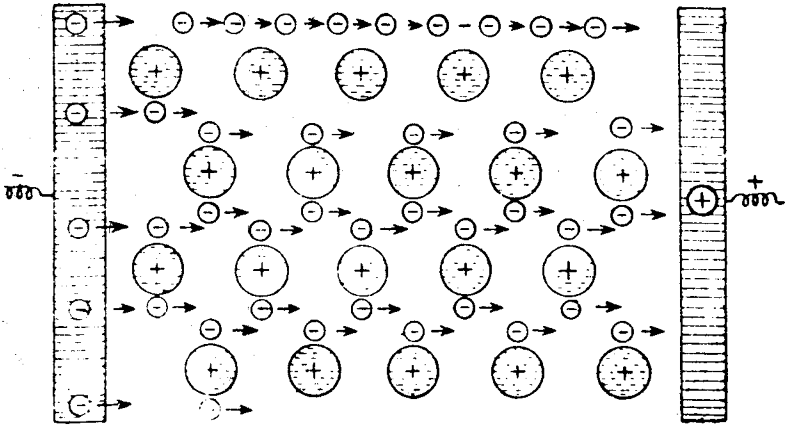


Fig. 4·12 Explanation of conduction of electricity in metallic crystals on the basis of electron-pool theory.

(*iii*) **Thermal Conductivity.** This property is also due to the presence of mobile electrons. When one part of a metal is heated, the electrons in that part acquire a large amount of kinetic energy. These electrons, being free, move rapidly through the crystal and

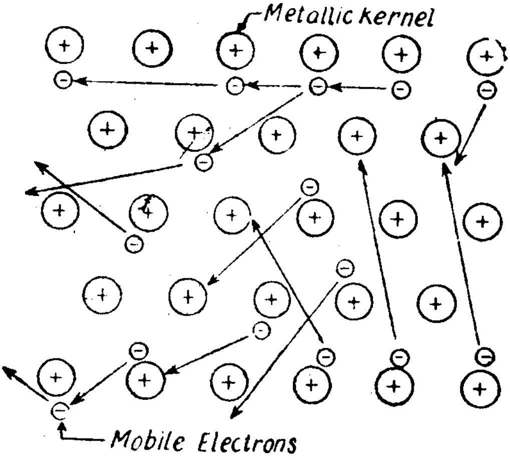


Fig. 4·13. Conduction of heat through metallic crystals on the basis of electron-pool theory.

conduct heat to the other parts of the metal. This process is repeated and results in quicker heat transfer to the other end of the metal (*see* Fig. 4·13).

(*iv*) **Malleability and Ductility**. Since mobile delocalised electrons in a metal crystal surround each kernel (*i.e.* metal ion, say M^+) symmetrically, the binding forces holding M^+ ions and valence-electrons are non-directional, *i.e.*, the force of attraction between M^+ ions and the valence-electrons is uniform in all directions and there are no localised bonds, and the bonds holding the crystal lattice in metals are not rigid as they are in covalent solids such as ice. This means that a layer of kernel can easily be shifted along a plane (indicated by broken lines in Fig 4·14) from one lattice site to the other one, when a shearing stress is applied on a metallic crystal. In the final state of the shifting process the relative positions of kernels remain the same as they were before shifting, since delocalised electrons are available everywhere. Thus we see that within the crystal each kernel has the same position with respect to its neighbours before and after shifting process and electron gas surrounds the kernel symmetrically in both the positions. The nearest neighbours can thus be changed easily and new metal bonds may be formed readily. The ease with which new metal bonds may be formed by moving the metal ions form one lattice site to another is responsible for the facts that metals can be beaten into their sheets (*i.e.* are malleable) and can be drawn into wires (*i.e.*, are ductile) by very little expenditure of energy.

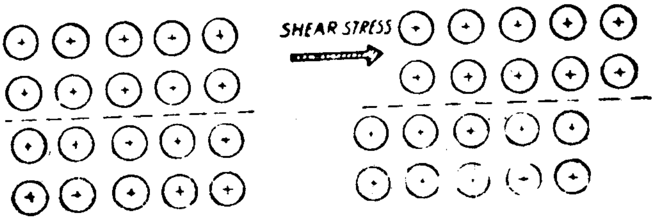
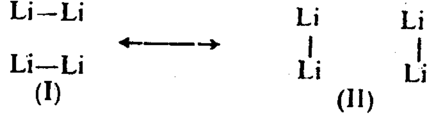


Fig. 4·14. **A layer of metal ions slides past another layer when a shearing stress is applied on a metallic crystal. Such type of shifting of metal ions layer does not produce any change in the overall crystal structure. The broken line indicates a plane along which the layer is shifted.**

(*v*) **High elasticity**. The fact that ions can change position without breaking the metallic crystal shows that under a stress the structure is temporarily changed and attains the original position on removing the stress.

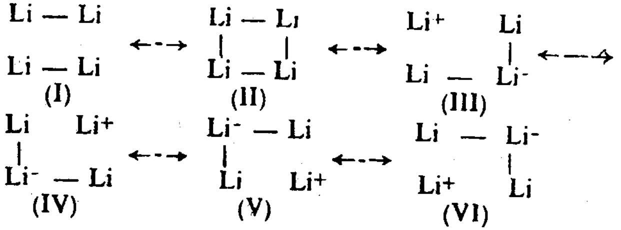
(2) **Resonance or Valence Bond Theory**. An alternative theory of metallic bonding was introduced by Pauling. According to it *the metallic bonding is essentially covalent in origin and metallic structure involves resonance of electron-pair bonds* (*i.e.* *ordinary covalent bonds*) *between each atom and its nearest neighbours.*

Let us consider the case of lithium metal in which each atom has 8 nearest neighbours as shown by X-ray studies. The configuration of lithium atom is $1s^2, 2s^1$ showing that lithium atom has only one valence-electron which is insufficient to form electron-pair bonds between each atom of lithium and all its 8 neighours. Consequently it is assumed that resonance takes place throughout the lithium solid. If each atom of lithium retains its single valence-electron, the resonance of pairs of bonds must be assumed to synchronised throughout the solid. Thus, in two dimensions, various resonance forms may be shown as follows :



Here it should be noted that although only four atoms have been shown in these forms, the actual bonding includes all of the atoms of the crystal and is three-dimensional.

The stability resulting from this type of resonance between covalent bonds (shown above) would relatively be smaller. Assuming unsynchronised resonance between the arrangements involving ions as well, we get in all the following contributing structures which are relatively more stable :



The contributing structures (III), (IV), (V), and (VI) contain lithium atom with a negative charge bonded to other two lithium atoms by two covalent bonds. These covalent bonds are resonating covalent bonds. How are these covalent bonds formed ? The answer to this question has been given as follows :

The electric configuration of lithium atom *viz* $1s^2, 2s^1 2p_x^\circ 2p_y^\circ 2p_z^\circ$ shows that there are three vacant $2p$-orbitals. Since the energy of these three $2p$-orbitals is not very different from that of the valence orbital *viz* $2s$-orbital, an electron from $2s$-orbital of one lithium atom can easily be transferred to one of three $2p$ vacant orbitals of the other lithium atom to convert it into Li^- ion with the configuration $1s^2, 2s^1 2p_x^1 2p_y^\circ 2p_z^\circ$. The lithium atom which is giving the electron from its $2s$-orbital is converted into Li^+ ion with the configuration $1s^2, 2s^\circ$. This point can more clearly be understood by distinguishing the four lithium atoms as Li_a, Li_b, Li_c and Li_d. All the atoms have $1s^2, 2s^1$ electronic configuration. Now suppose Li_d atom gives its $2s^1$ electron to Li_b atom so that Li_d becomes Li_d^+ (with configuration $1s^2$) and Li_b becomes Li_b^- (with configuration $1s^2, 2s^1 2p_x^1 2p_y^\circ 2p_z^\circ$). Now $2s$ and $2p_x$ orbitals on Li_b^- hybridise together to form two sp-hybrid orbitals. These hybrid orbitals which are singly filled form two covalent bonds, one with Li_a and other with Li_c atom as shown below : (In brackets we have shown the electronic configuration of the atom or ion. The orbitals shown in thick type are those which participate in covalent bond formation)

$$\begin{tikzcd} Li_a\,(1s^2,\ 2s^1) \arrow[r, dash] & Li_b^-[1s^2,\ (sp)^1, (sp)^1\ 2p_y^\circ\ 2p_z^\circ] \arrow[d, dash] \\ Li_d^+(1s^2) & Li_c(1s^2,\ 2s^1) \end{tikzcd}$$

Thus we find that the requirement, in terms of valence bond theory of metallic bonding, for the formation of resonating covalent bonds is that *there should be orbitals, energetically not very different from the outermost occupied orbitals, in the configuration of the metallic atom.*

The two vacant orbitals namely $2p_y^\circ$ and $2p_z^\circ$ on Li_b^- can accept the conductivity electrons and thus contribute to metallic conduction. These two $2p$ vacant orbitals are termed as *metallic orbitals.*

(3) **Molecular Orbital Theory—Band Theory.** This is the quantum mechanical treatment of the metallic crystal and is similar to molecular orbital theory of covalent molecules. The electrons in a metal are considered to belong to the crystal as a whole and not to individual or any pairs of atoms. According to this theory metallic bonding results from the delocalisation of the free electron orbitals over all the atoms of a metal structure.

We have already seen that when a diatomic molecule (a *two-centric system*) is formed, two atomic orbitals of equal energy combine together to give two molecular orbitals *viz.* one bonding molecular orbital and one anti-bonding molecular orbital. Similarly when three atomic orbitals of a three-centric system combine, three molecular orbitals are obtained *viz* bonding molecular orbital, anti-bonding molecular orbital and non-bonding molecular orbital. For an n-centric system where n is very large, we get n molecular orbitals.

In a metallic crystal n is generally of the order of 10^{23}. Thus if a very large number of atoms of a metal, say 10^{23}, are bought together to form the metallic crystal, 10^{23} molecular orbitals are formed. The energies of these molecular orbitals are so closely spaced that they appear to be a continuum, called a **quasi-continuous energy band.** Hence the name band theory. These molecular orbitals are delocalised, *i.e.* these belong to the crystal as a whole.

Let us see how the molecular orbitals (*i.e.* energy bands) are formed in a lithium crystal. Electronic configuration of lithium atom is $1s^2$. $2s^1\ 2p^\circ$. If n atoms of lithium metal are allowed to combine to form lithium crystal, they will form the following three energy bands.

(i) 1*s*-*band*. This band is formed by the combination of *n* 1*s* atomic orbitals of *n* lithium atoms and hence contains *n* energy levels all of which are completely filled. Total number of electrons in this completely filled 1*s*-band is $2\times n=2n$. Since 1*s* orbital is the inner-orbital, it is screened from the influence of other atoms by valence electron (*viz*. $2s^1$-electron) and does not appreciably interact and hence is narrow at equilibrium inter-atomic distance. 1*s*-band is the *non-conducting* or *non-conduction band*.

(ii) 2*s*-*band*. This is called the *valence-band*. Since 2*s* are the valence-energy levels, these are very much influenced by the presence of other atoms and are quite spread out. Since each lithium atom contains only one 2*s*-orbital, *n* lithium atoms in Li_n solid have *n* levels in 2*s*-bond. These *n* levels of 2*s*-band have *n* electrons (each 2*s*-level has only one electron). As the maximum capacity of *n* levels of 2*s*-band is to contain $2\times n=2n$ electrons, 2*s*-band is half-filled. *The upper-half of this band is empty while the lower-half is completely filled:* The levels of 2*s*-band are so near in energy that the electrons from the lower-half can go to the upper-half by energy available even at ordinary temperature.

(iii) 2*p*-*band*. *n* atoms of Li_n solid will give 3*n* levels in 2*p*-band whose maximum capacity to contain the electrons is $2\times 3n=6n$ electrons. Since 2*s* and 2*p* levels are near in energy, 2*s* and 2*p* bands overlap (*see* Fig. 4·15) and the electrons in 2*s*-band, therefore, have additional levels, differing very slightly in energy, to move about. The portion where 2*s* and 2*p* bands overlap is called **overlap zone.** This zone contains *n* electrons, i.e. it is 1 8th filled, since the maximum capacity of quasi-continuous band formed from 2*s* and 2*p* bands to contain the electrons is of $2n+6n=8n$ electrons.

The electronic energy bands where the electrons can move are called the **permitted bands.** These are also called **Brillouin zones.** Two Brillouin zones are separated from each other by empty bands which are called **forbidden zones** or **forbidden energy gap,** e.g. the filled 1*s*-band which is a non-conducting band is separated from the half-filled 2*s*-band by an empty zone—forbidden zone or forbidden energy gap. This zone, i.e. the energy gap between 1*s* and 2*s* bands is quite high and hence the promotion of electrons from the lower non-conducting 1*s*-band to the higher conducting 2*s*-band is prevented. The width of a Brillouin zone depends on the overlapping of electron clouds. The level below which all energy levels are filled is termed **Fermi level** which may fall within a band or within the gap between the bands.

Valence and conduction bands. As already stated a solid crystal may be supposed to contain energy bands. Energy bands formed by the inner energy levels are very narrow while those obtained from the valence levels are quite wide and are known as *valence bands.* The valence bands which are completely filled are called *non-conduc-*

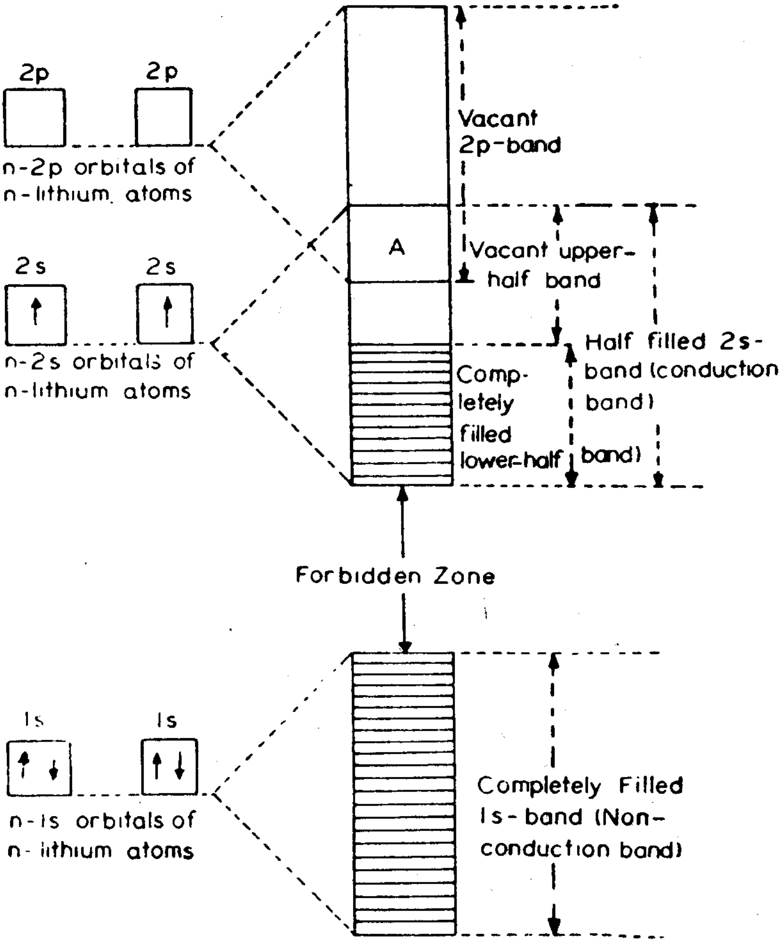


Fig. 4·15. Formation of 1*s*, 2*s* and 2*p* energy bands in lithium crystal. "A" represents the overlap zone where 2*s* and 2*p* bands overlap.

tion bands while those which are partially filled are called *conduction bands*. In conduction bands there is a large number of closely packed energy levels.

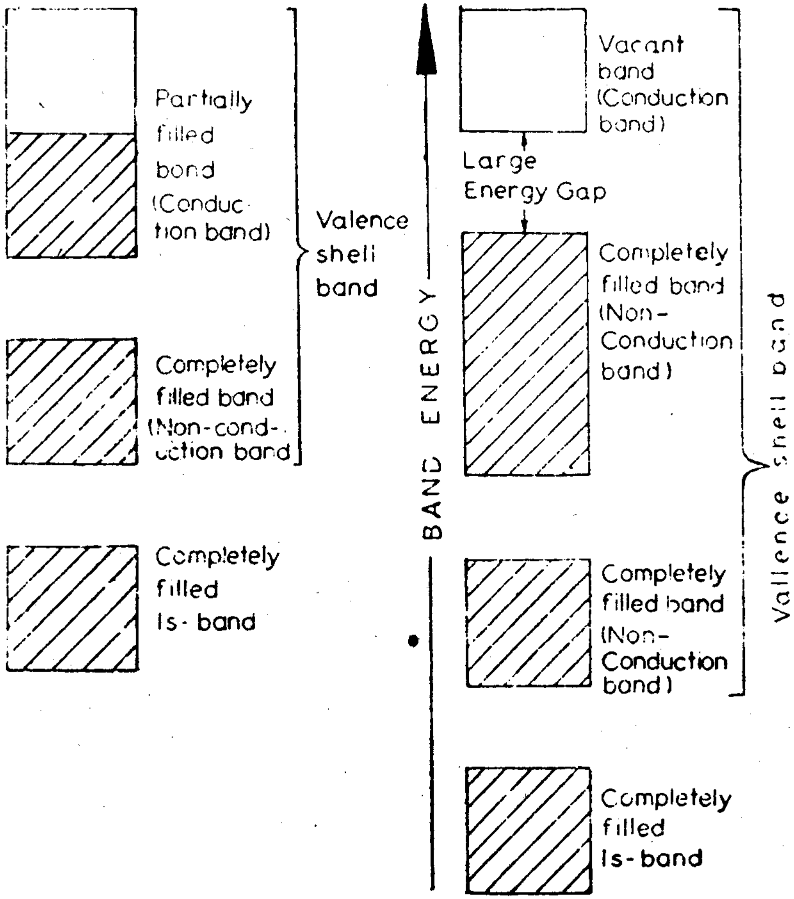
Band theory and physical properties of metals. With the help of band theory we can easily explain why some solids are good conductors (metals) of electricity and others are non-conductors or insulators (non-metals) or semi-conductors (semi-metals).

(*i*) **Conductors (Metals).** Conductors are those materials in which plenty of electrons are available for electric conduction.

In terms of energy bands the conduction band of a conductor is partly filled and contains a very large number of electrons. These electrons can be promoted to the nearby vacant levels in the same band by electric or thermal energy (*see* Fig. 4·16). This explains the high electrical and thermal conductivity of the metals.

(*ii*) **Non-conductors or Insulators** (**Non-metals**). Insulators are those materials in which valence-electrons are bound tightly to their parent atom and hence require very large electric current to remove them from the attraction of nuclei.

In terms of energy bands, an insulator has empty conduction band, i.e. there are no electrons in this high energy band of the valence-shell. The energy gap between the valence-shell band which is completely-filled (non-conduction band) and the conduction band is very large (*see* Fig. 4·16). Thus energy required for shifting an electron from the completely-filled valence-shell band to the empty conduction band is very high and is, therefore, not normally available. This explains that non-metals are insulators.



(*a*) Conductor (Metal) (*b*) Non-conductor or insulator (Non-metal)

Fig. 4·16. Energy bands in a (*a*) conductor (metal) and (*b*) non-conductor or insulator (non-metal)

(*iii*) **Semi-conductors.** Semi-conductors are those materials whose electrical properties lie between those of insulators and good conductors. When these semi-conductors are in their extremely pure form, these are called **intrinsic semi-conductors**· Germanium and silicon are the common examples of semi-conductors or intrinsic semi-conductors.

In terms of energy bands these have filled valence band (non-conduction band) and empty conduction band. The forbidden energy gap between them is so small that even at room temperature many electrons from the filled valence-band jump to the vacant conduction band. This shows low thermal conductivity. As the temperature is increased, width of the *forbidden energy gap* is decreased and hence some more electrons jump to the conduction band. In other words the increase in temperature increases the conductivity.

Recall that in case of metallic conductors increase in temperature decreases their conductivity as the movement of electrons is interfered by greater vibrations of the kernels.

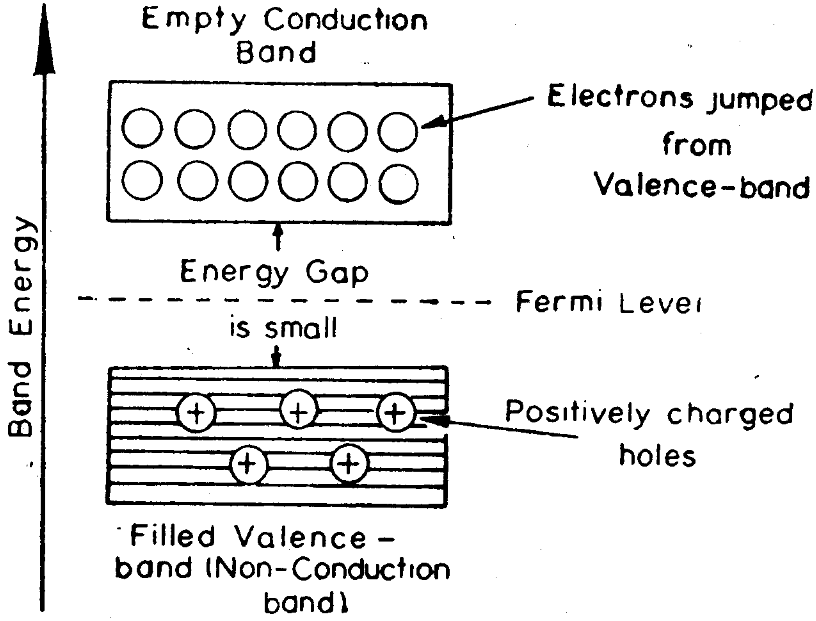


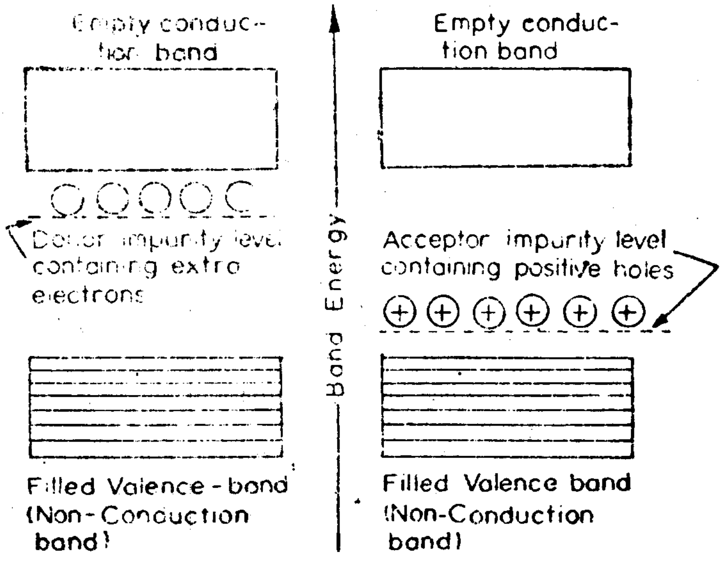
Fig. 4·17. Energy band diagram for an intrinsic semi-conductor at room temperature.

It is worth noting that for each electron liberated into the conduction band, a positively-charged hole is created in the valence-band. Number of holes is equal to the number of electrons jumped to the conduction band. Energy band diagram for an intrinsic semi-conductor at room temperature is shown in Fig. 4·17 in which Fermi-level lies exactly in the middle of the energy gap. Fermi level may be defined as a level below which all energy states are filled.

Sometimes substances, which are normally insulators, can be made semi-conductors when small amounts of impurities are added to them. Such substances are called **extrinsic** or **impurity semi-conductors**. Depending on the nature of impurity added extrinsic semi-conductors are of two types :

(*a*) ***n*-type extrinsic semi-conductors.** These are obtained when *an impurity atom to be added has more external electrons than the parent insulator atoms*, e.g. when phosphorus, arsenic or antimony (all containing five valence-electrons) atoms are added to pure silicon or germanium (both containing four valence-electrons), we get *n*-type extrinsic semi-conductor. Each antimony atom forms four covalent bonds with the surrounding four germanium atoms by using its four valence-electrons and its fifth electron is left unused. Thus there is an extra-electron at the lattice points occupied by antimony atoms compared to the lattice points occupied by germanium atoms. There are as many extra electrons in the lattice points of antimony as there are antimony atoms. These extra electrons occupy delocalised level (called **donor impurity level**) which is just below the empty conduction band of germanium crystal (*see* Fig. 4·18). These extra electrons can easily be excited to the empty conduction band by the application of electric field or by the increase in thermal energy and the crystal of germanium thereby becomes semi-conductor. In this case antimony is called a **donor impurity** because it donates an extra electron to the conduction band of pure germanium. Crystals of germanium are semi-conductors because of the presence of extra electrons in the donor impurities, hence the name *n*-type (*n* used for negatively charged electrons) extrinsic semi-conductors.

(*b*) ***p*-type extrinsic semi-conductors.** These are obtained when an impurity atom to be added has fewer external electrons than the



(*a*) (*b*)

Fig. .18 Energy bands for (*a*) *n*-type and (*b*) *p*-type extrinsic semi-conductors parent insulator atoms, *e.g.* when boron or aluminium (both containing three valence-electrons) atoms are added to pure silicon or germanium (both containing four valence-electrons), we get *p*-type extrinsic semi-conductors. In this case three valence-electrons of each boron atom form three covalent bonds with three germanium atoms and the fourth germanium atom is linked with boron atom by an incomplete bond containing only one electron (from germanium). Thus in this bond in the lattice there is an electron deficiency which creates a positive hole in the valence-band of germanium. There are as many positive holes as there are boron atoms. Positive holes are the places where the electrons are missing. These holes occupy the level (called **acceptor impurity level**) which exists close to the filled valence-band of germanium crystal. Electrons from the filled valence-band can thermally be promoted to this empty acceptor impurity level of positive holes. Under the influence of an applied potential an electron from an adjacent atom moves into a hole and in turn is replaced by an electron from another atom. Thus the molecule moves across the crystal in a direction which is opposite the direction of electron migration. The conduction can thus be thought of as being due to the migration of the positive hole, hence the name *p*-type (*p* used for positive holes) extrinsic semi-conductors.

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Nature of Covalent Bond and Shapes of Molecules

NATURE OF COVALENT BOND

While it is easy to understand that the ions forming an ionic bond are held together by electrostatic forces, it is not clear as to what holds two atoms together in a covalent bond.

It was only after the development of the wave mechanics that two alternative theories were put forward to explain the nature of covalent bond. These two approaches are : (*i*) *Valence bond theory*, (*ii*) *Molecular orbital theory*.

VALENCE BOND THEORY (VBT)

This theory is due to Heitler London, Pauling and Slater and was first applied by Heitler and London in 1927 to H_2-molecule. In case of H_2-molecule we consider the possibility of interchange of electrons between the two H-atoms. Although the two H-atoms in a H_2 molecule are identical, for convenience of treatment, let us call them H_A and H_B. Let these two H-atoms, H_A and H_B, be at an infinite distance from each other so that no appreciable interaction may occur. Thus there are two possible equivalent structures of H_2 molecule (I and II shown below) which are indistinguishable once the bond has been formed

$$\underset{\text{(I)}}{{}^1H_A\,{}^2H_B} \qquad \underset{\text{(II)}}{{}^2H_A\,{}^1H_B}$$

In structure (I) we have the nucleus H_A with electron 1 and nucleus H_B with electron 2. In structure (II) the electrons have been exchanged.

Now if ψ_I and ψ_{II} are the wave functions for the structure (I) and (II) respectively, then according to VBT

$$\psi_I = \psi_A(1)\,\psi_B(2) \qquad \text{...(5·1)}$$

and

$$\psi_I = \psi_A(2)\,\psi_B(1) \qquad \text{...(5·2)}$$

where $\psi_A(1)$, $\psi_B(2)$, $\psi_A(2)$ and $\psi_B(1)$ are the wave functions for the independent H-atoms namely ^1H_A, ^2H_B, ^2H_A and ^1H_B respectively. The true wave function, ψ, for H_2 molecule is given by

$$\psi = C_I\psi_I + C_{II}\psi_{II}$$

or

$$\psi = C_I\psi_A(1)\,\psi_B(2) + C_{II}\psi_A(2)\psi_B(1)$$

where C_I and C_{II} are the mixing coefficients. For H_2 molecule $C_I = \pm\, C_{II}$ *i.e.*, if $C_I = 1$, then $C_{II} = \pm 1$. There are thuse two possible values of ψ, one corresponding to $C_I = 1$ and $C_{II} = +1$ and other corresponding to $C_I = 1$ and $C_{II} = -1$. Let these two values of ψ be represented as ψ_s and ψ_a. Thus

$$\psi_s = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \qquad ...(5{\cdot}3)$$

and

$$\psi_a = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1) \qquad ...(5{\cdot}4)$$

Equation (5·3) represents a symmetric combination of $\psi_A(1)\psi_B(2)$ and $\psi(2)\psi_B(1)$, since ψ_s remains unchanged by exchange of electron 1 and 2, whereas equation (5·4) represents an antisymmetric combination, since ψ_a changes its sign by exchange of electrons. In Fig. 5·1 we have plotted the energy, E, against the internuclear distance R_{A-B} between the two hydrogen atoms, H_A and H_B, of H_2 molecule. As is evident from the plot, curve '*a*' represents ψ_a state. In this state two electrons are in parallel spins. As is evident from curve '*a*', if the two electrons in H_A and H_B have parallel spins, the energy continues to rise as the two atoms get closer together and no bond is formed. Thus ψ_a is a repulsive or non-bonding state. On the other hand, if the two atoms have opposed

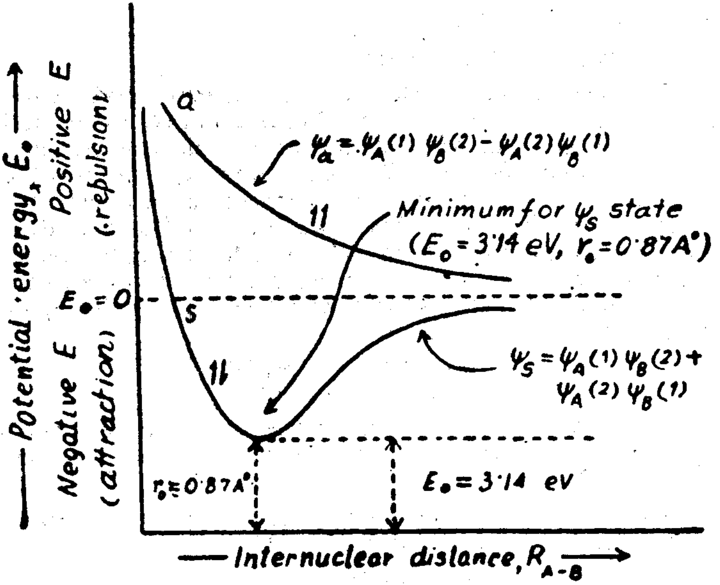


Fig. 5·1. Variation of energy with internuclear separation of two hydrogen atoms of a hydrogen molecule.

spins, energy curve which represents ψ_s state possesses a definite minimum which corresponds to the formation of the molecule. Thus ψ_s is an attractive or bond formation state. It would be evident from curve '*s*' representing ψ_s that at minimum the calculated dissociation energy E_0 (or bonding energy) and bond length r_0 are 3·14 eV and 0·87 Å respectively. The corresponding experimental values are 4·7 eV and 0·74 Å.

Improvement Suggested by Pauling. Pauling has shown that the calculations of E_0 made by Hitler-London method can be improved by considering two additional ionic structures for the molecule in which both the electrons 1 and 2 are attached to one atom. These two ionic structures (III) and (IV) as shown below :

$$\underset{\text{(III)}}{\overset{-1,2}{H_A}\ \overset{+}{H_B}} \qquad \underset{\text{(IV)}}{\overset{+}{H_A}\ \overset{-1,2}{H_B}}$$

Ionic Structure

Let these structures be represented by the wave functions ψ_{III} and ψ_{IV} which are given by

$$\psi_{III}=\psi_A(1).\ \psi_A(2) \qquad ...(5·5)$$

$$\psi_{IV}=\psi_B(1).\psi_B(2) \qquad ...(5·6)$$

The consideration of the ionic structures (III) and (IV) of H_2 molecule converts equation (5·3) to

$$\psi_s=\psi_A(1)\psi_B(2)+\psi_A(2)\psi_B(1)+\lambda(\psi_{III}+\psi_{IV})$$

$$=\psi_A(1)\psi_B(2)+\psi_A(2)\psi_B(1)+\lambda[\psi_A(1)\psi_A(2)+\psi_B(1)\psi_B(2)]$$

or

$$\psi_s=\psi_{cov}+\lambda\psi_{ion} \qquad ...(5·7)$$

Weinbaum used equation (5·7) and found the values of E_0 and r_0 equal to 3·21 eV and 0·88 Å respectively for $\lambda=0·158$.

The coefficient λ in Eqn. (5·7) is a measure of the degree to which the ionic forms (III) and (IV) contribute to the bonding *i.e.* λ offers a means of calculating the degree of the ionic character in the covalent bond.

CONCEPT OF RESONANCE

The physical interpretation of equation (5·7) is that the true structure of H_2 molecule cannot be represented by any of the four structures namely (I), (II), (III) and (IV) but is considered to be resonating between the two extreme structures—covalent structures (I) and (II) and ionic structures (III) and (IV), *i.e.* the actual structure of H_2 molecule is a resonance hybrid of (I), (II), (III) and (IV).

$$\underbrace{\underset{\text{(I)}}{{}^1H_A\ {}^2H_B} \longleftrightarrow \underset{\text{(II)}}{{}^2H_A\ {}^1H_B}}_{\text{Covalent structures}} \longleftrightarrow \underbrace{\underset{\text{(III)}}{\overset{-1,2}{H_A}\ \overset{+}{H_B}} \longleftrightarrow \underset{\text{(IV)}}{\overset{+}{H_A}\ \overset{-1,2}{H_B}}}_{\text{Ionic structures}}$$

The double-pointing arrows between these structures indicates that these structures are in resonance with one another.

When the properties of a molecule cannot be completely described by a single structure, but by two or more structures, its true structure is said to be a **resonance** or **mesomeric hybrid of** these structures. These various structures between which the resonance occurs are called **contributing** or **resonating structures.**

Resonance is the description of the electronic structures of a molecule or an ion by means of several schemes of pairing of electrons, with the features of each scheme contributing in the description.

As a result of resonance the energy of the molecule is lowered and acquires a *minimum value i.e.*, the energy of the true structure is less than that of any of the resonating structures. This lowering in energy is called the **resonance energy** In general it is equal to the difference between observed and calculated heats of formation. It is the greatest when all the resonating structures are of the same energy.

Resonance structures of some species.

(*i*) **Carbon monoxide molecule** (CO). The calculated bond lengths of $C=O$ and $C \overset{\leftarrow}{=} O$ bonds are 1·22Å and 1·10Å respectively. The experimental value equal to 1·13 Å is intermediate between these values. Thus CO is a resonance hybrid of (I) and (II)

$$\underset{\text{(I)}}{{}^{\times}_{\times}C = \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}} \longleftrightarrow \underset{\text{(II)}}{{}^{\times}_{\times}C \overset{\leftarrow}{=} O:}$$

The calculated and the observed heats of formation for $C=O$ bond are 175 kcal/mole and 256 kcal/mole respectively. Thus resonance energy is equal to $256-175=81$ kcal/mole.

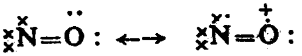
(*ii*) **Carbon dioxide molecule** (CO_2). For a long time its structure was thought to be $O=C=O$. The fact that the experimental value of $C-O$ bond distance ($=1\cdot15$ Å) is intermediate between the calculated values of $C=O$ and $C\equiv O$ bond distances ($=1\cdot22$ Å and $1\cdot10$ Å respectively) shows that the structure represented as $O=C=O$ for the molecule is inadequate. Its real structure is supposed to be a resonance hybrid of (I), (II) and (III) structures.

$$\underbrace{\underset{\text{(I)}}{O=C=O}}_{\text{symmetrical structure}} \longleftrightarrow \underbrace{\underset{\text{(II)}}{\overset{+}{O}\equiv C-\overset{-}{O}} \longleftrightarrow \underset{\text{(III)}}{\overset{-}{O}-C\equiv\overset{+}{O}}}_{\text{unsymmetrical structures}}$$

Since structure (I) is a symmetrical structure, its dipole moment is zero. Structures (II) and (III) are unsymmetrical and hence we should expect some finite values of dipole moment for these structures. The dipoles of (II) and (III) structures are equal and act in opposite directions so that the resultant dipole moment of the actual structure becomes zero. Observed dipole moment of CO_2 molecule is also equal to zero. Thus it is concluded that structures (II) and (III) make equal and opposite contributions to the overall structure of CO_2 molecule.

Structures (II) and (III) are equivalent and hence have the same energy. The resonance energy for this molecule is 33 kcal/mole.

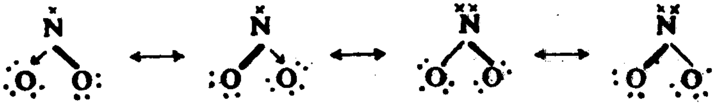
(iii) **Nitritic oxide molecule molecule** (NO). This molecule is supposed to be a resonance hybrid of the following structures.



$$ {}^{\times}_{\times}\overset{\times}{N}=\overset{\cdot\cdot}{O}: \longleftrightarrow {}^{\times}_{\times}\overset{\times\cdot}{N}=\overset{+}{\dot{O}}: $$

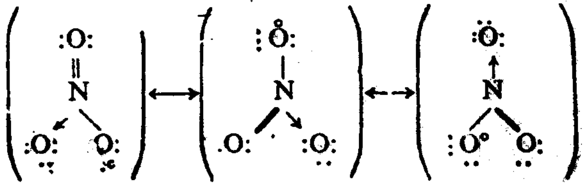
Evidently NO molecule is an odd-electron molecule. Thus it has effectively a structure, ${}^{\times}_{\times}N \overset{\times\cdot\cdot}{=} O$: with *one three-electron* and *two two-electron* (*i.e.*, two covalent single bonds or one double bond) *bonds* between N and O. Such a structure is in agreement with the small dipole moment equal to 0·16D of NO molecule and the observed N—O bond distance of 1·14 Å which is in between the calculated values of the distances for a double bond, N=O (=1·15 Å) and a triple bond, N≡O (=1·05 Å).

(*iv*) **Nitrogen dioxide molecule** (NO_2). It is a resonance hybrid of the following two sets of structures :



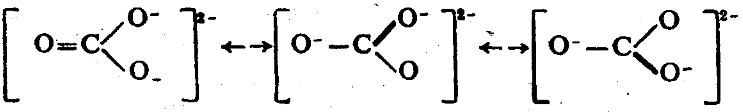
Due to the presence of an odd electron in the nitrogen atom, NO is paramagnetic in character. Due to resonance the two nitrogen-oxygen bonds are equivalent and the bond length is equal to 1·19Å. This experimental value (≐1·19Å) is intermediate between the calculated distances of the bonds : N--O and N=O which are equal to 1·36 Å and 1·15 Å respectively.

(*v*) **Nitrate ion** (NO^-_3). The true structure of this ion is a resonance hybrid of the following structures :



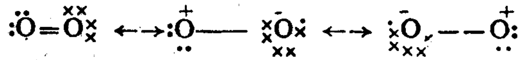
The observed nitrogen-oxygen bond length is 1·21Å. The calculated bond lengths for N—O and N=O bonds are 1·36Å and 1·15Å respectively. Thus the observed bond length is intermediate between the bond lengths for N–O (=1·36Å) and N=O (=1·15Å). The resonance energy is 45 kcal/mole.

(*vi*) **Carbonate ion (CO_3^{2-}).** It is a resonance hybrid of



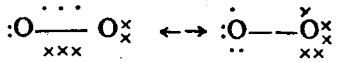
The observed bond length for carbon-oxygen bond in this ion is 1·31Å which is intermediate between the calculated values of the bond lengths for C=O (=1·22Å) and C—O (=1·43Å) bonds.

(*vii*) **Oxygen molecule (O_2).** The resonance structures of O_2 may be written as :



Although these structures can explain the bond energy and bond distance in O_2 molecule, these fail to explain the paramagnetic property of O_2.

In order to account for the paramagnetism, it can be represented as a resonance hybrid of the following structures :

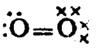


Thus O_2 molecule has *one two-electron* and *two three-electron* bonds. Each of the three-electron bonds has one unpaired electron. This explains the presence of two unpaired electrons in O_2 molecule.

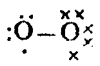
The conditions of resonance. For resonance to be possible the different contributing forms must satisfy the following conditions :

(*i*) *The relative position of all the atoms in each of the resonance forms must be the same ; the arrangement of electrons may differ.*

(*ii*) *The number of unpaired and paired electrons in each of the resonance forms must be the same so that a continuous change from one bond type to another may occur. For example,*



and



(I) (II)

can not be the contributing structures of O_2 molecule, since the number of paired and unpaired electrons in both the forms is different. Structure (II) contains two unpaired electrons and structure (I) has no unpaired electron.

(*iii*) *Like charges should not reside on atoms close together in a contributing form, but unlike charges should not be greatly separated.*

(*iv*) *Contributing structures should be of almost equal energy.*

Important results (or postulates) of VBT.—The overlap of atomic orbitals. The following points are significant :

(*i*) The atoms which unite to form a molecule completely retain their identities in the resulting molecule.

(*ii*) The formation of a covalent bond is due to overlap of atomic orbitals (abbreviated to AO's). If the two atoms, each having one unpaired electron, come together, the AO's accommodating these unpaired electrons overlap (*i.e.* electron waves interact) and the spins of the two electrons get mutually neutralised, resulting in the formation of a covalent bond which is localised between the two atoms. If the electrons present in the AO's have parallel spins, no bond formation will occur, *i.e.* no molecule will be formed.

(*iii*) If the AO's possess more than one unpaired electrons, more than one bond can be formed. Thus in N_2 molecule there are three bonds, since N-atom has three unpaired electrons ($N \rightarrow 2s^2, 2p^1_x\, 2p^1_y\, 2p^1_z$).

(*iv*) Electrons which are already paired in the valence-shell cannot participate in bond formation. They can, however do so, if they can be unpaired without using much energy. Because energy is released when a covalen bond is formed, the energy released by formation of more bonds may exceed the energy needed to unpair the electron by shifting it to the vacant orbital of slightly higher energy and of the same main energy level. Thus N atom ($2s^2, 2p^1_x, 2p^1_y, 2p^1_z$) shares its three unpaired 2*p*-electrons with fluorine atom to form NF_3 but cannot form NF_5, since the second main energy level does not possess any other orbital which may accommodate one of the 2*s* electrons after promotion. On the other hand $P(3s^2, 3p^1_x\, 3p^1_y\, 3p^1_z, 3d^0)$ can form PF_5, since in the third main energy level other orbital namely 3*d*-orbital is also available to accommodate one of the 3*s*-electrons giving five unpaired electrons : $P \rightarrow 3s^1, 3p^1_x 3p^1_y 3p^1_z, 3d^1$.

(*v*) The *strength of the covalent bond* is related in a rough way, to the extent to which the two combining AO's can overlap in space. The more the two bonding orbitals overlap, the more the bonding electrons are concentrated between the nuclei where they can minimise the nuclear repulsion and miximise the attractive forces between themselves and both nuclei jointly.

The greater the overlap between the AO's, the greater is the strength of the resulting covalent bond.

The extent of overlap of two AO's represented by wave functions ψ_A and ψ_B is expressed quantitatively by the overlap integral, S, which is given by

$$S = \int \psi_A \psi_B \, dr$$

When *S* is positive (*i.e.* $S > 0$), there is a build-up of electron charge (*i.e.*, electron density) between the nuclei of the two combining atoms and a bond can be formed. When *S* is negative (*i.e.* $S < 0$), there is a reduction in the electron density between the nuclei so that the repulsion between them is increased and they tend to move apart. When the overlap is zero (*i.e.* $S=0$), there is no net interaction (*i.e.* neither attraction nor repulsion) between the combining atoms.

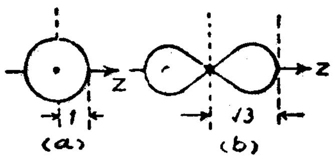


Fig. 5·2.
(*a*) radius of an *s*-orbital (*b*) Length of one lobe of a *p*-orbital

Now if the radius of an *s*-orbital is supposed to be equal to 1 unit, then the length of a lobe of *p*-orbital will be equal to $\sqrt{3}$ and the relative magnitudes or strength of the *p*- and *s*-orbitals would be in the ratio of $\sqrt{3}:1$ (Fig. 5·2). The bond strength is taken equal to the product of the magnitude of the bond orbitals of the two atoms forming the bond. Thus the strength of the *s—s* bond (*i.e.* bond formed by the overlap of *s*-orbitals) is equal to $1\times1=1$, that of *s-p* bond equal to $1\times\sqrt{3}=1{\cdot}732$ and that of *p-p* bond equal to $\sqrt{3}\times\sqrt{3}=3$.

The relative bond strengths are as follows :

s-s	*s-p*	*p-p*
$1\times1=1$	$1\times\sqrt{3}=1{\cdot}732$	$\sqrt{3}\times\sqrt{3}=3$

This shows that *p* orbitals can overlap with *s*- or *p*-orbitals more effectively than two *s*-orbitals.

Overlap of atomic orbitals—sigma (σ) and pi (π) bonds. Depending on the type of atomic orbitals involved in bond formation we may have different types of overlap. As a result, a covalent bond may be either a σ-covalent bond or a π-covalent bond.

σ-bond. *A covalent bond which is formed between two atoms by the overlap of orbitals along their axes (end-to-end or head-to-head overlap) is called a σ-bond.* All σ-bonds have axial symmetry. Since the overlap of two orbitals along their axes is maximum σ-bond is a strong bond.

If *z*-axis is assumed to be the molecular axis, σ-bond is given by *s-s*, $s\text{-}p_z$ and $p_z\text{-}p_z$ overlaps. These σ-bonds are called *s-sσ*-, $s\text{-}p_z\sigma$- and $p_z\text{-}p_z\sigma$-bonds respectively. Since p_z-orbitals on overlapping with other p_z-orbitals or with *s*-orbitals give σ- bonds, these are generally referred to as p_σ orbitals.

(*i*) ***s-s* overlap and structure of H_2 molecule.** 1*s* AO's of the two H-atoms in a H_2 molecule overlap with each other and give a covalent bond between them (Fig. 5·3).

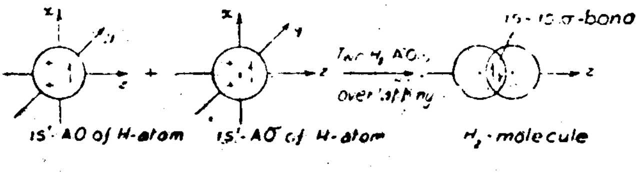


Fig. 5·3. Formation of H_2 molecule.

(*ii*) **p_z—p_z overlap and structure of X_2 molecule (X=F, Cl, Br, I).** The bond in X_2 molecule can be ascribed to the overlap of $2p_z$ AO's and is linearly directed (X $\longrightarrow$ $2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) as shown in Fig. 5·4.

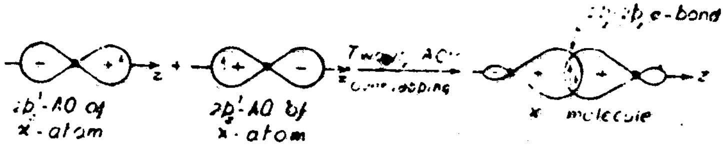


Fig. 5·4. Formation of an X_2-molecule (X = F, Cl, Br, I)

($2s$-, $2p_x$-, and $2p_y$- AO's of X-atom which are completely filled have not been shown).

(*iii*) **s-p_z overlap.** This type of overlap can be exemplified by considering the formation of HX (where X is F, Cl, Br or I), H_2O and NH_3 molecules.

(*a*) *HX Molecule* (*X is F, Cl, Br or I*). This molecule is also formed by the overlap of $1s$-AO of H-atom with $2p_z$-AO of X atom. Both the AO's are singly occupied (Fig. 5·5).

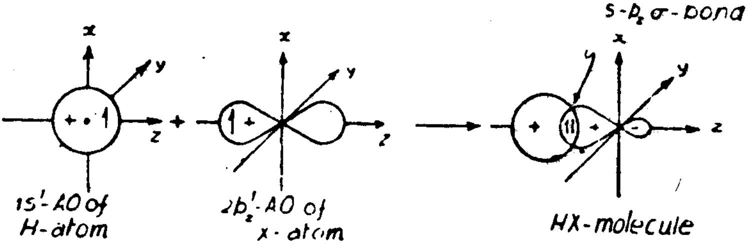


Fig. 5·5. Formation of HX-molecule

($2s$-, $2p_x$- and $2p_y$- AO's of X-atom have not been shown, since these are completely filled)

(*b*) *Water Molecule.* O-atom with its valence shell configuration $2s^2$, $2p_x^1$, $2p_y^1 . 2p_z^?$ has two unpaired p-electrons. These two AO's namely $2p_y$ and $2p_z$ having unpaired electrons overlap with two $1s$-orbitals of two H-atoms and thus two s—p σ-bonds are formed. Now since $2p_y$ and $2p_z$ AO's are at right angles to each other, an angular structure with two O—H bonds inclined at 90° to each other of H_2O molecule would be expected (Fig. 5·6), but the actual H—O—H angle found experimentally in H_2O molecule is 105°. The increase in the bond angle has been attributed to the mutual electrostatic repulsion between the two H-atoms which have fractional positive charge on them. This fractional positive charge is caused by the fact that the bond O—H is not purely covalent but has some ionic character. The experimental bond angles in other related molecules. ($H_2S = 92{\cdot}2^\circ$, $H_2Se = 91{\cdot}0^\circ$ and $H_2Te = 90^\circ$) approach closely the expected (*i.e.* theoretical) value of 90°. This close agreement in the theoretical and experimental value of bond angles is due to the fact that as the ionic character of the H—A bond (where A is O, Se, or Te) decreases, the repulsion between the H-atoms carrying small positive charge also decreases and the bond angles decrease and ultimately approach the theoretical values.

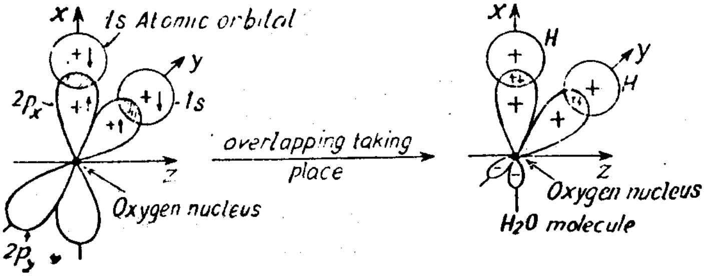


Fig. 5·6. Formation of H_2O molecule.

(2*s*-, 2*p*-AO's of O-atom which are completely filled have not been shown

(*c*) *NH_3 Molecule*. With N ($2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$), there are three unpaired 2*p*-orbital-electrons. Thus we shall expect three N—H bonds is NH_3 molecule perpendicular to each other (*i.e.* inclined at 90°) which would give a pyramidal shape to NH_3 molecule (Fig. 5·7).

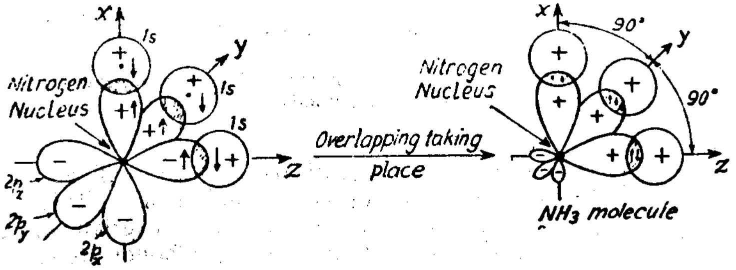


Fig. 5·7. Formation of NH_3 molecule (2*s*-AO of N-atom has not been shown, since it is completely filled).

The related molecules PH_3, AsH_3 and SbH_3 also have similar structure. The experimental H—N—H bond angle in NH_3 is 108°

which is greater than the theoretical value of 90°. Here also the greater value of experimental bond angle is attributed to the mutual repulsion between the two H-atoms. Bond angle of the related molecules ($PH_3=93°$, $AsH_3=92°$ and $SbH_3=91°$) approach 90° due to the reason that as the repulsion between the two H-atoms in these molecules on proceeding from $PH_3 \longrightarrow SbH_3$ diminishes, the bond angle H—A—H where A is P, As or Sb approaches 90°.

π-bond. *A covalent bond which is formed between two atoms by the overlap of orbitals along a line perpendicular to the molecular axis* (*side-to-side* or *lateral* overlap) *is called a π-bond.* If z-axis is assumed to be the molecular axis, π-bond is given by p_x-p_x and p_y-p_y overlaps.

p_x- and p_y-orbitals which on overlapping respectively with p_x and p_y-orbitals give π-bonds, are referred to p_π-orbitals.

(*i*) *O_2 Molecule.* O-atom has $2s^2$, $2p_x^1$, $2p_y^2$, $2p_z^1$ configuration. Evidently $2p_z$-AO (singly occupied) of one O-atom will overlap with $2p_z$-AO of the other O-atom to give a p_z-p_z σ-bond and the two $2p_x$-AO's (singly occupied) of both the O-atoms will overlap along a line perpendicular to z-axis (molecular axis) to give another type of covalent bond known as π-bond. It is a $p_x \rightarrow p_x$ π-bond. Thus O_2 molecule has two covalent bonds—one is p_z-p_z σ-bond and the other is $p_x - p_x$ π-bond (Fig. 5·8).

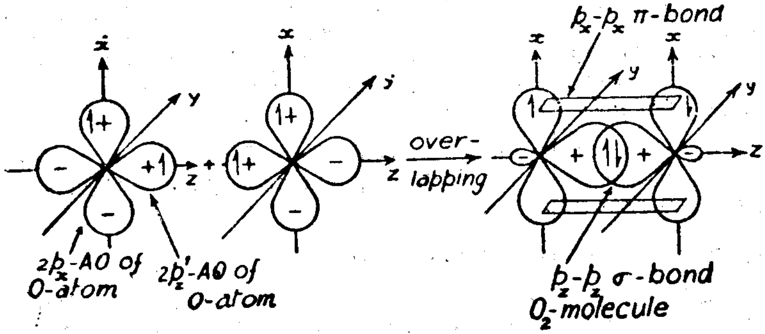


Fig. 5·8. Formation of O_2 molecule.

$2s$- and $2p_y$-AO's of both O-atoms have not been shown, since these are completely filled and hence do not participate in overlapping or bond formation process.

(*ii*) *N_2 Molecule.* N-atom has $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$ configuration. N_2 molecule has three covalent bonds : one is σ-bond ($2p_z-2p_z$ σ-bond) and two π-bonds ($2p_x-2p_x$ π-bond and $2p_y-2p_y$ π-bond).

σ-bonds *Vs* π-bonds. The following points may be noted :

(*i*) σ-bond is formed by the overlap of orbitals along their axes (end-to-end overlap) while π-bond results from side-to-side overlapping of the orbitals.

(*ii*) Since the extent of overlapping of orbitals along the same axes is always greater than the extent of overlapping at an angle, σ-bond is stronger than π-bond.

(*iii*) Electron cloud of a σ-bond is symmetrical about the line joining the two nuclei while that of a π-bond is unsymmetrical.

(*iv*) There can be free rotation of the atoms round the σ-bond. Such type of rotation is not possible round the π-bond, since the electron clouds overlap above and below the plane of atoms.

(*v*) σ-bond determines the direction of the bond and the extent of the internuclear distance. π-bond has no primary effect on the direction of the bond, but shortens the internuclear distance.

Limitations of VBT

(*i*) Since the two electrons of the shared pair constituting the covalent bond must come from two different atoms, it is evident that this theory does not give any explanation of the formation of a coordinate bond in which one of the bonded atoms furnishes both the electrons.

(*ii*) The two atoms in O_2 molecule should have close electronic shells resembling those of Ne which would give no unpaired electrons to the molecule and thus will make it diamagnetic. Actually experiments show that O_2 molecule is paramagnetic, indicating the presence of unpaired electrons in oxygen molecule.

(*iii*) This theory does not consider the formation of odd electron molecules or ions such as H_2^+ ion where no pairing of electrons occurs.

MOLECULAR ORBITAL THEORY (MOT)

In the study of VBT we have seen that the atoms in the resulting molecule retain their individual character, although they are chemically bonded in the molecule and a covalent bond between the two atoms is established by the sharing of electron pairs between the combining atoms.

According to the **molecular orbital theory** (MOT), put forward by Hund and Mulliken, orbitals are devised for the molecule as a whole. These orbitals consist of the nuclei of all the constituent atoms lying at a fixed equilibrium distance. These orbitals are called **molecular orbitals** (MO's). There is a difference between an atomic orbital (AO) and a molecular orbital (MO). In an AO the movement of an electron is influenced by only one positive nucleus, while that of an electron in a MO is influenced by two or more nuclei depending on the number of atoms contained in the molecule or on the number of MO's formed from the overlap of AO's. *Thus AO's are mono-centric while MO's are poly-centric.*

LCAO Approximation—Formation of Bonding and Antibonding MO's.

The wave function for MO's is obtained by a method known as **linear combination of AO's (LCAO)** approximation. In this method the linear combination of two AO's wave functions is brought about either by adding or by subtracting the two wave functions. Thus if ψ is the wave function of the MO obtained from two AO's, of two atoms A and B having ψ_A and ψ_B respectively as their wave functions, then

$$\Psi = \Psi_A \pm \Psi_B \qquad \ldots(5{\cdot}8)$$

Equation (5·8) holds good when the atoms A and B are identical. It clearly shows that the linear combination of Ψ_A and Ψ_B gives two MO's. One of these is represented as Ψ^b and the other as Ψ^*. These are thus given by

$$\Psi^b = \Psi_A + \Psi_B \qquad \ldots(5{\cdot}9)$$

and

$$\Psi^* = \Psi_A - \Psi_B \qquad \ldots(5{\cdot}10)$$

The MO, Ψ^b, has lower energy than that of either of the AO's from which it is formed. The MO thus leads to the formation of a

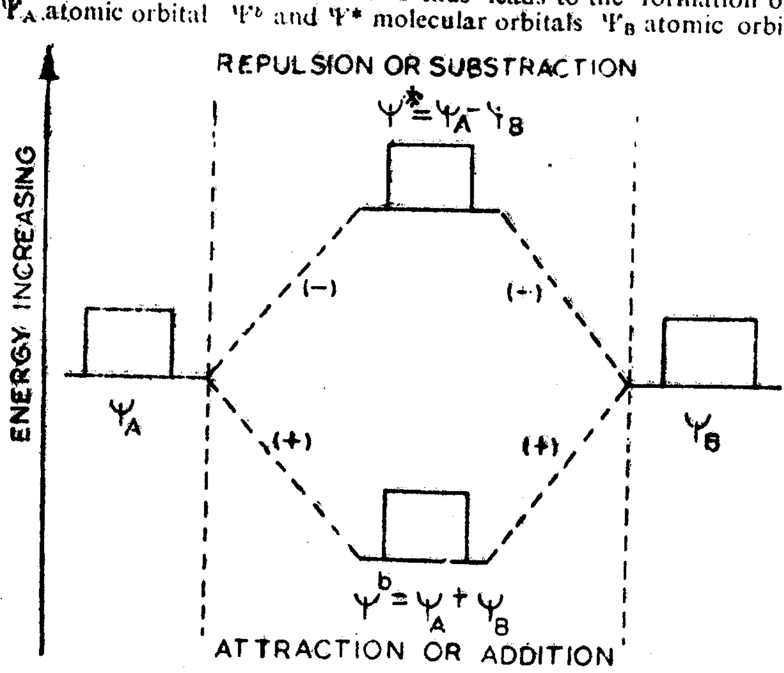


Fig. 5·9. An energy level diagram (drawn not to scale) showing the combination of two AO's having ψ_A and ψ_B as their wave functions to form MO's ; one bonding (Ψ^b) and one antibonding (Ψ^*).

stable molecule, A_2 and is, therefore, called a **bonding** MO. The other MO namely Ψ^* has higher energy than that of Ψ_A and Ψ_B and is, therefore, called an **antibonding** MO (Fig. 5·9). The superscript *b* used in Ψ^b indicates that the molecular orbital is bonding molecular orbital while * used in Ψ^* indicates that the molecular orbital is antibonding. The number of molecular orbitals is always equal to the number of atomic orbitals involved in the formation of molecular orbitals.

The plus sign in equation (5·9) indicates that the Ψ^b MO is obtained when the regions of AO's marked with positive sign overlap with each other. In this case it is said that the two AO's have been *added.* On the other hand in Eqn. (5·10) negative sign indicates that Ψ^* is obtained when the region of positive sign of one AO (say of Ψ_A) overlaps with the region of negative sign of the other (say of Ψ_B). In this case we say that the two AO's have been *subtracted.*

In order to understand the significance of bonding and antibonding molecular orbitals in terms of wave functions it is necessary to know the electric charge distribution of these orbitals.

Squaring the eqn. (5·9) we get

$$(\Psi^b)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B \qquad ...(5·11)$$

The terms Ψ_A^2 and Ψ_B^2 indicate the electronic charge densities of the wave functions Ψ_A and Ψ_B of the isolated atoms A and B while the term $(\Psi^b)^2$ indicates that of the wave function Ψ^b of the bonding molecular orbital. Obviously greater the value of $(\Psi^b)^2$, greater is the charge density between the two atomic nuclei and stronger the bond between them. It may be seen from equation (5·11) that $(\Psi^b)^2 > (\Psi_A^2 + \Psi_B^2)$ by a term $2\Psi_A\Psi_B$. This term results from the *interaction* or *overlap* of atomic orbitals. Thus larger is the overlap of atomic orbitals, greater is the charge density between the nuclei and more stable is the bond between A and B.

Fig. 5·10 contains the plot of electron charge density for bonding molecular orbital, $[(\Psi^b)^2]$ and for individual atomic orbitals (Ψ_A^2 and Ψ_B^2) against the internuclear distance (i.e. the distance between the two nuclei A and B). $(\Psi^b)^2$ has been shown by solid line and Ψ_A^2 and Ψ_B^2 by dotted lines. The points A and B represent the nuclei of the two atoms. It is obvious from this figure that there is more concentration of negative charge in the region between the two nuclei, A and B than for the individual atomic orbitals, Ψ_A and Ψ_B. Thus there is an accumulated negative charge between the nuclei which holds these together at an equilibrium internuclear distance.

Squaring eqn. (5·10), we get

$$(\Psi^*)^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B \qquad ...(5·12)$$

It may be seen from this equation that $(\Psi^*)^2 < (\Psi_A^2 + \Psi_B^2)$ by a term $2\Psi_A\Psi_B$. This means that in antibonding molecular orbital there is less charge density between the interacting atoms than there would be between the non-interacting atoms. Thus the energy of this antibonding molecular orbital is greater than the sum of the energies of the two interacting atoms A and B and the resulting bond is less stable.

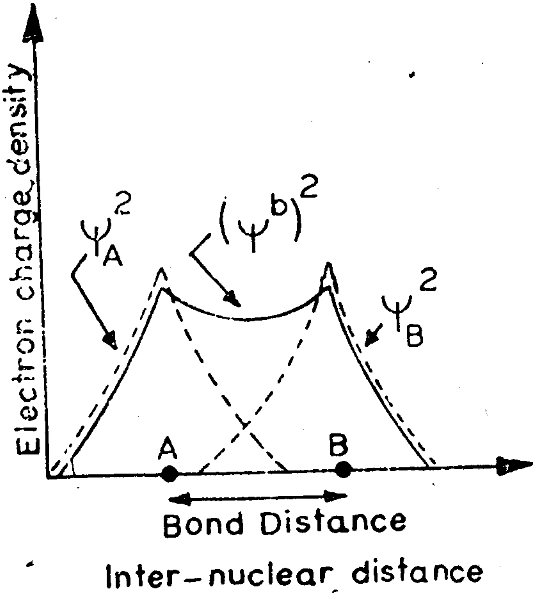


Fig. 5·10. Plots of electron charge density (square of wave function) for individual AO's (dotted lines) and Ψ^b MO (solid lines) against internuclear distance between A and B.

In Fig 5·11 $(\Psi^*)^2$ is shown by the solid line while Ψ_A^2 and Ψ_B^2 by dotted line. Plot of $(\Psi^*)^2$ touches the axis at mid-point N between the nuclei A and B. This point is called a **node point** and at this point the electron density is zero. Thus the formation of Ψ^* molecular orbital decreases the electron charge density in the region between the two nuclei A and B over that of the individual atoms. Negative charge is withdrawn from the region between the nuclei and is concentrated round the nucleus. This makes the electrons repel each other in the region between A and B. Thus we can say that in Ψ^* molecular orbital an electron, spends half of its time on each of the individual atoms and consequently is never found in the region between A and B *i.e.* the probability of finding the electron in the region between A and B is decreased.

We can say, therefore, that *a build-up of electronic charge between A and B is characteristic of the bonding or attractive state and a depletion of charge density between A and B is characteristic of antibonding or repulsive state.*

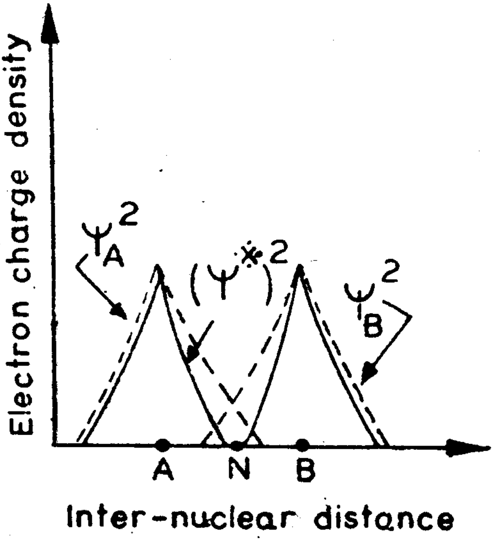


Fig. 5·11. Plots of electron charge density for individual AO's (dotted line) and Ψ^* MO (solid lines) against internuclear distance between A and B.

There are certain *conditions for effective combination of atomic orbitals* which are given below :

(*i*) The energies of the AO's combining together must be similar in magnitude or the AO's should have comparable energies. Thus in case of the formation of a homo-nuclear diatomic molecule of A_2 type, the $1s_a$-AO of the atom A_a will not combine with the $2s_b$-AO of another atom A_b of the same element, where A_a and A_b are the two atoms of the molecule A_2 since their energies are not equal. Similarly since the energy difference between 2*s*- and 2*p*- AO's is too great, they will also not combine.

But in case of the formation of hetero-nuclear diatomic molecule of AB type, such combinations may be expected.

(*ii*) The charge clouds of the AO's must overlap one another as much as possible, if they are going to combine together to form the MO's. This condition is often referred to as the *principal of maximum overlap.*

(*iii*) The AO's should have the same symmetry about the molecular axis. This condition is known as *symmetry condition for the combination of AO's.*

On the basis of this symmetry condition it is noted that some of the AO's which have comparable energies do overlap, but cannot combine to give MO's. Thus MO's cannot be formed by the overlap of an *s*-atomic orbital of atom A and one *p*-atomic orbital of atom B perpendicular to the molecular axis (*i.e.* either p_x- or p_y-orbital, since the molecular axis is the *z*-axis). The cause of non-formation of MO's is that the symmetry of *s*-orbital is not the same as that of *p*-orbital. Alternatively it can be said that + + overlap is neutralised by the + — overlap or in the other words the + — overlap cancels the bonding contribution from the + + overlap.

Thus the following pairs of AO's will not combine to from any MO's, provided that *z*-axis is assumed to be the molecular axis : (*a*) $s—p_x$ pair (*b*) $s—p_y$ pair (*c*) $p_x—p_y$ pair (*d*) $p_x—p_z$ pair (*e*) $p_y—p_z$ pair.

Molecular Orbital Configuration of Some Homo-Nuclear Diatomic Species

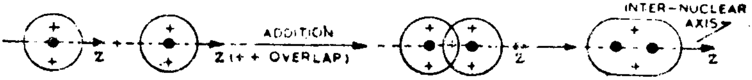
Homo-nuclear diatomic moleclues or ions have two identical atoms linked together. Thus these are A_2 type species.

The determination of molecular orbital configuration of these species can be studied under the following two headings :

(A) **Molecular orbital configuration of A_2 type species having only $\sigma_s{}^b$ and $\sigma_s{}^*$ molecular orbitals.** Under these species we shall consider the following systems :

(*i*) **The hydrogen molecule ion** ($H_2{}^+$). This ion has one hydrogen atom and one H^+ ion linked together. Each of these has 1*s*-atomic orbital. Using the LCAO method the two 1*s*-orbitals will combine together to give two molecular orbitals :

(*a*) One molecular orbital is obtained by the *addition* (*i,e.* + +overlap) of the two 1*s*-orbitals (Fig 5.12).



Two 1*s* atomic orbitals $\sigma_{1s}{}^b$-molecular orbital

Fig. 5.12 Addition (*i.e.*+ + overlap) of two 1*s*-orbitals to form $\sigma_{1s}{}^b$-molecular orbital.

It is clear from this figure that the electron in the molecular orbital will spend most of its time in the region between the two nuclei (shown by dots). The electron is now stabilised by two nuclear charges instead of one unlike an atomic orbital. *The resulting molecular orbital has lower energy than either of the two 1s orbitals and hence is called bonding molecular orbital.* Since this molecular orbital is symmetric to rotation about the inter-nuclear axis, *i.e.* it does not show any change of sign on rotation through 180° through the inter-nuclear axis, it is a sigma (σ) molecular orbital. Thus this molecular orbital is a *bonding sigma molecular orbital* and hence is represented as $\sigma_{1s}{}^b$.

(*b*) The other molecular orbital is obtained by the *subtraction* (*i.e.* + —overlap) of the two 1*s*-orbitals (Fig. 5.13).

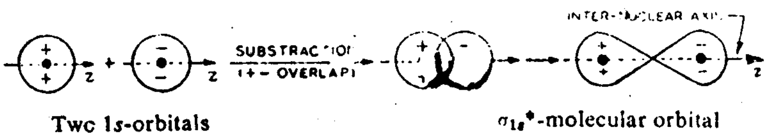


Fig 5·13 Subtraction (*i.e.* +—overlap) of two 1*s*- orbitals to form σ_{1s}^*-molecular orbital.

The resulting molecular orbital has zero electron density (*nodal plane*) in the region between the two nuclei (shown by dots). The electron in this molecular orbital is concentrated in region away from each nuclei. *The resulting molecular orbital is of higher energy than either of the two 1s-orbitals and hence is called antibonding molecular orbital.* Since this molecular orbital is also symmetric to rotation about the inter-nuclear axis, it is also a sigma (σ) molecular orbital. Thus this molecular orbital is an *antibonding sigma molecular orbital* and is, therefore, represented as σ_{1s}^*.

Molecular orbital energy level diagram as shown in Fig. 5.14 shows that the molecular orbital configuration of H_2^+ ion is : $(\sigma_{1s}^b)^1$ $(\sigma_{1s}^*)^0$.

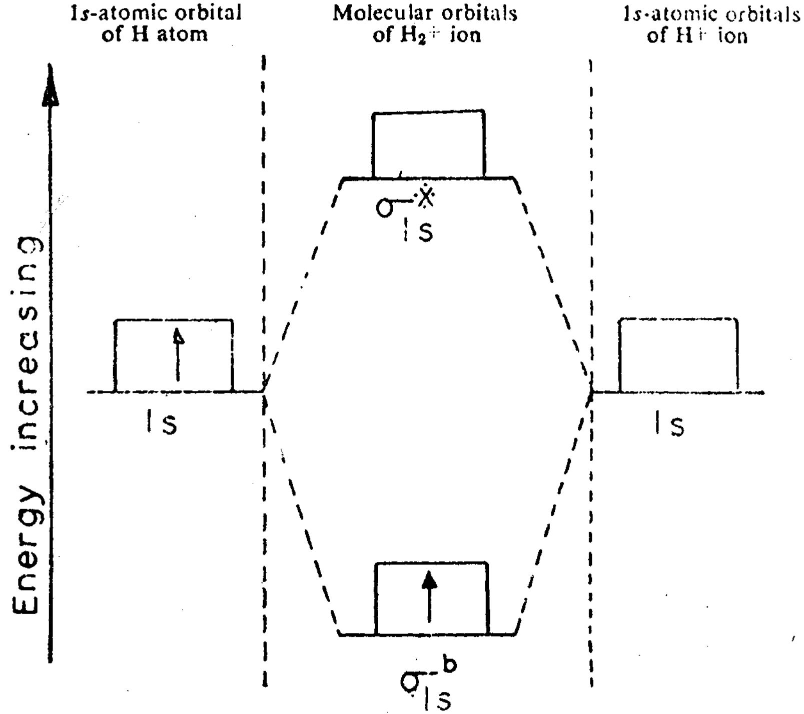


Fig 5.14 Molecular orbital energy level diagram (drawn not to scale) of H_2^+ ion.

In Fig. 5·14 the combining atomic orbitals are represented on the two extremes and the resulting molecular orbitals *viz.* σ_{1s}^b

σ_{1s}^* are shown in the centre column. In H_2^+ ion the 1*s*-orbitals of hydrogen atom and H^+ ion have the same energy and so these have been shown at the same level in the diagram. The difference between the energy of atomic orbitals and σ_{1s}^b depends on the extent to which the atomic orbitals overlap. A large overlap results in greater lowering and hence a strong bond. On the other hand a small overlap will result in a smaller lowering and hence a weak bond.

Bond order or bond multiplicity. The electrons in the bonding molecular orbitals help in the formation of bonds while those in the antibonding molecular orbitals oppose it. Bond order is defined as the number of covalent bonds between the two combining atoms of a molecule and *is equal to one-half of the difference between the number of electrons in bonding molecular orbitals* (n_b) *and in the antibonding molecular orbitals* (n_a). Thus :

$$\text{Bond order} = \tfrac{1}{2}\,(n_b - n_a)$$

$$\text{Bond order for } H_2^+ \text{ ion} = \tfrac{1}{2}\,(1-0) = \tfrac{1}{2}\sigma$$

Since the bond order of H^{2+} ion is one-half of a normal covalent bond, H_2^+ ion has low bond dissociation energy (=61 kcal/mole) and a large bond length (=1·06A°).

(*ii*) **The beryllium molecule (Be_2).** Each of the two Be atoms of Be_2 molecule has 1*s* and 2*s* atomic orbitals. Since 1*s*-atomic orbitals of both the atoms are deeply seated, the molecular orbitals formed by the overlap of these orbitals are considered to be non-bonding. Thus we are left only with the orbitals of the valence-shell namely 2*s* orbitals whose overlap should be considered.

The combination of two 2*s*-orbitals is exactly like that of 1*s*-orbitals. Thus their combination gives two σ-molecular orbitals : σ_{2s}^b which is obtained by ++ overlap (addition) and σ_{2s}^* which results from +− overlap (substraction).

Molecular orbital energy level diagram is shown in Fig. 5·15 which indicates that the molecular orbital configuration of Be_2 molecule which contains 2+2=4 electrons in valence-shell is : $(\sigma_{2s}^b)^2\,(\sigma_{2s}^*)^2$ and bond order=(2−2)/2=0.

The net energy change in zero showing that the molecular beryllium does not exist. This is in accordance with the experimental results.

(B) **Molecular orbital configuration of some A_2 type species composed of two identical atoms of *p*-block elements of second period of periodic table.** Each of the atoms of A_2 type species has 1*s*, 2*s* and 2*p* atomic orbitals. Since 1*s*-atomic orbitals of both the atoms are deeply seated, the molecular orbitals formed by the overlap of these orbitals are considered to be non-bonding. Thus we are left only with the atomic orbitals of the valence-shell *viz.* 2*s* and 2*p* orbitals whose overlap should be considered.

(a) **Overlap of two 2s-orbitals.** The combination of two 2s-orbitals, as already discussed under beryllium molecule, gives $\sigma_{2s}{}^{b}$ and $\sigma_{2s}{}^{*}$ molecular orbitals.

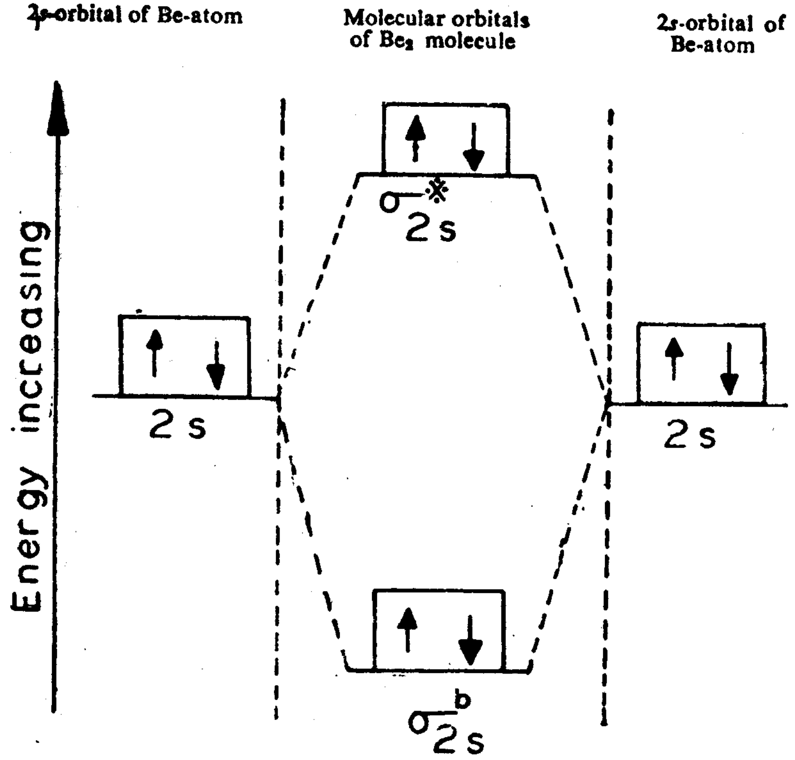
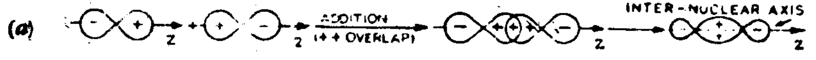


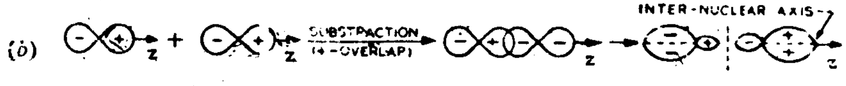
Fig. 5·15. Molecular orbital energy level diagram (drawn not to scale) of Be_2 molecule

(b) **Overlap of $2p_z$-orbitals.** z-axis is generally taken as the molecular (*i.e.* inter-nuclear) axis, though it is entirely arbitrary. Quite obviously x- and y-axes will be perpendicular to the molecular axis *viz.* **z-axis.**

Like the two 2s-orbitals, the two $2p_z$ orbitals will also give two σ-molecular orbitals : $\sigma_z{}^{b}$ and $\sigma_z{}^{*}$. $\sigma_z{}^{b}$ molecular orbital results from



Two $2p_z$ orbitals $\sigma_z{}^{b}$ molecular ortital



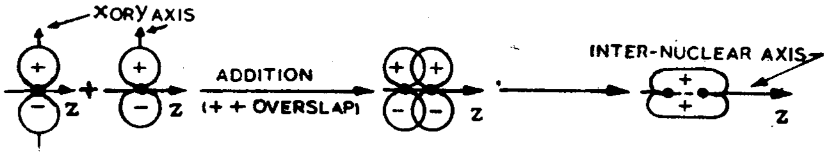
Two $2p_z$ orbitals $\sigma_z{}^{*}$ molecular orbital

Fig. 5·16. Overlap of two $2p_z$ orbitals by addition and subtraction method to form $\sigma_z{}^{b}$ and $\sigma_z{}^{*}$ molecular orbitals respectively.

++ overlap (addition) while σ_z^* is obtained from +− overlap (substraction). Both the overlaps take place along the molecular axis (Fig. 5·16).

(*c*) **Overlap of two $2p_x$ and $2p_y$ orbitals.** $2p_x$ orbital of one atom overlaps with $2p_x$ orbital of the other atom along the *x*-axis (which is perpendicular to the molecular axis *viz.* *z*-azis) to give two π-molecular orbitals : $\pi_x{}^b$ and $\pi_x{}^*$. Similarly the overlap of two $2p_y$ orbitals also gives two π-molecular orbitals : $\pi_y{}^b$ and $\pi_y{}^*$ (*see* Fig. 5·17).

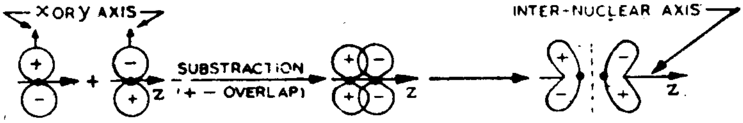
(*a*)



Two $2p_x$ or $2p_y$ orbitals

$\pi_x{}^b$ or $\pi_y{}^b$ molecular orbital

(*b*)



Two $2p_x$ or $2p_y$ orbitals

$\pi_x{}^*$ or $\pi_y{}^*$ molecular orbital

Fig. 5·17. Addition and substraction of two $2p_x$ atomic orbitals to form $\pi_x{}^b$ and $\pi_x{}^*$ molecular orbitals. Similarly the combination of two $2p_y$ atomic orbitals to form $\pi_y{}^b$ and $\pi_y{}^*$ molecular orbitals can also be shown.

Thus we find that $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on one atom on combining with $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals on the other atom give in all eight molecular orbitals which are :
$\sigma_{2s}{}^b$, $\sigma_{2s}{}^*$, $\sigma_z{}^b$, $\sigma_z{}^*$, $\pi_x{}^b$, $\pi_x{}^*$, $\pi_y{}^b$ and $\pi_y{}^*$. σ^b and σ^* molecular orbitals are *symmetric to rotation* about the internuclear axis, while π^b and π^* molecular orbitals are *unsymmetric to rotation*.

Relative order of energy of these molecular orbitals is :

Energy increasing ⟶

$$\sigma_{2s}{}^b < \sigma_{2s}{}^* < \pi_x{}^b = \pi_y{}^b < \sigma_z{}^b < \pi_x{}^* = \pi_y{}^* < \sigma_z{}^*$$

Stability decreasing ⟶

This order is based on the fact that there is an extra combination of $2s$-atomic orbital on one atom with $2p_z$ atomic orbital on the other atom.

From this order it may be noted that the $\pi_x{}^b$ and $\pi_y{}^b$ molecular orbitals are called **degenerate orbitals**. In a similar manner $\pi_x{}^*$ and $\pi_y{}^*$ molecular orbitals are also degenerate.

The molecular orbitals are filled with electrons in the increasing order of their energy, i.e. the molecular orbital having the lowest energy is filled up first while that with the highest energy is filled up in the last. Hund's rule is also obeyed by the degenerate molecular orbitals. According to this rule the orbitals are first singly filled and pairing starts when more electrons are to be accommodated.

Using the relative energy order of various molecular orbitals given above we may now determine the molecular orbital configuration of some molecules composed of *p*-block elements of second period of periodic table.

(*i*) **The boron molecule (B_2).** It is the first element in which *p*-orbital starts. Its valence-shell configuration is : $2s^2$, $2p_x^1\ 2p_y^0\ 2p_z^0$ with three electrons. Thus B_2 molecule has in all $3+3 = 6$ electrons and its molecular orbital configuration is :

$$(\sigma_{2s}^b)^2, (\sigma_{2s}^*)^2, (\pi_x^b)^1 = (\pi_y^b)^1 \quad (\textit{see}\ \text{Fig. 5·18})$$

Bond order of B_2 molecule in equal to $\frac{1}{2}(4-2) = 1$ which shows that the molecule is formed by a weak π-bond and has two unpaired electrons in π-molecular orbitals. This has been verified by experiments.

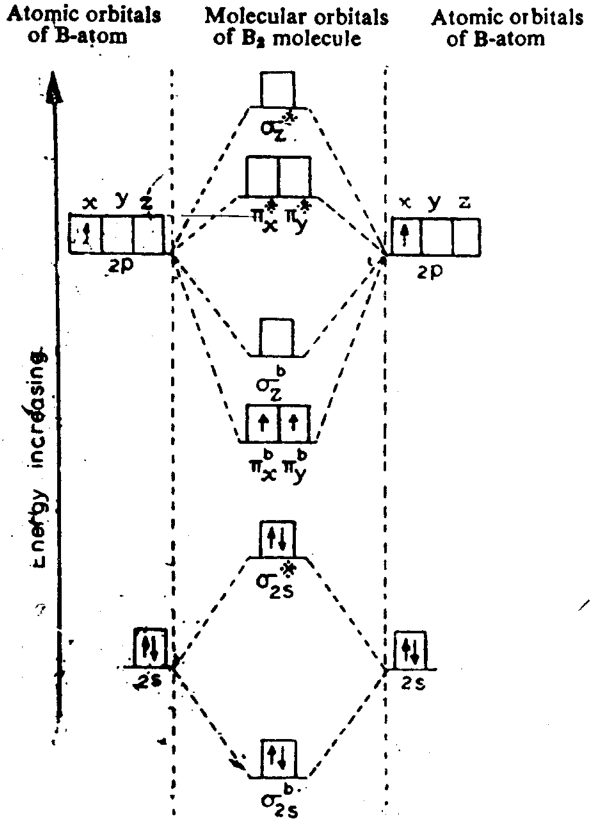


Fig. 5·18. Molecular orbital energy level diagram of B_2-molecule.

(*ii*) **The nitrogen molecule (N_2).** N-atom has $2s^2$, $2p^1_x\ 2p^1_y\ 2p_z^1$ electronic configuration with five electrons. Thus we have 10 electrons in all to be filled in molecular orbitals. The molecular orbital configuration of N_2 molecule is :

$$(\sigma_{2s}{}^b)^2,\ (\sigma_{2s}{}^*)^2,\ (\pi_x{}^b)^2 = (\pi_y{}^b)^2,\ (\sigma_z{}^b)^2 \quad (\textit{see}\ \text{Fig. 5·19})$$

and its bond order is equal to $\frac{1}{2}$ (8—2) = 3 which indicates that the molecule has one σ and two π-bonds. Bond order of three is in accordance with the very high bond energy (= 225 kcal/mole).

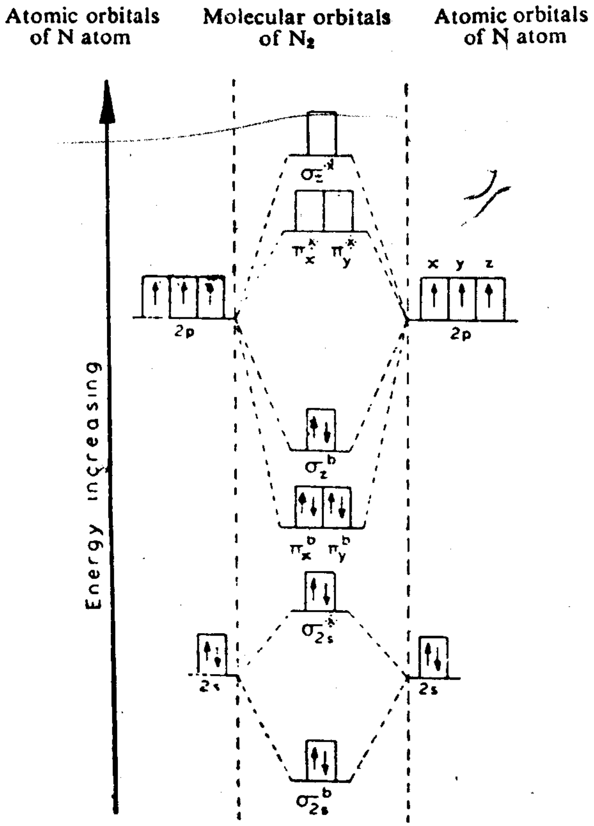


Fig. 5·19. Molecular orbital energy level diagram of N_2 molecule.

(*iii*) **The oxygen molecule (O_2).** Oxygen atom has the electronic configuration : $2s^2$, $2p^2_x\ 2p^1_y\ 2p^1_z$ with the six electrons. Thus in all there are 12 electrons to be accommodated in the molecular orbitals. The molecular orbital configuration of O_2 is :

$$(\sigma_{2s}{}^b)^2,\ (\sigma_{2s}{}^*)^2,\ (\pi_x{}^b)^2 = (\pi_y{}^b)^2\ (\sigma_z{}^b)^2,\ (\pi_x{}^*)^1, = (\pi_y{}^*)^1$$

Its bond order is equal to $\frac{1}{2}$ (8—4) = 2. Thus O_2 molecule consists of a double bond which is composed of one σ-, and one π-bond. It has bond dissociation energy = 118 kcal/mole and bond length = 1·21 Å. Its molecular orbital configuration as given above shows that it is paramagnetic due to the presence of two unpaired electrons which are in $\pi_x{}^*$ and $\pi_y{}^*$ molecular orbitals.

From the above discussion it is clear that a A_2 molecule having greater value of bond order is more stable than that having less value of bond order, *e.g.* since bond order of N_2 molecule (=3) is greater than that of O_2 molecule (=2), N_2 is more stable than O_2.

(*iv*) **O_2^- ion.** This ion has 6+7=13 electrons in its valence-shell and hence its molecular orbital configuration is :

$$(\sigma_{2s}{}^b)^2, (\sigma_{2s}{}^*)^2, (\pi_x{}^b)^2 = (\pi_y{}^b)^2, (\sigma_z{}^b)^2, (\pi_x{}^*)^2 = (\pi_y{}^*)^1$$

Thus its bond order is equal to $\frac{1}{2}(8-5)=1\frac{1}{2}$. This value shows that one bond is a two-electron σ-bond and the other bond is one-electron π-bond.

Molecular Orbital Configuration of Some Hetero-nuclear Diatomic Species

Hetero-nuclear diatomic species have two different atoms linked together. Thus these are AB type species. Here we shall consider those AB type species in which B has higher electronegativity than A and both the atoms A and B have 2*s* and 2*p* atomic orbitals, *i.e.* A and B are *p* block elements of second period of the periodic table.

The MOT treatment of such types of hetero-nuclear diatomic molecules and molecule ions by LCAO-approximation method is not fundamentally different from that of homo-nuclear diatomic molecules of A_2 type, except that MO's are not symmetric with respect to a plane perpendicular to and bisecting the internuclear axis.

Let as consider the following hetero-nuclear diatomic species.

(*i*) **Carbon monoxide molecule** (CO). Evidently CO molecule has 10 valence electrons : four from carbon atom ($2s^2p^2$) and six from oxygen atom ($2s^2p^4$). Its molecular orbital energy level diagram as represented in Fig. 5·20 shows that its molecular orbital configuration is :

$$(\sigma_{2s}{}^b)^2, (\sigma_{2s}{}^*)^2, (\pi_x{}^b)^2 = (\pi_y{}^b)^2, (\sigma_z{}^b)^2, (\pi_x{}^*)^0 = (\pi_y)^0, (\sigma_z{}^*)^0$$

Thus its bond order is equal to $\frac{1}{2}(8-2) = 3$ showing that carbon and oxygen atoms in CO molecule are linked together by one σ- and two π-bonds.

The following points may be noted from the molecular orbital energy level diagram shown in Fig. 5·20.

(*a*) Since the electronegativity of oxygen is greater than that of carbon, the 2*s* and 2*p* orbitals of oxygen have been placed lower than the 2*s* and 2*p* orbitals of carbon.

(*b*) Since CO is isoelectronic with N_2, it has the same molecular orbital configuration as N_2 molecule does.

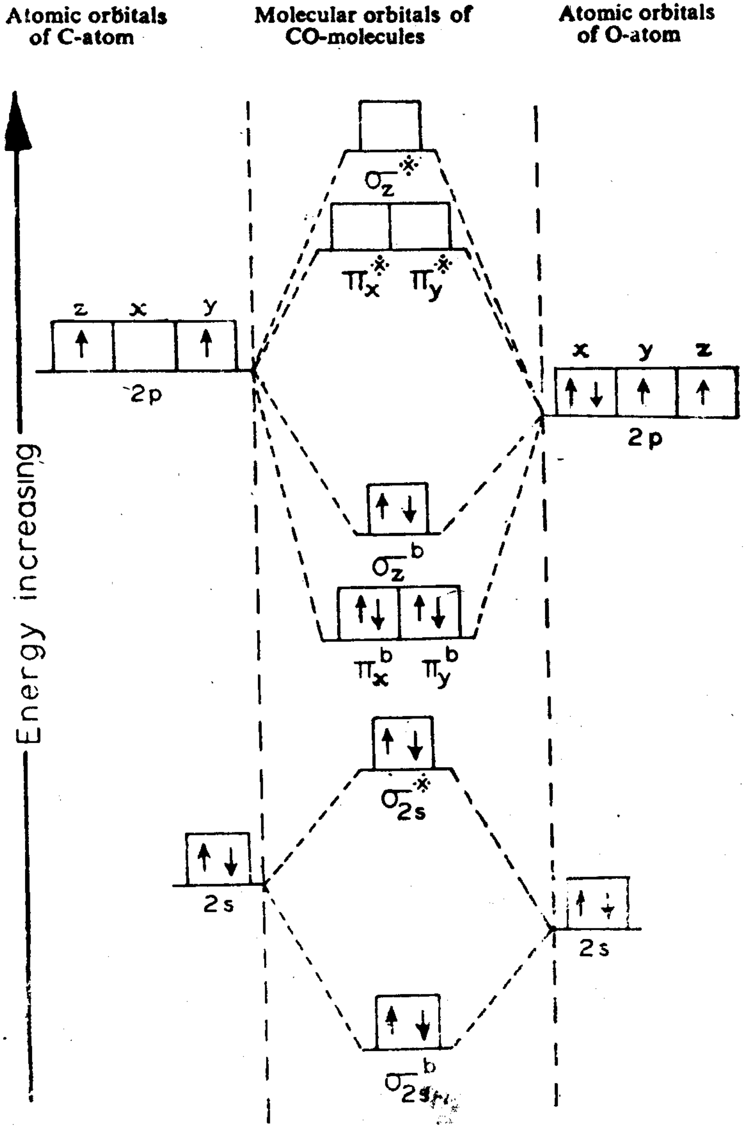


Fig. 5·20. Molecular orbital energy level diagram (drawn not to scale) of CO molecule.

Coulson's MOT treatment of CO molecule. Coulson has, however, suggested a modification of the above MO-configuration of CO molecule. According to him, the concept of hybridisation is used.

Valence-shell electronic configuration of carbon atom is $2s^2$, $2p_x^0\ 2p_y^1\ 2p_z^1$. $2s$ and $2p_z$ atomic orbitals hybridise to form two *sp*-hybrid orbitals which we have represented as $(sp)_C$. Thus, after carbon atom has been *sp*-hybridised, its configuration becomes $(sp)_C^2\ (sp)_C^1\ 2p_x^0\ 2p_y^1$. Similarly $2s$ and $2p_z$ atomic orbitals on oxygen atom ($O \longrightarrow 2s^2, 2p_x^2\ 2p_y^1\ 2p_z^1$) also give two *sp*-hybrid orbitals and the configuration of oxygen atom then becomes $(sp)_O^2$ $(sp)_O^1\ 2p_x^2\ 2p_y^1$. Thus

$$C \longrightarrow (sp)_C^2\ (sp)_C^1\ 2p_x^0\ 2p_y^1$$

$$O \longrightarrow (sp)_O^2\ (sp)_O^1\ 2p_x^2\ 2p_y^1$$

Electron-pair in $(sp)_C$ and $(sp)_O$ hybrid orbitals are not involved in bonding and hence are called σ-non-bonding electron-pairs (σ_{nb}-pairs). Thus CO molecule has two lone-pairs (*lp's*) : one is on carbon atom (see Fig. 5·21). $(sp)_C$ hybrid orbital containing a *lp* has higher energy than that having a single electron, points away from O-atom (*i.e.* extends away from the C—O bond), has a high degree of *p* character, is very reactive and hence accounts for the properties of CO. Thus we can say that there is a lone pair on C-atom which is predominantly *p*-orbital pointing away from O-atom.

$(sp)_O$ hybrid orbital containing a *lp* is of lower energy than that containing a single electron, has a high degree of *s*-orbital character and hence is very stable (*i.e.* unreactive) hybrid orbital.

Now we are left with two singly filled $(sp)_C$ and $(sp)_O$ hybrid orbitals and two 2*p*-atomic orbitals ($2p_x$ and $2p_y$) on both the atoms which overlap together in pair to give the following molecular orbitals.

$(sp)_C + (sp)_O$ give σ_{sp}^b and σ_{sp}^* molecular orbitals

$2p_x$-AO on C-atom$+2p_x$-AO on O-atom give π_x^b and π_x^* MO's

$2p_y$-AO on C-atom$+2p_y$-AO on O-atom give π_y^b and π_y^* MO's

The relative order of energy of these molecular orbitals and *sp*- hybrid orbitals containing *lp's* on each atom is :

$$(sp)_O < \sigma_{sp}^b < \pi_x^b = \pi_y^b < (sp)_C < \pi_x^* = \pi_y^* < \sigma_{sp}^*$$

and hence the molecular orbital configuration of CO is :

$$(sp)_O^2, (\sigma_{sp}^b)^2, (\pi_x^b)^2 = (\pi_y^b)^2, (sp)_C^2, (\pi_x^*)^0 = (\pi_y^*)^0, (\sigma_{sp}^*)^0$$

(*see* Fig. 5·21)

Thus bond order of CO $= \frac{1}{2}(6-0) = 3$ showing that carbon and oxygen in CO molecule are linked together by a triple bond ($1\sigma + 2\pi$ bonds).

σ_{sp}^b molecular orbital is mostly on oxygen atom. π_x^b and π_y^b molecular orbitals (degenerate MO's) are mostly on O-atom, since O-atom contributes more to the formation of these MO's than does C-atom (Note $x_O > x_C$). These MO's are leaning somewhat towards the O-atom. One of these two degenerate π MO's as shown in Fig. 5·22. The other π-MO is at right angles *i.e.* in front and behind the paper to the one shown.

In the formation of π_x^* and π_y^* molecular orbitals (degenrate molecular orbitals) carbon atom makes a larger contribution than the O-atom, since, $x_C < x_O$. Both of these degenerate π^* MO's are also at right angles to each other. One of these π^*-MO's is shown in Fig. 5·22.

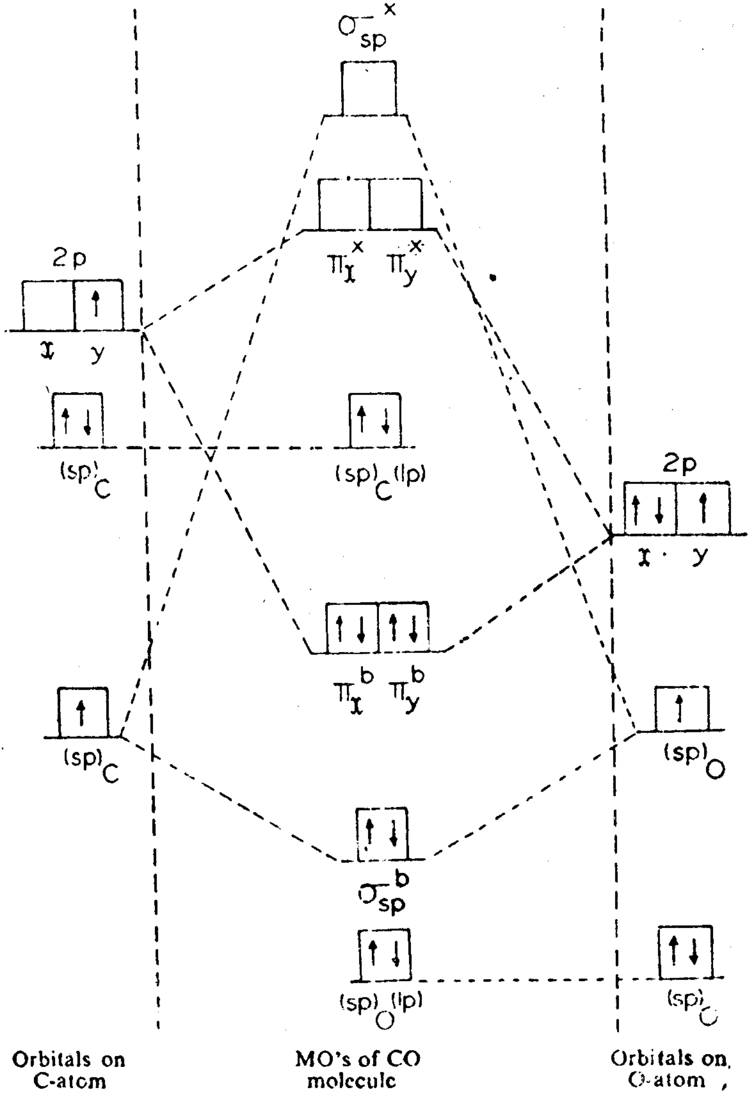


Fig. 5·21. MO energy level diagram (drawn not to scale) for CO molecule as suggested by Coulson.

These π^* MO's are much closer in energy to the *p*-orbitals of C-atom than the *p*-orbitals of O-atom and are, therefore, concentrated mostly on C-atom.

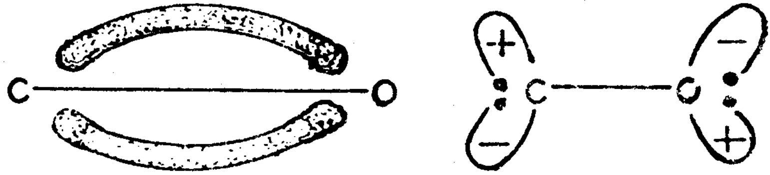
Both these π^* MO's are empty and can, therefore, accept electron pairs by interacting with appropriate filled orbitals of transitional elements. These π^* MO's are, therefore, called **acceptor MO's**. This acceptor property of these MO's is very important in considering the M ——→ L bond in metal carbonyls where M is the metal and L indicates a ligand such as CO.

$(sp)_C$ hybrid orbital having a *lp*

$(sp)_O$ hybrid orbital having a *lp*

Filled σ_{sp}^b molecular orbital

Empty σ_{sp}^* molecular orbital



One filled π_z^b molecular orbital. Similar is another filled π_y^b molecular orbital which is at right angles to the one shown.

One empty π_z^* molecular orbital. Similar is another empty π_y^* molecular orbital which is at right angles to the one shown.

Fig. 5·22. Different molecular orbitals of CO molecule.

(*ii*) **Nitrosyl ion** (NO^+). Since NO^+ ion is isoelectronic with N_2 molecule (both have 10 electrons in their valence-shell), it has the same molecular orbital configuration as N_2 molecule *viz*.

$$(\sigma_{2s}^b)^2, (\sigma_{2s}^*)^2, (\pi_x^b)^2 = (\pi_y^b)^2, (\sigma_z^b)^2$$

Its bond order is equal to ½ (8—2)=3 which represents one σ and two π-bonds.

(*iii*) **Nitric oxide molecule** (NO). This molecule has 11 electrons in its valence-shell : five from nitrogen atom ($2s^2p^3$) and six from oxygen atom ($2s^2p^4$). Thus it has the following molecular orbital configuration :

$$(\sigma_{2s}^b)^2, (\sigma_{2s}^*)^2, (\pi_x^b)^2 = (\pi_y^b)^2, (\sigma_z^b)^2, (\pi_x^*)^1 = (\pi_y^*)^0$$

The bond order equal to $(8-3)/2 = 5/2$ shows that nitrogen and oxygen in the molecule are linked together by one σ and two π-bonds. σ-bond is due to the electron pair in σ_z^b molecular orbital and the two π-bonds are due to π_x^b and π_y^b molecular orbitals. One unpaired electron is present in π_x^* molecular orbital. Thus, NO molecule has two 2-electron bonds and one 3-electron bond and can, therefore, be represented as

$$:\mathrm{N}\overset{\cdot\times\times}{=}\mathrm{O}^{\times}_{\times}$$

This structure well accounts for the lower bond strength and larger bond length as compared with N_2 molecule. It also explains the paramagnetic character of NO.

Valency Bond Theory *Vs* Molecular Orbital Theory

(A) Similarities

(*i*) Both the theories are the interpretation of covalent bond.

(*ii*) According to both the theories the AO's of the two atoms must overlap to from a covalent bond. The AO's overlapping each other must have the same symmetry and must be of the same energy.

(*iii*) According to both, the electronic charge resides in the region between the atomic nuclei.

(*iv*) Both the theories postulate that a covalent bond possesses directional properties.

(B) Differences.

MOT	*VBT*
(*i*) MO's are formed by LCAO approximation method. The AO's involved in the formation of these MO's are from valence shell of two atoms.	(*i*) Two AO's give an inter-atomic orbital obtained by the combination of the space functions of two unpaired electrons ; one being in each of the two AO's.
(*ii*) AO's of the resulting molecule lose their individual identity.	(*ii*) The resulting molecule consists of atoms which, although, interacting, retain a large measure of their individual character.
(*iii*) MO's are poly-centric.	(*iii*) AO's are mono-centric.

SHAPES OF COVALENT MOLECULES

The bonds formed by the central atom with other atoms in a covalent molecule may have different *orientations* (*or directions*) with respect to the central atom. Thus due to their different relative orientations the molecules have different shapes or geometries and different bond angles between a pair of bonds.

In order to predict the geometry of a molecule the following models have been proposed :

(1) Valence Shell Electron Pair Repulsion (VSEPR) Theory

This theory is largly due to Gillespie and Nyholm. The electrons already present in the valence-shell of the additional electrons aquired by it as a result of bonding with other atoms are called its valence-shell electrons. According to this theory, the geometry of a molecule depends on the number of bonding and non-bonding electron pairs in the central atom which arrange themselves in such a way that there is a minimum repulsion between them so that the molecule has minimum energy (*i.e.* maximum stability). Since there can only be one orientation of orbitals corresponding to minimum energy, the molecule has a definite shape.

The following rules have been proposed by Gillespie to explain the shape of some covalent molecules.

Rule 1. *If the central atom of a molecule is surrounded only by bonding electron pairs (bp's) and not by non-bonding electron pairs, called lone pairs lp's, the geometry of the molecule will be regular, i.e.* it will be *linear, triangular planar regular tetachedral, trigonal bipyramidal* and *regular octahadral* for 2, 3, 4, 5 and 6 bonding electron-pairs. $BeCl_2$ (*bp's* = 2, *linear*), BCl_3 (*bp's* = 3, *triangular planar*) $SnCl_4$ (*bp's* = 4, *regular tetahedral*), PCl_5, (*bp's* = 5, *trigonal bipyramidal*) and SF_6 (*bp's* = 6, *regular octahedral*) are important examples. In all these molecules *lp's* = 0.

Rule 2. *When the central atom in a molecule is surrounded by both bp's and lp's, the molecule does not have a regular shape.*

The alteration or distortion in shape is due to the alteration in bond angles which arises due to the presence of *lp's* on the central atom. How the presence of *lp* causes an alteration in bond angles can be explained as follows :

At a fixed angle the closer the electron-pairs are to the central atom, the closer they are to each other and hence greater is the repulsion between them.

Since the lone pair electrons are under the influence of only one positive centre (*i.e.*, nucleus), they would be expected to occupy a broader orbital with a greater electron density radially distributed close to the central atom than the bond pair electrons which are under the influence of two positive centres. Thus *lp* is much closer to the central atom than the *bp*, and so it is believed that *lp* will exert more repulsion on any adjacent electron pair than a *bp* will do on the same adjacent electron pair. Now if the adjacent electron pair is a *lp*, then

$$(lp-lp) > (lp-bp) \qquad \dots \quad (1)$$

where $(lp-lp)$ represents the repulsive force between two *lp*'s and $(lp-bp)$ represents the repulsive force between a *lp* and a *bp*.

If the adjacent electron pair is a *bp*, then

$$(lp-bp) > (bp-bp) \qquad \dots \quad (2)$$

where $(bp-bp)$ represents the repulsive force between two bonding pairs. Combination of relations (1) and (2) gives

$$(lp-lp) > (lp-bp) > (bp-bp)$$

Thus the repulsion between two *lp's* is maximum in magnitude, that between a *lp* and a *bp* is intermediate while that between two *bp*'s is the minimum. Thus since a *bp* experiences less repulsion from another *bp* than from a *lp* ; it (*i.e.*, *bp*) becomes closer to the *bp* and a contraction in the bond angle (*i.e.*, the angle between the two *bp's*) occurs.

More the number of *lp's* on a central atom, the greater is the contraction caused in the angle between the *bp's*. This fact is clear when we compare the bond angles in CH_4, NH_3 and H_2O molecules.

Molecules :	CH_4	NH_3	H_2O
No. of *lp's* on the central atom :	0	1	2
Bond angle (Angle between two *bp's*) :	109·5°	107 5°	105 5°
Contraction in bond angle relative to that of CH_4	0	109.5° − 107.5 = 2°	109.5° − 105.6 = 4°

Rule 3. B--A—B *bond angle decreases with the increase in electronegativity of atom* B *in* AB *molecule wherein* A *is the central atom*. This is due to the fact that with the increase in electronegativity of atom B, the average position of bonding electron-pair moves further from the central atom A and hence the repulsion exerted by bonding electron-pair on the electron-pair on atom A decreases. This decrease in repulsion decreases the bond engle. For example :

(*i*) PI_3 (102°) > PBr_3 (101·5°) > PCl_3 (100°)

(*ii*) AsI_3 (101°) > $AsBr_3$ (100·5°) > $AsCl_3$ (98.4°)

Rule 4. *Bond angles involving multiple bonds are generally larger than those involving only single bonds However, the multiple bonds do not affect the geometry of a molecule.*

Rule 5. *Repulsion between electron-pairs in filled shells are larger than the repulsion between electron-pairs in incompletely filled shells*, *e.g.* compare H—O—H and H—S—H bond angles in H_2O and H_2S molecules : OH_2 (105.5°) >> SH_2 (92·2°). The central atoms in these molecules *viz.* O and S respectively have eight electrons in their valence-shell (six electrons of the central atom + two electrons acquired from two H-atoms). Thus the valence-shell of O-atom in H_2O molecule which contains *four* orbitals (one 2*s* and three 2*p* orbitals) is completely filled while that of S-atom in H_2S molecule which contains *nine* orbitals (one 3*s*, three 3*p* and five 3*d* orbitals) is incompletely filled. The maximum capacity of the valence shell of S-atom is of $2(3s^2)+6(3p^6)+10\ (3d^{10}) = 18$ electrons.

Limitations of VSEPR Theory. (*i*) VSEPR theory cannot explain the shapes of molecules which have very polar bonds, *e.g.* Li_2O should have the same structure as H_2O but in fact it is linear.

(*ii*) This theory is unable to explain the shapes of molecules having extensive delocalised π-electron systems.

(*iii*) This theory cannot explain the shapes of certain molecule which have an inert-pair of electrons.

(*iv*) This theory is not able to predict the shapes of certain transition metal complexes.

(2) Hybridisation of Atomic Orbitals

We have seen that VBT according to which a covalent bond results by the overlap of atomic orbitals requires the presence of unpaired electrons in the overlapping atomic orbitals of an atom to enable it to form covalent bonds. Thus according to this theory Be($2s^2$), B($2s^2\ 2p_x^{\circ}\ 2p_y^{\circ}\ 2p_z^{\circ}$) and C ($2s^2$, $2p_x^1\ 2p_y^1\ 2p_z^{\circ}$) which have respectively 0, 1 and 2 unpaired electrons in their valence-shell should be expected to form no covalent bond, one covalent bond and two covalent bonds with a univalent atom like H or X (X = F, Cl, Br or I), but experiments show that Be, B and C form two (*i.e.* dicovalency) three (tricovalency), and four (teracovalency) covalent bonds respectively. VBT says that in order to enable these elements to show discovalency, tricovalency and tetracovalency, one of the paired $2s$-electrons is promoted to the vacant $2p$-orbitals. The promotion of a $2s$-electron to $2p$-level requires some energy which is generally available from the heat of reaction taking place when covalent bonds are formed, provided that there is no change of principal quantum number, n, during the promotion of the electron. The promotion of a $2s$-electron to $2p$-levels in case of Be, B and C gives respectively 2, 3 and 4 unpaired electrons which explains the discovalency, tricovalency and tetracovalency of these elements.

The arrangement of the electrons in the atom obtained after promtion of electrons is sometimes referred to as an **excited valence state** of the atom. Excited valence state of atoms are generally denoted by an asterisk. Thus :

Be (Ground state) : $2s^2$, $2p_x^{\circ}2p_y^{\circ}\ 2p_z^{\circ}$; Be* (Excited state) : $2s^1$, $2p_x^{\circ}2p_y^1 2p_z^{\circ}$

B (Ground state) : $2s^2$, $2p_x^{\circ}2p_y^1\ 2p_z^{\circ}$; B* (Excited state) : $2s^1$, $2p_x^{\circ}2p_y^1 2p_z^1$

C (Ground state) : $2s^2$, $2p_x^1 2p_y^1 2p_z^{\circ}$; C* (Excited state) : $2s^1$, $2p_x^1 2p_y^1 2p_z^1$.

Evidently, if for example, the structure of CH_4 molecule is explained on the basis of simple approach of overlap of AO's of C*-atom with $1s$-AO's of four H atoms (say H_a, H_b, H_c, and H_d), we should get a structure shown in Fig. 5·23 consisting of four covalent σ-bonds namely s-s σ-bond, s-p_x σ bond, s-p_y σ-bond, s-p_z σ-bond.

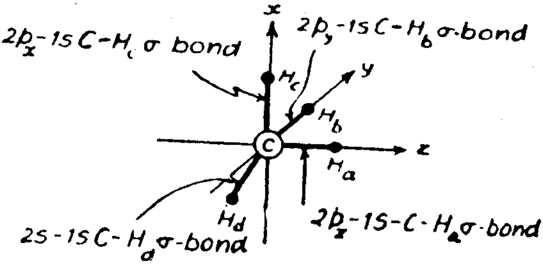


Fig. 5·23. Structure of CH_4 molecule if carbon atom uses pure AO's : $2s$, $2p_x$, $2p_y$ and $2p_z$ to form four C–H bonds

H_a-C-H_b bond angle = H_b-C-H_c bond angle = H_a-C-H_c bond angle = 90°
H_d-C-H_a bond angle = H_d-C-H_b bond angle = H_d-C-H_c bond angle = 125°

The three σ-bonds involving p-orbitals would be at right angles to each other while the fourth bond namely s-s σ-bond would be at about 125° with respect to the other three bonds.

Also s-s σ-bond would be weaker than the three σ-bonds involving p-orbitals which would be equivalent in energy.

Experiments show, however, that CH_4 does not have this type of structure. All the H—C—H bond angles are found to be equal, all the C—H bonds are equal in energy and these are arranged tetrahedrally so that a methane molecule has a regular tetrahedral shape.

Similarly, the three bonds in BX_3 or BH_3 are all equivalent and coplanar with bond angles of 120° which would not be possible if three bonds are derived from the overlap of two $2p$- and one $2s$ AO's of B atom with p-AO's of X-atom or $1s$-AO of H-atom.

BeX_2 has two bonds which are collinear and are of equal strength which would not be possible if the structure of BeX_2 ($X = Cl$, Br or I) involves the overlap of pure one $2s$ and one $2p$ AO's of Be with p-AO's of X-atom only.

In order to account for the equivalence of four C—H σ-bonds in CH_4 molecule we assume that the four orbitals of C* atom *viz.* $2s$ $2p_x$ $2p_y$ and $2p_z$ are mixed or hybridised together to form four equivalent (*i.e.* of the same energy) orbitals called *hybrid orbitals* or simply *hybrids* which are directed towards the four corners of a regular tetrahedron. *This type of mixing of pure atomic orbitals to give equal number of hybrid orbitals is referred to as hybridisation.* The carbon atom in this case is said to be sp^3 hybridised. This is a hypothetical process. Similarly Be and B atoms in BeX_2 and BX_3 molecules are said to be sp and sp^2 hybridised.

Rules for hybridisation. Following are the rules for hybridisation :

(*i*) *Only orbitals of similar energies belonging to the same atom or ion can hybridise together.*

(*ii*) *Number of hybrid orbitals produced is equal to the number of orbitals undergoing hybridisation. Hybrid bonds are stronger than the single-non-hybridised bonds of comparable energy.*

(*iii*) *Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They differ from one another in their orientation in space.*

(*iv*) For equivalent hybrids the orientation in space is determined by (*a*) *the number of orbitals mixed and consequently the number of hybrids obtained, and* (*b*) *which of x-, y-, and z-axes are preferred by the orbitals when pure.*

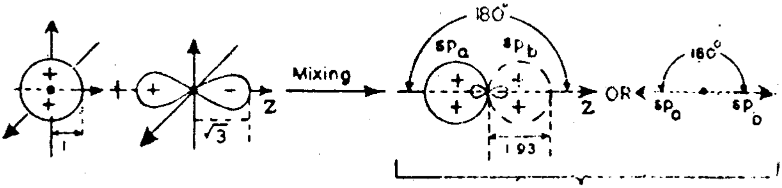
(*v*) *From the type of hybridisation one can predict the geometry and bond angles of a molecule.*

(*vi*) *An orbital which has been used to build up a hybrid orbital is no longer available to hold electron in its pure form.*

Types of hybridisation and shapes of some common molecules with σ- or $\sigma+\pi$-bonds.

Following are the common types of hybridisation.

(1) **sp-hybridisation** ($s+p_z$ AO's). A linear combination of one s- and one p_z wave functions (*i.e.* orbitals) in suitable proportion gives two sp-hybrid wave functions (or hybrid orbitals), sp_a and sp_b whose formation is shown in Fig. 5·24. This type of hybridisation is called **sp-hybridisation**; and the hybrid orbitals formed are called **linear** (or **digonal**) **hybrid orbitals.**



s-orbital p_z-orbital Two linear sp-hybrid orbitals *viz.* sp_a and sp_b

Fig 5.24. Formation of two linear (or digonal) sp-hybrid orbitals from the combination of s- and p_z-atomic orbitals.

Properties of sp-hybrids

(*i*) These have the properties of both s- and p-orbitals. These point in opposite direction along the axis of the p-orbital *i.e.*, their arrangement is linear (or digonal) and they make an angle of 180° with each other. Thus these have the directional properties of p-orbitals, but are fatter than pure p-orbitals.

(*ii*) sp_a and sp_b hybrid orbitals are completely equivalent in energy.

(*iii*) Each sp-hybrid orbital is stronger than both pure s- and p-orbitals from which it originates. Its predicted relative overlapping power is 19·3 (*see* Fig. 5·24).

(*iv*) The normalised wave functions, $\psi\,(sp_a)$ and $\psi\,(sp_b)$ for sp_a and sp_b hybrid orbitals are listed below :

$$\psi\,(sp_a) = \frac{1}{\sqrt{2}}\Big[\psi\,(s)+\psi(p_z)\Big]$$

$$\psi\,(sp_b) = \frac{1}{\sqrt{2}}\Big[\psi\,(s)-\psi(p_z)\Big]$$

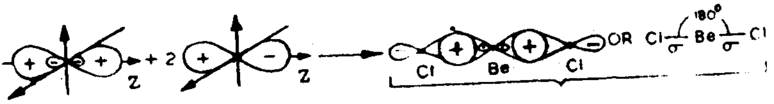
In the deduction of these equations it has been assumed that the molecular axis is the z-axis *i.e.*, the hybrids are pointing in the z-direction. One is pointing in the direction of the positive z-axis and the other in direction of the negative z-axis.

From these equations it is easy to see that the ratio of p-chracter to s-character is 1 : 1 in each of the two hybrid orbital wave functions and that both the hybrid orbital wave functions are orthogonal to each other.

(v) Each orbital has one large lobe and one small lobe. The large lobe is much bigger than the original *p*-orbitals. This larger lobe enables it to bring about a higher degree of overlapping with the orbital of the reacting atom. The resulting bond is, therefore, stronger.

Examples. Some of the molecules/ions which involve *sp*-hybridisation and hence are linear in shape are BeX_2 (2σ-bonds, $lp=0$) $O = N^+ = O$ ion ($2\sigma+2\pi$ bonds, $lp=0$, $\ddot{C} \equiv O$ ($1\sigma+2\pi$ bonds, $lp=1$), $H-C \equiv N$ ($2\sigma+2\pi$ bonds, $lp = 0$), $O = C = O$ ($2\sigma+2\pi$ bonds, $lp = 0$). The atoms in thick type are the central atoms that undergo *sp*-hybridisation and a pair of dots on them represents σ *lp*.

(*i*) **$BeCl_2$ molecule.** In this molecule Be-atom is the central atom that undergoes *sp* hybridisation. Be-atom in its excited state has the valence-shell configuration as : $2s^1$, $2p_z^1$. These atomic orbitals on hybridisation give two linear *sp*-hybrid orbitals. Each of these hybrids is singly-occupied and, therefore, overlaps with singly-filled $3p_z$ atomic orbital (*z*-axis has been assumed to be the molecular axis of each chlorine atom ($Cl \longrightarrow 3s^2, 3p_x^2 3p_y^2 3p_z^1$) to form two Be—Cl σ-bonds (*sp*-p_z σ-bonds). Both these bonds are coplanar and are at 180° to each other (*see* Fig. 5·25). Thus $BeCl_2$ molecule has **linear shape**.



Two half-filled *sp*-hybrids on Be-atom.

Two half-filled $3p_z$-atomic orbitals on two Cl-atoms

$BeCl_2$ molecule

Fig. 5·25. Linear $BeCl_2$ molecule resulted from *sp*-hybridisation.

(*ii*) **CO_2 molecule.** Let the two oxygen atoms be represented as O_a and O_b. Valence-shell electronic configurations of carbon (*in the excited state*) and of oxygen atoms (*in the normal state*) are :

C (*in the excited state*) : $2s^1, 2p_x^1 2p_y^1 2p_z^1$

O_a (*in the normal state*) : $2s^2, 2p_x^1 2p_y^1 2p_z^1$ ($lp = 2$)

O_b (*in the normal state*) : $2s^2, 2p_x^2 2p_y^1 2p_z^1$ (lp's $= 2$)

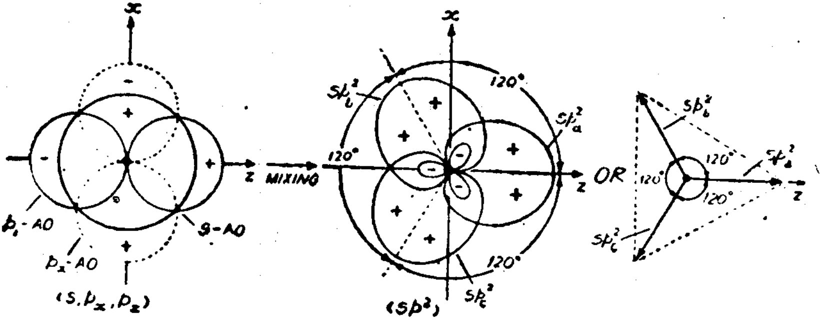
Linear shape of CO_2, $O = C = O$ suggests that carbon atom which is the central atom in this molecule is *sp*-hybridised. Thus, after *sp*-hybridisation ($s+p_z$), the electronic configuration of carbon atom becomes : $(sp)^1$ $(sp)^1$ $2p_x^1$ $2p_y^1$ Two half-filled *sp*-hybrid orbitals of carbon atom overlap with half-filled $2p_z$-orbitals of O_a and O_b respectively to form two σ-bonds which are $sp-p_z$ σ-bonds. The lateral overlap of the remaining two half-filled 2*p*-orbitals of carbon atom ($2p_x$ and $2p_y$ orbitals) with each of the two half-filled 2*p*-orbitals of O_a ($2p_x$) and O_b ($2p_y$) gives two π-bonds which are $p\pi-p\pi$-bonds.

Thus CO_2 molecule is **linear** in shape and its structure consists of two σ- and two π-bonds as shown :

$$:\ddot{O}\overset{\sigma}{\underset{\pi}{=}}C\overset{\sigma}{\underset{\pi}{=}}\ddot{O}:$$

Each pair of dots represents a *lp*.

(2) **sp^2-hybridisation** ($s+p_x+p_z$ AO's). On mixing, s-, p_x- and p_z-AO's give three sp^2 hybrids : sp_a^2, sp_b^2 and sp_c^2 whose formation is illustrated in Fig. 5·26. This type of mixing of atomic orbitals is called **sp^2-hybridisation**, and the hybrid orbitals formed are called **trigonal planar** (or **triangular**) **hybrid orbitals.**



s-, p_x- and p_z- AO's mixing together

Three trigonal planar sp^2- hybrid orbitals : sp_a^2, sp_b^2 and sp_c^2

Fig. 5·26. Formation of three trigonal planar sp^2 hybrid orbitals from the combination of s, p_x and p_z atomic orbitals.

Characteristics of sp^2 hybrids

(*i*) The three sp^2 hybrids have their maximum along one of the three axes. All these axes are lying in the plane of p-orbitals being used in the formation of sp^2 hybrids *i.e.*, these axes lie in the xz plane and make an angle of 120° to each other. Thus the three sp^2 hybrids lie in the plane of p-orbitals *i.e.*, in the xz-plane and are oriented at 120° with respect to each other.

(*ii*) All the three hybrids are equivalent in shape and energy.

(*iii*) Each hybrid, if rotated through 120°, would be exactly superposed on the hybrid orbital already on that axis.

(*iv*) The predicted relative overlapping power of each hybrid is 1·99.

(*v*) The normalised wave functions $\psi(sp_a^2)$, $\psi(sp_b^2)$ and $\psi(sp_c^2)$ for sp_a^2, sp_b^2 and sp_c^2 hybrids are listed below :

$$\psi(sp_a^2) = \frac{1}{\sqrt{3}}\,\psi(s) + \sqrt{\frac{2}{3}}\,\psi(p_z)$$

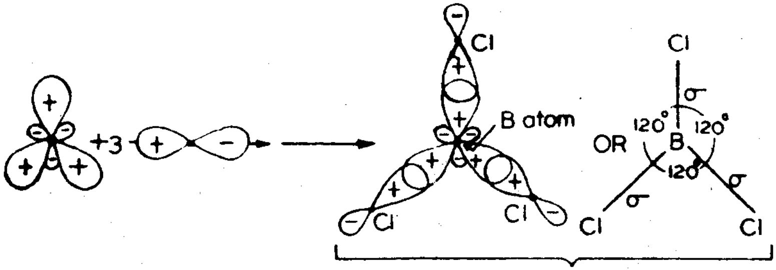
$$\psi(sp_b^2) = \frac{1}{\sqrt{3}}\,\psi(s) + \frac{1}{\sqrt{6}}\,\psi(p_z) + \frac{1}{\sqrt{2}}\,\psi(p_x)$$

$$\psi(sp_c^2) = \frac{1}{\sqrt{3}}\,\psi(s) - \frac{1}{\sqrt{6}}\,\psi(p_z) - \frac{1}{\sqrt{2}}\,\psi(p_x)$$

These equations have been deduced on the assumption that sp_a^2 hybrid has its maximum in the direction of *z*-axis *i.e.*, of the two *p*-orbitals (*i.e.*, p_x- and p_z-AO's) it is only p_z-orbital that is used to form the sp_a^2 hybrid ; p_x-orbital plays hardly any part in the formation of sp_a^2 hybrid. From these equations it is easy to see that the ratio of *p*-character to *s*-character is 2 : 1 in each of the hybrid wave functions.

Examples. Some molecules/ions which involve sp^2 hybridisation are : $\mathbf{B}X_3$ etc. (3 σ bonds, *lp* = 0, trigonal planar shape), $\mathbf{\ddot{Sn}X_2}$ (*gas*) (2σ bonds, *lp* = 1, V-shape), $\mathbf{HCO_2^-}$ ion (3 σ+1 π bonds, *lp* = 0, trigonal planar shape), $\mathbf{NO_3^-}$ ion (3 σ+1 π bonds, *lp* = 0, trigonal planar shape), $\mathbf{\dot{N}O_2^-}$ ion (2 σ+1 π bonds, *lp* = 1, V-shape), $\mathbf{\ddot{S}O_2}$ (2 σ+1 π bonds, *lp* = 1, V-shape). The atoms in thick type are the central atoms that undergo sp^2 hybridisation and the pair of dots represents a *lp* on them.

(*i*) **BCl_3 molecule.** B-atom is the central atom in this molecule. The valence-shell electronic configuration of this atom in the excited state is : $2s^1$, $2p_x^1 2p_z^1$. On hybridisation these atomic orbitals form three trigonal planar sp^2 hybrid orbitals which, being singly-occupied, overlap with three singly-filled $3p_z$ atomic orbitals of three Cl-atom to form three B—Cl σ-bonds (sp^2—p_z σ-bonds) which are coplanar and inclined to each other at 120° Thus BCl_3 molecule has **trigonal planar shape** (*see* Fig. 5·27).



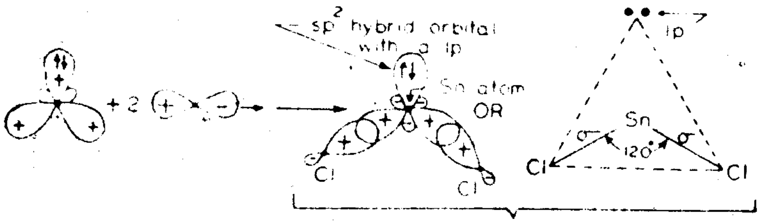
Three half-filled sp^2-hybrid orbitals on B-atom **Three half-filled $3p_z$-orbitals on Cl-atom** **BCl_3 molecule**

Fig. 5·27. Trigonal planar BCl_3 molecule by sp^2 hybridisation.

(*ii*) **$SnCl_2$ molecule.** The ground state configuration of Sn which is the central atom in this molecule is $5s^2$, $5p_x^1 5p_y^1 5p_z^0$. Its completely filled 5*s*-orbital and two half-filled 5*p*-orbitals hybridise together to give three sp^2-hybrid orbitals. One of these has a *lp* and the other two are singly filled.

The two singly occupied sp^2 hybrid orbitals of B-atom overlap with the two half-filled $3p_z$-orbitals of two Cl-atoms (Cl ⟶ $3s^2$, $3p_x^2 3p_y^2 3p_z^1$) to form two σ-covalent bonds. As one of the hybrid orbitals is occupied by a *lp*, the shape of $SnCl_2$ molecule is not triangular planar but a distorted one. Its actual shape is angular or

bent (**V-shape**). Due to the presence of a *lp*, the Cl—Sn—Cl bond angle is less than 120° (*see* Fig. 5·28).



Three sp^2-hybrid orbitals on Sn-atom | Two half-filled $3p_z$ orbitals on Cl-atom | $SnCl_2$ molecule

Fig. 5·28. V-shaped $SnCl_2$ molecule resulted from sp^2 hybridisation. Pair of dots represents a *lp* on Sn atom.

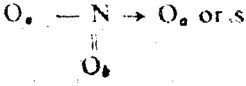
(*iii*) NO_3^- **ion.** Since X-ray diffraction studies have shown that the ion has **planar triangular shape,** N-atom which is the central atom in this ion undergoes sp^2-hybridisation. Since this ion carries a uni-negative charge, one of the three O-atoms may be considered to contain an extra electron. Let the three O-atoms be represented as O_a, O_b and O_c. The valence-shell configuration of N, O_a, O_b and O_c are :

$$N \longrightarrow 2s^2,\ 2p_x^1 2p_y^1 2p_z^1 \quad (lp = 1)$$
$$O_a \longrightarrow 2s^2,\ 2p_x^2 2p_y^1 2p_z^1 \ (lp\text{'s} = 2)$$
$$O_b \longrightarrow 2s^2,\ 2p_x^2 2p_y^1 2p_z^1 \ (lp\text{'s} = 2)$$
$$O_c^- \text{ (containing an extra electron)}$$
$$\longrightarrow 2s^2,\ 2p_x^2 2p_y^2 2p_z^1 \ (lp\text{'s} = 3).$$

$2s$, $2p_x$ and $2p_z$ atomic orbitals of N-atom hybridise to form three sp^2-hybrid orbitals. $2p_y$ orbital which is half-filled does not participate in the hybridisation process. Thus now the configuration of N-atom becomes as :

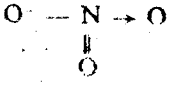
$$N \longrightarrow (sp^2)^2,\ (sp^2)^1,\ (sp^2)^1,\ 2p_y^1\ (lp = 1).$$

Hybrid orbital containing an electron-pair donates it to O_a-atom to form a coordinate covalent $N \xrightarrow{\sigma} O_a$ bond. A covalent σ-bond is formed by the overlap of half-filled hybrid orbital with half-filled $2p$-orbital of O_c atom. Similarly the overlap of the remaining half-filled hybrid orbital with half-filled $2p$-orbital of O_b-atom gives another covalent σ-bond. Half-filled $2p$-orbital of N-atom which did not participate in sp^2-hybridisation process overlaps *literally* with half-filled $2p$-orbital of O_b-atom to form a π-bond ($p\pi$—$p\pi$ bond). Thus the structure of NO_3^- ion can be represented as :



$$\begin{array}{c} O_c - N \rightarrow O_a \\ \| \\ O_b \end{array}$$

or simply as :



$$\begin{array}{c} O^- - N \rightarrow O \\ \| \\ O \end{array}$$

Double bond is composed of one σ- and one π-bond. sp^2-hybridisation gives a **planar trigonal and symmetrical shape** to this ion with O—N—O angle of 120° as shown in Fig. 5·29. It may be noted that all the three σ-bonds are sp^2-p σ-bonds. It may also be noted that the double bond involved in its structure does not influence its shape.

On the basis of sp^2-hybridisation of carbon atom it can be shown that CO_3^{2-} ion also has a **planar triangular shape**.

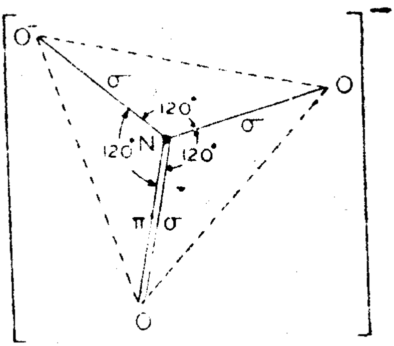


Fig. 5·29. Planar trigonal shape of NO_3^- ion resulted from sp^2 hybridisation.

(3) **sp^3-hybridisation ($s+p_x+p_y+p_z$ AO's).** One s- and three p-AO's on mixing together give a set of four equivalent sp^3 hybrids : sp_a^3, sp_b^3, sp_c^3 and sp_d^3. The formation of these hybrids is shown in Fig. 5·30. This type of mixing of atomic orbitals is called **sp^3-hybridisation**, and the hybrid orbitals thus produced are called **tetrahedral hybrid orbitals**.

Characteristics. (*i*) The four sp^3 hybrids are directed towards the corners of a regular tetrahedron at the centre of which lies the atom that has undergone hybridisation. The electron density associated with these sp^3 hybrids is much greater on one side of the nuclear of the central atom than on the other side.

(*ii*) *Normalised Wave Functions of sp³-hybrids.* All the four hybrid orbitals are equivalent with respect to the three coordinate axes and hence the coefficients for each component AO is $\sqrt{\frac{1}{4}}$. The coefficients of the p-component of all the four AO's are positive in sp_a^3 hybrid orbital since it points in the positive direction of the three axes. In sp_b^3, sp_c^3 and sp_d^3, the respective p_x, p_z and p_y component AO's are positive and others are negative. The normalised wave functions of the four sp^3 hybrids are thus :

$$\begin{aligned}\psi(sp_a^3) &= \tfrac{1}{2}[\psi(s)+\psi(p_x)+\psi(p_y)+\psi(p_z)]\\ \psi(sp_b^3) &= \tfrac{1}{2}[\psi(s)-\psi(p_x)-\psi(p_y)+\psi(p_z)]\\ \psi(sp_c^3) &= \tfrac{1}{2}[\psi(s)+\psi(p_x)-\psi(p_y)-\psi(p_z)]\\ \psi(sp_d^3) &= \tfrac{1}{2}[\psi(s)-\psi(p_x)+\psi(p_y)-\psi(p_z)]\end{aligned}$$

These equations clearly show that s-character in each of the hybrids is $(\frac{1}{2})^2 = \frac{1}{4}$ and the total contribution of the p-component orbital in sp_b^3 hybrid, for example, is

$$(-\tfrac{1}{2})^2+(-\tfrac{1}{2})^2+(+\tfrac{1}{2})^2 = \tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4} = \tfrac{3}{4}.$$

This is actually the total contribution made by p-orbitals in each of the four sp^3-hybrids. Thus the ratio of p-character to s-character in sp^3-hybrid is $\frac{3}{4}\times\frac{4}{1} = 3:1$.

All the s-p type hybrids are represented as sp^{λ^2} where $\lambda = \sqrt{1}$, $\sqrt{2}$ and $\sqrt{3}$ and $\lambda^2 = 1$, 2 and 3 for sp-, sp^2- and sp^3-hybrids. λ is called **hybridisation index**. The percent of *s*-character in each orbital is also given by :

$$\% \ s\text{-character} = \frac{1}{1+\lambda^2} \times 100$$

$$\text{and thus } \% \ p\text{-character} = 1 - \left[\frac{1}{1+\lambda^2} \times 100\right]$$

(*iii*) *Angle between hybrid orbitals.* The value of λ in a set of orbitals determines the angle, θ, between the hybrid orbitals. The angle, θ and the hybridisation index, λ are related as :

$$\lambda^2 \cos \theta = -1.$$

Thus :

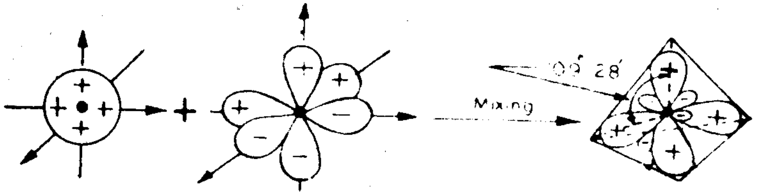
for *sp*-hybrids, $1 \cos \theta = -1, \quad \therefore \quad \theta = 180°$

for sp^2-hybrids, $2 \cos \theta = -1, \quad \therefore \quad \theta = 120°$

for sp^3-hybrids, $3 \cos \theta = -1, \quad \therefore \quad \theta = 109° \ 28'.$

(*iv*) The predicted relative overlapping power of each of the four sp^3-hybrids is 2.00.

The relative values of the overlapping power of *sp*-, sp^2- and sp^3-hybrids which are equal to 1·93, 1·99 and 2·00 respectively show that sp^3-hybrid orbitals are the strongest. This in other words means that the bonds established as a result of overlapping of sp^3-hybrid orbitals with other orbitals such as *s*- or *p*-AO's are strongest. The sequence of relative energy of *s-p* type hybrid orbitals is $sp < sp^2 < sp^3$.



One *s*-orbital Three *p*-orbitals Four tetrahedral sp^3-hybrid orbitals

Fig. 5·30. Formation of four tetrahedral sp^3-hybrid orbitals from the combination of *s*- and three *p*-atomic orbitals.

Examples. Some common molecules/ions whose formation involves sp^3 hybridisation are : **C**H_4, **N**H_4^+ etc. (4 σ-bonds, *lp* = 0, tetrahedral shape), $\ddot{\mathbf{N}}X_3$, $\ddot{\mathbf{P}}X_3$ etc. (3σ bonds, *lp* = 1, trigonal pyramidal shape), $H_2\ddot{\mathbf{O}}$:, :$\ddot{\mathbf{S}}Cl_2$ etc. (2 σ-bonds, *lp's* = 2, V-shape), $H\underset{..}{\ddot{\mathbf{X}}}$: (1 σ-bond, *lp's* = 3, linear shape), $\mathbf{S}O_4^{2-}$ (4 σ+2π bonds, *lp* = 0, tetrahedral shape) $\dot{\mathbf{Cl}}O_3^-$ ion (3 σ+3π bonds, *lp* = 1, trigonal pyramidal shape). The atoms in thick type are the central atoms that undergo sp^3 hybridisation and each pair of dots represents a *lp* on them.

(*i*) **CH$_4$ molecule.** The C-atom in the excited state has $2s^1 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1$ electronic configuration. On mixing, these four AO's give four equivalent sp^3-hybrid orbitals, namely, sp_a^3, sp_b^3, sp_c^3 and sp_d^3.

These hybrid orbitals are directed towards the corners of a regular tetrahedron. Each of these half-filled hybrid orbitals on overlapping along the axis with half-filled 1*s*-AO of H atom gives four localised bonding orbitals called σ-bonds (*see* Fig. 5·31).

Thus CH_4 molecule has a **tetrahedral shape** with a tetrahedral C—H—C bond angle equal to 109·5° (approximately).

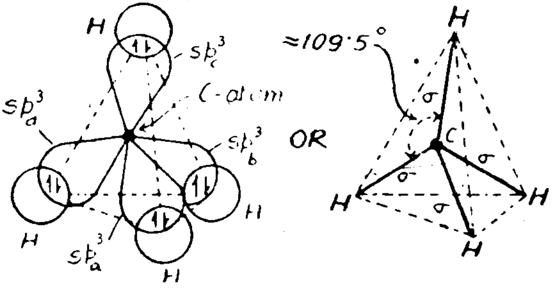


Fig. 5·31. Formation of tetrahedral CH_4 molecule by sp^3-hybridisation (*bp's* = 4, *lp* = 0).

(*ii*) **:NH_3, $H_2\ddot{O}$: and $H\ddot{F}$: molecules.** In NH_3 molecule nitrogen atom is the central atom whose valence-shell configuration in the ground state is $2s^2$, $2p_x^1$ $2p_y^1$ $2p_z^1$. All these four atomic orbitals on hybridisation give four equivalent sp^3 tetrahedral hybrid orbitals. Three of these four hybrid orbitals are singly-occupied and, therefore, overlap with singly-filled three 1*s*-atomic orbitals of three hydrogen atoms to form three N—H σ-bonds. The fourth hybrid orbital is occupied by a *lp* which does not participate in bond formation. Due to the presence of a *lp* on nitrogen atom, NH_3 molecule has a distorted tetrahedral shape, *i.e.*, it has **trigonal pyramidal shape**, with H—N—H bond angle, instead of tetrahedral angle of 109·5°, equal to 107·5° (*see* Fig. 5·32).

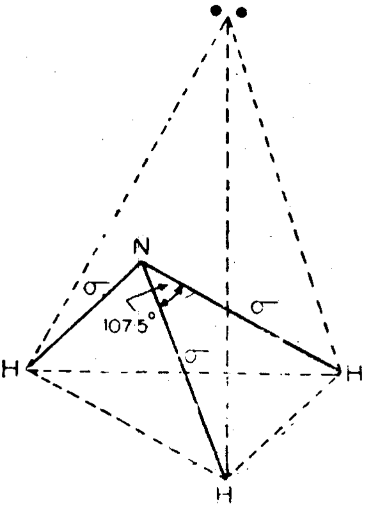


Fig. 5·32. Pyramidal shape of NH_3 molecule resulted from sp^3 hybridisation (*bp's* = 3, *lp* = 1). Pair of dots represents a *lp* in one of the sp^3 hybrids.

On the basis of similar arguments it can be shown that H_2O and HF molecules are also formed by sp^3-hybridisation of oxygen ($O \rightarrow 2s^2, 2p_x^2\ 2p_y^1\ 2p_z^1$) and fluorine ($F \rightarrow 2s^2, 2p_x^2\ 2p_y^2\ 2p_z^1$) atoms which are the central atoms in these molecules respectively. These molecules contain *bp's* = 2, *lp's* = 2 and *bp's* = 1, *lp's* = 3 respectively. Due to the presence of *lp*'s on the central atoms the shapes of these molecules are not regular tetrahedral. H_2O molecule is **V-shaped (angular or bent)** with H—O—H bond angle = 105·5° (*see* Fig. 5·33) while HF molecule is **linear** (*see* Fig. 5·34).

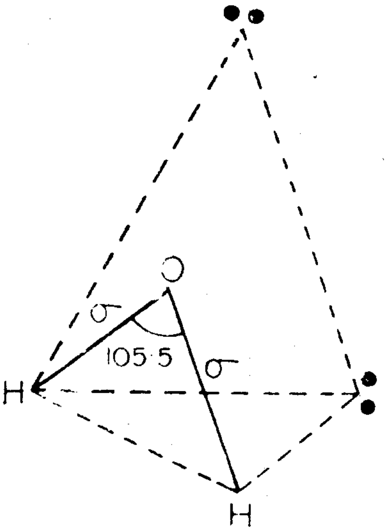


Fig. 5·33. V-shaped H_2O molecule resulted from sp^3 hybridisation (*bp's* = 2, *lp*'s = 2). Each pair of dots represents a *lp*.

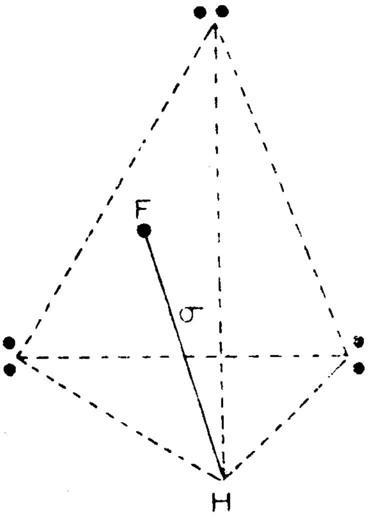


Fig. 5·34. Linear **HF** molecule formed by sp^3 hybridisation (*bp's* = 1, *lp*'s = 3). Each pair of dots represents a *lp*

(*iii*) **SO_4^{2-} ion.** X-ray studies of this ion **have** shown that this ion is **tetrahedral** in shape. Thus sulphur atom **which** is the central atom in this ion **undergoes** sp^3-hybridisation in its formation. Since SO_4^{2-} ion has two **negative** charges, two oxygen atoms may be considered to **have an extra** electron in their electronic configuration. The valence-shell **configuration** of sulphur atom and oxygen atoms are :

$$S \longrightarrow 3s^2, 3p^2\ 3p^1\ 3p^1$$
$$O \longrightarrow 2s^2, 2p^2\ 2p^1\ 2p^1$$
$$O^- \longrightarrow 2s^2, 2p^2\ 2p^2\ 2p^1$$

Configuration of sulphur atom in the doubly-excited state is obtained by promoting one 3*s* and one 3*p* electron to the next higher energy vacant 3*d*-orbitals. Thus the configuration of sulfur atom in the doubly-excited state is : $3s^1, 3p^1\ 3p^1\ 3p^1, 3d^1\ 3d^1$.

Now the 3*s*- and three 3*p*-orbitals in sulphur atom in the doubly-excited state hybridise to give four sp^3 singly-occupied hybrid orbitals. The two three 3*d*-orbitals do not take part in the hybridisation process.

These four singly filled sp^3 hybrid orbitals are used for the formation of four S-O σ-bonds with four singly-filled 2*p*-orbitals of four oxygen atoms. (Note that due to two negative charges on SO_4^{2-} ion, two oxygen atoms have an extra electron). The formation of four σ-bonds accounts for the tetrahedral shape of SO_4^{2-} ion. The two singly-filled 3*d* orbitals of sulphur atom which have not participated so far in hybridisation process overlap with two singly-filled 2*p*-orbitals of two oxygen atoms to form two S – Oπ-bonds. Thus SO_4^{2-} ion has four σ- and two π- bonds (see Fig. 5·35). σ-bonds are sp^3-*p* σ-bonds while π-bonds are *d*π-*p*π-π-bonds.

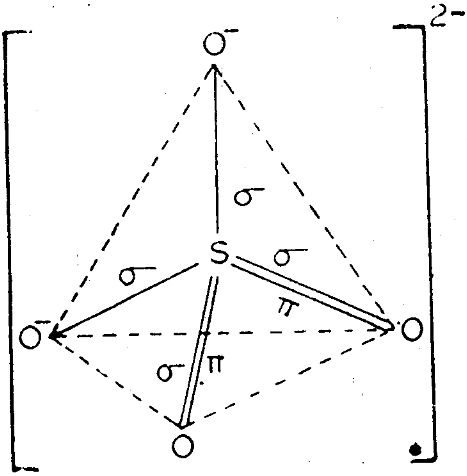


Fig. 5·35. Tetrahedral shape of SO_4^{2} in resulted from sp^3 hybridisation.

(4) sp^3d-**hybridisation** ($s+p_x+p_y+p_z+d_{z^2}$ **AO's**). Combination of one *s*-, three *p*- and $d_z{}^2$-atomic orbitals gives five sp^3d hybrid orbitals. Such type of mixing of AO's is called sp^3d **hybridisation** and the resulted hybrid orbitals are called **trigonal bipyramidal hybrid orbitals**, since these are directed towards the apices of a trigonal bipyramid (*see* (Fig. 5·36).

Characteristics. All these five hybrid orbitals are *non-equivalent*. Thus these can be divided into two sets :

(*a*) **equatorial hybrids.** This set consists of three hybrids which are equivalent and are directed towards the corners of an equatorial triangle. Thus these are planar and the angle between them is 120°. It is for this reason that these hybrids are called **equatorial** (or **basal** or **planar**) **hybrids**. These hybrids may be regarded as being formed by the combination of *s*, p_x and p_y atomic orbitals. Thus this set consists of three sp^2 hybrid orbitals. The bonds formed by the overlap of these hybrids with the orbitals of the surrounding atoms are called **equatorial bonds**. In Fig. 5·36 the equatorial hybrids are shown as unshaded hybrids.

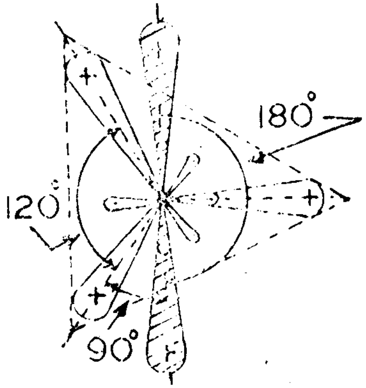


Fig. 5·36. Five sp^3d trigonal bipyramidal hybrid orbitals formed by the combination of *s*, p_x, p_y, p_z and $d_z{}^2$ orbitals. The unshaded three orbitals are equatorial (or basal or planar) hybrid orbitals while the shaded ones are axial (or polar) hybrid orbitals.

(*b*) **axial or polar hybrids.** This set consists of two hybrids which are equivalent and are oriented perpendicular (90°) to the plane containing the equatorial hybrids. Quite obviously these are called **axial or polar hybrids**. These make an angle of 180° with each other but with the equatorial hybrids they make an angle of 90°. These may be regarded as being formed by the combination of p_z and d_{z^2}- orbitals.

Thus this set consists of two $p_z\, d_{z^2}$ hybrids. The bonds formed by the overlap of these hybrids with the orbitals of the surrounding atom are called axial bonds. In Fig. 5·36 the shaded hybrids are axial hybrids.

Since the equatorial hybrids have lower energy than the axial, the *lp*'s, if present in a molecule, occupy equatorial hybrids. The reason for this can also be given by saying that a *lp* is under the influence of only one positive nucleus and as such it tends to be closer to the central atom than is a *bp* which is under the influence of two positive nuclei. Being closer to the nucleus means being at a lower energy level. Thus *lp*'s are situated in the equatorial sp^2 orbitals which are of lower energy.

Examples. Some common molecules/ions that are formed by sp^3d hybridisation are : $\mathbf{PF_5}$ (5σ- bonds, *lp* = 0, trigonal bipyramidal shape), $\mathbf{\dot{S}F_4}$ (4σ-bonds, *lp* = 1, distorted trigonal bipyramidal shape), $:\mathbf{\dot{C}lF_3}$ (3σ-bonds, *lp*'s = 2, T-shape), $:\ddot{X}eF_2$, $\dot{I}:Cl_2^-$ (2σ-bonds, *lp's* = 3, linear shape). The atoms in thick type are the central atoms that are sp^3d hybridised and each pair of dots on them represents a *lp*. *lp's* always occupy the equatorial positions of the trigonal bipyramid.

(*i*) **$\mathbf{PF_5}$ molecule.** Ground state configuration of phosphorus atom which is the central atom in this molecule is $3s^2$, $3p^1_x\ 3p^1_y\ 3p^1_z$. In order to make available five atomic orbitals for sp^3d hybridisation one of the paired $3s$-electrons is promoted to the higher energy vacant $3d_{z^2}$-orbital to give phosphorus the excited state configuration as : $3s^1$, $3p_x^1\ 3p_y^1\ 3p_z^1$, $3d^1_{z^2}$. These five atomic orbitals now hybridise to form singly-occupied trigonal bipyramidal sp^3d hybrid orbitals which overlap with the singly-filled p-atomic orbitals of five fluorine atoms (F→$2s^2$, $2p_x^2\ 2p_y^2\ 2p_z^1$) to form five P—F σ-bonds in PF_5 molecule with trigonal bipyramidal shape. In this molecule the three bond distances between phosphorus and equatorial fluorine atoms are the *same* but are *shorter* than the two bond distances between phosphorus and axial fluorine

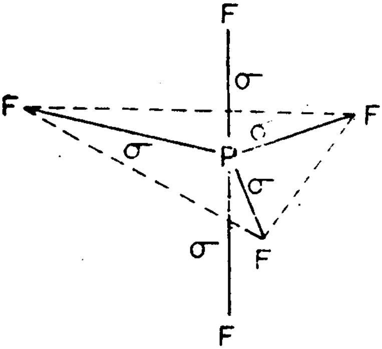


Fig. 5·37. Formation of trigonal bipyramidal PF_8 molecule resulted from sp^3d hybridisiation.

atoms which are also same. This fact confirms the non-equivalent nature of the five sp^3d hybrids orbital (Fig. 5·37).

(*ii*) **:SF$_4$ molecule**. The excited-state configuration of sulphur atom (central atom) is $3s^2$, $3p_x^1$ $3p_y^1$ $3p_z^1$, $3d_{z^2}^1$. On hybridisation these five atomic orbitals form five sp^3d hybrid orbitals one of which has a *lp*. The remaining four which contain one electron each form four σ-bonds with four singly-filled $2p_z$-atomic orbitals of four fluorine atoms. *lp* occupies equatorial position, since in this case the lone-pair repulsion is minimum. Due to the presence of a *lp* SF$_4$ molecule has a **distorted trigonal bipyramidal shape** and bond angles, instead of being 90° and 180°, are 89° and 177° respectively (*see* Fig. 5·38).

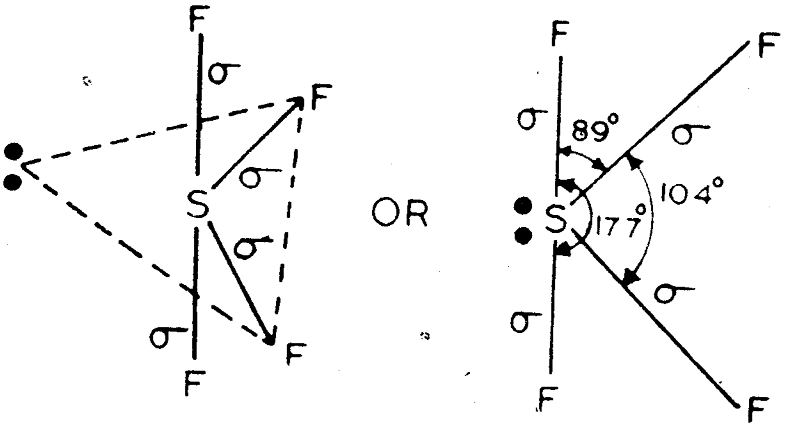


Fig. 5·38. Formation of distorted trigonal bipyramidal SF$_4$ molecule by sp^3d hybridisation (*bp*'*s*=4, *lp* = 1). Pair of dots on sulphur atom represents a *lp*.

(*iii*) **:$\dot{\mathrm{C}}$lF$_3$ molecule**. The $3s$, $3p_x$, $3p_y$, $3p_z$ and $3d_{z^2}$ atomic orbitals of the excited-state configuration of chlorine atom (central atom) *viz*. $3s^2$, $3p_x^2$ $3p_y^1$ $3p_z^1$, $3d_{z^2}^1$ on hybridisation form five sp^3d hybrid orbitals. Three half-filled hybrid orbitals are used to form three Cl—F σ-bonds by overlapping with half-filled $2p_z$ orbitals of three fluorine atoms while the remaining two hybrid orbitals which contain *lp*'s do not participate in bonding. *lp*'s occupy the equatorial positions. Due to the greater repulsion caused by the presence of two *lp's* the molecule has distorted trigonal bipyramidal shape. The molecule is actually known to have **T-shaped structure**. On account of distortion the F—Cl—F bond angle is, instead of 90°, equal to 87·6° (*see* Fig. 5·39).

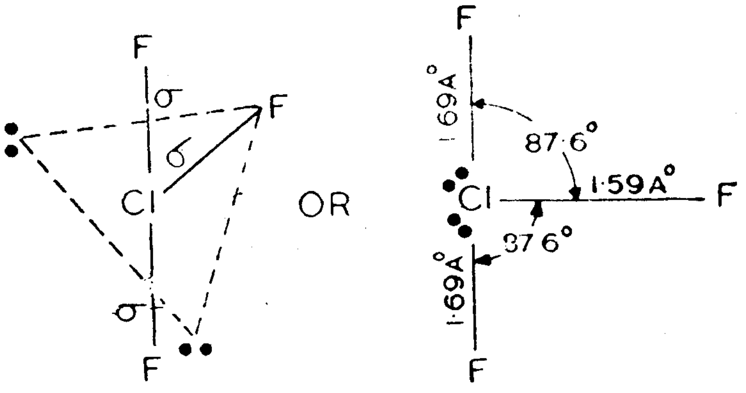


Fig. 5·39. Formation of T-shaped ClF_3 molecule by sp^3d hybridisation (bp's = 3, lp's = 2. Each pair of electrons on chlorine atom represents a lp.

(*iv*) **$:\dot{X}eF_2:$ molecule**. The $5s$, $5p_x$, $5p_y$, $5p_z$ and $5d_{z^2}$ atomic orbitals of the excited-state configuration of Xenon atom (central atom) *viz.* $5s^2$, $5p_x^2$ $5p_y^2$ $5p_z^1$, $5d_{z^2}^1$ undergo hybridisation to form five sp^3d hybrid orbitals. Two of these which are singly-occupied are used to form two F— Xe—F σ-bonds by overlapping with half-filled $2p_z$-atomic orbitals of two fluorine atoms while the remaining three hybrids which are occupied by lp's do not participate in bonding. The lp's occupy the equatorial positions. XeF_2 molecule has thus **linear shape** (*see* Fig. 5·40).

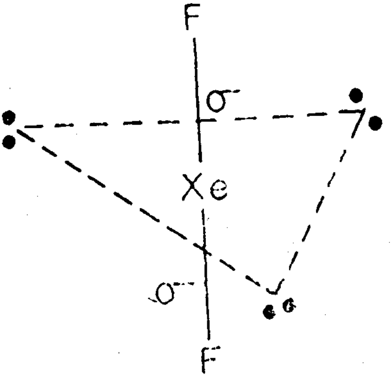


Fig. 5·40. Formation of linear XeF_2 molecule by sp^3d hybridisation (bp's = 2, lp's = 3). Each pair of electrons represents a lp.

(*v*) **$:\dot{X}eOF_2$ molecule.** Electronic configurations of xenon atom (central atom) in the ground state and in the excited state are $5s^2$, $5p_x^2$ $5p_y^2$ $5p_z^2$ and $5s^2$, $5p_x^2$ $5p_y^1$ $5p_z^1$, $3d_{z^2}^1$, $3d^1_{x^2-y^2}$ respectively. $5s$, $5p_x$, $5p_y$, $5p_z$ and $5d_{z^2}$ atomic orbitals of the excited state configuration hybridise to form five sp^3d hybrid orbitals. $5d_{x^2-y^2}$ orbital does not participate in hybridisation process. Three of these hybrid orbitals are singly-occupied and are, therefore, used to form two Xe—F σ- bonds with two fluorine atoms and one

Xe—O σ-bond with oxygen atom. In both the cases singly-filled $2p_z$ orbital of fluorine and oxygen is used. (F→$2s^2$, $2p_x^2 2p_y^2 2p_z^1$, O→$2s^2$, $2p_x^2\ 2p_y^1\ 2p_z^1$). The remaining two hybrid orbitals are occupied by two *lp*'s. $3d_{x^2-y^2}$ orbital which has not participated in hybridisation process overlaps with singly-filled $2p_y$ orbital of oxygen atom to form a Xe—O π-bond which is a $d\pi-p\pi$ π-bond. Thus $XeOF_2$ has **T-shaped structure** (*see* Fig. 5·41). *lp's* occupy equatorial positions.

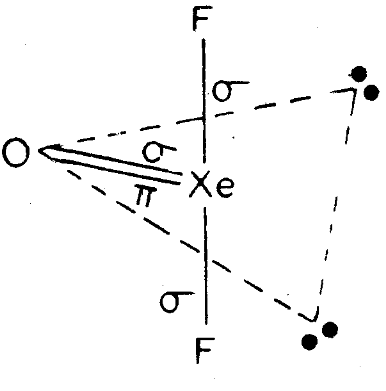


Fig. 5·41. T-shaped $XeOF_2$ molecule resulted from sp^3d hybridisation of Xe. Each pair of electrons represents a *lp*.

(5) **sp^3d^2-hybridisation.** ($s+p_x+p_y+p_z+d_{z^2}+d_{x^2-y^2}$ AO's). Combination of s, p_x, p_y, p_z, d_{z^2} and $d_{x^2-y^2}$ atomic orbitals gives six equivalant sp^3d^2 hybrid orbitals. This type of mixing of atomic orbitals is called sp^3d^2 hybridisation. These hybrids are directed towards the corners of a regular octahedron, *i.e.*, these are pointing away from the origin in the $\pm x$, $\pm y$ and $\pm z$ direction of the x-. y-, and z- axes (Fig. 5·42). It is for this reason that these are called **octahedral hybrid orbitals**. The angle between a pair of the hybrid orbitals is equal to 90°. It is obvious from Fig. 5·42 that four hybrid orbitals, namely, ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are in the xy-plane and the remaining two (*i.e.*, ϕ_5 and ϕ_6) point along the $+z$ and $-z$ axes.

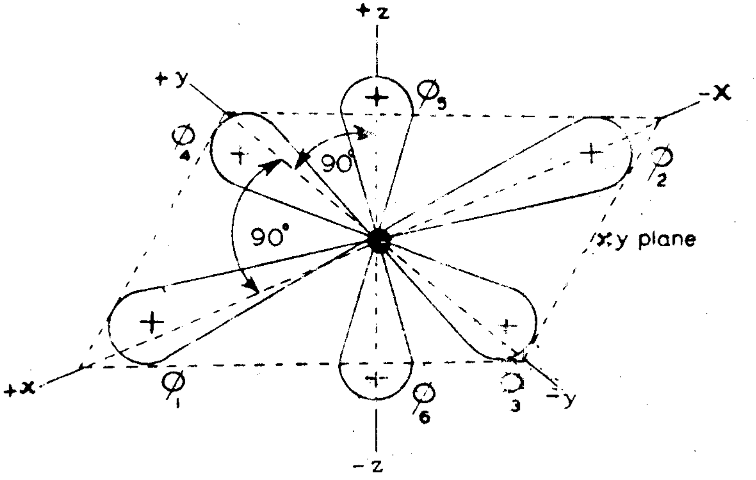


Fig. 5·42. Six equivalent sp^3d^2 octahedral hybrid orbitals formed by the combination of $s, p_x, p_y, p_z, d_{z^2}$ and $d_{x^2-y^2}$ atomic orbitals.

The normalised equations representing the wave functions of these hybrids are :

$$\Psi(\phi_1) = \sqrt{\frac{1}{6}}\,\Psi(s)+\sqrt{\frac{1}{2}}\,\Psi(p_x)+\sqrt{\frac{1}{4}}\,\Psi(d_{x^2-y^2})-\sqrt{\frac{1}{12}}\,\Psi(d_{z^2})$$

$$\Psi(\phi_2) = \sqrt{\frac{1}{6}}\,\Psi(s)-\sqrt{\frac{1}{2}}\,\Psi(p_x)+\sqrt{\frac{1}{4}}\,\Psi(d_{x^2-y^2})-\sqrt{\frac{1}{12}}\,\Psi(d_{z^2})$$

$$\Psi(\phi_3) = \sqrt{\frac{1}{6}}\,\Psi(s)+\sqrt{\frac{1}{2}}\,\Psi(p_y)-\sqrt{\frac{1}{4}}\,\Psi(d_{x^2-y^2})-\sqrt{\frac{1}{12}}\,\Psi(d_{z^2})$$

$$\Psi(\phi_4) = \sqrt{\frac{1}{6}}\,\Psi(s)-\sqrt{\frac{1}{2}}\,\Psi(p_y)-\sqrt{\frac{1}{4}}\,\Psi(d_{x^2-y^2})-\sqrt{\frac{1}{12}}\,\Psi(d_{z^2})$$

$$\Psi(\phi_5) = \sqrt{\frac{1}{6}}\,\Psi(s)+\sqrt{\frac{1}{2}}\,\Psi(p_z)+\sqrt{\frac{1}{3}}\,\Psi(d_{z^2})$$

$$\Psi(\psi_6) = \sqrt{\frac{1}{6}}\,\Psi(s)-\sqrt{\frac{1}{2}}\,\Psi(p_z)+\sqrt{\frac{1}{3}}\,\Psi(d_{z^2})$$

Examples. Some molecules/ions that involve sp^3d^2 hybridisation are $\mathbf{S}F_6$, $\mathbf{Al}F_6^{3-}$, $\mathbf{Si}F_6^{2-}$, $\mathbf{P}F_6^-$ (6σ-bonds, $lp = 0$, octahedral shape), $\ddot{\mathbf{I}}F_5$, $\mathbf{Sb}F_5^{2-}$ (5 σ-bonds, $lp = 0$, square pyramidal shape), $:\ddot{\mathbf{Xe}}F_4$, $:\ddot{\mathbf{Br}}F_4^-$ (4σ-bonds, $lp's = 2$, square planar shape), $\ddot{\mathbf{Xe}}\,OF_4$ (5 σ+1 π bonds, $lp = 1$, square pyramidal shape). The atoms in thick type are the central atoms that undergo sp^3d^2 hybridisation and each pair of dots on them represents a *lp*. *lp's* always occupy the polar positions.

(*i*) **SF$_6$ molecule.** Electronic configuration of sulphur atom (central atom) in the doubly-excited state is : $3s^1$, $3p_x^1$ $3p_y^1$ $3p_z^1$, $3d^1_{z^2}$ $3d^1_{x^2-y^2}$. These orbitals hybridise to form six equivalent sp^3d^2 hybrid orbitals. All the six hybrid orbitals which are singly-filled overlap with singly-occupied $2p_z$ orbitals of six fluorine atoms to form six S—F σ-bonds. Thus we get an octahedral SF$_6$ molecule in which all S—F bonds are equal and F—S—F angle equal to 90° (*see* Fig. 5·43).

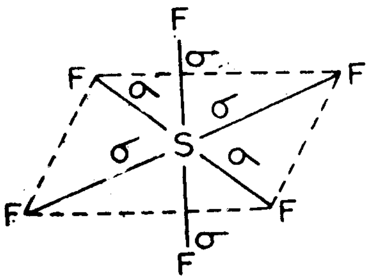


Fig. 5·43. Octahedral SF$_6$ molecule resulted from sp^3d^2 hybridisation ($bp's = 6$, $lp = 0$).

(*ii*) **:IF$_5$ and :$\ddot{\text{Xe}}$F$_4$ molecules.** In IF$_5$ molecule iodine is the central atom whose electronic configuration in the doubly-excited state is :

$5s^2$, $5p_x^1$ $5p_y^1$ $5p_z^1$, $5d^1_{z^2}$ $5d^1_{x^2-y^2}$. These atomic orbitals when hybridised give six equivalent sp^3d^2 octahedral hybrid orbitals. Five of these hybrid orbitals are singly-occupied and, therefore, overlap with five singly-filled $2p_z$-atomic orbitals of five fluorine atoms to form five I—F σ-bonds. Sixth hybrid orbital which is at the axial position of the octahedron is occupied by a *lp* due to which the shape of IF_5 molecule is not regular octahedral but it is **square pyramidal** (*see* Fig. 5·44).

On the basis of similar arguments it can be shown that XeF_4 molecule in which xenon [Xe (in doubly-excited state) → $5s^2$, $5p_x^1$ $5p_y^1$ $5p_z^1$ $5d_z^1$ $5d^1_{x^2-y^2}$] atom is the central atom is also formed by sp^3d^2 hybridisation. This molecule has *bp*'s = 4 and *lp*'s = 2. Two *lp*'s occupy two axial hybrid orbitals. Due to the presence of *lp*'s the molecule is **square planar** in shape. (*see* Fig. 5·45).

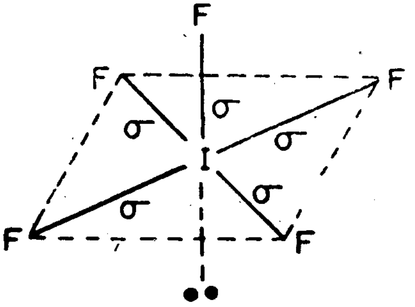


Fig. 5·44. Square pyramidal IF_5 molecule resulted from sp^3d^2 hybridisation. Pair of dots represents a *lp* on iodine atom.

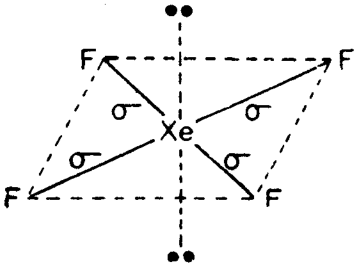


Fig. 5·45. Square planar XeF_4 molecule formed by sp^3d^2 hybridisation. Pair of dots represents two *lp*'s.

(*iii*) **$\ddot{\text{X}}\text{eOF}_4$ molecule.** In this molecule Xe-atom is the central atom whose electronic configuration in the triply-excited state is $5s^2$, $5p_x^1$ $5p_y^1$ $5p_z^1$, $5d^1_{z^2}$ $5d^1_{x^2-y^2}$ $5d^1_{xy}$. $5s$, $5p_x$, $5p_y$, $5p_z$, $5d_{z^2}$ and $5d_{x^2-y^2}$ atomic orbitals hybridise to give six sp^3d^2 hybrid orbitals. $5d_{xy}$-atomic orbital does not take part in hybridisation process. Five hybrid orbitals are singly-filled while the sixth one is occupied by a *lp*. Four out of five hybrid orbitals which are singly-filled overlap with singly-occupied four $2p$-atomic orbitals of four fluorine atoms (F → $2s^2$, $2p_x^2$ $2p_y^2$ $2p_z^1$) to form four Xe—F σ-bonds which are sp^3d^2—p σ-bonds. Similarly the remaining fifth singly-occupied hybrid orbital forms a Xe—O σ-bond with singly-filled $2p$-atomic orbital on oxygen atom (O → $2s^2$, $2p_x^2$ $2p_y^1$ $2p_z^1$). $5d_{xy}$ atomic orbital of Xe-atom which has not participated in hybridisation process overlaps with the remaining singly-filled $2p$-orbital of oxygen atom to form a Xe—O π-bond (oxygen atom has two singly-filled $2p$-orbitals) which is a $d\pi$—$p\pi\pi$-

bond. Due to the presence of a *lp* in one of the six sp^3d^2 hybrid orbitals the shape of the molecule is **square pyramidal** as shown in Fig. 5·46. Thus $XeOF_4$ molecule has five σ- and one π-bonds. *lp* occupies the hybrid orbital situated at the axial (*i.e.* polar) position.

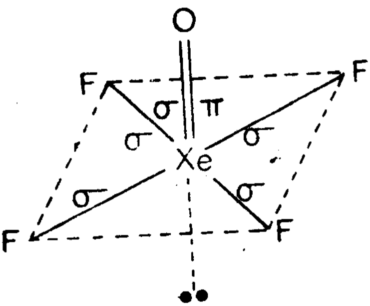


Fig. 5·46. Square pyramidal shape of $XeOF_4$ resulted from sp^3d^2 hybridisation (bp's = 5, lp = 1).

(6) **sp^3d^3 hybridisation** ($s+p_x+p_y+p_z+d_{xy}+d_{yz}+d_{zx}$ AO's). Combination of these atomic orbitals gives seven sp^3d^2 hybrid orbitals which are directed towards the corners of a pentagonal-bipyramid. These are not equivalent hybrid orbitals. Five of them point towards the vertices of a regular pentagon while the other two are oriented perpendicular (90°) to the plane containing the first set of five hybrids.

Examples : (*i*) **IF_7 molecule**. Electronic configuration of iodine atom (central atom) is $5s^2$, $5p_x^2$ $5p_y^2$ $5p_z^1$. In order to make available seven singly-occupied orbitals for sp^3d^3 hybridisation one $5s$ and two $5p$ electrons are promoted to the vacant high energy $5d_{xy}$, $5d_{yz}$ and $5d_{zx}$ orbitals. These seven atomic orbitals then hybridise to form seven sp^3d^3 hybrid orbitals all of which are singly-filled and, therefore, overlap with seven singly-occupied $2p_z$ atomic orbitals of seven fluorine atoms to form seven I—F σ-bonds. All these are $sp^3d^3-p_z$ σ-bonds and the molecule is **pentagonal bipyramidal** in shape (*see* Fig. 5·47). Axial I—F distances are not the same as equatorial I—F distances. This confirms the non-equivalent nature of sp^3d^3 hybrid orbitals.

(*ii*) **XeF_6 molecule**. In this molecule Xe-atom is the central atom whose valence-shell configuration is : $5s^2$, $5p_x^2$ $5p_y^2$ $5p_z^2$. In the triply-excited state its configuration becomes : $5s^2$, $5p_x^1$ $5p_y^1$ $5p_z^1$, $5d_{xy}^1$ $5d_{yz}^1$ $5d_{zx}^1$. These orbitals are hybridised to give seven sp^3d^3 hybrid orbitals one of which is occupied by a *lp* while the remaining six are singly-occupied. These singly-filled hybrid orbitals overlap with $2p_z$ atomic orbitals of fluorine atoms to form σ-bonds. Thus XeF_6 has a **pentagonal bipyramidal structure** with one *lp* residing in the hybrid orbital at the **axial position (*see* Fig. 5·48).**

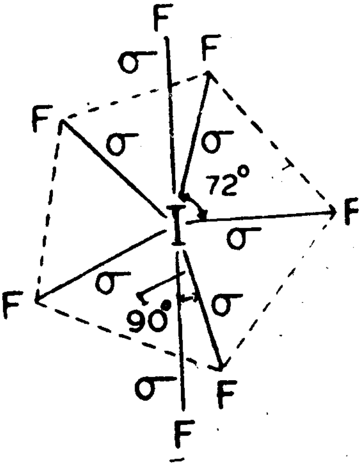


Fig. 5·47. Pentagonal bipyramidal IF_7 molecule resulted from sp^3d^3 hybridisation.

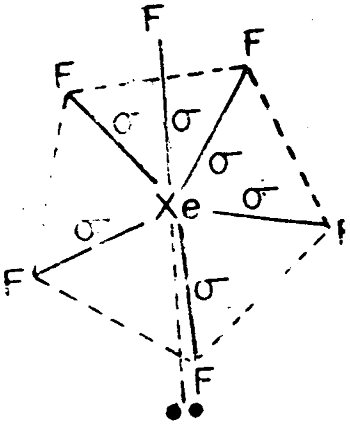


Fig. 5·48. Pantagonal bipyramidal shape of XeF_6 with one axial position being occupied by a *lp*.

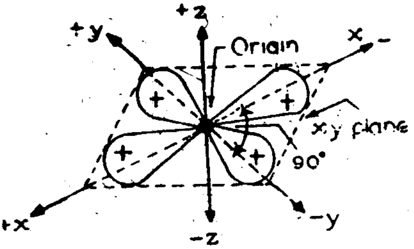


Fig. 5·49. Four square planar dsp^2 hybrid orbitals.

(7) dsp^2 **hybridisation** ($s+p_x+p_y+d_{x^2-y^2}$ **AO's**). Combination of these atomic orbitals gives four dsp^2 equivalent hybrid orbitals which are directed towards the corners of a square in the xy- plane, *i.e.*, these hybrids point away from the origin in the $\pm x$ and $\pm y$ directions of x- and y- axes (Fig. 5·49).

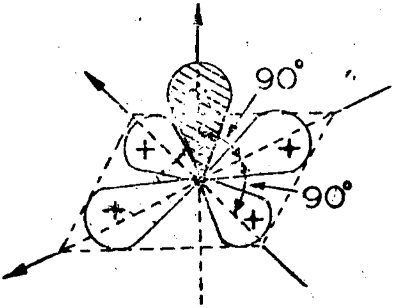


Fig. 5·50. Five-square-pyramidal dsp^3 hybrid orbitals.

(8) dsp^3 **hybridisation** ($s+p_x+p_y+p_z+d_{x^2-y^2}$ **AO's**). Combination of these atomic orbitals gives five non-quivalent dsp^3 hybrids which are directed towards the apices of a square pyramid. Four orbitals form the basal set of equivalent orbitals, while the remaining fifth hybrid orbital (shown as shaded orbital in Fig. 5·50) is the axial orbital.

Some Important Results

The formation of σ- and π-bonds in different molecules/ions which we have considered so far discloses the following facts ;

(*i*) Single bonds are always σ-bonds. double bonds have one σ- and one π-bond and triple bonds are composed of one σ- and two π-bonds.

(*ii*) The shape of a molecule is essentially determined by σ-bonds and generally π-bonds have no effect on it, *e.g.*, consider the shapes of CH_4, NH_3 and H_2O molecules. Although the respective central atoms in all these molecules are sp^3 hybridised, yet their shapes are different. This is because of the fact that these molecules have different number of σ-bonds ($CH_4=4\sigma$-bonds, $NH_3=3\sigma$-bonds, $H_2O=2\sigma$-bonds).

(*iii*) If the number of electron-pairs used in the formation of σ-bonds plus *lp's* in a molecule/ion is equal to 2 or 3, the central atom will undergo *sp* or sp^2 hybridisation respectively. In a multiple-bonded molecule (*i.e.* a molecule having $\sigma+\pi$ bonds) which has *bp's*+*lp's*=2 or 3 (*i.e. sp* or sp^2 hybridisation), π-bond, if present, is a $p_\pi-p_\pi$ π-bond. In this case the central atom has a *p*-orbital available to overlap with a *p*-orbital of the adjacent atom to form a $p_\pi-p_\pi$ π-bond. On the other hand in a multiple bonded molecule having *bp's*+*lp's*=4, 5 or 6, the π-bond will be $p_\pi-d_\pi$ π-bond. In this case the central atom uses all its *p*-orbitals for hybridisation and has only *d*-orbitals available to overlap with *p*-orbitals of the adjacent atom to give $p_\pi-d_\pi$ π-bond.

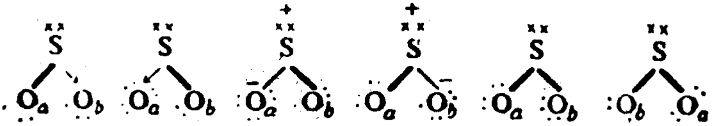
The formation of $p_\pi-p_\pi$ π-bond is common for the second period elements and is not important for the elements of third and higher periods. The $p_\pi-d_\pi$ π-bonding is more favourable than the $p_\pi-p_\pi$ π-bonding for higher atoms *i.e.* atoms of third and higher periods, since in these cases *d*-orbitals project out in the general direction of the bond.

DELOCALISED OR EXTENDED π-MO's

In molecules like ethylene or acetylene, the π-MO's formed are localised (*i.e.* bi-centric) between the two bonded atoms. But it must be remembered that all the electrons in a molecule repel all other electrons and attract all the nuclei so that the idea of localised MO's is only an approximation. There are some poly-atomic molecules and ions in which the electron pair in the π-MO is not necessarily confined to the individual pair of bonded atoms but is **extended** or **delocalised** over the whole molecule or ion *i.e.*, the π-MO's belong to the molecule as a whole and not just to a pair of bonded atoms. These π-MO's extend over all the nuclei *i.e.* are associated with more than two nuclei and the electrons move in the region encompassing all the nuclei of the molecule or ion.

To discuss the formation of these delocalised MO's let us consider the structure of SO_2 molecule. This molecule has a delocalised π-MO.

Recalling the octet rule the following structures can be written for SO_2. To distinguish the two oxygens these have been designated as O_a and O_b.



(I) (II) (III) (IV) (V) (VI)

The actual structure of SO_2 molecule in regarded as a resonance hybrid of the above structures. Here we shall discuss the banding in (III) and (IV) structures only. O—S—O bond angle in SO_2 molecule is approximately 120° (actual value=119·5°) which suggests that it is formed by sp^2 hybridisation. In structures (III) and (IV) S^+, O_a^- and O_b all are sp^2 hybridised. For the time being let us consider structure (III) in which $2s$, $2p_x$ and $2p_z$ atomic orbitals of S^+ ($S^+ \rightarrow 2s^2, 2p_x^1\ 2p_y^1\ 2p_z^1$) hybridise to give three sp^2 hybrid orbitals out of which one is occupied by a *lp* and the remaining two are half filled. $2p_y$-atomic orbital which is half-filled does not participate in hybridisation process. Similarly $2s$, $2p_x$ and $2p_z$ atomic orbitals of O_a^- ($O^- \rightarrow 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$) and O_b ($O \rightarrow 2s^2, 2p_x^2\ 2p_y^1\ 2p_z^1$) also give three sp^2 hybrid orbitals. Two hybrid orbitals of both oxygen atoms contain *lp*'s. $2p_y$ atomic orbitals on each oxygen atom remain as pure atomic orbitals, since they do not participate in hybridisation process. In O_a^- $2p_y$ orbital has a *lp* while that in O_b is singly filled. Thus S^+, O_a^- and O_b have *lp*'s=1, 3 and 2 respectively as shown below.

$$O_a^- \longrightarrow (sp^2)^2\ (sp^2)^2\ (sp^2)^1,\ 2p_y^2\ (lp\text{'s}=3)$$
$$S^+ \longrightarrow (sp^2)^2\ (sp^2)^1\ (sp^2)^1,\ 2p_y^1\ (lp=1)$$
$$O_b \longrightarrow (sp^2)^2\ (sp^2)^2\ (sp^2)^1,\ 2p_y^1\ (lp\text{'s}=2)$$

The singly occupied hybrid orbital on S^+ overlaps with the singly-occupied hybrid orbital on O_a^- to form a $S^+—O_a^-$ σ-bond which is a $sp^2—sp^2$ σ-bond. Similarly the other singly-filled hybrid orbital of S^+ overlaps with singly-filled hybrid orbital on O_b atom to form a $S^+—O_b$ σ-bond. This is also a $sp^2—sp^2$ σ-bond. Now $2p_y$ orbital (singly-filled) of S^+ overlaps laterally with $2p_y$ orbital (half-filled) of O_b atom to form a $S^+—O_b$ π-bond (or a π-MO) which is a $p_\pi—p_\pi$ π-bond. Thus structure (III) has two $S^+—O_a^-$ and $S^+—O_b$ σ-bonds and one $S^+—O_b$ π-bond (or π-MO).

Now if we consider structure (IV) we shall have two $S^+—O_b^-$ and $S^+—O_a$ σ-bonds and one $S^+—O_a$ π-bond. Actually the electron-pair in π-MO is not localised in one S—O region, but is *delocalised* (*extended*) over both S—O bonds, *i.e.*, the electron-pair in π-MO is free to move all over the molecule (*see* Fig. 5·51). The de-localised π-MO which extends over the whole molecule has

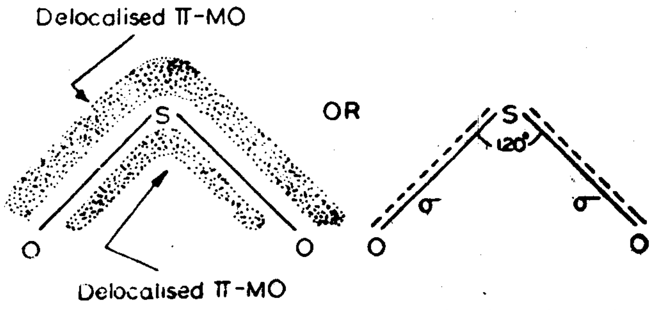


Fig. 5·51. Structure of SO_2 having two σ-bonds and one delocalised (or extended) π-MO. Delocalised π-MO can also be shown by dotted lines.

been obtained by the superimposition of $S^+—O_b$ and $S^+—O_a$ π-MO's. Actually all the three $2p_y$ atomic orbitals of S^+, O_a^- and O_b which have participated neither in sp^2 hybridisation nor in π-bonds formation overlap together and form a de-localised π-MO in which all the four $2p_y$-electrons (two electrons of O_a^- in $2p_y$ orbital + one electron of S^+ in $2p_y$ orbital + one electron of O_b in $2p_y$ orbital) are wandering. Actually this de-localised π-MO (or π-cloud) is not a single MO but is a smear of MO's and AO's.

When does delocalisation occur ? One may ask when delocalisation occurs ? To explain the condition for delocalisation let us again consider the case of SO_2. We have seen that after two σ-bonds have been formed and one electron pair on S^+ and two electron pairs on each of the two O-atoms have been localised as *lp's*, there remains in all three $2p_y$ AO's perpendicular to the plane of the molecule (one $2p_y$-AO on each of the three atoms) which have not so far participated in overlapping process and contain two electron pairs.

Thus the number of AO's is more than that of electron pairs still to be used. Whenever alternative electron pair structures can be written, it is found that the number of orbitals left unused is more than the number of electron pairs, once the σ-bonds and *lp*'s have been assigned. It is under this situation that delocalisation of electrons over all the remaining orbitals results.

ELECTRON DEFICIENT COMPOUNDS

The compounds in which the number of usable orbitals is greater than the number of electrons, to use all the orbitals, are known as electron deficient compounds.

In other words *the molecules in which there are not enough electrons to form two-electron bonds between the atoms are called electron deficient molecules, e.g.* $(BH_3)_2$, $[Be(CH_3)_2]_n$, $[Al(CH_3)_3]_2$ etc. are electron deficient molecules, since they do not contain enough electrons to form the two-electron bonds between the atoms.

Electron deficient compounds are given more by the elements of III A group than those of any other group, because the atoms of III A group have the tendency to be 4-covalent but have only three valence electrons (ns^2p^1). This, however, does not lead to the property of electron deficiency in all types of compounds, *e.g.*, the trivalent halides such as $AlCl_3$ are not electron-deficient.

To discuss the structure and bonding in electron deficient molecules we shall discuss diborane (B_2H_6) as an example.

Structure and Bonding of B_2H_6.

The ethane-like structure and the ionic form, $(H^+)_2$ $(B_2H_4)^{2-}$ are now known to be incorrect.

Electron diffraction studies have shown that B_2H_6 has a hydrogen-bridged structure as shown in Fig. 5·52 in which two irregular BH_4 tetrahedra have one edge in common. Thus two boron atoms (represented as B^I and B^{II}) and four hydrogen atoms (called terminal H-atoms and hence represented as H_t-atoms) lie in the plane of the paper (*i.e.*, these are co-planar) while the remaining two H-atoms (called bridging H-atoms and hence represented as H_b-atoms) are located centrally above and below the plane having two B-atoms (B^I and B^{II} atoms) and four H-atoms more or less bridging the borons B^I and B^{II} and thus prevent the rotation between the two B-atoms. Specific heat measurements also confirm that rotation is hindered.

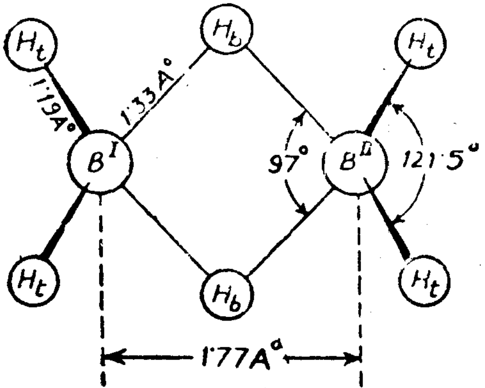


Fig 5·52. Bridge type structure of diborane (B_2H_6).

From Fig. 5·52, it is evident that length of B^I —H_t bond = length of B^{II} —H_t bond which is equal to 1·19 A°. This bond length is almost equal to that expected for a single bond given by the sum of the single-bond normal covalent radii of boron and hydrogen, *i.e.* $r_B + r_H$ which is equal to $0{\cdot}85+0{\cdot}30 = 1{\cdot}15\ \text{Å} \approx 1{\cdot}19\ \text{Å}$. On the other hand $B^I - H_b = B^{II} - H_b = 1{\cdot}33\ \text{Å} > r_B + r_H = 1{\cdot}15\ \text{Å}$ indicating the presence of fractional bond.

Facts supporting the bridge structure. (*i*) Nuclear magnetic resonance study and Raman spectra have shown that four hydrogens namely H_t-atoms are of one type while the remaining two namely H_b atoms are of different type.

(*ii*) Specific heat measurements have shown that the two ends of the molecule cannot be rotated against each other. This hindered rotation clearly indicates that the two bridging hydrogen atoms (*i.e.*, H_b atoms) lie in a plane at right angles to that in which the two boron atoms (*i.e.*. B^I and B^{II}) and the four terminal hydrogen atoms (*i.e.*, four H_t-atoms) lie.

(*iii*) One of the most revealing reactions of B_2H_6 is a redistribution reaction that occurs with methyl borane, BMe_3.

$$B_2H_6 + BMe_3 \rightleftharpoons \underbrace{B_2H_5Me + B_2H_4Me_2 + B_2H_3Me_3 + B_2H_2Me_4}_{\text{Di-borane derivatives}}$$

Only the $B\overset{t}{-}H$ bonds are subject to hydrolysis in these di-borane derivatives and hence the location of methyl groups may be determined from the hydrolysis products.

Hydrolysis of $B_2H_2Me_4$ gives $Me_2B(OH)$, showing that a maximum of the two methyl groups may be joined to a given B-atom in the dimer. Hydrolysis of $B_2H_3Me_3$ gives $Me_2B(OH)$ and $MeB(OH)_2$, *i.e.* 1, 1, 1-trimethyl di-borane does not exist. This suggests that all the six hydrogen atoms in B_2H_6 are not equivalent, a suggestion which is completely supported by structural studies.

(*iv*) All the four terminal B—H bonds have the same length as those in borone-carbonyl, which is not electron-deficient. The electron-deficiency in B_2H_6 lies with the $B^{I}-H_b-B^{II}$ bridge system in which $B^{I}-H_b$ or $B^{II}-H_b$ bond is abnormally long.

Explanation of the formation of hydrogen-bridge in terms of MOT. According to MOT the hydrogen bridge, $B^{I}-H_b-B^{II}$, in B_2H_6 is regarded as a three-centre, two electron bond denoted as ($3c-2e$) bond. This ($3c-2e$) bond is a special type of bond which is formed by two electrons and which binds three nuclei together, namely B^{I}, H_b and B^{II}. Thus B_2H_6 molecule has two ($3c-2e$) $B^{I}-H_b-B^{II}$ bonds. On the basis of MOT, the formation of two ($3c-2e$) $B^{I}-H_b-B^{II}$ bonds in B_2H_6 is explained as follows :

We know that boron atom has the configuration : $B \longrightarrow 2s^2p^1$. The promotion of one of the two $2s$-electrons to $2p$-orbital gives three unpaired electrons ($B \longrightarrow 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^0$). The hybridisation of the orbitals containing the unpaired electrons (*i.e.*, $2s$-, $2p_x$- and $2p_y$- AO's) together with the empty AO, namely, $2p_z$ orbital gives four sp^3 hybrid orbitals : three containing one electron each and the fourth one empty.

Now in terms of MOT, the 3-centre bond, $B^{I}-H_b-B^{II}$ (or more correctly to call a 3-centre MO) results from the overlap of $1s$-AO of a bridging H-atom (*i.e.*, H_b-atom) with two sp^3-hybrid orbitals : one from each boron atom. For the formation of a 3-centre MO, one of the sp^3-hybrids must be empty. A second 3-centre MO also arises in a similar way.

The formation of a 3-centre MO is shown in Fig. 5·53. The two 3-centre MO's are indicated by two lobes (upper and lower) which are of the banana shape. Each lobe links two B-atoms (B^{I} and B^{II}) and one bridging H-atom (*i.e.*, H_b-atom), but encloses only two electrons. A 3-centre MO is also sometimes called a *banana bond*. Thus each of the two ($3c-2e$) $B^{I}-H_b-B^{II}$ MO's involves three nuclei or atoms (namely, B^{I}, H_b and B^{II}) bonded together by only two electrons which are delocalised (mobile) between the three centres. Clearly these two 3-centre MO's are formed by sp^3-s-sp^3 overlap.

The four (2c-2e) B-H_t σ-bonds (*i.e.* two B^I —H_t and two B^{II}—H_t σ-bonds) arise from the overlap of the remaining two sp^3-hybrids (each having one electron) of each B-atom with 1s-AO's of H_t-atoms. Thus these four (2c—2e) σ-bonds are formed by sp^3-s overlap. The 3c—2e bond is called an *open* (3c—2e) bond.

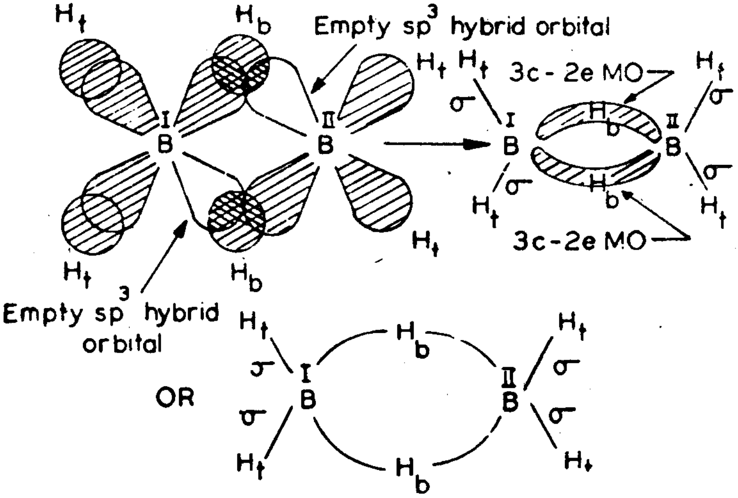


Fig. 5·53. Formation of two (3c—2e) MO's (or σ-bonds) in B_2H_6 on the basis of MOT.

Thus we see that B_2H_6 has the following two types of bonds :

(*i*) Four terminal (2c—2e) boron-hydrogen σ-bonds : two B^I —H_t σ-bonds and two B^{II} —H_t σ- bonds and

(*ii*) Two (3c—2e) hydrogen bridge bonds.

Both (2c—2e) and (3c—2e)-bonds are merely simple special cases of multi-centre bonds, which may be four-, five-, six-, and, in general, *n*-centred bonds [denoted as (*nc*—2*e*) bonds].

References

See the references of chapter 4.

6

Modern Concepts of Acids and Bases

Following are the important modern concept of acids and bases :

1. ARRHENIUS CONCEPT—THE WATER ION SYSTEM

According to this concept, an acid is any hydrogen containing compound which gives H^+ ions in aqueous solution and a base which gives OH^- ions in aqueous solution. Thus HCl is an acid and NaOH is a base and the neutralisation process can be represented by a reaction involving the combination of H^+ and OH^- ions to form H_2O.

$$HCl \underset{H_2O}{\overset{H_2O}{\rightleftharpoons}} H^+ + Cl^-$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

Utility. (*i*) Since the reaction representing neutralisation process involves the combination of H^+ and OH^- ions, the approximately constant molar heat of neutralisation would be expected. Thus the constant heat of neutralisation of a strong acid by a strong base is readily understandable in terms of this concept.

(*ii*) This concept has offered a means of correlating catalytic behaviour with the concentration of the H^+ ion.

Limitations. (*i*) According to this concept, HCl is regarded as an acid only when dissolved in H_2O and not in some other solvent such as C_6H_6 or when it exists in the gaseous form.

(*ii*) It cannot account for the acidic and basic character of the materials in non-aqueous solvents, *e.g.*, NH_4NO_3 in liq. NH_3 acts as an acid, through it does not give H^+ ions. Similarly many organic materials and NH_3, which do not have OH^- ions at all, are actually known to show basic character.

(*iii*) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in many other solvents and even in the absence of solvents.

(*iv*) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aquous solution.

2. BRONSTED-LOWRY THEORY – THE PROTON-DONOR-ACCEPTOR SYSTEM

Bronsted and Lowry in 1923 independently proposed a more general definition of acids and bases. According to them, *an acid is defined as any hydrogen containing material* (a molecule or a cation or an anion) *that can release a proton* (H^+) *to any other substance, whereas a base is any substance* (a molecule or a cation or an anion) *that can accept a proton from any other substance.* In short, **an acid is a proton-donor and a base is a proton-acceptor.**

$$\text{Bronsted Acids}\left\{\begin{array}{ll} \textit{Molecular}: & HCl \longrightarrow H^+ + Cl^- \\ \textit{Cationic}: & [Al(H_2O)_6]^{3+} \longrightarrow H^+ + [Al(H_2O)_5(OH)]^{2+} \\ \textit{Anionic}: & HCO_3^- \longrightarrow H^+ + CO_3^{2-} \end{array}\right.$$

$$\text{Bronsted Bases}\left\{\begin{array}{ll} \textit{Molecular}: & py + H^+ \longrightarrow [pyH]^+ \\ \textit{Cationic}: & [Al(H_2O)_5(OH)]^{2+} + H^+ \longrightarrow [Al(H_2O)_6]^{3+} \\ \textit{Anionic}: & HCO_3^- + H^+ \longrightarrow H_2CO_3 \end{array}\right.$$

py stands for pyridine molecule

Conjugate Acid-Base Pairs

Consider a reaction

one proton (H+) going to H_2O — one proton (H+) going to Cl^-

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

In this reaction HCl donates a proton to H_2O and is, therefore, an acid. Water, on the other hand, accepts a proton from HCl, and is, therefore, a base. In the reverse reaction which at equilibrium proceeds at the same rate as the forward reaction, the H_3O^+ ion donates a proton to Cl^- ion, hence H_3O^+ ion is an acid. Cl^- ion, because it accepts a proton from H_3O^+ ion, is a base. Acid base pairs such as

$$HCl \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Cl^- \quad \text{and} \quad H_3O^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_2O,$$

the *members of which can be formed from each other mutually by the gain or loss of proton* are called **conjugate acid-base pairs.**

If in the above reaction, the acid HCl is labelled $Acid_1$ and its conjugate base *viz.* Cl^- as $Base_1$ and further, if H_2O is designated $Base_2$ and its conjugate acid *viz.* H_3O^+ as $Acid_2$, the equilibrium can be represented by a general equation

Table 6·1. *Acid-Base Chart containing some common conjugate acid-base pairs.*

Acid		*Conjugate Base*	
Name (In the order of decreasing strength as an acid i.e., K_a decreasing)	*Formula*	*Formula*	*Name (In the order of increasing strength as a base i.e., K_b increasing)*
Perchloric acid (Strongest acid)	$HClO_4$	ClO_4^-	Perchlorate ion (Weakest base)
Sulphuric acid	H_2SO_4	HSO_4^-	Hydrogen sulphate ion
Hydrogen chloride	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogen sulphate ion	HSO_4^-	SO_4^{2-}	Sulphate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion
Hexa aquo aluminium (III) ion	$[Al(H_2O)_6]^{3+}$	$[Al(H_2O)_5(OH)]^{2+}$	Hydroxo penta aquo aluminium (III) ion
Carbonic acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion
Hydrogen sulphide	H_2S	HS^-	Hydro sulphide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	Carbonate ion
Phenol	C_6H_5OH	$C_6H_5O^-$	Phenoxide ion
Water	H_2O	OH^-	Hydroxide ion
Ethyl alcohol	C_2H_5OH	$C_2H_5O^-$	Ethoxide ion
Ammonia	NH_3	NH_2^-	Amide ion
Methyl amine	CH_3NH_2	CH_3NH^-	Methyl amide ion
Hydrogen	H_2	H^-	Hydride ion
Methane (Weakest acid)	CH_4	CH_3^-	Methide ion (Strongest base)

$$\overbrace{\text{Acid}_1\ (HCl) + \underbrace{\text{Base}_2\ (H_2O) \rightleftharpoons \text{Acid}_2\ (H_3O^+)}_{\text{Conjugate acid-base pair}} + \text{Base}_1\ (Cl^-)}^{\text{Conjugate acid-base pair}}$$

This is the fundamental equation representing the relationship between an acid and a base on the basis of Bronsted concept. Thus on the basis of this concept Acid_1 and Base_1 form one conjugate acid-base pair and Acid_2 and Base_2 form another conjugate acid-base pair.

Two important axioms of the Bronsted concept and position of equilibrium in acid-base reactions :

Let us again consider the reaction

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{Cl^-}$$

In the equilibrium mixture two acids HCl and H_3O^+ ion are competing to donate protons to a base. Since HCl wins, it is the stronger acid. Similarly two bases, H_2O and Cl^- ion, are competing to accept protons. Here H_2O is the stronger base. It will be seen that the stronger acid, HCl, has the weaker conjugate base, Cl^- ion and the stronger base, H_2O, has weaker conjugate acid, H_3O^+ ion. *The stronger acid and weaker base form one conjugate acid-base pair and weaker acid and stronger base form another conjugate acid-base pair.* Some common acid-base pairs are listed in acid-base chart given in Table 6·1. From this chart it is quite evident that $HClO_4$ is the strongest acid ; its conjugate base ClO_4^- ion, is consequently the weakest base. CH_4 and H_2 are the weakest acids ; their conjugate bases, CH_3^- ion and H^- ion respectively, are consequently the strongest bases.

As a stronger acid, HCl is highly ionised even in concentrated aqueous solution. At equilibrium, the above reaction proceeds far to the right, with most of HCl ionised to form H_3O^+ and Cl^- ions. This fact can be illustrated by using arrows of unequal length to designate the forward and reverse reactions respectively. Thus

$$\text{Stronger Acid} + \text{Stronger Base} \overset{\longrightarrow}{\leftarrow} \text{Weaker Acid} + \text{Weaker Base}$$

$$HCl + H_2O \overset{\longrightarrow}{\leftarrow} H_3O^+ + Cl^- \quad \ldots(1)$$

The longer arrow indicates that the position of equilibrium lies to the right.

In the ionisation of CH_3COOH in H_2O, equilibrium is reached when the reaction has proceeded to the right only to a slight extent, with only a small fraction of the CH_3COOH present in the form of ions.

$$\text{Weaker Acid} + \text{Weaker Base} \overset{\rightarrow}{\longleftarrow} \text{Stronger Acid} + \text{Stronger Base}$$

$$CH_3COOH + H_2O \overset{\rightarrow}{\longleftarrow} H_3O^+ + CH_3COO^- \quad \ldots(2)$$

Here the longer arrow indicates that the position of equilibrium lies to the left.

Evidently H_3O^+ ion in equilibrium (2) is stronger acid and CH_3COO^- ion is a stronger base. It is also evident that the stronger acid H_3O^+ ion has the weaker conjugate base, H_2O and the stronger base, CH_3COO^- has the weaker conjugate acid, CH_3COOH. We thus see that all the proton transfer reactions (*i.e.*, protolysis reactions) run downhill to form predominantly the weaker acid and the weaker base.

Relative Strengths of Acids and Bases

According to Bronsted concept, a strong acid has a strong tendency to donate a proton and a strong base has a strong tendency to accept a proton. At least two general methods are generally used for the comparison of relative acidity of given acids.

(*i*) The first of these consists of making a comparison of proton-donating tendencies of different acids towards the same base. For moderately strong acids, H_2O is generally used as the base. Suppose we have to compare the acidic strengths of CH_3COOH and HCN. Experimentally it has been observed that the ionisation or acidity constant, K*a*, for CH_3COOH and HCN at 25° is $1{\cdot}8 \times 10^{-5}$ and $4{\cdot}0 \times 10^{-10}$ respectively.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \quad (Ka = 1{\cdot}8 \times 10^{-5})$$

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- \quad (Ka = 4{\cdot}0 \times 10^{-10})$$

CH_3COOH is, therefore, a stronger acid than HCN and CN^- ion is a stronger base than CH_3COO^- ion.

(*ii*) The second method is the *competitive protolysis method.* In this method one acid is added to the conjugate base of another and the equilibrium concentrations are determined experimentally. For example, when $NaOC_2H_5$ is added to H_2O, it is experimentally. seen that $OC_2H_5^-$ ion, which is the conjugate base of C_2H_5OH reacts fairly completely with H_2O to form C_2H_5OH and OH^- ion.

$$\underset{\text{Stronger acid}}{H_2O} + \underset{\text{Stronger base}}{C_2H_5O^-} \rightleftharpoons \underset{\text{Weaker acid}}{C_2H_5OH} + \underset{\text{Weaker base}}{OH^-}$$

Ethoxide ion, $C_2H_5O^-$ is, therefore, a stronger base than OH^- and H_2O is a stronger acid than C_2H_5OH.

Periodic variations of acidic and basic properties.

The discussion of this topic is made under the following heads.

(A) Hydracids of the elements of the same period. We can consider the hydracids of the elements of 2nd period *viz.* CH_4, NH_3, H_2O and HF. *These hydrides become increasingly acidic as we move from* CH_4 *to* HF. Thus CH_4 has negligible acidic properties, but NH_3 donates a proton (H^+) to strong bases to form NH_2^-, H_2O loses a proton even more readily and HF is a fairly strongly acid. The increase in the acidic properties of these hydrides is due to the fact that as we move from CH_4 to HF, the stability of their conjugate bases *viz* CH_3^-, NH_2^-, OH^- and F^- increases in the order :

$$CH_3^- < NH_2^- < OH^- < F^-.$$

The increase in acidic properties is supported by the successive increase in the dissociation constant values of these hydrides as shown :

$$CH_4(=10^{-58}) < NH_3(=10^{-35}) < H_2O\ (=10^{-14}) < HF(=10^{-4})$$

(*B*) **Hydracides of the elements of the same group.** The following examples make this point clear :

(*i*) *Hydracids of VA group elements* (NH_3, PH_3, AsH_3, SbH_3, BiH_3). All these hydrides show basic character. *With the increase in size and decrease in electronegativity from* N to Bi, *there is a decrease in electron density in* sp^3 *hybrid orbital and thus electron donor capacity* (*i.e. basic character*) *decreases.*

(*ii*) *Hydracids of VI A group elements* (H_2O, H_2S, H_2Se, H_2Te). Aqueous solution of the hydrides of this group behave as weak diprotic acids and ionise as :

$$H_2R \rightleftharpoons H^+ + HR^-$$
$$HR^- \rightleftharpoons H^+ + R^{2-}.$$

The strength of the hydrides as acids increases in the order :

$$H_2O < H_2S < H_2Se < H_2Te.$$

This order is supported by the successive increase of their dissociation constants as shown :

$$H_2O(=1\cdot3\times10^{16}) < H_2S\ (=1\cdot1\times10^{-7}) < H_2Se(2\times10^{-4})$$
$$< H_2Te(=2\cdot3\times10^{-3}).$$

The increasing acidic character reflects decreasing trend in the electron donor ability of OH^-, HS^-, HSe^- or HTe^- ions. *The increasing acidic character is explained by saying that as the charge density on the conjugate base decreases from* OH^- to HTe^-, *the proton is less tightly held in higher members and, therefore, acidic character increases.*

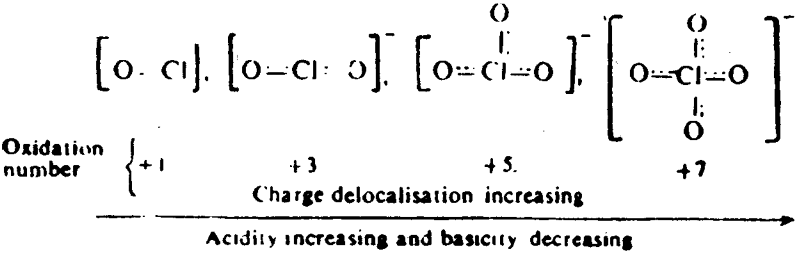
(*iii*) *Hydracids of VIIA group elements* (HF, HCl, HBr, HI). The aqueous solutions of these hydrides show acidic character which increases in the order HF < HCl < HBr < HI. This order is explained by saying that as we pass from HF to HI, there is a gradual decrease in the bond energies of H—X bonds (H—F=135 kcal/mole, H—Cl=103, H—Br=88, H—I=71). This decreasing order of bond energies increases the tendency of HX molecule to split up into H^+ and X^- ions in aqueous solution and thus the acidic character increases from HF to HI.

(*C*) **Oxyacids.** (*i*) ***The acidic character of oxyacids of the same element which is in different oxidation states increases with the increase of its oxidation state.*** The following series follow this rule (called ***oxidation number*** or ***oxidation state rule***)

(*a*) $HCl^{+}O < HCl^{3+}O_2 < HCl^{5+}O_3 < HCl^{7+}O_4$

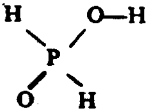
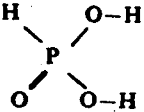
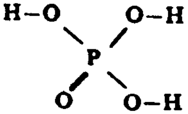
(*b*) $H_2S^{4+}O_3 < H_2S^{6+}O_4$ (c) $HN^{3+}O_2 < HN^{5+}O_3$.

Explanation. With reference to the oxyacids of halogens explanation of the oxidation rule can be given as follows. It is well known that *the stronger the acid, the weaker will be its conjugate base and vice versa.* Now the conjugate bases of the acids are : ClO^-, ClO_2^-, ClO_3^- and ClO_4^- respectively. The oxyanions in which the central atom (*i.e.* chlorine atom) has larger oxidation number has the larger number of lone oxygen atoms for participation in extension of the π-bond. Thereby the charge on the ion is delocalised which greatly stabilises the ion and thus decreases its tendency to accept a proton *i.e.*, causes the ion to be a very weak base with the result that the strength of the acid increases.



When the oxidation state rule as given above is applied to the oxyacids of phosphorus *viz.* $H_3P^{+}O_2$, $H_3P^{3+}O_3$ and $H_3P^{5+}O_4$, it is predicted that the acidic character of these acids should be in the order : $H_3P^{+}O_2 < H_3P^{3+}O_3 < H_3P^{5+}O_4$, but the experimental observation suggests the reverse order *viz* $H_3PO_2 > H_3PO_3 > H_3PO_4$.

Explanation. The experimental order can be explained when we consider the structures of these acids as given below. In these the number of protonated and unprotonated oxygen atoms have also been indicated. The oxygen atom attached with a proton is called *protonated oxygen* while that attached directly with phosphorus (central atom) is known as *unprotonated oxygen.*

Structure :			
	H_3PO_2	H_3PO_3	H_3PO_4
Nature of the acid :	monobasic	dibasic	tribasic
No. of protonated oxygen atoms :	1	2	3
No. of unprotonated oxygen atoms :	1	1	1

The proton attached to any oxygen atom has a far greater chance of dissociation than that linked directly with phosphorus atom (which is the central atom). Thus in this series, since the number of protonated oxygen atoms and consequently the number of dissociable protons increases from one in H_3PO_2 to three in H_3PO_4, the acidity of these acids decreases in the order : $H_3PO_2 > H_3PO_3 > H_3PO_4$.

(*ii*) *The acidic character of the oxyacids of different elements which are in the same oxidation state decreases with the increase in the atomic number of the central atom.* The following series follow this rule (*a*) $HOCl^{1+} > HOBr^{1+} > HOI^{1+}$ (*b*) $HCl^{7+}O_4 > HI^{7+}O_4$ (*c*) $H_2S^{4+}O_3 > H_2Se^{4+}O_3$.

Explanation. As the atomic number of the central atom increases, its electronegativity decreases and its size increases. As a result of this the tendency of the acid to lose a proton to water decreases. This makes the acid a weaker acid.

(*D*) **Hydrated metal ions.** Under favourable conditions one or more protons may dissociate from the coordinated aquo groups :

$$\underset{\text{Hydrated metal ion}}{[M(H_2O)_6]^{n+}} + H_2O \longrightarrow [M(H_2O)_5\,(OH)]^{(n-1)+} + H_3O^+$$

Thus hydrated metal ions also develop acidity. The other things being equal, *acidity increases with the increase of positive charge and basicity increases with the increase of negative charge.* Thus $[Fe(H_2O)_6]^{3+}$ ion is a stronger acid than $[Fe(H_2O_6]^{2+}$ ion and $[Ni(OH)_4]^{2-}$ is a stronger base than $[Ni(OH)_4]^-$ ion.

Amphiprotonic substances. H_2O can act as an acid in the presence of bases stronger than itself such as NH_3, amine, $C_2H_5O^-$ ion, OH^- and CO_3^{2-} ions.

proton (H^+) being transferred

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$$

Water can act as a base in the presence of acids stronger than itself such as $HClO_4$, HCl, CH_3COOH and phenol.

[H^+]

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$

In fact the amphiprotonic nature of H_2O is well illustrated in the extremely slight dissociation or self-ionisation :

$$\underset{\text{Weaker acid}}{H_2O} + \underset{\text{Weaker base}}{H_2O} \rightleftharpoons \underset{\text{Stronger acid}}{H_3O^+} + \underset{\text{Stronger base}}{OH^-}$$

$(K_w = 1{\cdot}0 \times 10^{-14})$

The levelling effect, levelling and differentiating solvents

The apparent strength of a protonic acid is dependent on the solvent in which the acid is dissolved. When all the acids in the acid chart (Table 6·1) which are stronger than H_3O^+ ion (*i.e.*, the acids above H_3O^+ ion in the acid chart namely $HClO_4$, H_2SO_4, HCl, and HNO_3 acids) are added to H_2O, they donate a proton to H_2O to form H_3O^+ ion and appear to have equal strength, since all these acids are levelled to the strength of H_3O^+ ion which is left in solution and is common to all such solutions. This phenomenon *viz.* the strength of all the acids becomes equal to that of H_3O^+ ion is called **levelling effect** of the solvent, water and here water is called a **levelling solvent** for all these acids.

In aqueous solution all very strong bases like Na^+H^-, $Na^+NH_2^-$, $Na^+OC_2H_5$ are levelled to the strength of OH^- ion, for they react completely with H_2O to produce OH^- ions.

The solvent in which complete proton-transfer occurs are called levelling solvents. In other words, the solvent in which the solute is ~100% ionised, are called levelling solvents. Since HF and HCl both are ~ 100% ionised in liquid NH_3 to give ~ 100% NH_4^+ ions, these appear to be of equal strength and liq. NH_3 acts as a levelling solvent for HF and HCl. In H_2O, HF is only partially ionised, whereas HCl and HBr are ~ 100% ionised. Thus H_2O is a differentiating solvent for HF, but for HCl and HBr it is a levelling solvent. Several mineral acids are partially ionised in glacial CH_3COOH medium because CH_3COOH is a poor proton-acceptor but rather a better proton donor. CH_3COOH, therefore, acts as a differentiating solvent towards the mineral acids. But, for bases, CH_3COOH acts as a levelling solvent.

Utility of Bronsted Concept. (*i*) It defines acids and bases in terms of the substances themselves and not in terms of their ions in aqueous solution. Thus HCl is an acid because of the fact that it can give a H^+ ion.

$$HCl \rightleftharpoons H^+ + Cl^-$$

(*ii*) The Bronsted concept recognises that acid-base behaviour is neither restricted to, nor depends on, any particular solvent.

(*iii*) This concept is useful in accounting for the hydrolysis of salt solution. When a salt is dissolved in water, an unbalance in the concentration of the solvent cation (H_3O^+) and anion (OH^-) will result, if the salt cation and anion differ in their proton-donor and proton-acceptor properties towards H_2O. This point can be illustrated by considering the aqueous solution of $FeCl_3$. Aqueous solution of $FeCl_3$ is acidic, since the proton-donor ability of the hydrated ferric ion, $[Fe(H_2O)_x]^{3+}$, exceeds the proton-acceptor ability of Cl^- ion and a considerable excess of H_3O^+ ion is produced in the solution, making $FeCl_3$ acidic.

$$FeCl_3 + xH_2O \rightleftharpoons [Fe(H_2O)_x]^{3+} + 3Cl^-$$

Aqueous solution of a Na_2CO_3 is alkaline in character, because the proton acceptor ability of CO_3^{2-} ion exceeds the proton-donor ability of hydrated sodium ion, $[Na(H_2O)_x]^+$.

$$2x\ H_2O + Na_2CO_3 \rightleftharpoons 2\ [Na(H_2O)_x]^+ + CO_3^{2-}$$

Limitations: (i) This concept lays excessive emphasis on the proton-transfer. Although it is true that most common acids are protonic in nature, yet there are many which are not.

(*ii*) There are a number of acid-base reactions in which no proton transfer takes place, *e.g.*,

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

Thus the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, SO_2, N_2O_4 and $BrFe_3$.

3. GENERAL THEORY OF SOLVENT SYSTEM

The protonic definition of acids and bases given by Bronsted can be extended to the reactions occurring in non-aqueous solvents containing hydrogen such as NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, HCN, and alcohols.

In an attempt to have more general definition of acids and bases applicable to protonic and non-protonic solvents, several definitions have been proposed. One of these is due to Cady and Elsey (1928) according to whom *an acid is a solute that, either by direct dissociation or by reaction with the solvent gives the anion characteristic of the solvent and a base is a solute that, either by direct dissociation or by reaction with the solvent,* gives the cation characteristic of the solvent. If for example, we consider the solvent H_2O, its characteristic cation and anion are H_3O^+ and OH^- respectively as shown below :

$$\overset{\text{acid}}{H_2O} + \overset{\text{base}}{H_2O} \rightleftharpoons \overset{\text{acid}}{H_3O^+} + \overset{\text{base}}{OH^-}$$

Thus all those compounds which can give H_3O^+ ions in H_2O will act as acids and all the compounds which can give OH^- ions in H_2O will behave as bases.

Similarly in N_2O_4 as solvent substances such as NOCl which yield NO^+ ions are acids and the substances such as $NaNO_3$ which yield NO_3^- ions are bases.

$$\overset{\textbf{Acid}}{N_2O_4} + \overset{\textbf{Base}}{N_2O_4} \rightleftharpoons \overset{\textbf{Acid}}{2NO^+} + \overset{\textbf{Base}}{2NO_3^-}$$

Evidently this definition of acids applies equally well to protonic and non-protonic solvents.

The auto-ionisation of some protonic and non-protonic solvents is shown below.

	Acid		**Base**		**Acid**		**Base**
Protonic solvents	H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
	NH_3	+	NH_3	$\rightleftharpoons$	NH_4^+	+	NH_2^-
	CH_3COOH	+	CH_3COOH	$\rightleftharpoons$	$CH_3COOH_2^+$	+	CH_3COO^-
Non-protonic solvents	SO_2	+	SO_2	$\rightleftharpoons$	SO^{2+}	+	SO_3^{2-}
	BrF_3	+	BrF_3	$\rightleftharpoons$	BrF_2^+	+	BrF_4^-
	N_2O_4	+	N_2O_4	$\rightleftharpoons$	$2NO^+$	+	$2NO_3^-$

Just as with the Arrhenius definition, neutralisation is a reaction between an acid and a base to produce a salt and the solvent. Neutralisation reactions in some non-aqueous solvents are given below :

	Acid		*Base*		*Salt*		*Solvent*
In liq. NH_3	: NH_4Cl	+	$NaNH_2$	$\rightleftharpoons$	$NaCl$	+	$2NH_3$
In N_2O_4	: $NOCl$	+	$NaNO_3$	$\rightleftharpoons$	$NaCl$	+	N_2O_4
In CH_3COOH	: HCl	+	CH_3COONa	$\rightleftharpoons$	$NaCl$	+	CH_3OOH
In liq. SO_2	: $SOCl_2$	+	$[N(CH_3)_4]_2SO_3$	$\rightleftharpoons$	$2[N(CH_3)_4]Cl$	+	$2SO_2$

It may be seen from the following reactions that there is a complete analogy between the solvolytic and amphoteric behaviours in aqueous solvents.

Solvolytic behaviour

$$\left[\begin{array}{ll} \text{In liq. } NH_3 : & AlCl_3 + NH_3 \longrightarrow [Al(NH_2)]^{2+} + H^+ + 3Cl^- \\ \text{In } H_2O : & AlCl_3 + H_2O \longrightarrow [Al(OH)]^{2+} + H^+ + 3Cl^- \end{array}\right.$$

Amphoteric behaviour

$$\left[\begin{array}{ll} \text{In liq. } NH_3 : & Zn(NH_2)_2 + 2NH_2^- \longrightarrow [Zn(NH_2)_4]^{2-} \\ \text{In } H_2O : & Zn(OH_2) + 2OH^- \longrightarrow [Zn(OH)_4]^{2-} \end{array}\right.$$

Utility of the concept. Evidently this concept of solvent system can be used to explain the acid-base reactions occurring in aqueous and non-aqueous solvents (protonic and non-protonic both)

Limitations. (*i*) This theory does not consider a number of acid-base reactions included in the protonic definition.

(*ii*) It limits acid-base phenomena to solvent systems only. Thus it does not explain the acid-base reactions which may occur in the absence of solvent.

(*iii*) It cannot explain the neutralisation reactions occurring without the presence of ions.

Thus this theory can simply be said to be an extension of the Arrhenius water-ion system.

4. THE LEWIS CONCEPT—THE ELECTRON-DONOR-ACCEPTOR SYSTEM

This theory explains the acid-base phenomena not in terms of ionic reactions but in terms of electronic structure of the acid and base along with the formation of a coordinate covalent bond. According to Lewis (1923), *an acid is any species* (molecule, radical or ion) *that can accept an electron-pair to form a coordinate covalent bond and a base is any species that can donate an electron-pair to the formation of a coordinate covalent bond.* Thus, in the Lewis system, *an acid is an electron pair-acceptor and a base is an electron pair-donor.*

Thus according to Lewis theory, the process of neutralisation is simply the formation of a coordinate bond between an acid and a base. The neutralisation product, termed as coordinate complex or adduct, may be either non-ionisable or may undergo dissociation or condensation reaction depending on its stability.

Now consider the reaction between a proton (H^+) and $:NH_3$ molecule as shown below :

An electron pair from $:NH_3$ being transferred to H^+

$$\underset{\substack{\text{(proton)}\\ \text{Acid}}}{H^+} + \underset{\text{Base}}{:NH_3} \rightarrow \underset{\text{Adduct}}{(H \leftarrow NH_3)^+}$$

Evidently in the above reaction proton (H^+) accepts one electron pair from $:NH_3$ molecule and is, therefore, an acid, whereas $:NH_3$ molecule which donates an electron pair, is a base. The adduct is NH_4^+ ion.

Lewis bases and Bronsted-Lowry bases are the same substances, since any molecule or ion which accepts protons does so because of the presence of an unshared pair of electrons. In the above example NH_3 molecule is a proton acceptor (*i.e.* Bronsted-base) and an electron pair donor (*i.e.* Lewis-base).

Bronsted and Lewis theories are thus identical as far as bases are concerned except that the wording used for definition of the bases is different in both the theories. Thus NH_3, H_2O, OH^-, Cl^-, CN^- etc. are the bases on the Bronsted as well as on the Lewis systems. There are however, few compounds such as amides, ethers, nitriles, C_2H_4, C_2H_2, C_6H_6 etc. which have little or no tendency to accept protons but react readily with Lewis-acids.

Classification of Lewis Acids.

Any Lewis acid must contain at least one empty orbital in the valence shell of one of its atoms to accept an electron pair from a Lewis-base. Lewis-acids may be classified as :

(*i*) *Molecules containing a central atom with an incomplete octet.* Typical examples of this class of acids are electron deficient molecules such as alkyls and halides of Be, B and Al. Some reactions of this type of Lewis acid with Lewis bases are shown below :

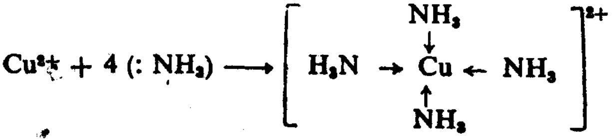
Lewis Acid	+	*Lewis base*	⟶	*Adducts*
F_3B	+	$O(C_2H_5)_2$	⟶	$F_3B \longleftarrow O(C_2H_5)_2$
Cl_3Al	+	NC_5H_5	⟶	$Cl_3Al \longleftarrow NC_5H_5$
Me_3B	+	N_2H_4	⟶	$Me_3B \longleftarrow N_2H_4$

(*ii*) *Molecules containing a central atom with vacant d-orbitals.* The central atom of the halides such as SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3, PF_5, SF_4, SeF_4, $TeCl_4$, etc. have vacant *d*-orbitals. These substances can, therefore, accept an electron pair from the Lewis base to accommodate in their vacant *d*-orbital and can thus form adducts with a number of halide ions and organic bases. These substances are, therefore, Lewis acids. These halides are vigorously hydrolysed by H_2O to form an oxy acid or oxide of the central atom and the appropriate HX. The hydrolytic reactions take place presumably through the intermediate formation of unstable adducts with H_2O,

(*iii*) *Simple cations.* Theoretically all simple cations are potential Lewis acids. Reactions of some cations as Lewis acids with Lewis Bases are shown below. It will be seen that these reactions are identical with those which produce Werner complexes.

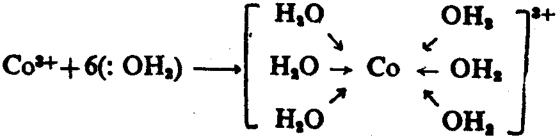
Lewis acid + *Lewis base* ⟶ *Adduct or Addition compounds*

Ammonation : $Ag^+ + 2(:NH_3) \longrightarrow [NH_3 \rightarrow Ag \leftarrow NH_3]^+$



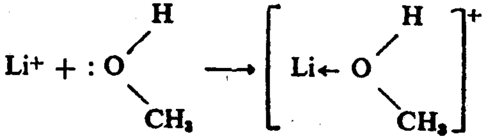
$$Cu^{2+} + 4(:NH_3) \longrightarrow \left[\begin{array}{ccccc} & & NH_3 & & \\ & & \downarrow & & \\ H_3N & \rightarrow & Cu & \leftarrow & NH_3 \\ & & \uparrow & & \\ & & NH_3 & & \end{array}\right]^{2+}$$

Hydration :



$$Co^{3+} + 6(:OH_2) \longrightarrow \left[\begin{array}{ccccc} H_2O & & & & OH_2 \\ & \searrow & & \swarrow & \\ H_2O & \rightarrow & Co & \leftarrow & OH_2 \\ & \nearrow & & \nwarrow & \\ H_2O & & & & OH_2 \end{array}\right]^{3+}$$

Alcoholation :



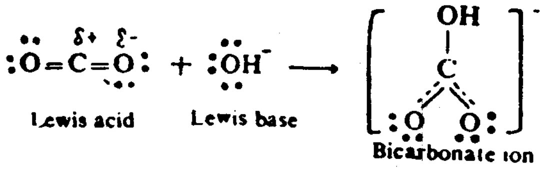
$$Li^+ + :O\begin{matrix}\diagup H \\ \diagdown CH_3\end{matrix} \longrightarrow \left[Li \leftarrow O\begin{matrix}\diagup H \\ \diagdown CH_3\end{matrix}\right]^+$$

The Lewis acid strength or coordinating ability of the simple cations which, according to Lewis, are Lewis acids, increases with (*a*) an increase in the positive charge carried by the cation (*b*) an increase in the nuclear charge for atoms in any period of the periodic table. (*c*) a decrease in ionic radius. (*d*) a decrease in the number of shielding electron shells.

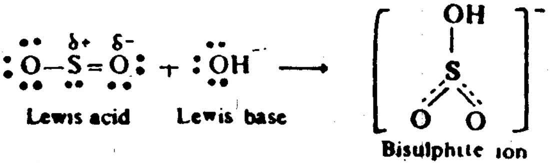
Evidently the acid strength of simple cations increases for the elements on moving from left to right in a period and from bottom to top in a group of periodic table. Thus :

$Fe^{2+} < Fe^{3+}$ (positive charge increases, +2 ⟶ +3)
$K^+ < Na^+$ (on moving from bottom to top in a group)
$Li^+ < Be^{2+}$ (on moving from left to right in a period)
——strength of Lewis acids increasing——⟶

(*iv*) ***Molecules having a multiple bond between atoms of dissimilar electro-negativity.*** Typical examples of molecules falling in this class of Lewis acids are CO_2, SO_2 and SO_3. In these compounds the oxygen atoms are more electronegative than S- or C-atom. As a result, the electron density of π-electrons is displaced away from carbon or sulphur atoms which are less electronegative than oxygen, towards the O-atom. The C- or S-atom thus becomes electron deficient and is, therefore, able to accept an electron pair from a Lewis base such as OH^- ions to form dative bond.



SO_2 also reacts in the same manner with OH^- ion



(*v*) *Elements with an electron sextent.* Oxygen and sulphur atoms contain six electrons in their valence shell and can, therefore, be regarded as Lewis acids. The oxidation of SO_3^{2-} to SO_4^{2-} ion by oxygen and to $S_2O_3^{2-}$ ion by sulphur are the acid-base reactions.

Lewis base		Lewis acid		Adduct
SO_3^{2-}	+	$:\ddot{\underset{..}{O}}$	$\longrightarrow$	$[O \longleftarrow SO_3]^{2-}$
SO_3^{2-}	+	$:\ddot{\underset{..}{S}}$	$\longrightarrow$	$[S \longleftarrow SO_3]^{2}$

Utility of Lewis concept. (*i*) This concept also includes those reactions in which no protons are involved.

(*ii*) Lewis concept is more general than the Bronsted-Lowry concept (*i.e.* protonic concept) in that acid-base behaviour is not dependent on the presence of one particular element or on the presence or absence of a solvent.

(*iii*) It explains the long accepted basic properties of metallic oxides and acidic properties of non-metallic oxides.

(*iv*) This theory also includes many reactions such as gas-phase, high temperature and non-solvent reaction as neutralisation processes.

(*v*) The Lewis approach is, however, of great value in cases where the protonic concept is inapplicable, for example, in reaction between acidic and basic oxides in the fused state.

Limitations. (*i*) Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, for example, experiments show that fluoride complex of Be^{2+} ion is more stable than that of Cu^{2+} ion, indicating that Be^{2+} ion is more acidic than Cu^{2+} ion. On the other hand amine complex of Cu^{2+} is more stable than that of Be^{2+} ion indicating that Cu^{2+} is more acidic than Be^{2+} ion.

(*ii*) According to the phenomenological criteria, an acid-base reaction should be a rapid reaction. There are, however, many Lewis acid-base reactions which are slow.

Classification of Lewis Acids and Bases into Hard and Soft Acids and Bases :

Soft and Hard Bases. Soft Lewis bases are those in which the donor atoms are easily polarised and have low electro-negativity. Hard Lewis bases are those in which the donor atoms have low polarisabilities and high electro-negativities. Table 6·2 contains some typical bases which are classified as hard, intermediate and soft bases. It will be seen that within a group of the periodic table, softness of the Lewis bases increases with the increase in the size of the donor atom. Thus, among the halide ions, softness increases in the order: $F^- < Cl^- < Br^- < I^-$ Thus F^- is the hardest and I^- is the softest Lewis base.

Table 6·2. *Classification of Lewis bases as hard, intermediate and soft bases (R=alkyl or aryl group)*

Hard bases	*Boderline (i.e. intermediate) bases*	*Soft bases*
H_2O, OH^-, F^-, CH_3COO^-, PO_4^{3-}	$C_6H_5NH_2$, C_5H_5N, Br^-	R_2S, RSH, RS^-, I^-, SCN^-
SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	NO_2^-, SO_3^{2-}, N_2	$S_2O_3^{2-}$, R_3P, R_3As, $(RO)_3P$, CN^-, RNC, CO, C_2H_4. C_6H_6, H^-
ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4		

Soft and Hard Acids. A hard acid, like a hard base, is difficult to polarise. A cationic hard acid, such as Al^{3+}, generally has (*i*) a small size (*ii*) a high positive charge and (*iii*) a noble gas electronic configuration.

Soft acids, like soft bases, are readily polarised. These (*i*) have a large size (*ii*) have low positive or zero charge and (*iii*) do not have a noble gas electronic configuration.

In Table 6·3 are given some hard, soft and intermediate Lewis acids.

Table 6·3. *Classification of Lewis acids as hard, intermediate and soft acids.*

Hard acids	*Borderline (i.e. intermediate) acids*	*Soft acids*
H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	Cu^+, Ag^+, Au^+, Tl^+, Hg^+
Sr^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}, In^{2+}	Pb^{2+}, Sn^{2+}, Sb^{3+}, Br^{3+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
La^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+},	Rh^{3+}, SO_2, NO^+, GaH_3	Tl^{3+}, BH_3, $GaCl_3$, $InCl_3$
Fe^{3+}. As^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}		I^+, Br^+, I_2, Br_2
Th^{4+}, U^{4+}, Ce^{3+}, Sn^{4+}, VO^{2+}		Zerovalent metal atoms
UO_2^{2+}, MoO^{3+}, BF_3, SO_3, Cr^{6+}		
I^{7+}, I^{5+}, CO_2, $(HF)_n$		

SHAB principle and stability of the complex A : B

The typical Lewis acid-base reaction can be generalised as :

$$\underset{\substack{\text{Lewis acid}\\ \text{(acceptor)}}}{A} + \underset{\substack{\text{Lewis base}\\ \text{(donor)}}}{:B} \longrightarrow \underset{\text{Adduct or complex}}{A:B}$$

A concept known as **Principle of Soft and Hard Acids and Bases** (abbreviated to SHAB principle) is very helpful in making a prediction of the stability of the complex A : B. This principle was proposed by Ralph G. Pearson (1963). According to this principle the complex A : B is most stable when A and B are either both soft or both hard. The complex is least stable when one of the reactants (namely A and B) is very hard and the other one is very soft.

This principle also means that if there is a choice of reaction between an acid and two bases, or between a base and two acids, *a hard acid will prefer to combine with a hard base and a soft acid will prefer to combine with a soft base and thus a more stable product will be obtained.*

Applications of the SHAB principle. For this let us consider some typical examples.

(*i*) AgI_2^- is stable, but AgF_2^- does not exist. It will be seen from Tables 6·2 and 6·3 that Ag^+ is a soft acid, F^- is a hard base and I^- is a soft base. Hence AgI_2^- (soft acid + soft base) is a stable complex and AgF_2^- (soft acid + hard base) does not exist. Similarly it can also be shown that CoF_6^{3-} (hard acid + hard base) is more stable than CoI_6^{3-} (hard acid + soft base).

(*ii*) Consider the case of $Hg(OH)_2$ and HgS. Evidently HgS (soft acid+soft base) will be more stable than $Hg(OH)_2$ (soft acid+hard base). More stability of HgS than that of $Hg(OH)_2$ explains why $Hg(OH)_2$ dissolves readily in acidic aqueous solution but HgS does not.

(*iii*) The existence of certain metal ores can also be rationalised by applying the SHAB principle. Thus, hard acids such as Mg^{2+}, Ca^{2+}, and Al^{3+} occur in nature as $MgCO_3$, $CaCO_3$, and Al_2O_3 and not as sulphides (MgS, CaS, and Al_2S_3), since the anions CO_3^{2-} and O^{2-} are hard bases and S^{2-} is a soft base. Soft acids such as Cu^+, Ag^+, and Hg^{2+}, on the other hand, occur in nature as sulphides. The borderline (*i.e.*, intermediate) acids such as Ni^{2+}, Cu^{2+}, Pb^{2+} occur in nature both as carbonates and sulphides. The combination of hard acids and hard bases occurs mainly through ionic bonding as in $Mg(OH)_2$ and that of soft acids and soft bases occurs mainly by covalent bonding as in HgI_2.

If we arrange the donor atoms (*i.e.* As, P, C, Se, S, I, Br, N, Cl, O and F) of most common Lewis bases in an increasing order of their electro-negativity values (*i.e.* x_A values), we will get

$$\xrightarrow{} \text{electro-negativity increasing} \xrightarrow{}$$

$$\begin{array}{lcccccccc} & \text{As}, & \text{P} & < \text{C}, & \text{Se}, & \text{S}, & \text{I} & <\text{Br} & <\text{N}, \text{Cl} & <\text{O} & <\text{F} \\ x_A\text{- values}: & 2{\cdot}0, & 2{\cdot}1, & 2{\cdot}5, & 2{\cdot}4, & 2.5, & 2.5 & <2.8 & <3{\cdot}0\ 3{\cdot}0 & <3.5 & <4.0. \end{array}$$

Soft Lewis acids will form more stable complexes with left hand members of the above series and hard Lewis acids will do so with right hand members, *e.g.* a rare earth ion (Ln^{3+} ion) which is a hard Lewis acid, will form complexes with N, O and F donor atoms (*i.e.* right hand members of the above series) or with hard bases.

5. THE USANOVICH CONCEPT—THE POSITIVE-NEGATIVE SYSTEM

The most comprehensive of all the acid-base theories is the Usanovich concept according to which *an acid is any species capable of giving cations, combining with anions or electrons or neutralising a base to give a salt. In other words an acid is a cation, a cation donor, an electron pair acceptor.*

A base is defined as any species capable of giving up anions or electrons, combining with cation or neutralising an acid to give a salt.

It is thus obvious that this concept includes all the previous acid-base definitions. It also includes many reactions such as oxidation reduction reactions as a special class of acid-base reactions.

The acidic and basic character of a molecule depends on the valence of the atoms of which the molecule is composed and usually the atom of the highest valence affects most the acidic and basic character of the molecule. *The acidic character of the elements increases on moving from left to right in a period in the periodic table. The basic character of the elements increases on passing from top to bottom of a group of the periodic table.* Thus the oxides of the alkali and alkaline earth metals are essentially basic whereas those of N and S are acidic. *The acidic character of a molecule increases with the increase in the oxidation state of the element in a molecule* ; thus $\overset{IV}{Sn}S_2$ is more acidic than $\overset{II}{Sn}S$.

Acid-Base Relationships according to Usanovich concept with some specific examples : According to Usanovich concept acid-base relationships can be represented by considering some specific examples such as :

Acid-base reactions	*Explanation*
Acid + *Base* ⟶ *Salt*	
$SO_3 + Na_2O \longrightarrow Na_2SO_4$	Na_2O gives O^{2-} ion ; SO_3 combines with O^{2-} ion. $Na_2O \longrightarrow 2Na^+ + O^{2-}$ $SO_3 + O^{2-} \longrightarrow SO_4^{2-}$ $2Na^+ + SO_4^{2-} \longrightarrow Na_2SO_4$ (salt)
$\overset{II}{Fe}(CN)_2 + 4KCN \longrightarrow K_4[\overset{II}{Fe}(CN)_6]$	KCN gives CN^- ion, $Fe(CN)_2$ combines with CN^- ion. $4KCN \longrightarrow 4K^+ + 4CN^-$ $\overset{II}{Fe}(CN)_2 + 4CN^- \longrightarrow [\overset{II}{Fe}(CN)_6]^{4-}$ $4K^+ + [\overset{II}{Fe}(CN)_6]^{4-} \longrightarrow K_4[\overset{II}{Fe}(CN)_6]$
$Cl_2 + 2Na \longrightarrow 2NaCl$	Na atom loses an electron ; Cl combines with this electron. $2Na \xrightarrow{-2e^-} 2Na^+ + 2e^-$ $2Cl + 2e^- \longrightarrow 2Cl^-$ $2Na^+ + 2Cl^- \longrightarrow 2NaCl.$

Utility. This concept is particularly advantageous in classifying together all examples of acids and bases. It is thus the most general of all acid-base concepts.

Limitations. (*i*) It is extremely general.

(*ii*) It includes many reactions such as oxidation-reduction reactions which can perhaps be better considered from some other point of view.

(*iii*) This theory virtually considers all the chemical reactions as acid-base reactions.

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7

Non-Aqueous Solvents

Most of the chemical reactions take place in aqueous solutions. The reacting substances should be in a dispersed condition (*i.e.*, as ions, atoms or molecules) in a suitable medium (solvent) before appreciable interaction can take place. It is rather unfortunate that we usually lay stress on reacting substances only and ignore the importance of the solvent on the course of a chemical reaction. By changing the solvent, the reactants may give altogether different products or even the course of a chemical reaction may be reversed, *e.g.* NH_4Cl and $LiNO_3$ do not react in aqueous solution but give a precipitate of LiCl in liq. NH_3.

$$NH_4Cl + LiNO_3 \xrightarrow{NH_3(l)} \underset{\text{ppt.}}{LiCl\downarrow} + NH_4NO_3$$

Again $AgNO_3$ and $BaCl_2$ in aqueous solution react to form a precipitate of AgCl

$$2AgNO_3 + BaCl_2 \xrightarrow{H_2O} \underset{\text{ppt.}}{2AgCl\downarrow} + Ba(NO_3)_2$$

But in liq. NH_3 reverse reaction takes place and a precipitate of $BaCl_2$ is formed

$$2AgCl + Ba(NO_3)_2 \xrightarrow{NH_3(l)} \underset{\text{ppt.}}{BaCl_2\downarrow} + 2AgNO_3$$

The above description shows that while choosing a solvent various practical factors are to be taken into consideration.

CLASSIFICATION OF SOLVENTS

Solvents have been classified in a number of ways depending on their physical and chemical properties.

(I) This is a common classification which is based on *proton-donor* and *proton-acceptor property* of the solvents. On the basis of this classification the solvents may be classified into three types :

(*i*) **Protic or protonic solvents.** These solvents have hydrogen atom in their formule and are of two types. (*a*) *Acidic or protogenic solvents.* These have *strong tendency to donate protons* (*e.g.* H_2SO_4, HF, CH_3COOH, HCN etc.), (*b*) *Basic or protophilic solvents.* These have *strong tendency to accept protons* (*e.g.*, NH_3, C_5H_5, amines, N_2H_4).

(*ii*) **Aprotic or non-protonic solvents.** These may or may not have hydrogen in their formula and *neither donote nor accept protons* (*e.g.*, C_6H_6, $CHCl_3$, SO_2, CCl_4, BrF_3)

(*iii*) **Amphi-protic or amphoteric solvents.** These have hydrogen in their formula and donate or accept protons depending on the nature of reacting species, *i.e., these can act both as acids and bases and consequently are amphoteric in nature.* These solvents dissociate feebly into protons and anions. Examples : CH_3COOH, H_2O

(II) This classification is based on the fact that "*like dissolves like*". Thus this classification gives (*i*) *Ionising* (*polar* or *ionic*) *solvents* and (*ii*) *Non-ionising* (*non-polar* or *non-ionic solvents*).

(*i*) **Ionising solvents.** Ionising solvents are polar or ionic in nature and hence dissolve ionic compounds and initiate ionic reactions. These exist as ions in their pure state and thus are weak conductors of electricity. These have high values of dielectric constants. Because of their polar nature they have strong tendency to form assotiated structures. Examples : H_2O, NH_3, HF, SO_2 etc. These solvents undergo self-ionisation as shown below.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \; ; \; NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^- \; ;$$

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

(*ii*) **Non-ionising solvents.** These are non-polar or non-ionic in nature and hence dissolve only non-polar or neutral compounds and do not initiate ionic reactions. These have low dielectric constants. They have little associating and solvating tendency between the solute and solvents. Examples : C_6H_6, CCl_4 etc. These solvents do not undergo self-ionisation.

(III) **Aqueous and non-aqueous solvents.** The solvents other than water are called non-aqueous solvents. The groups obtained as a result of self-ionisation of H_2O and non-aquoeus solvents are analogous to each other, *e.g.*, H_3O^+ and OH^- groups obtained from the self-ionisation of H_2O are analogous to NH_4^+ and NH_2^- groups respectively resulted from the self-ionisation of liq. NH_3. This is called *parent solvent concept* and a large number of chemical reactions have been correlated in terms of this concept.

Some of the parent solvents and analogous groups are given below :

✓ $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

✓ $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

✓ $NH_2OH + NH_2OH \rightleftharpoons NH_3OH^+ + NHOH^-$

✓ $H_2S + H_2S \rightleftharpoons H_3S^+ + SH^-$

Solvents — Analogous groups

In this chapter we shall confine our attention to the study of ionising solvents only in which inorganic substances ionise and give ionic reactions similar to water. Non-ionising solvents are of interest particularly in organic chemistry.

GENERAL PROPERTIES OF IONISING SOLVENTS

Physical Properties.

Some of the physical properties of some ionising solvents are given in Table 7·1.

Table 7·1. *Physical properties of some ionising solvents.*

Solvent	*Viscosity (millipoise)*	*Dipole moment (in Debye units)*	*Dielectric constants*
Water	10·08	1.84	78·5 (25°C)
Ammonia	2·65	1·46	22·0 (−33·5°C)
Hydrogen fluoride	2·40	1·90	83·6 (0·0°C)
Hydrogen cyanide	2·00	2·93	106·8 (25°C)
Sulphur dioxide	2·28	1·61	17·27 (−16·5°C)

Auto-ionisation	*Ionic product*
$2H_2O \rightleftharpoons H_3O^+ + OH^-$	10^{-14}
$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$	10^{-33}
$3HF \rightleftharpoons H_2F^+ + HF_2^-$	$> 10^{-14}$
$2HCN \rightleftharpoons H_2CN^+ + CN^-$	10^{-19}
$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$	10^{-13}

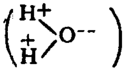
(*i*) **Dipole moment.** The product of charge and distance between the two charges is called dipole moment. Greater is the polarity of the bond, greater will be the charge separation and higher will be the dipole moment. *Solvents having higher values of dipole moment dissolve the polar substances (i.e. solutes) readily.* This is because of the fact *that greater the polarity of a solvent molecule, greater is the solvation energy released on dissolution of a solute.*

Dipole moment value of solvent also gives an idea about the extent of association in the liquid state and hence its liquid temperature range.

(*ii*) **Dielectric constant and dissolution of ionic compounds in polar solvents.** Coulombic force of attraction, F between a cation and an anion in an ionic crystal is given by the expression

$$F=\frac{q^+q^-}{Dr^2}$$

where q^+ and q^- = charges on the cation and anion respectively, r = distance between the cation and anion and D=a constant, called *dielectric constant* which depends on the nature of the solvent in which the ionic crystal is kept. The above expression shows that for the same values of q^+, q^- and r, if F is small, D will be large, *i e.*, a solvent having a high value of D will reduce F. In other words a solvent with a high value of D will weaken the force holding the ions of ionic crystal together and ultimately will dissolve the ionic crystal in it, *e.g.* water which has greater value of dielectric constant (=78·5) than liq. NH_3(=22·0) is a better solvent for dissolving ionic compounds like NaCl.

When NaCl is dissolved in water ; the positive ions *viz.* Na^+ ions are attracted by the negative dipolar end of H_2O  $\left(\begin{matrix}H^+ \\ H^+\end{matrix}\!>O^{--}\right)$ and the negative ions *viz.* Cl^- ions are attracted by the positive end of H_2O molecules and thus NaCl passes into H_2O. Na^+ and Cl^- ions removed fro the ionic crystal (*i.e.* NaCl) get attached with some H_2O molecul Such ions are called *hydrated* or *solvated* or *aquated ions*. Na^+ and Cl^- ions probably contain a least six water molecules attached with them.

It is imperative that in order to have a solute dissolve in an ionic solvent, the solute itself must be ionic. This explains why a non-polar substance does not dissolve in ionic solvents like water.

The dissolution of an ionic compound in a polar solvent occurs only when the energy of solvation of the ions exceeds the lattice energy of the crystal.

The reader should note that solvent-solute interaction leading to solubility is more involved than would appear from a series of dielectric constants alone. Other factors that might influence, in specific case are ion-dipole, dipole-dipole, hydrogen bonding and even π-complexing interactions.

(*iii*) **Electrical conductance.** These solvents are self-ionising, hence, electrical conductance gives an idea about the extent of such ionisation. Greater is the ionisation, easier it is for acid-base reactions to occur in the solvent.

(*iv*) **Viscosity.** Viscosity is an important property of a liquid solvent. Some solvents are highly fluid, *e.g.* water, low molecular weight alcohols, liq. NH_3, while some are viscous *e.g.* anhydrous

H_2SO_4, high molecular weight alcohols etc. Solvents with low viscosity can be handled rather easily. Precipitation, crystallisation and filtration are carried out, on the other hand, with considerable difficulty in solvents of high viscosity.

(*v*) **Proton affinity.** It is applicable for protonic solvents only. It greatly affects the behaviour of a solute in a given solvent system. NH_3 has greater proton affinity than water. Acetamide which behaves as a very weak base in aqueous solution, shows acidic properties in liq. NH_3.

$$CH_3.CO.NH_2 + H_2O \rightleftharpoons CH_3.CO.NH_3^+ + OH^-$$

$$CH_3.CO.NH_2 + NH_3 \rightleftharpoons CH_3.CO.NH^- + NH_4^+$$

Chemical reactions

Chemical reactions that can occur in ionising solvents are of the following types :

(1) **Acid-base reactions** (or **salt formation** or **neutralisation reactions**). In these reactions an acid and a base react together to produce a salt and the solvent.

Ionising solvents are polar compounds and hence undergo self-ionisation to some extent. Self-ionisation of some polar solvents are shown below :

Acid$_1$		Base$_2$		Acid$_2$		Base$_1$
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
NH_3	+	NH_3	$\rightleftharpoons$	NH_4^+	+	NH_2^-
SO_2	+	SO_2	$\rightleftharpoons$	SO^{2+}	+	SO_3^{2-}
HF	+	H_2F_2	$\rightleftharpoons$	H_2F^+	+	HF_2^-
N_2O_4	+	N_2O_4	$\rightleftharpoons$	NO^+	+	NO_3^-

According to the definition of acids and bases given by Cady and Elsey (1928) an acid is a substance which increases the concentration of positive ions characteristic of the solvent and base is a substance which increases the concentration of negative ions characteristic of the solvent, *e.g.* all ammonium salts in liquid ammonia will behave as acids, since they will provide NH_4^+ ions and thus increase the concentration of positive ions which are characteristic of the solvent, liq. NH_3. Similarly all soluble amides will behave as bases, as they will increase the concentration of NH_2^- ions (negative ions) characteristic of the solvent, liq. NH_3. Thus the reaction between NH_4Cl and KNH_2 is an acid-base reaction which can be followed by using phenolphthalein as indicator.

$$\underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{K^+NH_2^-} \rightleftharpoons \underset{\text{salt}}{K^+Cl^-} + \underset{\text{solvent}}{2NH_3}$$

The above equation can also be written ionically as :

$$NH_4^+ + NH_2^- \rightleftharpoons 2NH_3$$

(2) **Solvation reaction** (**or solvate formation reaction**). When one or more solvent molecules are attached to a solute species (which may be a cation, an anion or a neutral molecule) by any of the

chemical linkage, the reaction is known as **solvation reaction.** The products obtained as a result of solvation reactions are called **solvates**. The solvation reaction taking place in water, liq. NH_3, alcohol, hydrazine and ether are known as **hydration, ammonation, alcoholation, hydrazination** and **etheration** respectively and the solvates obtained in these reactions are called **hydrates**, **ammoniates**, **alcoholates, hydrozinates** and **etherates** respectively.

The attachment of the solvent molecule to the solute species may be through ion-dipole, hydrogen bonding or coordinate bonding. In the last type of bonding the solvent may act as a Lewis base or as a Lewis acid depending on the acceptor or donor property of the solute respectively, *e.g.*,

$$BF_3 + NH_3 \longrightarrow \underset{\textbf{Ammoniate}}{BF_3.NH_3}$$

$$\underset{\substack{\textbf{solute acting}\\\textbf{as a Lewis}\\\textbf{acid}}}{CuCl_2} + \underset{\substack{\textbf{solvent}\\\textbf{acting}\\\textbf{as a Lewis}\\\textbf{base}}}{4H_2O} \longrightarrow \underset{\textbf{hydrate}}{[Cu(H_2O)_4]^{2+}} + 2Cl^-$$

$$\underset{\substack{\textbf{solute acting}\\\textbf{as a Lewis}\\\textbf{base}}}{KI} + \underset{\substack{\textbf{solvent acting}\\\textbf{as a Lewis}\\\textbf{acid}}}{4SO_2} \longrightarrow \underset{\textbf{solvate}}{K^+[(SO_4)_4I]^-}$$

The solvates are addition compounds or adducts.

(3) **Solvolysis or solvolytic reactions.** Solvolysis reactions (or solvolytic reactions) are those in which the solvent is split into two parts and one or both parts get attached to a solute molecule or ion. In solvolysis reactions the concentration of either cation or anion is increased which is characteristic of auto-ionisation of the solvent. The solvolysis reactions taking place in water, liq. NH_3 and alcohol are called **hydrolysis**, **ammonolysis** and **alcoholysis** respectively. Examples of solvolysis reactions in different solvents are :

$$\left.\begin{array}{ll} H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- & \ldots(i)\\ CuSO_4 + 4H_2O \rightleftharpoons Cu(OH)_2 + SO_4^{2-} + 2H_3O^+ & \ldots(ii)\\ CN^- + H_2O \rightleftharpoons HCN + OH^- & \ldots(iii) \end{array}\right\}\begin{array}{l}\textbf{hydrolysis}\\\textbf{reactions}\end{array}$$

Evidently in reactions (*i*) and (*ii*) the concentration of H_3O^+ ion is increased by the auto-ionisation of H_2O while in reaction (*iii*) the concentration of OH^- ion is increased.

In the solvolysis reaction in *lia.* SO_2 the concentration of either SO^{2+} or SO_3^{2-} ion is increased

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$
$$Zn(C_2H_5)_2 + 2SO_2 \rightleftharpoons Zn^{2+} + SO_3^{2-} + (C_2H_5)_2SO$$

In case of ammonolysis the concentration of either NH_4^+ or NH_3^- ion is increased.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_3$$
$$SiCl_4 + 8NH_3 \rightleftharpoons Si(NH_2)_4 + 4NH_4^+ + 4Cl^-$$
$$H^- + NH_3 \rightleftharpoons NH_2^- + H_2$$

(4) **Metathetical or precipitation reactions.** One of the familiar chemical reactions is the formation of a precipitate when two solutions are mixed together. The formation of a precipitate depends on the solubilities of various products formed in a particular solvent and these depend critically on the solvation energies of the ions considered in that solvent. Hence the precipitation reaction mainly depends on the nature of the solvent used in the reaction, *e.g.* when aqueous solutions of $BaCl_2$ and $AgNO_3$ are mixed together, AgCl in precipitated

$$2AgNO_3 + BaCl_2 \xrightarrow{\text{water}} 2AgCl\downarrow + Ba(NO_3)_2$$

However, in *liq.* NH_3, on mixing solution of AgCl and $BaNO_3$, it is $BaCl_2$ which is precipitated.

$$Ba(NO_3)_2 + 2AgCl \xrightarrow{\textit{liq.}\ NH_3} BaCl_2\downarrow + 2AgNO_3$$

(5) **Redox reactions.** In general, same type of redox reactions occur in non-aqueous media as occur in aqueous system. However, a solvent itself may be susceptible to redox reactions, *e.g.* water is susceptible to reduction, hence strong reducing agents whose electrode potentials are above hydrogen in the electrode potential series cannot be used in aqueous system. However, oxidation reactions can be easily carried out in aquoeus systems. The reverse is true for NH_3. It is stable towards reduction but susceptible to oxidation. Thus, water is a suitable medium for oxidation reactions while NH_3, for reduction reactions. Liquid SO_2, on the other hand, is inert towards redox reaction. Hence, it serves as a suitable medium for oxidation-reduction reactions.

LIQUID AMMONIA AS SOLVENT

The ease of the availability of liq. ammonia and its water like properties have made it a very useful solvent and reaction medium for carrying out various types of organic and inorganic syntheses.

The melting point and boiling point of ammonia are abnormal with respect to PH_3, AsH_3 and SbH_3 due to the inter-molecular association occurring in it due to H-bonding. Its freezing point and boiling point are lower than those of water. The lower value of its dielectric constant (=22) as compared to that of water (78·5) shows that liq. NH_3 is a poorer electrolytic solvent than water. However, the lower viscosity of liq. NH_3 might be expected to promote greater ionic mobilities and thereby overcome, to some extent the dielectric constant effect.

NH_3 molecule has some degree of polarity which results from pyramidal structure of the molecule and the polarity of the bond $N^{\delta-}—H^{\delta+}$. The N atom in it is sp^3 hybridised. The three sp^3 hybrids are used for bonding with three H atoms and the fourth has an electron lone pair. In NH_3 molecule there are bond dipoles which add vectorially to give NH_3 a net dipole. The total dipole moment, 1·46 D, also includes a contribution from the lone pair in sp^3 hybride orbital.

The bond angle H—N—H is 107° which is somewhat less than the tetrahedral angle (=109·5°) because of the fact the repulsion between lone pair and bonding pair of electrons is greater than that between two bonding pairs of electrons.

Solubility of Substances in liq. NH_3

(*i*) **Inorganic compounds.** Since dielectric constant of NH_3 is much less than that of H_2O, liq.NH_3 is a poorer solvent for ionic substances. Molecules having many electrons such as iodine compounds and non-polar substances such as hydrocarbons are, however, soluble in liq. NH_3. Nitrates, thiocyanates, perchlorates and most cyanides are soluble. Oxides, hydroxides, sulphates, carbonates, phosphates, sulphites, and most sulphides are insoluble. The general order of the solubility of halides in liq. NH_3 is $I^- > Br^- > F^-$. Most iodides are soluble, bromides are less soluble, only NH_4^+, Be^{2+} and Na^+ chlorides are soluble and most fluorides are insoluble.

Most of the ammonium salts (except those of multivalent anions) such as NH_4NO_3, NH_4SCN, $NH_4(CH_3COO)$ are soluble in liq. ammonia. All the metal amides, except those of alkali metals, are insoluble. $LiNH_2$ is also insoluble.

(*ii*) **Organic compounds.** Alcohols, halogen compounds (*e.g.* chloroform etc.), ketones, esters, simple ethers and phenol and its derivatives are soluble. The aromatic hydrocarbons are in general sparingly soluble.

(*iii*) **Non-metals.** The non-metals (*e.g.* P, S and I) dissolve in liq. NH_3 reacting with it.

$$\frac{5}{4}S_8 + 16\,NH_3 \longrightarrow N_4S_4 + 6\,(NH_4)_2S$$

Advantages of using Liquid Ammonia as Solvent :

(*i*) One of the greatest advantages of using liq. NH_3 as a solvent is that liq. NH_3 without reacting dissolves alkali-metals. The dissolved alkali-metals can be recovered simply by evaporating the alkali metal-ammonia solution.

(*ii*) If a reducing agent stronger than hydrogen is to be used in an aqueous medium, it will react with H_2O to liberate H_2 and hence cannot be used in aqueous solution. In such cases many alkali-metal-ammonia solutions which contain mobile ammoniated electrons, $e^-_{(am)}$, can be used for reducing the materials soluble in liq. NH_3.

(*iii*) NH_3 has lesser tendency than H_2O to undergo solvolysis reactions with dissolved solutes.

Disadvantages of using Liquid NH_3 as a solvent :

(*i*) The boiling point of liq. NH_3 is —33·5° and hence while working with this solvent, a lower temperature is to be maintained, if high pressures are to be avoided.

(*ii*) The use of liq. NH_3 as a solvent and a reaction medium requires elaborate equipment and special techniques are to be used.

(*iii*) Due to the hydroscopic nature of liq. NH_3, reactions are done in sealed tubes so as not to allow ammonia to come in contact with moisture.

Auto-ionisation of liq. NH_3. Liq. NH_3 undergoes auto-ionisation similar to H_2O but to a lesser extent than H_2O. This is clear from its lower electrical conductance value as compared to water.

$$NH_3+NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$H_2O+H_2O \rightleftharpoons H_3O^+ + OH^-$$

The ionic product of NH_3, $[NH_4^+][NH_2^-] = 1{\cdot}9\times10^{-33}$ at 50°C is a very low value as compared to that of water, $[H_3O^+][OH^-] = 1\times10^{-14}$ at 25°C.

On the basis of auto-ionisation of liq. NH_3 as shown above it is said that *any substance which gives* NH_4^+ *ions in liq.* NH_3 (e.g. NH_4Cl) *is an* **ammono acid**, *while the substance which gives* NH_2^-, NH^{2-} or N^{3-} *ions* (*e.g.*, $NaNH_2$, PbNH, BiN) *is called an* **ammono base**. The interaction of an ammono acid and an ammono base gives a salt (called **ammono salt**) and the solvent, liq. NH_3.

Chemical reactions occurring in liquid ammonia.

Chemical reactions that can take place in liquid ammonia, can be of the following types :

(1) **Metathetical or precipitation reactions.** Because of differences in solubilities of various substances in liq. NH_3 and in water numerous precipitation reactions that normally do not occur in water may take place in liq. NH_3. Some of the reactions of this type are mentioned below :

(*i*) Most of the chlorides, except those of Na, Be and ammonium, are insoluble in liq. NH_3. When solutions of KI and ammonium chlorides in liq. NH_3 are mixed together, a white precipitate of KCl is obtained.

$$KI + NH_4Cl \xrightleftharpoons{NH_3(l)} \underset{\text{white ppt.}}{KCl\downarrow} + NH_4I$$

(*ii*) When solutions of various nitrates [*e.g.* $Sr(NO_3)_2$, $Zn(NO_3)_2$] in liq. NH_3 are mixed with the solutions of NH_4Br or NH_4I, the corresponding metallic bromides and iodides are precipitated.

$$Sr(NO_3)_2 + 2NH_4Br \xrightleftharpoons{NH_3(l)} SrBr_2\downarrow + 2NH_4NO_3$$

$$Zn(NO_3)_2 + 2NH_4I \xrightleftharpoons{NH_3(l)} ZnI_2\downarrow + 2NH_4NO_3$$

(*iii*) Sodium carbamate is precipitated in liq. NH_3

$$NH_4[NH_2CO.O] + NaNO_3 \xrightarrow{NH_3(l)} \underset{\text{sodium carbamate ppt.}}{Na[NH_2CO.O]} + NH_4NO_3$$

(*iv*) $(NH_4)_2S$ dissolved in liq. NH_3 can precipitate the sulphides of various metals such as Mg, Zn, Cd, Mn, Co, Ag, Pb, Hg, Bi, Cu and Ba from the nitrate solutions of these metals

$$(NH_4)_2S + 2AgNO_3 \overset{NH_3(l)}{\rightleftharpoons} Ag_2S \downarrow + 2NH_4NO_3$$

$$(NH_4)_2S + \underset{\text{metal nitrates}}{Cd(NO_3)_2} \overset{NH_3(l)}{\rightleftharpoons} \underset{\text{metal sulphides}}{CdS} \downarrow + 2NH_4NO_3$$

(*v*) The metal alcoholates, $M^{n+}(OR)_n$, can be precipitated by the reaction of an appropriate metal salt with K-alcoholate, K(OR) in liq. NH_3

$$M^{n+} + nK(OR) \xrightarrow{\text{liq. } NH_3} M^{n+}(CR)_n \downarrow + nK^+$$

$$Ba(NO_3)_2 + 2K(OC_2H_5) \xrightarrow{\text{liq. } NH_3} Ba(OC_2H_5)_2 \downarrow + 2KNO_3$$

(*vi*) Many insoluble halides can be precipitated as complex amines

$$2NaCl + Ca(NO_3)_2 + 8NH_3 \rightleftharpoons [Ca(NH_3)_8]Cl_2 \downarrow + 2NaNO_3$$

(2) **Ammonia as a proton-acceptor.** Liq. NH_3 has a strong tendency to pick up protons even from apparently neutral or weakly basic substances. It picks up a proton from H_2O molecule

$$H_2O \rightleftharpoons OH^- + H^+$$

$$H_3N + H^+ \rightleftharpoons [H_3N \leftarrow H]^+$$

$$\overline{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-}$$

The very high solubility of NH_3 in water or of water in NH_3 is because of the strong tendency of the above reaction to occur.

It is on the basis of proton-acceptor property of liq. NH_3 that the following facts can be explained

(*a*) CH_3COOH is a weak acid in aqueous solution but behaves as a strong acid in liq. NH_3 because NH_4^+ ions are produced in the reaction.

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

(*b*) Acetamide and urea are weakly basic in aqueous solution, but show acidic property in liq NH_3.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NH_3 \longrightarrow CH_3CONH^- + NH_4^+$$

$$\underset{\text{Urea}}{NH_2CONH_2} + NH_3 \longrightarrow NH_2CONH^- + NH_4^+$$

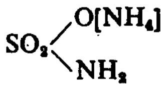
(*c*) Similarly $AgNH_2$ which is a weak base in aqueous solution behaves as an acid in liq. NH_3

$$AgNH_2+2NH_3 \rightleftharpoons [Ag(NH_2)_2]^-+NH_4^+$$

In all the above reactions the concentration of NH_4^+ ion is increased in liq. NH_3. According to Cady and Elsey, all these substances, therefore, behave as acids in liq. NH_3.

(3) **Ammonation reactions and formation of ammoniates.** *Ammonation reactions are those in which one or more molecules of liq.* NH_3 *are attached with the solute species containing an acceptor atom by any of the chemical linkage and give the products, known as* **ammoniates.** In these reactions NH_3 molecule acts as a *Lewis base* (i.e. *electron donor*), since it has a lone pair. The lone pair focuses its negative charge on the empty orbital of the acceptor atom in the solute species to form the ammoniate which are simply *addition compounds or adducts.*

The formation of some typical ammoniates is shown below:



$$SO_3+2NH_3 \longrightarrow SO_2\langle^{O[NH_4]}_{NH_2} \quad (\text{or } SO_3.2NH_3)$$

$$SiF_4+2NH_3 \longrightarrow SiF_4.\,2NH_3$$

$$BF_3+NH_3 \longrightarrow BF_3.NH_3$$

$$[Cu\,(H_2O)_4]^{2+}+4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}+4H_2O$$

$$[Ag(H_2O)_2]^{+}+2NH_3 \longrightarrow [Ag(NH_3)_2]^{+}+2H_2O$$

The first two ammoniates formed in the above reactions are 1 : 2 adducts while the third one is a 1 : 1 adduct.

As we go down a group of the periodic table (*e.g.* Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), the ions increase in their size and the ammonia molecules become more weakly attached.

NH_3 is a better Lewis base than water. Presence of an extra electron pair on oxygen atom in water hinders the approach of water molecule towards acceptor molecule.

(4) **Reactions of ammono acids.** As already stated *the ammono acids are the substances which in liq.* NH_3 *give* NH_4^+ *ions.* The reactions of ammono acids with various substances (*e.g.* metals, metal oxides etc.) are illustrated by the following examples:

(*i*) Liq. NH_3 solutions of ammonium salts can react with active metals to give hydrogen *e.g.*, when blue solutions of alkali-metals in liq. NH_3 react with ammonium salts, they are decolorised.

$$Na+NH_4^+ \longrightarrow Na^++\tfrac{1}{2}H_2+NH_3$$

Metal oxides (*e.g.* Na_2O) and hydroxides (*e.g.*, NaOH) get dissolved in ammono acids.

$$Na_2O+2NH_4Cl \xrightarrow{NH_3(l)} 2NaCl+2NH_3+H_2O$$

$$NaOH+2NH_4NO_3 \xrightarrow{NH_3(l)} NaCl+NH_3+H_2O$$

(*ii*) When magnesium silicide, Mg_2Si, and Mg-germanide, Mg_2Ge, react with liq. NH_3 solution of NH_4Br, high yields of lower silanes and germanes respectively are obtained :

$$Mg_2Si \xrightarrow{NH_4Br,\ NH_3(l)} SiH_4$$

$$Mg_2Ge \xrightarrow{NH_4Br,\ NH_3(l)} GeH_4$$

(*iii*) There are compounds, which do not donate protons to water but readily undergo protolysis in liq. NH_3. Thus guanidine, urea, acetamide, acetamidine and sulphamide which cannot donate protons in aqueous solutions, donate protons to NH_3 in liq. NH_3. This fact is evident from the following reactions.

$$\underset{\text{Guanidine}}{H_2N\,.\,C = NH.NH_2}+NH_3 \longrightarrow {}^-HN.\,C = NH.\,NH_2+NH_4^+$$

$$\underset{\text{Urea}}{H_2N.\,C = NH.\,NH_2}+NH_3 \longrightarrow {}^-HN.\,C = O.\,NH_2+NH_4^+$$

$$\underset{\text{Acetamide}}{H_3C.\,C = O.\,NH_2}+NH_3 \longrightarrow H_3C.\,C = O.NH^-+NH_4^+$$

$$\underset{\text{Acetamidine}}{H_3C.\,C= NH.\,NH_2}+NH_3 \longrightarrow H_3C.C = NH.\,NH^-+NH_4^+$$

$$\underset{\text{Sulphamide}}{H_2N.\,SO_2.\,NH_2}+NH_3 \longrightarrow H_2N.\,SO_2.\,NH^-+NH_4^+$$

Similarly sulphamic acid acts as a monobasic acid in aqueous solution but in liq. NH_3 it acts as a dibasic acid.

$$H_2N.SO_2.\,OH+H_2O \longrightarrow H_2N.\,SO_2.O^-+H_3O^+$$

$$\underset{\text{Sulphamic acid}}{H_2N.\,SO_2.OH}+2NH_3 \longrightarrow {}^-HN.\,SO_2.\,O^-+2NH_4^+$$

(5) **Reactions of ammono bases**. Many metal salts react with ammono bases to give amides, imides and nitrides which get precipitated in liq. NH_3, *e.g.*

$$\text{salt+ammono base} \xrightarrow{NH_3(l)} \text{salt}$$

$$AgNO_3+KNH_2 \xrightarrow{NH_3(l)} \underset{\text{amide}}{AgNH_2}\downarrow +KNO_3$$

$$PbI_2+2KNH_2 \xrightarrow{NH_3(l)} \underset{\text{imide}}{PbNH}\downarrow + 2KI+NH_3$$

$$BiI_3+3KNH_2 \xrightarrow{NH_3(l)} \underset{\text{nitride}}{Bi\,N}\downarrow +3KI+2NH_3$$

(6) **Acid-base reactions and formation of ammono salts.** These are also called **neutralisation reactions.** *In these reactions ammono acids and ammono bases react together and give the ammono salt and the solvent liq.* NH_3.

The following reactions illustrate the acid-base reactions in liq. NH_3.

$$\text{Ammono acid} + \text{Ammmono base} \xrightarrow{NH_3(l)} \text{Ammono salt} + \text{solvent}$$

$$NH_4NO_3 + KNH_2 \xrightarrow{NH_3(l)} KNO_3 + 2NH_3$$

$$\underset{\text{Guanidine}}{H_2N.C = NH.NH_2} + KNH_2 \xrightarrow{NH_3(l)} K^+[HN.C = NH.NH_2]^- + NH_3$$

$$\underset{\text{Acetamide}}{H_3C.C = O.NH_2} + KNH_2 \xrightarrow{NH_3(l)} K^+[H_3C.C = O.NH]^- + NH_3$$

$$\underset{\text{urea}}{H_2N.C = O.NH_2} + KNH_2 \xrightarrow{NH_3(l)} K^+[H_2N.C = O.NH]^- + NH_3$$

$$2NH_4I + PbNH \xrightarrow{NH_3(l)} PbI_2 + 3NH_3$$

$$3NH_4I + BiN \xrightarrow{NH_3(l)} BiI_3 + 4NH_3$$

(7) **Ammonolysis reactions (or ammonolytic reactions).** In these reactions the concentration of either NH^{4+} or NH_2^- ion is increased.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$SiCl_4 + 8NH_3 \rightleftharpoons Si(NH_2)_4 + 4NH_4^+ + 4Cl^-$$

$$H^- + NH_3 \rightleftharpoons NH_2^- + H_2$$

In these reactions an atom, ion or radical from the compound undergoing ammonolysis is replaced by $-NH_2$, $=NH$ or $\equiv N$ groups. Let us study the ammonolytic reactions under the following headings :

(*i*) *Ammonolysis of Inorganic halides.* The ammonolytic reactions of inorganic halids have been studied in detail. Many inorganic covalent halides undergo ammonolysis in liq. NH_3, while the ionic halides do not tend to ammonolyse. The ammonolytic reactions and the formation of corresponding ammonolysis products in case of some inorganic halides are shown below :

$$BX_3 \xrightarrow{NH_3(l)} B(NH_2)_3 + 3NH_4X$$

$$SO_2Cl_2 \xrightarrow{NH_3(l)} SO_2(NH_2)_2 + NH_4Cl$$

$TiCl_4$ is ammonolysed in steps in excess of liq. NH_3

$$TiCl_4 \xrightarrow{+NH_3(l)} TiCl_3(NH_2) \xrightarrow{+NH_3(l)} TiCl_2(NH_2)_2$$

$$\xrightarrow{+NH_3(l)} TiCl(NH_2)_3 \xrightarrow{+NH_3(l)} Ti(NH_2)_4$$

$HgCl_2$ and SnX_4 halides are not completely ammonolysed.

$$Hg_2Cl_2 \xrightarrow{NH_3(l)} Hg + HgCl(NH_2) + NH_4Cl$$

$$SnX_4 \xrightarrow[-33{\cdot}5^\circ C]{NH_3(l)} SnX(NH_2)_3$$

(*ii*) *Ammonolysis of Organic Compounds.* Organic halides also undergo slow ammonolysis at the boiling point of liq. NH_3 and give mixtures of primary, secondary and tertiary amines ·

$$RX + 2NH_3 \longrightarrow RNH_2 + NH_4X$$

$$RX + RNH_2 \xrightarrow{+NH_3} R_2NH + NH_4X$$

$$RX + R_2NH \xrightarrow{+NH_3} R_3N + NH_4X$$

$$(X = F, Cl, Br, I)$$

(*iii*) *Ammonolysis of alkali metal hydrides and oxides* has also been found possible.

$$MH \xrightarrow{NH_3(l)} M(NH_2) + H_2$$

$$M_2O \xrightarrow{NH_3(l)} 2M(NH_2) + H_2O$$

(8) **Complex formation reactions.** We know that hydroxides or oxides of certain metals dissolve in excess of alkali to yield *soluble hydroxo complex, e.g.*

$$\underset{\text{(Insoluble)}}{Zn(OH)_2} + 2NaOH \xrightarrow{H_2O} \underset{\substack{\text{Soluble hydroxo}\\\text{complex}}}{Na_2[Zn(OH)_4]}$$

Similarly many insoluble metal amides, immides and nitrides dissolve in solution of KNH_2 in liq. NH_3 to form *soluble amido complex, e.g.*

$$\underset{\text{(Insoluble)}}{Zn(NH_2)_2} + 2KNH_2 \xrightarrow{NH_3\ (l)} \underset{\substack{\text{Soluble amido}\\\text{complex}}}{K_2[Zn(NH_2)_4]}$$

Aluminium amalgam reacts with KNH_2 solution in liq. NH_3 and forms soluble complex ion, ammono aluminate, $[Al(NH_2)_4]$

$$Al^{3+} + 3NH_2^- \overset{NH_3(l)}{\rightleftharpoons} \underset{\text{insoluble}}{[Al(NH_2)_3]\downarrow} \underset{+NH_2^-}{\overset{NH_3\ (l)}{\rightleftharpoons}} \underset{\substack{\text{Soluble amide}\\\text{complex}}}{[Al(NH_2)_4]^-}$$

$SnCl_4$ reacts with NH_3 at $-63^\circ C$ and an ammonolysis product, $SnCl(NH_2)_3$, is formed by the replacement of three chlorine atoms in $SnCl_4$ by three $-NH_2$ groups. At $-36^\circ C$ it has been observed with the help of ion-exchange experiments that the resulting solution contains only one mole of ammonium chloride, the probable explanation of which is that the higher temperature (namely $-36^\circ C$) gives a more concentrated solution of NH_4Cl which breaks down the polymeric structure of $SnCl(NH_2)_3$ and forms the complex compound.

$$SnCl_4 + 6NH_3 \xrightarrow{-63°C} \underset{\substack{\text{Ammonolysis product}\\ \text{with polymeric structure}}}{SnCl(NH_2)_3} + 3NH_4Cl$$

$$\xrightarrow{-36°C} \underset{\text{Complex compound}}{(NH_4)_2[SnCl_3(NH_2)_3]} + NH_4Cl$$

Similar is the case with TiI_4.

$$TiI_4 + 6NH_3 \longrightarrow TiI(NH_2)_3 + 3NH_4I \xrightarrow[\text{temp.}]{\text{higher}} \underset{\text{Complex compound}}{(NH_4)_2[TiI_3(NH_2)_3]} + NH_4I$$

(9) **Reduction-oxidation (Redox) reactions.** Redox reactions are those in which the nitrogen or hydrogen of ammonia molecule undergoes a change in its oxidation number.

Following are the important redox reactions occurring in liq. NH_3.

(*i*) Catalytic oxidation of NH_3 to NO.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

(*ii*) Reduction of metal oxide with liq. NH_3 at high temperature.

$$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$$

(*iii*) *Oxidation of active metals* :

$$3Mg + 2NH_3 \longrightarrow Mg_3N_2 + 3H_2$$

(*iv*) The following reactions illustrate the reduction reactions which may be carried out in liq. NH_3.

$$(a)\ \overset{\text{II}}{[Ni(CN)_4]^{2-}} + 3e^-_{(am)} \longrightarrow \underbrace{\overset{\text{I}}{[Ni(CN)_3]^{2-}} + CN^-}$$

$$\Big\downarrow +e^-_{(am)}$$

$$[Ni^0(CN)_4]^{4-}$$

Evidently in reaction (*a*), Ni^{II} is reduced to Ni^0.

$$(b)\ CuI + Na \xrightarrow{NH_3(l)} Cu + NaI.$$

$$(c)\ 4ZnI_2 + 9Na \xrightarrow{NH_3(l)} NaZn_4 + 8NaI$$

(*v*) In liq. NH_3 elementary iodine acts as a weak oxidising agent and can, therefore, oxidise $K_4[Sn^{II}(NH_3)_6]$ to $K_2[Sn^{IV}(NH_3)_6]$.

$$\underset{\text{Petassium ammono-stannite}}{K_4[Sn^{II}(NH_2)_6]} + I_2 \underset{}{\overset{+NH_3(l)}{\rightleftharpoons}} \underset{\text{Pot. ammono-stannate}}{K_2[Sn^{IV}(NH_2)_6]} + 2KI$$

(*vi*) The oxidising action of very strong oxidising agents in liq. NH_3 is considerably weaker than in water solution, *e.g.*, HNO_3 in liq. NH_3 does not act as an oxidising agent and permanganate (*e.g.*, $KMnO_4$) acts as a weaker oxidising agent in liq. NH_3. $KMnO_4$ is reduced by a solution of potassium in liq. ammonia first to K_2MnO_4 and finally to MnO. The latter reaction is represented as :

$$K_2MnO_4 + 4K + 3NH_3 \rightleftharpoons MnO + 3KNH_2 + 3KOH$$

$KMnO_4$ is also reduced to K_2MnO_4 by a liq. NH_3 solution of KNH_2 :

$$6KMnO_4 + 6KNH_2 \overset{NH_3(l)}{\rightleftharpoons} 6K_2MnO_4 + 4NH_3 + N_2$$

(*vii*) Various organo-metallic compounds have been reduced by an alkali metal solution in liq. NH_3

$$(C_6H_5)_2BiI + 2Na \xrightarrow{NH_3(l)} [(C_6H_5)_2Bi]Na + NaI$$

(10) **Metal-ammonia solutions and their reactions.** (*a*) *Solutions of metals in liquid ammonia.* Metals that have low ionisation energies, low energies of sublimation and high energies of solvation, alkali metals, alkaline earth metals, Al, europium and ytterbium readily dissolve in liq. NH_3 and give metal-ammonia solutions. These are blue in colour in dilute and bronze-coloured in concentrated solutions. The absorption spectra of the blue solutions are alike, regardless of the metal dissolved in the solution. The blue solutions are excellent electrolytes. The bronze-coloured solutions (*i.e.* concentrated solutions) have high thermal coefficient of electrical conductance approaching that of the free metal whereas the electrolytic conductance of the blue-coloured solutions (*i e.* dilute solutions) is of the magnitude of an electrolytic solution.

By simply evaporating the alkali-metal-ammonia solutions, alkali metal can be recovered. Alkaline earth metal-ammonia solutions on evaporation give hexammonate, $M(NH_3)_6$, where M = alkaline earth metal, indicating that the solvent action is chemical.

All metal ammonia solutions, upon long standing or in presence of a suitable catalyst, undergo decomposition and give H_2 gas and the metal amide.

$$M + nNH_3 \longrightarrow \frac{n}{2}H_2\uparrow + M(NH_2)_n$$

This decomposition reaction proceeds rapidly in presence of small amounts of certain catalysts such as Fe_2O_3 or Pt-black.

The blue metal ammonia dilute solutions are paramagnetic in character (*i.e.* if these solutions are placed in magnetic field, they will be attracted into the field), indicating the presence of unpaired electrons. As the concentration of the solutions increases, the magnetic susceptibility per mole of the solute decreases.

It is now believed that in concentrated solutions the electrons are largely free *i.e.*

$$M \rightleftharpoons M^+ + e^- \qquad ...(1)$$

On the other hand in dilute solutions the electrons and the metal ions, M^+, are solvated (*i.e.* ammoniated) reversibly as :

$$M^+ + xNH_3 \rightleftharpoons \underset{\text{ammoniated cation}}{M(NH_3)_x^+} \qquad ...(2)$$

$$e^- + yNH_3 \rightleftharpoons \underset{\text{ammoniated electron}}{e(NH_3)_y^-} \qquad ...(3)$$

Thus the properties of metal-ammonia solutions are best accounted for in terms of an equilibrium represented by (4) obtained by adding (1), (2) and (3),

$$e + M + (x + y)NH_3 \rightleftharpoons [M(NH_3)_x]^+ + [e(NH_3)_y]$$

or

$$M \overset{NH_3(l)}{\rightleftharpoons} M^+_{(am)} + e^-_{(am)} \qquad ...(4)$$

where the ammoniated cation and ammoniated electron have been represented as $M^+_{(am)}$ and $e^-_{(am)}$ respectively.

The electrons are believed to occupy the cavities in the solvent surrounded by NH_3 molecules whose protons are oriented towards the free electrons. As the concentration increases, the $M^+_{(am)}$ cations tend to bond together by $e^-_{(am)}$ into aggregates such as M_2, M_3, etc. In the concentrated bronze-coloured solutions, the $M^+_{(am)}$ cations and $e_{(am)}$ are bonded together in a manner which is similar to that of ordinary metal ions of the same size in a molten metal.

(*b*) *Reaction of metal-ammonia solutions.* Since the blue metal-ammonia solutions contain highly mobile, ammoniated electrons, such solutions can act as strong reducing agents, particularly for reducing those substances which are soluble in liq. NH_3.

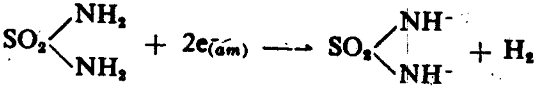
Now since the reducing agents which are stronger than hydrogen, react with water to liberate hydrogen, these cannot generally be used in aqueous solutions. It is for this reason that many metal ammonia solutions which are strong reducing agents are widely used to bring about a number of reduction reactions. Some typical reactions are mentioned below :

(*i*) *Reduction of non metallic elements.* If metal-ammonia solution is treated with non-metallic element, reduction products are obtained by direct combination.

(*ii*) Metal-ammonia solutions are quickly decolorised by ammonium salts or by other acids which are reduced.

$$NH_4^+ + e_{(am)} \longrightarrow NH_3 + \tfrac{1}{2} H_2$$

This further supports the view that the blue colour is due to ammoniated electrons



$$SO_2\begin{matrix}NH_2\\NH_2\end{matrix} + 2e_{(am)} \longrightarrow SO_2\begin{matrix}NH^-\\NH^-\end{matrix} + H_2$$

(*iii*) Many organic compounds undergo reduction in metal-ammonia solutions.

$$\underset{\text{Acetylenic hydrocarbon}}{RC\equiv CH} + e^-_{(am)} \xrightarrow[\text{NH}_3(l)\text{ not in excess}]{\text{metal dissolved in}} \underset{\text{Acetylide ion}}{RC\equiv C^-} + H$$

$$RC\equiv CH + \tfrac{1}{2}H_2 \xrightarrow[\text{in NH}_3(l)\text{ in excess}]{\text{metal dissolved}} \underset{\text{ethylenic derivatives}}{RC=CH_2}$$

(*iv*) A large number of organometallic compounds of various types can react with metal-ammonia solutions and form a series of compounds containing metal bonds.

LIQUID SULPHUR DIOXIDE AS SOLVENT

Liquid sulphur dioxide is a water like solvent and as such is used extensively for carrying out a number of chemical reactions. Its boiling point is 10°C and freezing point —75·5°C. Since the liquid range is sufficiently high, it can be used as a solvent.

The auto-ionisation occurring in liq. SO_2 takes place as follows:

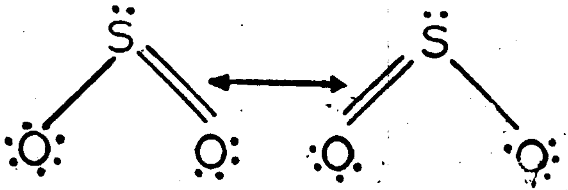
$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

The thionyl ion (SO^{2+}) is analogous to the hydronium ion (H_3O^+) and NH_4^+ ion and SO_3^{2-} ion corresponds to OH^- and NH_2^- ion of the aqueous and liq. NH_3 system

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

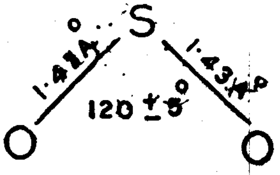
Dipole moment of SO_2 is 1·61 D. Its dielectric constant is 17·27 (at —16·5°C) and it can dissolve many salts.

The true structure is considered to be a resonance hybrid of I and II structures shown below :



I II

Electron diffraction has shown that its structure is



Since S-atom contains a vacant bonding orbital, it can act as an electron acceptor and can, therefore, form molecular complexes.

Solubility of Inorganic materials in liq. SO_2. In general, iodides are most soluble followed by thiocyanates. The solubilities of alkali metal halides decrease in the order MI > MBr > MCl > MF. Alkali metal sulphites and acetates are soluble. Metal sulphates, alkali metal thiocyanates and cyanides are soluble. Metal sulphates, sulphides, oxides and hydroxides are virtually insoluble. Many of the ammonium, thallium and mercuric salts are soluble, The substances such as IBr, PBr_3, CCl_4, $SiCl_4$, $GeCl_4$ and $SnCl_4$ are quite soluble in liq. SO_2.

Many substances such as Br_2, ICl, BCl_3, PCl_3, $AsCl_3$ CS_2, $POCl_3$, $SOCl_2$, $SO(CH_3COO)_2$ and many sulphuryl compounds, SO_2X_2, are completely miscible with liq. SO_2. The miscible nature of $SOCl_2$ has been utilised in the preparation of a large number of thionyl derivatives by the metathetical reactions of liq. SO_2.

Solubility of Organic Compounds in liq. SO_2. As might be expected from the value of dielectric constant of SO_2, covalent organic compounds are more soluble in liq. SO_2 than the ionic compounds. Aromatic hydrocarbons and alkenes are more soluble than the alkanes. Liq. SO_2 has also been used as a medium for conducting a number of organic reactions such as Friedel-Crafts' sulphonation and bromination reactions.

Conductivity of salt solutions in SO_2. The solutions of alkali metals, ammonium and tetraalkyl ammonium chlorides, bromides, iodides and thiocyanates in liq. SO_2 are moderately good conductors. On the other hand the mono-, di- and tri-alkyl ammonium salts are very poor conductors.

The conductivity of electrolyte solutions in liq. SO_2 roughly increases with the size of the cation. Thus the order of conductivity may be shown as: $Na^+ < NH_4^+ < K^+ < Rb^+ < (CH_3)_3S^+ < (CH_3)_4N^+$ etc. The conductivity of the anions increases ir the order $SCN^- < ClO_4^- < Cl^- < I^-$ etc.

Many covalent compounds such as Br_2, I_2, PBr_5, $AsBr_3$, $SbCl_5$, S_2Br_2, IBr, ICl, ICl_3, $SOBr_2$, $(C_6H_5)_3CCl$ etc. behave as electrolytes in liq. SO_2.

The solutions of many tri-substituted hydronium salts such as $[(C_2H_5)_3O]BF_4$, $[(CH_3)_3O]BF_4$ and $[(C_2H_5)_3O]_5SbCl_6$ in liq. SO_2 are moderately good conductors.

Chemical reactions that can occur in liquid sulphur dioxide.

Chemical reactions that can occur in liq. SO_2 can be classified under the following headings :

(1) **Metathetical or precipitation reactions.** Precipitation reactions in liquid SO_2 have been studied by Jander. There are many precipitation reactions which may conveniently be carried out in liq. SO_2 due to the specific solubility relationships. Equations illustrating the precipitations of several insoluble materials upon mixing the soluble compounds in liq. SO_2 are as follows :

$$BaI_2 + Zn(CNS)_2 \rightleftharpoons Ba(CNS)_2\downarrow + ZnI_2$$
$$SbCl_3 + 3LiI \rightleftharpoons SbI_3\downarrow + 3LiCl$$
$$AlCl_3 + 3NaI \rightleftharpoons 3NaCl\downarrow + AlI_3$$
$$PbF_2 + Li_2SO_4 \rightleftharpoons PbSO_4\downarrow + 2LiF$$

A large number of new thionyl derivatives have been prepared from the miscible solutions of $SOCl_2$ in liq. SO_2,

$$2Ag(CH_3COO) + SOCl_2 \xrightarrow{SO_2(l)} 2AgCl\downarrow + \underset{\text{Thionyl acetate}}{SO(CH_3COO)_2}$$

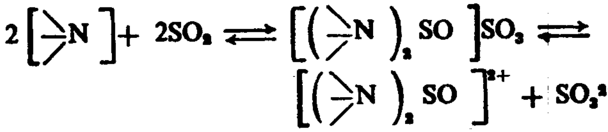
$$2KI + SOCl_2 \xrightarrow{SO_2(l)} 2KCl\downarrow + \underset{\text{Thionyl iodide}}{SOI_2}$$

$$2KBr + SOCl_2 \xrightarrow{SO_2(l)} 2KCl\downarrow + \underset{\text{Thionyl bromide}}{SOBr_2}$$

$$2NH_4(SCN) + SOCl_2 \xrightarrow{SO_2(l)} 2NH_4Cl\downarrow + \underset{\text{Thionyl thiocyanate}}{SO(SCN)_2}$$

$SO(CH_3COO)_2$, SOI_2 and $SO(SCN)_2$ have not been isolated from the mother liquor of these reactions, presumably due to secondary decomposition reactions that occur,

The reaction of NH_3 and its organic derivatives with the solvent, namely SO_2, can be represented as :



(2) **Acid-base (or salt formation or neutralisation) reactions.** For the first time Cody and Elsey proposed the auto-ionisation of liq. SO_2 which was later on supported by Jander and Wickert.

$$\underset{\text{Acid}_1}{SO_2} + \underset{\text{Base}_2}{SO_2} \rightleftharpoons \underset{\text{Acid}_2}{SO^{2+}} + \underset{\text{Base}_1}{SO_3^{2-}}$$

From the equation representing the auto-ionisation of liq. SO_2, it is clear that the compounds containing or making available SO_3^{2-} ions will act as typical bases in liq. SO_2. Thus the alkali metal sulphites such as Na_2SO_3 behave as bases in liq. SO_2.

Similarly the compounds containing or making available SO^{2+} ions will behave as typical acids in liq. SO_2. The compounds such as $SOCl_2$ and $SOBr_2$ behave as acids in liq. SO_2.

Some of the neutralisation reactions studied by Jander in liq. SO_2 are mentioned below :

Acid	*Base*		*Salt*	*Solvent*
$SOCl_2$	$+ Cs_2SO_3$	$\longrightarrow$	$2CsCl$	$+ 2SO_2$
$SOBr_2$	$+ [N(CH_3)_4]_2SO_3$	$\longrightarrow$	$2[N(CH_3)_4]Br$	$+ 2SO_2$
$SO(SCN)_2$	$+ K_2SO_3$	$\longrightarrow$	$2K(SCN)$	$+ 2SO_2$

The reactions occurring between sulphites and thionyl compounds in liq. SO_2 are assumed to occur by ionic mechanism.

$$SO_3^{2-} + SO^{2+} \longrightarrow 2SO_2$$

When $SOCl_2$ or $SOBr_2$ is dissolved in SO_2 tagged with radioactive isotope, S^{35}, exchange is very low which makes it clear that free SO^{2+} plays no important role in the mechanism of reaction in liq. SO_2.

(3) **Solvolysis or solvolytic reactions and formation of solvolytic products.** It is only a limited number of salts that undergo solvolysis reactions in liq. SO_2.

Many halides except $SbCl_3$, $SbCl_5$, $SiCl_4$, and $SnCl_4$, VCl_5, SCl_2, SCl_4 and M Cl_6 readily undergo solvolysis in liq. SO_2.

$$PCl_5 + SO_2\,(l) \longrightarrow POCl_3 + SOCl_2$$

$$\left.\begin{aligned} NbCl_5 + SO_2\,(l) &\xrightarrow{70°C} NbOCl_3 + SOCl_2 \\ WCl_6 + SO_2\,(l) &\xrightarrow{70°C} WOCl_4 + SOCl_2 \\ UCl_6 + 2SO_2(l) &\longrightarrow UO_2Cl_2 + 2SOCl_2 \end{aligned}\right\}\ \text{In sealed tubes.}$$

However, the halides such as $SbCl_3$, $SiCl_4$, $SnCl_4$ undergo hydrolysis, form clear solutions in liq. SO_2, with no sign of solvolysis.

(4) **Solvation reactions and formation of solvates.** Many of the most soluble salts form the addition compounds with the solvent. The addition compounds are called solvates which are analogous to hydrates and ammoniates formed in water and liq NH_3 respectively. Typical examples of solvates are : $NaI.4SO_2$, $KI.4SO_2$, $RbI.4SO_2$, $SrI_2.4SO_2$, $K(SCN).2SO_2$, $Cs(SCN).0.5SO_2$, $[(CH_3)_4N].3SO_2$, Dioxane . $5SO_2$, Dioxane . $2SO_2$, Anisole . SO_2.

(5) **Complex formation reactions.** Walden and his collaborators for the first time reported that the formation of complex compounds in liq. SO_2 is also possible.

A large number of complex compounds is formed by $SbCl_3$ and $SbCl_5$ in liq. SO_2, *e.g.*,

$$\left.\begin{aligned} SbCl_3 + 3KCl &\xrightarrow{SO_2(l)} K_3\,[SbCl_6] \\ SbCl_5 + KCl &\xrightarrow{SO_2(l)} K\,[SbCl_6] \\ SbCl_5 + [N(CH_3)_4]\,Cl &\xrightarrow{SO_2(l)} [N(CH_3)_4][SbCl_6] \\ SbCl_5 + CH_3COCl &\xrightarrow{SO_2(l)} [CH_3CO][SbCl_6] \end{aligned}\right]\ \text{Complex compounds}$$

Liq. SO_2 has also been used as a medium in the reactions for the preparation of hexa chloro-antimonates, *e.g.*,

$$\left.\begin{aligned} 2SbCl_5 + 3SOCl_2 &\xrightarrow{SO_2(l)} [SO]_3\,[SbCl_6]_2 \\ SbCl_5 + NOCl &\xrightarrow{SO_2(l)} [NO]\,[SbCl_6] \end{aligned}\right\}\ \text{Hexa chloro-antimonates}$$

(6) **Amphoterism reactions.** The salts of the metals whose hydroxides are emphoteric behave in aquoeus and liq. SO_2 in an analogous way, *e.g.* the reaction of $AlCl_3$ with OH^- ions in aqueous medium is analogous to its reaction with SO_3^{2-} ions in liq. SO_2, since in both the cases a precipitate is obtained.

$$AlCl_3 + 3OH^- \xrightarrow{H_2O} \underset{\text{ppt.}}{Al(OH)_3\downarrow} + 3Cl^-$$

$$2AlCl_3 + 3SO_3^{2-} \xrightarrow{SO_2(l)} \underset{\text{ppt.}}{Al_2(SO_3)_3\downarrow} + 6Cl^-$$

These precipitates dissolve in excess of the precipitant *viz.* OH^- and SO_3^{2-} ions respectively to form the soluble complex

$$\underset{\text{ppt.}}{Al(OH)_3} + \underset{\text{(excess)}}{OH^-} \xrightarrow{H_2O} \underset{\text{soluble complex}}{[Al(OH)_4]^-}$$

$$\underset{\text{ppt.}}{Al_2(SO_3)_3} + \underset{\text{(excess)}}{3SO_3^{2-}} \xrightarrow{SO_2(l)} \underset{\text{soluble complex}}{2[Al(SO_3)_3]^{3-}}$$

The behaviour of $GaCl_3$ is also similar to that of $AlCl_3$.

The amphoterism reactions of liq SO_2 are included in complex formation reactions.

(7) **Reduction-oxidation (Redox) reactions.** At high temperatures gaseous SO_2 may act either as an oxidising agent or as a reducing agent, depending on the nature of the substance with which gaseous SO_2 reacts. On the other hand liq. SO_2 does not have any strong oxidising or reducing properties, although it may serve as a medium for oxidation-reduction reactions.

Although liq. SO_2 cannot reduce bromine or iodine, a sulphite in liq. SO_2 reduces iodine as is indicated by the reactions shown below :

$$I_2 + 2\,RSO_3 \longrightarrow RSO_4 + RI_2 + SO_2$$

$$I_2 + 2[(NEt_3)_2\,SO]\,SO_3 \longrightarrow [(NEt_3)_2\,SO]SO_4 + [(NEt_3)_2\,SO]\,I_2 + SO_2$$

Conversely soluble iodides such as KI can be oxidised to free iodine by the reagents such as $SbCl_5$.

$$6KI + 3SbCl_5 \rightleftharpoons 3I_2 + SbCl_3 + 2K_3[SbCl_6]$$

Some other reactions in liq. SO_2 are :

$$\underset{\text{acetyl fluoborate}}{CH_3COBF_4} + CH_3COOK \xrightarrow{SO_2(l)} (CH_3CO)_2O + KBF_4$$

$$CH_3COBF_4 + \underset{\text{Triphenyl chloromethane}}{(C_6H_5)_3CCl} \xrightarrow{SO_2(l)} (CH_3CO)Cl + \underset{\text{yellow powder}}{(C_6H_5)_3CBF_4\downarrow}$$

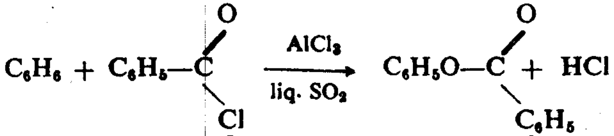
(8) **Reactions with organic compounds.** Various organic compounds are soluble in liq. SO_2. It is a useful solvent for several types of organic synthetic reactions due to its non-inflammability, relative inertness and convenient temperature range. It serves as a

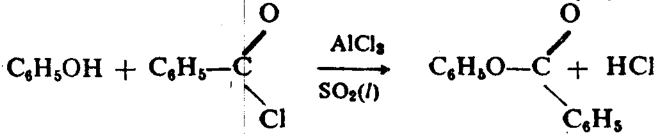
medium for a number of organic reactions some of which are mentioned below :

(*a*) *Sulphonation.* Various aromatic hydrocarbons undergo sulphonation in liq. SO_2 and thus give good yields, *e.g.*,

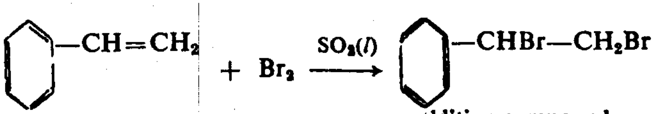
$$C_6H_6 + ClSO_3H \xrightarrow{SO_2\,(l)} C_6H_5SO_3H + HCl$$

(*b*) *Friedel-Craft's reactions.* Since $AlCl_3$ which is used as a catalyst in this reaction is highly soluble in liq. SO_2, Friedel-Craft's reaction is carried out in liq. SO_2 medium.

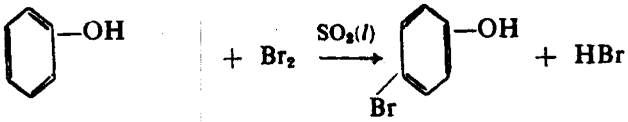




(*c*) *Bromination.* Liq. SO_2 is also used as a solvent in various bromination reactions



addition compound



substitution compound

LIQUID DINITROGEN TETRAOXIDE (liq. N_2O_4)

Because of its convenient liquid range its very interesting chemical characteristics and ease of preparation and purfication, liq. N_2O_4 has been the subject of much research during the years 1935-40 as a medium for chemical reactions. Since it is a powerful oxidising agent, it can oxidise reducing substances explosively particularly of organic nature. Consequently extreme care must be taken in carrying out the reactions with reducing agents so that the possibility of such substances being oxidised explosively may be minimised.

It has a low dielectric constant and hence is a poor solvent for ionic substances but good solvent for organic compounds. The auto-ionisation of liq. N_2O_4 takes place as

$$N_2O_4 + N_2O_4 \rightleftharpoons \underset{\text{Nitrosyl ion}}{2NO^+} + \underset{\text{Nitrate ion}}{2NO_3^-}$$

The auto-ionisation of liq. N_2O_4 can be promoted by solvents of high dielectric constant such as nitromethane.

Chemical reactions

Following are the important chemical reactions that occur in liq. N_2O_4.

(1) **Acid-base (or neutralisation or salt formation) reactions.** Auto-ionisation of liq. N_2O_4 as shown above indicates that, according to solvent system concept, substances furnishing NO^+ ions (*e.g.* NOCl, NOBr etc.) would behave as acids in liq. N_2O_4 and those furnishing NO_3^- ions (*e.g.* $AgNO_3$, $[Et_2NH_2]NO_3$) would behave as bases. Thus the solution of NOCl in liq. N_2O_4 reacts with solid $AgNO_3$ to give AgCl (salt) and the solvent.

$$\underset{\text{acid}}{NOCl} + \underset{\text{base}}{AgNO_3\,(s)} \longrightarrow \underset{\text{salt}}{AgCl\downarrow} + \underset{\text{solvent}}{N_2O_4}$$

(2) **Reactions with metals.** Very active metals like alkali metals react with liq. N_2O_4 in the same manner as water does.

$$M + N_2O_4 \longrightarrow NO + MNO_3$$

$$M + H_2O \longrightarrow MOH + \tfrac{1}{2}H_2$$

Addition of HCl to H_2O increases the reactivity of H_2O towards metals. Similarly the addition of NOCl to liq. N_2O_4 also increases its reactivity towards metals, *e.g.* Zn, Fe, Sn react with solution of NOCl in liq. N_2O_4.

$$Zn + 2NOCl \xrightarrow{N_2O_4(l)} ZnCl_2 + 2NO$$

$$Sn + 4NOCl \xrightarrow{N_2O_4(l)} (NO_2)\,SnCl_4 + 2NO$$

$$M + 2HCl \xrightarrow{H_2O} MCl_2 + H_2$$

(3) **Complex formation.** $Zn(NO_3)_2$ dissolves readily in a solution of diethyl ammonium nitrate, $[Et_2NH_2]NO_3$ in liq. N_2O_4 to yield a nitrato zinc complex which is of undetermined composition.

$$\underset{\text{solid}}{Zn(NO_3)_2} + x\,[Et_2NH_2]\,NO_3 \xrightarrow{N_2O_4(l)} \underbrace{[Et_2NH_2]_x\,[Zn(NO_3)_{x+2}]}_{\substack{\text{Diethyl ammonium}\\ \text{nitrato zincate}}}$$

The above reaction also indicates the *amphoteric reaction.* Some solvate are also formulated as complex salts as shown under *solvate formation reactions* given below.

(4) **Solvate formation reactions.** Nitrates of some metals such as Zn, U and Fe react with liq. N_2O_4 to form the solvates, *e.g.* $Zn(NO_3)_3 \cdot 2N_2O_4$, $UO_2(NO_3)_2 \cdot N_2O_4$ and $Fe(NO_3)_3 \cdot N_2O_4$ respectively. These solvates may also be formulated as complex salts : $(NO)_2[Zn(NO_3)_4]$, $NO[UO_2(NO_3)_3]$ and $NO[Fe(NO_3)_4]$.

(5) **Solvolysis reactions.** A number of solvolysis reactions have been studied in liq. N_2O_4. Some examples are :

$$[Mg(H_2O)_6]Cl_2 + N_2O_4(l) \longrightarrow [Mg(H_2O)_6](NO_2)_2 + 2NOCl$$

$$[Et_2NH_2]Cl + N_2O_4(l) \longrightarrow [Et_2NH_2]NO_3 + NOCl$$

$$Mg(ClO_4)_2 + 2N_2O_4(l) \longrightarrow Mg(NO_3)_2 + 2NOClO_4$$

$LiCO_3$ gets solvated in presence of traces of water.

$$Li_2CO_3 + 2N_2O_4(l) \xrightarrow[\text{traces of } H_2O]{\text{In presence of}} 2LiNO_3 + N_2O_3 + CO_2 \uparrow$$

LIQUID HYDROGEN FLUORIDE (liq. HF)

Liq. HF has a wide but convenient liquid range (—83°C to 19·4°C). The disadvantages of using HF as a solvent and reaction medium are that it can dissolve only relatively few substances without chemical reaction and that it has poisonous character.

Although HF has a rather low specific conductance, its high dielectric constant makes it an excellent ionising solvent. It is regarded as one of the most water-like of all non-aqueous solvents. It dissolves many inorganic and organic compounds to give highly conducting solutions. Inorganic substances are generally more soluble than organic compounds.

The dissolution of a solute in HF takes place by any of the following mechanisms :

(*i*) HF *may dissociate into* [illegible] *viz.* H and F^- *ions as other ionizing solvents do.*

$$HF \longrightarrow H^+ + F^-$$

$$AF_5 + F^- \longrightarrow AF_6^-$$

$$(A = Sb, As, P)$$

$$\overline{AF_5 + HF \longrightarrow AF_6^- + H^+}$$

Such solutions behave as acidic solutions.

(*ii*) *Chemical addition of* HF *to the solute followed by its dissociation to give* F^- *ion*, e.g.

$$CH_3COOH + HF \longrightarrow CH_3COOH \, . \, HF \longrightarrow CH_3COOH_2^+ + F^-$$

$$HNO_3 + HF \longrightarrow HNO_3 \, . \, HF \longrightarrow HNO_3H^+ + F^-$$

$$KNO_3 + 2HF \longrightarrow KNO_3 \, . \, 2HF \longrightarrow K^+ + H.HNO_3^- + 2F^-$$

(*iii*) *The anion of the solute may be replaced by* F^- *ion*, e.g.

$$KCN + HF \longrightarrow KF + HCN$$

$$KI + HF \longrightarrow KF + HI$$

(*iv*) *Chemical reactions involving more than simple replacement may take place*, e.g.

$$H_2SO_4 + HF \longrightarrow HSO_3F + H_2O$$

$$H_2O + HF \longrightarrow H_3O^+ + F^-$$

$$\overline{H_2SO_4 + 2HF \longrightarrow HSO_3F + H_3O^+ + F^-}$$

Auto-ionisation of HF. The auto-ionisation of HF can be represented as :

$$\underset{}{HF+HF} \longrightarrow \underset{\text{Fluoronium ion}}{H_2F^+} \quad \underset{\text{Fluoride ion}}{+F^-}$$

According to the theory of solvent system any substance capable of giving H_2F^+ ions will behave as an acid in this solvent whereas any substance giving F^- ions will act as a base.

There are only a few substances which can donate protons readily to HF. Thus the substances like HNO_3, H_2SO_4 etc. which can behave as strong acids in aqueous solution behave as bases in HF, *e.g.*

$$HNO_3+HF \longrightarrow H_2NO_3^++F^-$$
$$H_2SO_4+HF \longrightarrow H_3SO_4^++F^-$$

$HClO_4$ which is probably the strongest acid in aqueous solution is amphoteric in HF.

$$HClO_4+HF \longrightarrow HClO_4^++F^- \quad (HClO_4 \text{ acts as a base})$$
$$HClO_4+HF \longrightarrow ClO_4^-+H_2F^+ \quad (HClO_4 \text{ acts as an acid})$$

The only compounds acting as acids in liq. HF are certain electron-acceptor fluorides (*e.g.* BF_3, AsF_3, PF_5 and SbF_5).

$$BF_3+2HF \longrightarrow H_2B^++BF_4^-$$
$$SbF_5+2HF \longrightarrow H_2F^++SbF_6^-$$

These acceptor molecules dissolve in HF to give solutions which dissolve electropositive metals like Mg. This is an evidence in favour of the acidic nature of these solutes.

Substances acting as bases in HF are ionic fluorides which increase the concentration of F^- ions and decrease that of H_2F^- ions.

Weak acids in other systems behave as bases in HF, *e.g.* CH_3COOH behaves as a base in HF.

$$CH_3COOH+HF \longrightarrow CH_3COOH.HF \longrightarrow CH_3COOH_2^++F^-$$

Oxidation-reduction reactions. Oxidation-reduction reactions between hydrofluo acids and metals in HF are not generally different from those taking place between HNO_3 and metals in the aqueous system, *e.g.*

$$3HAsF_6+2Ag \longrightarrow 2AgAsF_6+AsF_3+3HF$$
$$7HIF_6+6Ag \longrightarrow 6AgIF_6+HI+6HF$$
$$4HNO_3+3Ag \longrightarrow 3AgNO_3+NO+2H_2O$$

Precipitation reactions. Some of the precipitation reactions occurring in liq. HF are exemplified by the following reactions.

$$Na_2SO_4+2AgF \xrightarrow{HF(l)} Ag_2SO_4\downarrow+2NaF$$

$$KClO_4 + TlF \xrightarrow{HF(l)} TlClO_4 \downarrow + KF$$

$$NaClO_4 + AgF \xrightarrow{HF(l)} AgClO_4 \downarrow + NaF$$

The precipitation reaction resulting in the formation of silver tetrafluoroborate, $AgBF_4$ is the most important. $AgBF_4$ is obtained as a precipitate when $AgNO_3$ and BF_3 solutions in HF are mixed.

$$AgNO_3 + BF_3 + 2HF \longrightarrow \underset{\text{ppt}}{AgBF_4} + H_2NO_3F$$

Formation of addition compounds. HF also forms a number of addition compounds with metallic fluorides, *e.g.* KF.HF, KF.2HF, KF.3HF, $NH_4F.HF$ etc.

LIQUID HYDROGEN SULPHIDE (liq. H_2S)

Liquid H_2S behaves more like an organic solvent than like water and is thus a much poorer solvent for ionic compounds than water. Only few inorganic compounds dissolve in this solvent without chemical reaction.

Liquid H_2S possesses a very narrow and inconveniently low range (—85° to —60°C) for experimental work and is highly poisonous.

Auto-ionisation of liq. H_2S and acid-base reactions. H_2S ionises as :

$$H_2S + H_2S \rightleftharpoons H_3S^+ + HS^-$$

Thus the substances yielding H_3S^+ ions (or H^+-ions) behave as acids in liq. H_2S while those giving HS^- ions behave as bases in this solvent. Some acid-base reactions have been observed in this solvent, *e.g.* neutralisation reaction between HCl and triethyl ammonium hydrosulphide, $[N(Et)_3H]SH$ has been studied in this medium.

$$\underset{\text{base}}{[N(Et)_3H]SH} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{salt}}{[N(Et)_3H]Cl} + \underset{\text{solvent}}{H_2S}$$

Solvolysis reactions. A number of solvolysis reactions have been studied in liq. H_2S. The following reactions illustrate these reactions.

Compound	+ Solvent	$\longrightarrow$	Solvolysis product + xHCl
$SnCl_4$	$+ 2H_2S(l)$	$\longrightarrow$	$SnS_2 + 4HCl$
PCl_5	$+ H_2S(l)$	$\longrightarrow$	$PSCl_3 + 2HCl$
$SbCl_5$	$+ H_2S(l)$	$\longrightarrow$	$SbSCl_3 + 2HCl$
$HgCl_2$	$+ H_2S(l)$	$\longrightarrow$	$HgS + 2HCl$

LIQUID HYDROGEN CYANIDE (liq. HCN)

Liquid hydrogen cyanide is a highly associated liquid through hydrogen bonding. It has the highest dielectric constant and dipole moment of any other water-like solvent. On the basis of these special properties we would expect liq. HCN to be the best of all ionising solvents. But surprisingly, as an ionising solvent, HCN does not come up to our expectations. In comparison to water it is undoubtedly an inferior solvent. The poisonous nature of HCN has seriously limited the studies in this solvent.

Solubility of different compounds. Many organic compounds like benzene, aniline, methanol, glycerine, urea and ethanol are readily soluble in HCN. Triethyl ammonium chloride, triethyl ammonium picrate and potassium dichloro acetate are also readily soluble in HCN and give solutions with high electric conductivity Propylamine is also soluble but its solution does not conduct electricity.

HCN dissolves both covalent and ionic compounds. NaCl, KCl, NH_4Cl, $NaNO_3$, K_2SO_4 and KI are either soluble or sparingly soluble in HCN. Many covalent chlorides like $POCl_3$, $SOCl_2$, $BiCl_3$, $SbCl_5$ and HCl are soluble and produce ions in the solvating process. $SnCl_4$, $SnBr_4$, SnI_4 and I_2 dissolve in HCN without undergoing ionisation.

Auto-ionisation and acid-base reactions. There is an evidance to show that liq. HCN ionises according to the equation

$$HCN + HCN \rightleftharpoons H_2CN^+ + CN^-$$

$$H_2CN^+ \rightleftharpoons 2H^+ + CN^-$$

$$\overline{HCN + HCN \rightleftharpoons 2H^+ + 2CN^-}$$

Thus, on the basis of acid-base concept the substances capable of releasing protons (*e.g.* soluble acids like H_2SO_4, HNO_3, HCl etc.) act as acids and the compounds giving CN^- ions (*e.g.* alkali metal and substituted ammonium cyanides) act as bases in liq. HCN.

The examples illustrating the conductometric and potentiometric titration reactions are given below :

Solute Titrant Products formed

(*i*)

$$KCN + H_2SO_4 \xrightarrow{HCN(l)} KHSO_4 + HCN$$

$$C_5H_5N + H_2SO_4 \longrightarrow C_5H_5NHHSO_4$$

$$C_5H_5NHHSO_4 + C_5H_5N \longrightarrow (C_5H_5NH)_2SO_4$$

(*ii*)

$$2C_5H_5N + H_2SO_4 \xrightarrow{HCN\ (l)} (C_5H_5NH)_2SO_4$$

(*iii*)

$$SO_3 + (C_2H_5)_3N \xrightarrow{HCN\ (l)} SO_3.(C_2H_5)_3N$$

$$Cl_2CHCOOH + (C_2H_5)_3N \longrightarrow Cl_2CHCOO(C_2H_5)_3NH$$

$$Cl_2CHCOO\ C_2H_5)_3NH + Cl_2CHCOOH \longrightarrow Cl_2CHCOO(C_2H_5)_3NH\text{-}Cl_2CHCOOH$$

(*iv*)

$$2Cl_2CHCOOH + (C_2H_5)_3N \xrightarrow{HCN\ (l)} Cl_2CHCOO(C_2H_5)_3NH.Cl_2\text{-}CHCOOH$$

Complex farmation reactions. The following reactions illustrate the complex formation reaction in liq. HCN.

$$FeCl_3 + 3\underset{\text{Triethyl ammonium cyanide}}{[(C_2H_5)_3NH]CN} \xrightarrow{HCN\ (l)} \underset{\text{Blue ppt}}{Fe(CN)_3} \downarrow + 3[(C_2H_5)_3NH]Cl$$

$$Fe(CN)_3 + 3[(C_2H_5)_3NH]CN \xrightarrow{HCN\ (l)} \underset{\text{soluble complex}}{[(C_2H_5)_3NH]_3^{3+}[Fe(CN)_6]^{3-}}$$

Solvolysis reactions. Solvolysis reactions in liq. HCN correspond to hydrolysis reactions in H_2O. $AgSO_4$ and CH_3COCl are solvolysed according to the equations.

$$Ag_2SO_4 + 2HCN \longrightarrow 2AgCN + H_2SO_4$$

$$CH_3COCl + HCN \longrightarrow CH_3COCN + HCl$$

Formation of solvates. HCN forms few solvates. The solvate $AlCl_3.2HCN$ is best described as iminoformyl carbylamine and hence is formulated as $Al_3.NHCHNC$. $SO_3.3HCN$ or $(OH)_3S(CN)_3$ is another important solvate with SO_3.

ACETIC ACID (CH_3COOH

It is an associated solvent and exists as a dimer in the liquid state. It has a conveniently wide liquid range (16·6°C to 118°C). It is non-ionic and stable under ordinary conditions. A most serious disadvantage of this solvent is the difficulty which is involved in the preparation of anhydrous acid. Its dipole moment is zero and the value of dielectric constant is low (=9·7). From these properties CH_3COOH would be expected to be a poor solvent for ionic compounds but surprisingly a large number of such compounds is soluble in this solvent.

Auto-ionisation and acid-base reactions. There is an evidence which, indicates that CH_3COOH ionises as :

$$CH_3COOH + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$$

Thus on the basis of solvent system concept of acid-base, substances giving the solvated proton ($CH_3COOH_2^+$) in solution are regarded as acids while those giving the CH_3COO^- ions are considered as bases. Typical acid-base reaction between soluble acetate and strong acid is shown below :

$$\underset{\text{base}}{CH_3COONa} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{solvent}}{CH_3COOH}$$

Weak organic bases like acetamide and acetanilide cannot be titrated in aqueous medium but they may be titrated in CH_3COOH medium. Perchloric acid, which is the most highly dissociated of the strong acids in CH_3COOH, is generally used as the titrant. The neutralisation reaction is followed potentiometrically and also by indicators. The weak organic bases function as quite strong bases due to the occurrence of the reaction *viz.*

$$\underset{\text{Weak organic base}}{B} + CH_3COOH \longrightarrow BH^+ + CH_3COO^-$$

Precipitation reactions. The following reactions are the precipitation reactions taking place in liq. CH_3COOH.

$$AgNO_3+CaCl_2 \xrightarrow{CH_3COOH(l)} 2AgCl\downarrow+Ca(NO_3)_2$$

$$Pb(CH_3COO)_2+2NaCl \xrightarrow{CH_3COOH(l)} PbCl_2\downarrow+2CH_3COONa$$

$$Cd(CH_3COO)_2+H_2S \xrightarrow{CH_3COOH(l)} CdS\downarrow+2CH_3COOH$$

Amphoteric reactions. Certain compounds such as $Zn(CH_3COO)_2$ exhibit amphoteric behaviour in liq. CH_3COOH

$$Zn^{2+}+2CH_3COO^- \longrightarrow \underset{\text{Insoluble}}{Zn(CH_3COO)_2} \xrightarrow{+2CH_3COO^-} \underset{\text{soluble complex}}{[Zn(CH_3COO)_4]^{2-}}$$

Complex formation reactions. Certain complex formation reactions take place in liq. CH_3COOH just like in aqueous medium, *e.g.* Fe^{3+} and CNS^- ions react in this medium to form red-coloured complex (insoluble), $[Fe(CNS)_6]^{3-}$. The same complex is formed in aqueous solution.

$$Fe^{3+}+6CNS^- \xrightarrow{CH_3COOH(l)} \underset{\substack{\text{Red-coloured}\\ \text{insoluble complex}}}{[Fe(CNS)_6]^{3-}}$$

The amphoteric behaviour of $Zn(CH_3COO)_2$ in liq. CH_3COOH as shown above may also be included under complex formation reactions.

Solvolysis reactions. These reactions are exemplified by the following reactions :

$$SO_2Cl_2+4CH_3COOH \longrightarrow SO_2(CH_3COO)_2+2CH_3COOH_2^+ +2Cl^-$$

$$CN^-+CH_3COOH \longrightarrow CH_3COO^-+HCN$$

Solvate formation reaction. $CH_3COOK.2CH_3COOH$ is a typical example of a solvate formed in liq. CH_3COOH.

LIQUID BROMINE TRIFLUORIDE (liq.

A fairly high specific contance of liq. BrF_3 indicates that it ionises as :

$$BrF_3+BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

SbF_5 acts as an acid in liq. BrF_3 because it increases the concentration of BrF_2^+ ions as shown below :

$$SbF_5+BrF_3 \longrightarrow BrF_2^+ + SbF_6^-$$

KF, on the other hand, acts as a base in this solvent, because it increases the concentration of BrF_4^- ions as shown :

$$KF+BrF_3 \longrightarrow K^+ + BrF_4^-$$

Neutralisation reactions. Neutralisation reaction occurs on mixing the solutions of SbF_5 and KF in liq. BrF_3 and the salt $K^+[SbF_6]^-$ is formed.

$$KF + BrF_3 \longrightarrow K^+ + BrF_4^-$$
$$SbF_5 + BrF_3 \longrightarrow SbF_6^- + BrF_2^+$$

$$KF + SbF_5 + 2BrF_3 \longrightarrow K^+[SbF_6]^- + 2BrF_3$$

or $$\underbrace{K^+[BrF_4]^-}_{\text{base}} + \underbrace{[BrF_2]^+[SbF_6]^-}_{\text{acid}} \longrightarrow \underbrace{K^+[SbF_6]^-}_{\text{salt}} + \underbrace{2BrF_3}_{\text{solvent}}$$

Neutralisation reactions of this type help us to synthesise many compounds which are difficult to prepare by other methods. Some examples of such syntheses which can be carried out by neutralisation in liq. BrF_3 are given below :

$$\begin{array}{llcll} \text{base} & \text{acid} & & \text{salt} & \text{solvent} \\ Ag^+[BrF_4]^- + & [BrF_2]^+[AuF_4]^- & \longrightarrow & Ag^+[AuF_4]^- & + 2BrF_3 \\ 2[NO]^+[BrF_4]^- + & [BrF_2]_2^+[GeF_6]^{2-} & \longrightarrow & [NO]_2^+[GeF_6]^{2-} & + 4BrF_3 \\ Ag^+[BrF_4]^- + & [BrF_2]^+[SbF_6]^- & \longrightarrow & Ag^+[SbF_6]^- & + 2BrF_3 \end{array}$$

OXYHALIDES

A number of oxyhalides such as phosphorus oxychloride ($POCl_3$), selenium oxychloride ($SeOCl_2$), NOCl, $COCl_2$, CH_3COCl etc. have been used as solvents. The auto-ionisation of these solvents takes place as :

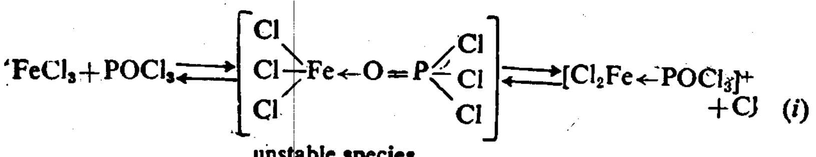
$$POCl_3 + POCl_3 \longrightarrow 2POCl_2^+ + 2Cl^- \quad (\text{Dielectric constant} = 13{\cdot}0)$$
$$SeOCl_2 + SeOCl_2 \longrightarrow 2SeOCl^+ + 2Cl^- \quad (= 46{\cdot}2)$$
$$COCl_2 + COCl_2 \longrightarrow 2COCl^+ + 2Cl^- \quad (= 4{\cdot}34)$$
$$CH_3COCl + CH_3COCl \longrightarrow 2CH_3CO^+ + 2Cl^- \quad (= 16{\cdot}9)$$

Formation of adducts. $POCl_3$ with halides like $FeCl_3$, $SbCl_5$, $AlCl_3$, $TiCl_4$ etc. forms adducts. Since the solutions of these adducts are conducting and can be titrated with bases like $[Et_4N]^+Cl^-$, their structures are $POCl_2^+FeCl_4^-$, $POCl_2^+SbCl_6^-$, $POCl_2^+AlCl_4^-$, $POCl_2^+TiCl_5^-$ and consequently the titration reaction can be shown as :

$$\underbrace{POCl_2^+SbCl_6^-}_{\text{acid}} + \underbrace{[Et_4N]^+Cl^-}_{\text{base}} \longrightarrow \underbrace{POCl_3}_{\text{solvent}} + \underbrace{[Et_4N][SbCl_6]}_{\text{salt}}$$

These adducts behave as acids.

Mechanism of adduct formation. All the Cl^- ions to form $FeCl_4^-$ ion come from $FeCl_3$ as shown below :



(i)

unstable species

$$Cl^- + FeCl_3 \longrightarrow FeCl_4^- \qquad (ii)$$

On adding (*i*) and (*ii*) we get

$$2FeCl_3+POCl_3 \rightleftharpoons FeCl_4^-+[Cl_2Fe\leftarrow POCl_3]^+$$

$$\rightleftharpoons [FeCl_4]^-[POCl_2]^++FeCl_3$$

or

$$FeCl_3+POCl_3 \rightleftharpoons \underset{\text{Adduct}}{[FeCl_4]^-[POCl_2]^+}$$

The reaction of $SnCl_4$ with $SeOCl_2$ to form the adduct $SnCl_6^{2-}$ $2SeOCl^+$ can be shown as :

$$SeOCl_2+SeOCl_2 \rightleftharpoons 2SeOCl^++2Cl^-$$

$$SnCl_4+2Cl^- \rightleftharpoons SnCl_6^{2-}$$

$$2SeOCl_2+SnCl_4 \rightleftharpoons SnCl_6^{2-}.2SeOCl^+$$

This adduct behaves as an acid. Alkali metal chlorides and organic bases (*e.g.* C_5H_5N) form *bases* with $SeOCl_2$ while $SnCl_4$, $TiCl_4$, $AsCl_3$, $FeCl_3$, SO_2 etc. form *acids*.

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8

Transition Elements (d-Block Elements)

DEFINITION AND ELECTRONIC CONFIGURATIONS OF ATOMS

The elements lying between *s*- and *p*-block elements of the periodic table are collectively known as **transition** or **transitional elements (T.E.'s)**: *These elements either in their atomic state or in any of their common oxidation state have partly filled* $(n-1)d$ *orbitals of* $(n-1)$*th main shell. In these elements the differentiating electron enters* $(n-1)d$ *orbitals of* $(n-1)$*th main shell and as such these are called* ***d*-block elements**

The valence-shell configurations of these elements can be represented by $(n-1)d^{1-10}.ns^{0,1,2}$. The predicted and observed valence-shell configurations of these elements are given in Table 8·1.

The configurations clearly show that strictly, according to the definition of *d*- block elements, Cu, Ag and Au should be excluded from *d*- block elements, since these elements, both in their atomic state [with configuration $(n-1)d^{10}ns^1$] and in their +1 oxidation state [with configuration $(n-1)d^{10}$], do not have partly filled $(n-1)\ d$ orbitals. Similarly Zn, Cd and Hg which both in their atomic state $[(n-1)d^{10}ns^2]$ and in +2 oxidation $[(n-1)d^{10}]$ do not contain partly filled $(n-1)\,d$ orbitals, should also be excluded from *d*-block elements. Similar is the case with Pd atom with configuration $4d^{10}5s^0$. Yet, in order to maintain a rational classification of elements, these elements (*viz* Cu, Ag, Au, Zn, Cd, Hg and Pd) are also generally studied with *d*- block elements.

All the *d*-block elements are classified into four series *viz* 3*d*, 4*d*, 5*d* and 6*d* series corresponding to the filling of 3*d*, 4*d*, 5*d* and 6*d* orbitals of $(n-1)$*th* main shell. Each of 3*d*, 4*d* and 5*d* series has ten elements (*see* Table 8·1) while 6*d* series has at present only one element *viz* Ac_{89} whose valence shell configuration is $6d^1\,7s^2$

Irregularities in Configurations. Table 8·1 clearly shows that the observed configurations of the elements shown with asterisk ar

Table [illegible]·1. Observed and predicted valence-shell configurations of *d*-block elements.

Elements of 3d-series	Valence shell configuration		Elements of 4 d-series	Valence shell configuration		Elements of 5d-series	Valence shell configuration	
	Observed	Predicted		Observed	Predicted		Observed	Predicted
Sc_{21}	$3d^1$ $4s^2$	$3d^1$ $4s^2$	Y_{39}	$4d^1$ $5s^2$	$4d^1$ $5s^2$	La_{57}	$4f^0$ $5d^1$ $6s^2$	$4f^0$ $5d^1$ $6s^2$
Ti_{22}	$3d^2$ $4s^2$	$3d^2$ $4s^2$	Zr_{40}	$4d^2$ $5s^2$	$4d^2$ $5s^2$	Hf_{72}	$4f^{14}$ $5d^2$ $6s^2$	$4f^{14}$ $5d^2$ $6s^2$
V_{23}	$3d^3$ $4s^2$	$3d^3$ $4s^2$	*Nb_{41}	$4d^4$ $5s^1$	$4d^3$ $5s^2$	Ta_{73}	$4f^{14}$ $5d^3$ $6s^2$	$4f^{14}$ $5d^3$ $6s^2$
*Cr_{24}	$3d^5$ $4s^1$	$3d^4$ $4s^2$	*Mo_{42}	$4d^5$ $5s^1$	$4d^4$ $5s^2$	W_{74}	$4f^{14}$ $5d^4$ $6s^2$	$4f^{14}$ $5d^4$ $6s^2$
Mn_{25}	$3d^5$ $4s^2$	$3d^5$ $4s^2$	Tc_{43}	$4d^5$ $5s^2$	$4d^5$ $5s^2$	Re_{75}	$4f^{14}$ $5d^5$ $6s^2$	$4f^{14}$ $5d^5$ $6s^2$
Fe_{26}	$3d^6$ $4s^2$	$3d^6$ $4s^2$	*Ru_{44}	$4d^7$ $5s^1$	$4d^6$ $5s^2$	Os_{76}	$4f^{14}$ $5d^6$ $6s^2$	$4f^{14}$ $5d^6$ $6s^2$
Co_{27}	$3d^7$ $4s^2$	$3d^7$ $4s^2$	*Rh_{45}	$4d^8$ $5s^1$	$4d^7$ $5s^2$	Ir_{77}	$4f^{14}$ $5d^7$ $6s^2$	$4f^{14}$ $5d^7$ $6s^2$
Ni_{28}	$3d^8$ $4s^2$	$3d^8$ $4s^2$	*Pd_{46}	$4d^{10}$ $5s^0$	$4d^8$ $5s^2$	*Pt_{78}	$4f^{14}$ $5d^9$ $6s^1$	$4f^{14}$ $5d^8$ $6s^2$
*Cu_{29}	$3d^{10}$ $4s^1$	$3d^9$ $4s^2$	*Ag_{47}	$4d^{10}$ $5s^1$	$4d^9$ $5s^2$	*Au_{79}	$4f^{14}$ $5d^{10}$ $6s^1$	$4f^{14}$ $5d^9$ $6s^2$
Zn_{30}	$3d^{10}$ $4s^2$	$3d^{10}$ $4s^2$	Cd_{48}	$4d^{10}$ $5s^2$	$4d^{10}$ $5s^2$	Hg_{80}	$4f^{14}$ $5d^{10}$ $6s^2$	$4f^{14}$ $5d^{10}$ $6s^2$

*Note the irregularities in configurations.

different from their predicted configurations. The irregularities in the observed configurations of Cr, Cu, Mo, Pd, Ag and Au are explained on the basis of the concept that *half-filled and completely-filled d-orbitals are relatively more stable than other d-orbitals.*

On the basis of the above concept it is, however, not easy to explain the irregularities found in the observed electronic configurations of the atoms of other elements, since one has to consider the net effect of so many other factors such as (*i*) nuclear-electronic attraction (*ii*) shielding of one electron by several other electrons (*iii*) inter-electronic repulsion (*iv*) the exchange-energy forces etc. All these factors play an important part together in determining the final stability of an electronic configuration of an atom. It is not easy to explain why W unlike Cr($3d^5\ 4s^1$) and Mo($4d^5\ 5s^1$) should have the idealised electronic configuration ($4f^{14}\ 5d^4\ 6s^2$).

GENERAL CHARACTERISTICS OF TRANSITION ELEMETNS

Some important properties of 3*d*- series elements are given in Table 8·2.

The properties of transition elements of any given period are not so much different from one another as those of the same period of non-transition elements. The reason of this fact lies in the electronic configurations of transition elements. We know that electronic configurations of transition elements is invariably $(n-1)d^{1-10}\ ns^{0 \text{ or } 1 \text{ or } 2}$ which indicates that (*i*) the electronic configurations of transition elements differ from one another only in the number of electrons in in *d* orbitals in the (*n*—1)th shell and (*ii*) the number of electrons in the outermost shell, *ns*, is invariably 1 or 2.

Some of the important characteristic properties of *d*-block elements are mentioned below :

(1) Metallic Character

All the transition elements are metals, since the number of electrons in the outer-most shell is very small, being equal to 2. They are hard, malleable and ductile. They exhibit all the three types of structures : *face centred cubic* (*fcc*), *hexagonal close packed* (*hcp*) *and body centred cubic* (*bcc*). Metals of VIII and IB Groups are softer and more ductile than other metals.

It appears that covalent and metallic bonding both exist in the atoms of transition metals. The presence of *unfilled d-orbitals* favours covalent bonding. These metals are good conductors of heat and electricity.

(2) Melting and Boiling Points

The transition elements have very high melting and boiling points as compared to those of *s* and *p* block elements. Zn, Cd and Hg have relatively low values. The reason for these low values is that these metals have completely filled *d*-orbitals with no unpaired electron that may be available for covalent bonding amongst the atoms of these metals. The formation of covalent bonding occurs in

Table 8·2. Some properties of the elements of first transition series (3*d*-series) (fourth period)

Property	*III B*	*IV B*	*V B*	*VI B*	*VII B*	*VIII*			*I B*	*II B*
Elements with atomic numbers	Sc_{21}	Ti_{22}	V_{23}	Cr_{24}	Mn_{25}	Fe_{26}	Co_{27}	Ni_{28}	Cu_{29}	Zn_{30}
Valence-shell configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^3$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Atomic volume (c.c.)	15·0	16·6	8·3	7·2	7·3	7·1	6·7	6·6	7·1	9·2
Density (g/c.c.)	3·0	4·5	6·1	7·2	7·4	7·8	8·9	8·9	8·9	7·1
Melting point (°C)	1539	1668	1900	1875	1245	1536	1495	1453	1083	419·5
Boiling points (°C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
Atomic (covalent) radii (A°	1·44	1·32	1·22	1·18	1·17	1·17	1·16	1·15	1·17	1·25
Ionic radii (A°) for M^{2+} ions	—	0·90	—	—	0·80	0·76	0·74	0·72	0·69	0·74
for M^{3+} ions	0·81	0·68	0·73	0·69	—	0·64	0·63	0·62	—	—
Hydration energies (Kcal) of M^{2+} ions	—	446	453	460	445	468	497	509	507	491
of M^{3+} ions	947	1027	1053	1105	1098	1072	1126	—	—	—
Ionisation potentials (*e*V) I_1 I_2	6·56 12·91	6·83 13·69	6·74 14·26	6·76 16·95	7·43 15·69	7·90 16·21	7·86 17·08	7·63 18·21	7·72 20·34	9·39 18·00
Standard oxidation potentials (volts) for M $\longrightarrow$ $M^{2+} + 2e^-$ reaction for M $\longrightarrow$ $M^{3+} + 3e^-$ reaction	— 2·10	1·60 —	1·20 —	— 0·74	1·18 —	0·41 —	0·28 -	0·25 —	—0·34 —	0·76 —
Electronegativity (Pauling's)	1·3	1·5	1·6	1·6	1·5	1·8	1·8	1·8	1·9	1·6

the rest of the *d*-block elements on account of the presence of unfilled *d*-orbitals.

Although melting and boiling points show no definite trends in the three transition series, the metals having the highest melting and boiling points are towards the middle of each transition series.

(3) Atomic (Covalent) and Ionic Radii

The atomic and ionic radii (M^{2+} ions) for the elements of 3*d*-series are given in Table 8·2. It will be seen that these values decrease generally, on moving from left to right in the period. This is due to the fact that an increase in the nuclear charge tends to attract the electron cloud inwards. The atomic radii for the elements from Cr to Cu are, however, very close to one another. This is due to the fact that simultaneous addition of electron to 3*d*- level exercises the reverse effect by screening the outer 4*s*- electrons from the inward pull of the nucleus. As a result of these two opposing effects, the atomic radii do not alter much on moving from Cr to Cu.

The ionic radii of M^{2+} and M^{3+} ions follow the same trends as their atomic radii. The radii of M^{2+} ions, although somewhat smaller than that of Ca^{2+} ion (=0·99A°) are comparable with it. Thus MO oxides of transition element should be similar to CaO in many ways, although somewhat less basic and less soluble in water. Similarly the hydration energies of M^{2+} ions should be similar to but somewhat greater than that of Ca^{2+} ion. This is borne out by facts, since the hydration energy of Ca^{2+} ion is 395 kcal and the observed values of hydration energies for the elements Ti^{2+}...Cu^{2+} are between 446 kcal and 597 kcal (Table 8·2).

The radii of M^{3+} ions are slightly greater than that of Ga^{3+} ion (=0·62A°). Thus M_2O_3 oxides of transitional elements should be similar to but slightly less acidic (more basic) than Ga_2O_3 and the hydration energies of M^{3+} ions should be less than 1124 kcal which is the hydration energy of Ga^{3+} ion. The observed values of hydration energies for the series Sc^{3+}...Fe^{3+} are between 947 kcal and 1072 kcal.

(4) Ionisation Potentials

The first ionisation potentials of transitional elements lie between the values of those of *s*- and *p*- block elements. The first ionisation potentials of all the transition elements lie between 5 to 10 electron volts. In case of transition elements the addition of the extra electron in the $(n-1)$ *d* level provides a screening effect which shields the outer *ns* electrons from the inward pull of positive nucleus on the outer *ns* electrons. Thus the effects of the increasing nuclear charge and the shielding effect created due to the expansion of $(n-1)$ *d* orbital oppose each other. On account of these counter affects, the ionisation potentials increase rather slowly on moving in a period of the first transition series.

First ionisation potentials. Table 8·2 contains the values of first and second ionisation potentials (in *eV*) for the elements of IV period. From this table it is evident that the values for the first four 3*d* block elements (Sc, Ti, V and Cr) differ only slightly from one another. Similarly the values for Fe, Co, Ni and Cu also are fairly close to one another. The value of I_1 for Zn is considerably higher. This is due to the extra-stability of $3d^{10}$ level which is completely filled in Zn-atom.

Second ionisation potentials. The second ionisation potentials are seen to increase more or less regularly with the increase of atomic number. The value of I_2 for Cr and Cu are higher than those of their neighbours. This is due to the fact that the electronic configurations of Cr^+ and Cu^+ ions have extra stable $3d^5$ and $3d^{10}$ levels.

There is a sudden fall in the values of ionisation potentials in going from II B (Zn-group elements) to IIIA sub-group. This sudden fall is explained on the basis that in case of IIIA group elements the electron to be removed is from a 4*p*-orbital which is incompletely filled, while in case of the II B group elements, the electron to be removed is from 4*s*-orbital which is completely filled. Thus more energy will be required to remove an electron from a filled 4*s*-orbital in comparison to that used to remove an electron from a 4*p*-orbital which is incompletely filled.

Electropositive character of transitional elements as compared to that of alkali metals and alkaline earth metals. The values of first ionisation potentials of transitional elements in most cases lie between those of *s*- and *p*-block elements. Thus the transitional elements are less electropositive than the elements of I A and II A groups. Thus, although the transitional elements do form ionic compounds, yet they do not form ionic compounds so readily as the alkali and alkaline earth metals do. Also, unlike the alkali and alkaline earth metals, the transitional elements also have a tendency to form the covalent compounds under certain conditions. Generally the compounds in which the transitional elements show a smaller valency are ionic, while those in which a higher valency is exhibited are covalent in character.

(5) **Oxidation States**

One of the most important property that distinguishes transition elements from *s*- and *p*-block elements is that they show variable oxidation states. *s*- and *p*-block elements have oxidation states either equal to their group number, G or equal to (8—G). The transition elements on the other hand exhibit variable oxidation states.

This unique property is due to the fact that the energy levels of 3*d*, 4*d* and 5*d* orbitals are fairly close to those of 4*s*, 5*s* and 6*s* orbitals respectively and, therefore, in addition to *ns* electrons and variable number of (*n*—1) *d* electrons are also lost in getting various oxidation states

More common oxidation states shown by 3*d*, 4*d* and 5*d* series elements are shown in Table 8·3. The following points may be noted from this Table :

Table 8·3. *Different oxidation states exhibited by transitional metals (most stable oxidation states are in brackets)*

IIIB	*IVB*	*VB*	*VIB*	*VIIB*	*VIII*			*IB*	*IIB*
Elements of 3*d*- series (Period 4)									
Sc$_{21}$	Ti$_{22}$	V$_{23}$	Cr$_{24}$	Mn$_{25}$	Fe$_{26}$	Co$_{27}$	Ni$_{28}$	Cu$_{29}$	Zn$_{30}$
			+1					+1	
+2	+2	+2	+2	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)
(+3)	+3	+3	(+3)	+3	(+3)	(+3)	+3		
	(+4)	+4	+4	(+4)	+4		+4		
		(+5)	+5						
			(+6)	+6	(+6)				
				(+7)					
Elements of 4*d*- series (Period 5)									
Y$_{89}$	Zr$_{40}$	Nb$_{41}$	Mo$_{42}$	Tc$_{43}$	Ru$_{44}$	Rh$_{45}$	Pd$_{46}$	Ag$_{47}$	Cd$_{48}$
								(+1)	
		+2 (?)	+2 (?)		(+2)	+2	(+2)	+2(?)	(+2)
(+3)	+3	+3 (?)	+3 (?)		(+3)	(+3)	+3(?)	(+3)	
	(+4)	+4 (?)	+4	(+4)	(+4)	(+4)	+4		
		(+5)	+5		+5	+5	+5		
			(+6)	+6	+6	+6	+6		
				(+7)	+7				
Elements of 5*d*- series (Period 6)									
La$_{57}$	Hf$_{72}$	Ta$_{73}$	W$_{74}$	Re$_{75}$	Os$_{76}$	Ir$_{77}$	Pt$_{78}$	Au$_{79}$	Hg$_{80}$
								+1	+1
		+2 (?)	+2 (?)	+2(?)	+2	+2	(+2)		(+2)
(+3)	+3 (?	+3 (?)	+3 (?)	+3(?)	+3	(+3)		(+3)	
	(+4)	+4 (?)	+4	+4 (?)	(+4)	(+4)	(+4)		
		(+5)	+5	+5 (?)		+5 (?)	+5		
			(+6)	(+6)	(+6,	+6	+6		
				(+7)	+8				

(*i*) *Minimum oxidation state.* All the transition elements with the exception of Cr, Cu, Ag, Au and Hg which have a minimum oxidation state of +1 exhibit a minimum oxidation state of +2. In most cases this +2 oxidation state arises due to the loss of two *s*-electrons.

(*ii*) *Maximum oxidation state.* Each of the elements in groups III B to VII B can show the maximum oxidation state equal to its group number. Thus, Cr in group VIB shows a maximum oxidation state of +6 in $Cr_2O_7^{2-}$ ion. Most of the elements in VIII group show a maximum oxidation state equal to +6. However, Ru and Os have a maximum oxidation state equal to +8 which is the highest oxidation state shown by any element.

(*iii*) There is an increase in the number of oxidation states in going from left to right in a period. However, the elements towards the middle of a period show more oxidation states than those towards the end of the period. The increase in the number of oxidation states in proceeding from left to right in a period is due to the ready availability of *s*- and *d*- electrons for binding. Maximum number of oxidation states is reached somewhere in the middle of a series.

(*iv*) *Relative stability of various oxidation states.* The relative stabilities of various oxidation states of 3*d*- series elements can be correlated with the extra stability of $3d^0$, $3d^5$ and $3d^{10}$ configurations to some extent. Thus Ti^{4+} ($3d^0$) is more stable than Ti^{3+} ($3d^1$) and similarly Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^4$). It may, however, be pointed out that such a generalisation for the relative stability of various oxidation states of 4*d*- and 5*d*- series elements is often rather difficult to realise.

The higher oxidation states of 4*d* and 5*d* series elements are generally more stable than those of the elements of 3*d* series, *e.g.*, Mo, Te (4*d*-series elements) and W, Re (5*d*-series elements) form he oxyanions : $Mo^{VI}O_4^{2-}$, $Tc^{VIII}O_4^-$, $W^{VI}O_4^{2-}$, $Re^{VII}O_4^-$ which are stable and in which the transition elements concerned show their maximum oxidation states. The corresponding oxyanions of Cr and Mn namely $Cr^{VI}O_4^{2-}$ and $Mn^{VII}O_4^-$ are strong oxidising agents.

Furthermore, the highest oxidation states of second and third row elements are encountered in compounds containing the more electronegative elements *viz*. F, O and Cl. Thus for the compounds $Ru^{VIII}O_4$, $Os^{VIII}O_4$, $W^{VI}Cl_6$ and $Pt^{VI}F_6$ there are no analogs being formed by the first row elements. The lower oxidation states particularly +2 and +3 are important in the chemistry of aquated and complex ions of the 3*d*-series (*i.e* first row) elements but these ions are not very important in the chemistry of second (*i.e.* 4*d* series) and third (5*d*- series) row elements. In short it may be said that in going down a sub-group the stability of the higher oxidation states increases while that of lower oxidation states decreases.

(*v*) *Formation of ionic and covalent compounds.* Transition elements cannot form ionic compounds in higher oxidation states because the loss of more than three electrons is prevented by the higher attractive force exerted (on the electrons) by the nucleus. Higher oxidation states of these metals are not formed by the actual loss of electrons but due to the formation of new hybrid orbitals involving $(n-1)d$, ns and np orbitals.

The transition elements form ionic bonds in the lower oxidation states and the ionic character of the bond decreases with the increase in the oxidation state. With this decrease in the ionic character of the bond the basic character of the oxides decreases, *e.g.* MnO (oxidation states of $Mn=+2$) is basic, $MnO_2(Mn=+4)$ is amphoteric and MnO_3 $(Mn=+6)$ is acidic.

(6) Magnetic Properties

First of all we describe the principles of magnetism and definition of some terms.

Pole strength. The unit pole is defined as the pole which when placed in air (or in vacuum) one cm. away from a pole of unit strength repels or attracts it with a force of one dyne.

Intensity of magnetisation or magnetic moment per unit volume, I is defined as the pole strength induced per unit area. Thus, if m=pole strength, l=distance between the poles and A=area of the pole, then

$$I=\frac{m}{A}=\frac{m\,.\,l}{A\,.\,l}=\frac{\text{magnetic moment}}{\text{Volume}}$$

Hence I is *the magnetic moment per unit volume.*

Gauss's law and total magnetic induction, B. A magnetic field has one unit intensity when one unit of force passes through 1 sq. cm. When a substance is placed in a magnetic field of strength H gauses, magnetic effect is induced in the substance and the total magnetic induction or magnetic flux (*i.e.* total number of lines of magnetic force per unit area in the sample), B induced in the sample is equal to the sum of H and 4π times of pole strength induced per unit area, I (Gauss's law). Thus :

$$B=H+4\pi I$$

or

$$\frac{B}{H}=1+4\pi\,\frac{I}{H} \qquad \ldots(8{\cdot}1)$$

Magnetic permeability, P represents the ratio of the lines of magnetic force per unit area in the sample to the lines of force per unit area of magnetic field in vacuum. Thus P is given by :

$$P=B/H.$$

Susceptibility per unit volume (or simply *volume susceptibility*), χ [pronounced as *chi*, (काई) is given by $\chi=I/H$, and gives the extent to which the material is susceptible (*i.e.* sensitive) to the external magnetic field or susceptible to magnetisation. It may be noted that if I and H are measured in the same unit, χ becomes dimensonless quantity. P and χ both are dimensionless quantities.

By placing $B/H=P$ and $I/H=\chi$ in equation (8·1), we get

$$P=I+4\pi\chi \qquad ...(8\cdot 2)$$

Gram susceptibility. In practice, susceptibility is usually expressed per unit mass (*i.e. gram, specific* or *weight susceptibility*, χ_g) rather than per unit volume. χ_g is given by

$$\chi_g = \frac{\text{volume susceptibility}}{\text{density}} = \frac{\chi}{d} \qquad ...(8\cdot 3)$$

The molar susceptibility, χ_M, is then given as :

$$\chi_M = \text{gram susceptibility} \times \text{mol. wt.}$$
$$= \chi_g \times M$$
$$= \frac{\chi}{d} \times M \qquad ...(8\cdot 4)$$

For normal paramagnetic and diamagnetic substances χ, χ_g and χ_M are constants independent of field strength.

Origin of magnetism. If an electric current which is a flow of electron is allowed to flow through a wire coiled a round core, a field is produced which behaves as if it were due to a magnet, *i.e.* magnetic field is produced. Now we know that, according to classical model of an atom (Bohr's model) the electron has two types of motion (*i*) *orbital motion* which is due to the motion of the electron round the nucleus in an orbit. Orbital motion can be compared to the flow of electric current through a coiled wire. *The orbital motion, therefore, like an electric current flowing in a coiled wire, also produces magnetic field or magnetic moment which is called orbital magnetic moment or simply orbital moment of the electron* (*ii*) *spin motion* which is due to the spinning of the electron round its own axis. *This spin motion also produces magnetic field or magnetic moment which is called spin magnetic moment* or *simply spin moment of the electron*. These two magnetic moments (*i.e.* orbital magnetic moment and spin magnetic moment) make an atom behave like a small magnet, *i.e. it is these two magnetic moments which produce magnetic properties in substances.*

Now we know that when one magnet is placed in the field of another magnet, the magnetic field produced by one magnet will interact with that produced by the other. This in other words means that when a substance (which behaves as a magnet due to orbital and spin motion of its electrons as we have seen above) is placed between the poles of a magnet, the magnetic field produced by the orbital and spin motion of the electrons interacts with the externally applied magnetic field. It is interesting to note that when the various substances are placed between the poles of a magnet (*i.e.* in a magnetic field), they do not behave in a similar way, *i.e.* they *show different behaviours which are known as magnetic behaviours.* These are classified as *diamagnetism, paramagnetism, ferromagnetism antiferromagnetism* and *ferrimagnetism*. Of these the last three are of rare occurrence and will, therefore, not be considered in detail. On the other hand, paramagnetism and diamagnetism are of great importance.

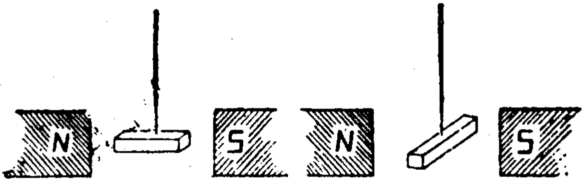
Magnetically dilute substance. A magnetically dilute substance is that in which the individual magnetic centres in the crystal lattice are sufficiently apart to minimise any further magnetic interaction between near neighbours. Conversely substances in which the individual magnetic centres in the crystal lattice are close enough to initiate the further magnetic interaction are called *magnetically concentrated substances.*

The various magnetic behaviours differ in regard to : (*i*) sign and magnitude of χ (*ii*) temperature dependence of χ (*iii*) field strength dependence of χ.

The salient features of various types of magnetic behaviours are summarised in Table 8·4.

Diamagnetism.

The substances which, when placed in a magnetic field, decrease the intensity of the magnetic field than in vacuum are called **diamagnetic substances** and the property due to which they show this behaviour is called **diamagnetism.** The magnetic lines of force tend to avoid such substances and as such *diamagnetic substances are repelled by the magnetic field and such substances set themselves at right angles to the magnetic field* [*see* Fig. 8·1(*b*)].



(*a* Paramagnetic substance in a magnetic field.

(*b*) Diamagnetic substance in a magnetic field.

Fig. 8·1 Effect of magnetic field on paramagnetic and diamagnetic substances.

Origin of diamagnetism. If two electrons with opposite spins are paired in the same orbital, the magnetic field produced by one electron is cancelled by that caused by the other electron, because each of the two electrons has equal and opposite magnetic moment. *Thus the substance having only paired electrons give zero resultant magnetic moment and consequently are diamagnetic.*

Diamagnetic is temperature-independent and is shown by all types of substances (even by paramagnetic substances). Since diamagnetism is much weaker than paramagnetism (1 to 100 times weaker) and both act opposite to each other, it is difficult for the substances having unpaired electrons to show diamagnetism, *i.e. the substances having unpaired electrons show a net paramagnetism.*

For diamagnetic substances B < H. As P is less than 1, χ will be negative. Hence I is opposing H.

Table 8·4. *Main types of magnetic behaviour and their salient properties.*

Type	*Caused by*	*Sign and magnitude of* χ_g	*Temperature and field* (H) *dependence of* χ_g	*Examples*
Diamagnetism	Cancellation of orbital angular moment of electrons, *i.e.* electrons with closed shells (paired electrons)	Small and negative $\sim -1 \times 10^{-6}$ *cgs* units	Independent of temperature and H	H_2, N_2, O_2, KCl, $MgCl_2$, $NiCl_2 \cdot 6H_2O$, $K_3[Mn(CN)_6]$, organic ligands
Paramagnetism	Orbital and spin motion of electrons (unpaired electrons)	Small and positive ~ 10 to $10^4 \times 10^{-6}$ *cgs* units	Varies inversely with temperature and independent of H	$[Ni(H_2O)_6]Cl_2$, $[CoCl_4]^{2-}$
Ferromagnetism	Lattice of particles having electrons with parallel spins	Very large and positive 10^{-2} to 10^4 *cgs* units	Large decrease below Curie temperature and indepedent of H	Metallic iron, Mn—Cu alloys
Antiferromagnetism	Two lattices of particles having spins of one lattice antiparallel to the spins of the other lattice	Very small and positive $\sim 0{\cdot}1$ to $10^2 \times 10^{-6}$ *cgs* units	Increases below Neel temperature	$KNiF_3$, many dimeric complexes of Cu(II) and oxovanadium (IV)

Paramagnetism.

The substances which, when placed in a magnetic field, allow the magnetic lines of force to pass through them rather than through vacuum, are called **paramagnetic substances** and the property due to which they show this behaviour is called **paramagnetism.** *A paramagnetic substance tends to set itself with its length parallel to the magnetic field* [*see* Fig. 8·1 (*a*)]. Thus *a paramagnetic substance is attracted into a magnetic field.*

Paramagnetism is sub-divided into (*i*) *normal paramagnetism* (*ii*) *temperature independent or Van Vleck paramagnetism* (TIP) and (*iii*) *Pauli or free electron paramagnetism.*

For paramagnetic substances $B > H$. As P is greater than 1, χ will be positive. Hence I is acting in the direction of H.

Origin of paramagnetism. Paramagnetism of a substance consisting of atoms, ions or molecules *is caused by the presence of unpaired electrons in the substance.* The greater the number of unpaired electrons, the greater will be paramagnetism shown by the substance.

In substances containing one or more unpaired electrons the magnetic fields caused by these unpaired electrons are not mutually cancelled, since each of the unpaired electrons has equal magnetic moment and thus some permanent and definite value of resultant magnetic moment is obtained. This resultant magnetic moment which is a combination of spin and orbital magnetic moments is sufficiently of high magnitude to overcome the small magnetic moments induced by the externally applied magnetic field. Such a substance, therefore, instead of experiencing repulsion like diamagnetic substance, experiences *attraction* in a magnetic field, *i.e.* it shows paramagnetic behaviour.

Paramagnetic molecules are free to orient themselves ideally in the gas phase, but in practice also in solution and even in the solid state, if magnetically dilute. They are subject to two opposing effects : (*i*) *the magnetic field,* H *which tends to align the molecular magnets in the same direction as that of the field,* and (*ii*) *thermal agitation or thermal energy,* *k*T (called *k*T *effect*) *which tends to orient the molecular magnets randomly.* The effect of the applied magnetic field becomes more pronounced with the decrease in the value of absolute temperature, T.

Magnetic moments from magnetic susceptibility. Paramagnetic susceptibility, χ_p is given by :

$$\chi_p = \frac{N\mu^2}{3kT} \qquad \text{...(8·5)}$$

where N=Avogadro's Number, μ=magnetic moment, k=Boltzman constant=$1{\cdot}38\times10^{-16}$ ergs/deg and T=absolute temperature.

The value of χ_M calculated from the experimental value of χ_g is the algebraic sum of χ_p, χ_{TIP} and χ_{dia}, *i.e.*

$$\chi_M = \chi_p + \chi_{TIP} + \chi_{dia}$$

As we do not usually know the value of χ_{TIP}, corrected molar susceptibility, χ_M^{corr} which is equal to $\chi_M - \chi_{dia}$ is also used in place of χ_p in the above equation (8·5). The value of magnetic moment obtained by putting χ_M^{corr} in place of χ_p in equation (8·5) is called **effective magnetic moment** and hence is represented by μ_{eff}. Thus equation (8·5) becomes :

$$\chi_M^{corr} = \frac{N\mu^2_{eff}}{3kT} \qquad \text{...(8·6)}$$

or

$$\mu_{eff} = \sqrt{\frac{3kT \times \chi_M^{corr}}{N^2}} \text{ B.M.}$$

On substituting the values of k and N in this equation we get

$$\mu_{eff} = 2{\cdot}83\sqrt{\chi_M^{corr} \times T} \text{ B.M.} \qquad \text{...(8·7)}$$

Magnetic moments are expressed in Bohr magneton (B.M.) One B.M. is given by : $1 \text{ BM} = eh/4\pi mc = 9{\cdot}27 \times 10^{-21}$ ergs/gauss where h = Plank's constant, e = electronic charge (measured in electrostatic units), c = velocity of light and m = mass of the electron. If e is measured in electromagnetic units, then $1 \text{ BM} = eh/4\pi m$. Note that one BM which is equal to $eh/4\pi mc$ is not, however, the magnetic moment of a single electron.

Curie's Equation. From expression (8·6) it is evident that χ_M^{corr} *is inversely proportional to* T. This is called **Curie's law.** Thus :

$$\chi_M^{corr} \propto \frac{1}{T}$$

or

$$\chi_M^{corr} = \frac{C}{T} \qquad \text{...(8·8)}$$

where C is a constant which is equal to $N\mu^2_{eff}/3k$. This constant is characteristic of the substance and is called **Curie's constant** and the expression (8·8) is called **Curie's equation.** From this equation it is evident that the plot of χ_M^{corr} values against 1/T (or of $1/\chi_M^{corr}$ against T) will give us a straight line of slope C which intercepts the origin. Although many paramagnetic substances obey Curie's law given by equation (8·8), yet there are many paramagnetic substances which do not obey this law, *i.e.* in many cases the line does not go through the origin but cuts the T axis (x-axis) at a temperature below 0°K or above 0°K. For such substances a modified law known as **Curie-Weiss law** has been suggested which is defined by :

$$\chi_M^{corr} = \frac{C}{T - \theta} \qquad \text{...(8·9)}$$

where θ is the temperature at which the line cuts the T axis and is called **Weiss-constant.** *If the value of θ is positive (i.e. above 0°K), the substance is said to be ferromagnetic and if θ is negative (i.e. below 0°K), the substance is said to be antiferromagnetic.*

The value of μ_{eff} for the substances which obey Curie-Weiss law is given by :

$$\mu_{eff} = 2.83\sqrt{\chi_M^{corr} \times (T - \theta)} \text{ B.M.} \qquad \text{...(8·10)}$$

Thermal energy and magnetic moment.

We know that, according to Russel-Saunders L-S coupling scheme, the ground term symbol of an atom or ion is represented as:

Ground term symbol $= {}^{multiplicity}L_J = {}^{2S+1}L_J = {}^{n+1}L_J$

where the superscript $2S+1 = n+1$ is the *multiplicity of* L *state*. It is simply the permitted values of J for a given value of L. $n =$ No. of unpaired electrons, S = *resultant spin quantum number*, L = *resultant orbital quantum number*. Its different values have been represented by particular term letters as shown :

Values of L	= 0	1	2	3	4	5	6...
Term letters	= S	P	D	F	G	H	I...

The subscript J is called *resultant inner quantum number* and is obtained by coupling L and S. J is a measure of the total angular momentum (spin angular momentum) and atomic orbital angular momentum of the atom. Thus J is also called *total angular momentum*. Different values of J obtained by coupling L and S vary in integral steps between $|L+S|$ and $|L-S|$, total number of values which J can have are $(2S+1)$ if $L>S$ and $(2L+1)$ if $L<S$. In particular if $L=0$ (*i.e.* S state), J can have only one value *viz* $J=S$. *J must always be positive, never negative, since it represents the total angular momentum of the atom.*

Let us consider ${}^3F$ term, as an example, to calculate different J values. Since for ${}^3F$ term $2S+1=3$ or $S=1$ and $L=3$ (for F letter $L=3$), $J=4, 3, 2$. Thus ${}^3F$ term is split by spin orbit (*ls*) coupling into three states *viz* ${}^3F_4$, ${}^3F_3$ and ${}^3F_2$. Each of these states corresponds to a particular energy. The last one is the lowest in energy. In a magnetic field these three states are again split into $(2J+1)$ levels each of which is separated from its immediate neighbour by an energy $g\beta H$ which is equal to $eh/4\pi mc$. Here g = *Lande splitting factor for the substance*, β = *Bohr magneton* and H = *field strength*. All these $(2J+1)$ levels taken together constitute a multiplet. The energy difference between two successive J levels of a multiplet is called **multiplet width of the levels** (*i.e. energy separation between the levels*). *In which J level the atoms of a particular substance will go will depend on the value of multiplet width of the successive J energy levels relative to the* **thermal energy** (or **thermal agitation**). *k*T *available to the atoms*. *k*T is approximately 200 cm^{-1} (or 0·6 kcal/mole) at 300°K. Such considerations lead to the following cases :

(*i*) **Multiplet width large compared to *k*T.** If the multiplet width is large compared to *k*T (as it is for some, though not all, tripositive lanthanide ions), the L and S vectors couple very strongly *i.e.* the spin-orbital (L – S) coupling of unpaired electrons is significant in this case. Lowest energy J levels obtained by this type of strong L—S coupling is only populated by atoms. The other J levels are much above the ground state J level and are not populated.

In this case the effective magnetic moment, μ_{eff} is given by

$$\mu_{eff} = \mu_J = g\sqrt{J(J+1)}\ \text{BM} \qquad \ldots(8{\cdot}11)$$

where g is known as Lande splitting factor and is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \qquad \ldots(8{\cdot}12)$$

The values of magnetic moments of lanthanide tripositive ions can be calculated by using the above equation (*see magnetic properties of lanthanides in the chapter on Lanthanides*).

(*ii*) **Multiplet width small compared to kT.** When the multiplet width of different J-levels is small compared to kT (as it is for some, through not all, ions of the metals of first transition series), J levels are so close together that the thermal energy leads to virtually equal population of all these J levels with atoms. This means that *the coupling of* L and S *vectors is weak and hence these vectors maintain their individuality.* Consequently L and S vectors interact independently with the externally applied magnetic field. The effective magnetic moment is then obtained by adding the magnetic moments due to orbital motion (*i.e.* orbital magnetic moment, μ_L) and that due to the spin motion (*i.e.* spin magnetic moment, μ_S) of the electron given by :

Orbital magnetic moment, $\mu_L = g_L\sqrt{L(L+1)}$,

and Spin magnetic moment, $\mu_S = g_S\sqrt{S(S+1)}$

Here g_L and g_S are the *Lande splitting factors* for orbital and spin magnetic moments. Since for μ_L, $g_L = 1$ and for μ_S, $g_S = 2$, μ_L and μ_S are given by :

$$\mu_L = \sqrt{L(L+1)},$$

$$\mu_S = 2\sqrt{S(S+1)} = \sqrt{4S(S+1)}$$

Thus μ_{eff} is given by :

$$\mu_{eff} = \mu_{L+S} = \sqrt{L(L+1)+4S(S+1)} \text{ B.M.} \qquad ...(8{\cdot}13)$$

This equation is generally used to calculate the values of μ_{eff} of the ions of the metals of first transition series (*see* Table 8·5).

For the ions with S term symbol (*e.g.* Mn^{2+} and Fe^{3+} ions), $L=0$ ($L=0$ for S term symbol), *i.e. there is no contribution of orbital magnetic moment to μ_{eff} for the ions which contain* S *term symbols.* For these ions for which $L = 0$, the above equation (8·13) giving the value of μ_{eff} becomes :

$$\mu_{eff} = \sqrt{4S(S+1)}\text{B.M.} \qquad ...(8{\cdot}14)$$

Now since $S = \frac{1}{2}\times n = n/2$ (n = No. of unpaired electrons),

$$\mu_{eff} = \sqrt{4n/2(n/2+1)} = \sqrt{n(n+2)}\text{BM} \qquad ...(8{\cdot}15)$$

Since the value of μ_{eff} given by equation (8·14) or (8·15) is that which contains only the contribution made by the spin magnetic moment resulting from the spin motion of the electron, it is called **spin-only magnetic moment,** $\mu_{spin\ only}$ whose value is thus given by :

$$\mu_{spin\ only} = \sqrt{4S(S+1)}\text{BM} = \sqrt{n(n+2)}\text{BM} \qquad ...(8{\cdot}16)$$

The formula represented by equation (8·16) is called **spin-only formula** and the values of magnetic moments calculated from this formula are called *spin only values.* Thus we see that for the ions with S ground state (*e.g.* Mn^{2+} and Fe^{3+} —d^5 ions), the magnetic moment is due to the spin magnetic moment and *the orbital magnetic moment is largely suppressed or quenched by the electrostatic field of other atoms, ions or molecules surrounding the metal ion. The atom,*

Table 8·5. *Calculated and experimental values of magnetic moments of the ions of the metals of first transition series in high spin configurations at ordinary temperatures.*

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Ions with configurations	n	Ground term $= {}^{2S+1}L_J$	$S=n/2$	L	J	$\mu_J = g\sqrt{J(J+1)}$ B. M.	$\mu_{S+L} = \sqrt{L(L+1)+4S(S+1)}$ B.M.	$\mu_{spin\ only} = \sqrt{4S(S+1)}$ B.M. $= \sqrt{n(n+2)}$ B.M.	μ_{exp} (B.M.)
$Ti^{3+}(3d^1)$	1	${}^2D_{3/2}$	1/2	2	3/2	1·55	3·01	1·73	1·7—1·8
$V^{3+}(3d^2)$	2	${}^3F_2$	1	3	2	1·63	4·49	2·83	2·8—3·1
V^{2+}, $Cr^{3+}(3d^3)$	3	${}^4F_{3/2}$	3/2	3	3/2	0·70	5·21	3·87	3·7—3·9
Cr^{2+}, $Mn^{3+}(3d^4)$	4	${}^5D_0$	2	2	0	0·00	5·50	4·90	4·8—4·9
Mn^{2+}, $Fe^{3+}(3d^5)$	5	${}^6S_{5/2}$	5/2	0	5/2	5·92	5·92	5·92	5·7—6·0
Fe^{2+}, $Co^{3+}(3d^6)$	4	${}^5D_4$	2	2	4	6·71	5·50	4·90	5·0—5·6
$Co^{2+}(3d^7)$	3	${}^4F_{9/2}$	3/2	3	9/2	6·63	5·21	3·87	4·3—5·2
$Ni^{2+}(3d^8)$	2	${}^3F_4$	1	3	4	5·59	4·49	2·83	2·9—3·9
$Cu^{2+}(3d^9)$	1	${}^2D_{5/2}$	1/2	2	5/2	3·55	3·01	1·73	1·9—2·1

ion or molecules surrounding the metal ion restrict the motion of the electrons round the nucleus (the so-called orbital motion) *and thus the contribution due to the orbital magnetic moment is quenched.*

According to *crystal field theory,* as the six ligands in an octahedral complex approach the central metal, any electrons in the *d*-orbitals of the metal ion are repelled *i.e.*, the energy of the *d*-orbitals is increased. In addition, the degeneracy of the *d*-orbitals is removed. It is this removal of degeneracy of the *d*-orbitals which is responsible for the quenching of the orbital contribution to the effective magnetic moment.

Table 8·5 also shows that, in addition to Mn^{2+} and Fe^{3+} ions (with S ground state), the spin-only formula also holds good for other ions for calculating their magnetic moments. From this formula it is evident that the values of magnetic moments for the ions containing unpaired electrons, $n=1, 2, 3, 4$...etc are 1·73, 2·83, 3·87, 4·90...BM respectively. This fact is also obvious from this Table. It may also be seen from the Table that μ_J and μ_{S+L} values are, except for Mn^{2+} and Fe^{3+} ions (d^5 configuration), in worse agreement with the experimental values.

For the elements of second and third transition series the orbital and spin magnetic moments interact with each other in a complicated way and as such spin-only formula cannot be used for calculating the magnetic moments of these elements.

Experimental determination of magnetic susceptibility by Gouy's method.

The magnetic susceptibility of substances can be determined by several methods but the Gouy's method is the most simple and hence is commonly used.

In this method a thin cylindrical glass tube, filled with the sample, is vertically suspended from the beam of a balance (kept on a table) in draught free enclosure in such a way that its lower end lies between the poles of a magnet, preferably an electromagnet (placed under the table) and the upper end lies in a negligible field (*i.e.*, the magnetic field at the upper end of the tube is zero). The weight of the sample is determined *with the field off and with the field on.* Similar determination is also made with the same sample tube so as to allow for a diamagnetic correction of the glass tube.

The small force dF experienced by the sample of volume susceptibility, χ and small volume, dv in a magnetic field H is given by :

$$dF = H.\chi\ dv.\ \frac{dH}{dx},$$

where $\frac{dH}{dx}$ is the field gradient.

Now if A is the cross-sectional area and dx is the small height of the sample, then $A.dx = dv$ and hence,

$$\begin{aligned} dF &= H.\chi.A.dx.\frac{dH}{dx} \\ &= H.\chi.A.dH. \end{aligned}$$

On integrating we get

$$\int_{H_0}^{H} dF = \int_{H_0}^{H} H.\, \chi.\, A.\, dH$$

or $$F = A.\, \chi.\, \tfrac{1}{2}\,(H^2 - H^2_0)$$

where H and H_0 are the lower and upper limits of magnetic fields.

Now since $\chi_g = \dfrac{\text{Volume susceptibility}}{\text{density}} = \dfrac{\chi}{d}$,

$$F = A.\, \chi_g.\, d.\, \tfrac{1}{2}\,(H^2 - H_0^2)$$

Now since density $(d) = \dfrac{\text{Mass } (m)}{\text{Volume}}$

$$= \frac{\text{mass } (m)}{\text{area } (A) \times \text{length } (l)}$$

or $$d = \frac{m}{Al}$$

or $$Ad = \frac{m}{l},$$

above equation becomes :

$$F = \chi_g.\frac{m}{l}.\ \frac{1}{2}\,(H^2 - H_0^2)$$

If H_0 is neglected, then

$$\chi_g = \frac{2l \times F}{H^2 \times m}$$

Since the force, F acting on the sample is measured as a change in the weight of the sample in the magnetic field, the above equation becomes :

$$\chi_g = \frac{2l \times \text{change in weight of the sample}}{H^2 \times \text{Weight of the sample}}$$

or $$\chi_M = \left[\frac{2l \times \text{change in weight of the sample}}{H^2 \times \text{weight of the sample}}\right] \times \begin{matrix}\text{molecular weight}\\ \text{of the sample(M)}\end{matrix} \quad ...(i)$$

The quantity $2l/H^2$ is called the *tube calibration constant*. This constant is first determined by taking a measurement on a standard substance such as $CuSO_4.\ 5H_2O$ ($\chi_g = 5{\cdot}92 \times 10^{-6}$ cgs units), $Hg[Co(SCN)_4]$ ($\chi_g = 16{\cdot}44 \times 10^{-6}$ cgs units] for which χ_g is accurately determined. The same tube is then cleaned and used to determine the χ_g of the substance under investigation. For paramagnetic substances the value of χ_M as calculated from equation (*i*) is corrected for the diamagnetism of the ligands using Pascal's constants. The corrected value of χ_M (represented as χ_M^{corr}) is then used to calculate the effective magnetic moment, μ_{eff} with the help of Curie equation given below :

$$\mu_{eff} = 2{\cdot}83 \sqrt{\chi_M^{corr} \times (T-\theta)} \text{ BM}$$

(7) Colour of Transition metal ions

Unlike the cations, anions, and oxyanions of the representative elements all of which are colourless, the transition metal ions and their oxyanions such as CrO_4^{2-} (yellow), $Cr_2O_7^{2-}$ (orange) and MnO_4^- (purple) are generally coloured. The colours of the hydrated cations of some transition series elements are given below. For simplicity, water molecules associated with each ion are omitted.

$3d^1$ ($n=0$) → Sc^{3+}, Ti^{4+} (all are colourless), $3d^1$ ($n=1$) → Ti^{3+} (purple), V^{4+} (blue) ; $3d^2$ ($n = 2$) → V^{3+} (green), $3d^3$ ($n = 3$) → Cr^{3+} (dark green), V^{2+}(violet) ; $3d^4$ ($n=4$)→Mn^{3+} (violet), Cr^{2+}(blue); $3d^5$ ($n=5$)→Mn^{2+} (faintly pink or flesh colourless) ; $3d^6$ ($n=4$)→ Fe^{2+} (pale green or faintly green), Co^{3+} (blue) ; $3d^7$ ($n=3$)→Co^{2+} (pink), $3d^8$ ($n=2$)→Ni^{2+} (green), $3d^9$ ($n=1$) →Cu^{2+} (blue), $3d^{10}$ ($n=0$) →Cu^+, Zn^{2+} etc. (all are colourless). Here n indicates the number of unpaired electrons present in the ions.

These colours show that the ions such as Sc^{3+}, Ti^{4+} which have no d-electrons (d°) are colourless. Ions such as Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+} etc. are also colourless, since these have completely filled d-orbitals (d^{10}) which are not involved in coordination with water molecules. Zn^{2+}, for example, uses sp^3 hybrid orbitals to give $[Zn(H_2O)_4]^{2+}$ ion where no d-orbitals are involved. Thus the complex ions of transition metals with partially filled d-orbitals are frequently coloured.

Origin of colour according to Crystal Field Theory

The origin of colour shown by transition metal ions can be explained with the help of Crystal Field Theory (CFT). For this *see the applications of* CFT *described in chapter on Nature of Metal-Ligand Bonding in Complexes.*

Factors affecting the colour of the complexes

An increase in the magnitude of Δ_0 decreases the wavelength (λ) of the light absorbed by the complexes. Thus with a decrease in the wavelength the colour of the complexes changes from red→ violet. All the factors which change the magnitude of Δ_0 also change the colour of the complexes. These factors are :

(*i*) **Change in the number of d-electrons.** An increase in the number of d electrons in the central metal ion decreases the magnitude of Δ_0 and hence increases the wavelength (λ) of the absorbed light. Thus :

$$\text{No. of } d\text{-electrons} \propto \frac{1}{\Delta_0} \propto \lambda$$

The increase in λ changes the colour of the complex from violet→red.

(*ii*) **Field strengths of the ligands.** In order to see the effect of the field strengths of the ligands on the colour of the complex ions let us consider the octahedral complex ions *viz* $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3+}$ which contain the ligands whose field strengths are in the increasing order $H_2O < NH_3 < CN^-$ (*see* spectrochemical series). Quite obviously the magnitude of Δ_0 which is the energy difference between t_{2g} and e_g orbitals will also be in the same order, *i.e.* $\Delta_0(H_2O) < \Delta_0(NH_3) < \Delta_0(CN^-)$, but the wavelengths ($\lambda$) of the colours absorbed by these ions will be in the reverse order, since $\Delta_0 \propto \frac{1}{\lambda}$. Thus : $\lambda(H_2O) > \lambda(NH_3) > \lambda(CN^-)$. Consequently the colour of the light absorbed by the complex will shift from red → violet and the colour of the light transmitted by the complex (*i.e.*, colour of the complex) will shift from blue-green → yellow-green. The colour of the transmitted light which is the colour of the complex is called complementary colour to that of absorbed light.

Colours which are absorbed and those which are transmitted by these ions are given below :

Complex ions :	$[Co(H_2O)_6]^{3+}$	$[Co(NH_3)_6]^{3+}$	$[Co(CN)_6]^{3-}$
Ligand field strength :	H_2O <	NH_3 <	CN^-
Magnitude of Δ_0 :	$\Delta_0(H_2O) <$	$\Delta_0(NH_3) <$	$\Delta_0(CN^-)$
Magnitude of λ :	$\lambda(H_2O) >$	$\lambda(NH_3) >$	$\lambda(CN^-)$
Colour of absorbed light :	orange	Green-blue	violet
Colour of the transmitted light (*i.e.* colour of the complex) :	Green-blue	Orange	Yellow-green

(*iii*) **Geometry of the complex.** A change in the geometry of the complex having the same cation also changes the value of Δ which in turn changes the colour of the complex. Thus tetrahedral and square planar complexes of Ni^{2+} have different colours. The tetrahedral complexes are blue or green while square planar complexes are yellow or brown. To illustrate the point again some of the complexes of Co^{2+} and Mn^{2+} ions having different geometry are given below. It will be evident that these complexes have different colours.

Central cation	*Complex ion*	*Geometry of the complex ion*	*Colour of the complex*
Co^{2+}	$[Co(H_2O)_6]^{2+}$	octahedral	pink
Co^{2+}	$[CoCl_4]^{2-}$	tetrahedral	blue
Mn^{2+}	$[Mn(H_2O)_6]^{2+}$	octahedral	pink
Mn^{2+}	$[MnCl_4]^{2-}$	tetrahedral	green

(*iv*) Occasionally the value of Δ_0 is so small that the radiation in the infra red region may cause excitation. In such cases the complex ion is colourless. Hence lack of colour in a complex ion of a coloured cation may be due to either a very large or very small value of Δ_0.

(8) Standard oxidation potentials and reducing properties.

The values of standard oxidation potentials of 3*d*-series elements for the reactions M/M^{2+} and M/M^{3+} as given in Table 8·2 reveal that the value for any element, excepting Cu, is higher than that of standard hydrogen electrode (taken as zero). It is, therefore, expected that these metals, excepting Cu, would evolve H$_2$ gas from acid solutions according to the equation

$$M + 2H^+ \ (\textit{from acid}) \longrightarrow M^{2+} + H_2 \ (\textit{gas})$$

In actual practice the rate with which most of the metals react with acid is very slow. Some of the metals get protected from further attack of the acids due to the formation of a thin protective layer of their oxide which prevents the acid to come in further contact with the metals, *e.g.* although electrode potential of Cr is high, it gets coated with its non-reactive oxide, Cr$_2$O$_3$ which makes the chromium metal so unreactive that it can be used as a protective non-oxidising metal.

Reducing properties. In spite of the fact that the metals of first transition series, excepting Cu, have high values of standard electrode potentials, these are not as good reducing agents as the metals of IA, IIA and IIIA groups, although some of the metals of these groups (*e.g.* Al) have smaller oxidation potentials. The poor reducing capacity of the transition metals is due to high heats of vaporisation, high ionisation potentials and low heats of hydration of their ions.

The tendency of Cu to change into Cu^{2+} ions is *extremely low* due to its negative electrode potential. The metal is also not able to displace H$^+$ ions from acid solutions Cu is, therefore, particularly poor reducing agent, *i.e.* oxidation of copper metal by H$^+$ to Cu^{2+} does not occur readily and consequently Cu metal will not dissolve in acids.

(9) Tendency to form complex compounds

The cations of the transition metals have a great tendency to form complexes with several ligands such as neutral molecules (NH$_3$, H$_2$O etc.) and anions (CN$^-$, Cl$^-$ etc.). These ligands possess invariably lone pairs of electrons which they donate to the transition metals cations in the formation of complex compounds.

The tendency of the transition metals cations to form the complexes is due to the following reasons :

(*i*) The transition metals cations are relatively very small in size and hence have high positive charge density which makes it easy for the transition metals cations to accept the lone pairs of electrons from the ligands.

(*ii*) The transition metals cations have vacant $(n-1)$ *d*-orbitals which are of approximately the right type of energy to accept lone pairs of electrons.

(*iii*) The transition metals are capable of showing several oxidation states.

The structure commonly found in such complexes are linear (*i.e.* co-ordination number, C.N. = 2), square planar (C.N. = 4), tetrahedral (C.N. = 4) or octahedral (C.N. = 6).

Since the electropositive character decreases on moving down in each group of transition metals, the members of the first transition series form more stable complexes with ligands containing nitrogen and oxygen while the members of the second and third series form more stable complexes with P, S and As donors. Here it should be noted that this generalisation is true only for few families of the transition metals.

(10) Catalytic properties

Most of the transition metals and their compounds have good catalytic properties. Some examples are (*i*) *Vanadium* is used as V_2O_5 or as metavanadates such as NH_4VO_3 in the manufacture of sulphuric acid by contact process. (*ii*) *Nickel* is used as finely divided or active nickel in hydrogenation reactions, *e.g.* (*a*) Conversion of oils into fats, (*b*) Conversion of CO and steam into CO_2 and H_2. (*iii*) *Platinum* is used as spongy platinum in a number of processes such as (*a*) Conversion of SO_2 into SO_3 by air (manufacture of H_2SO_4). (*b*) Oxidation of NH_3 to nitric oxide (manufacture of HNO_3 by Ostwald process). (*iv*) *Iron* is used as a catalyst in the manufacture of NH_3 by the Haber process, about 1% of Na_2O or K_2O and about 1% SiO_2 or Al_2O_2 are added as promoters. Mo is also sometimes used as a promotor.

Comparison of the elements of first transition series (3d-series) with those of second (4d-series) and third (5d-series) series

(*i*) **Elements having irregular electronic configurations.** In the first transition series, only two elements namely Cr and Cu have irregular electronic configuration (Cr $\longrightarrow 3d^5\,4s^1$ and Cu $\longrightarrow 3d^{10}4s^1$)

In the second series six elements namely Nb, Mo, Ru, Rh, Pd and Ag have irregular electronic configurations; in the third series it is only two elements namely Pt and Au that have irregular configurations. The irregular configurations of Cr and Cu (first transition series), of Mo and Ag (second transition series) and of Au (third transition series), can be explained on the basis of special stability associated with half-filled and completely filled $(n-1)d$-orbitals. The irregular configurations of other elements have got no reasonable explanation.

(*ii*) **Reactivity of elements.** The reactivity of the transition elements generally decreases in going from first transition series to the third transition series. Thus the elements of the first transition series are much more reactive than those of the second and third series.

(*iii*) **Stability of oxidation state.** As we proceed from the first transition series to the third transition series, the lower oxidation states become progressively less stable and higher ones more stable.

(*iv*) **Maximum oxidation state.** The maximum oxidation state in each series is exhibited by Fe-group elements. Fe shows a maximum oxidation state of +6 in FeO_4^{2-} and Ru and Os exhibit maximum oxidation state of +8 in their tetraoxides, $M^{VIII}O_4$.

(*v*) **Application of spin-only formula.** Spin-only formula can give interpretation of the magnetic data for the elements of first transition series only. To interpret the magnetic data for the elements of the second and third series is difficult.

(*vi*) **Stability of complexes.** Elements of the first transition series form more stable complexes with N, O and F donors, while those of the second and third series form more stable complexes with P S and heavier halogen donors.

(*vii*) **Co-ordination number.** The elements of the first series rarely show co-ordination number, C.N., greater than six. C.N. = 7 and 8 are quite common with the elements of second and third series.

References

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9

Lanthanides or Rare Earths (4f-Block Elements)

DEFINITION

The elements in which the additional electron enters $(n-2)\,f$ orbitals are called **inner transition elements.** The valence-shell electronic configuration of these elements can be represented as : $(n-2)\,f^{0,\,2\cdots14}.\ (n-1)\,d^{0,\,1,\,2}.\ ns^2$. These are also called ***f*-block elements** because the extra electron goes to *f*-orbitals which belong to $(n-2)$*th* main shell. *f*-block elements have been classified as 4*f* and 5*f* block elements corresponding to the filling of 4*f* and 5*f* orbitals of $(n-2)$*th* main shell.

The complete and valence-shell electronic configurations of 4*f* and 5*f*-block elements can be represented as : (*n* represents the outermost shell).

Block elements	Complete configuration	Valence-shell configuration
f-block elements	$2, 8, 18, 4s^2p^6d^{10}f^{0,\,2\cdots14}, 5s^2p^6d^{0,\,1}, 6s^2$	$4f^{0,\,2\cdots14}, 5d^{0,\,1}, 6s^2$ $(n=6)$
5*f*-block elements	$2, 8, 18, 32, 5s^2p^6d^{10}f^{0,\,2\cdots14}, 6s^2p^6d^{0,\,1,\,2}, 7s^2$	$5f^{0,\,2\cdots14}\,6d^{0,\,1,\,2}, 7s^2$ $(n=7)$

4*f*-block elements are also called **lanthanides, lanthanones** or **rare-earths.** The first two names are given because of their strong resemblance to lanthanum. The name rare earth was given to them because they were originally extracted from oxides for which ancient name was *earth* and which were considered to be rare. The term *rare-earths* is avoided now because many of these elements are no longer rare but are abundant. Thus strictly according to this definition of lanthanides only *thirteen* elements from Ce_{58} ($4f^2 5d^0 6s^2$) to Yb_{70} ($4f^{14} 5d^0 6s^2$) should be the members of lanthanide series. However, all the *fifteen* elements from La_{57} ($5d^1 6s^2$) to Lu_{71} ($4f^{14} 5d^1 6s^2$) are considered as the members of lanthanide series, since all the fifteen elements have similar physical and chemical properties. In fact the name *lanthanides* has been derived from lanthanum which is the *prototype* of lanthanides.

5*f*-block elements are called **actinides** or **actinones.**

Lanthanides constitute the *First Inner Transition Series* while actinides constitute the *Second Inner Transition Series.*

POSITION OF LANTHANIDES IN THE PERIODIC TABLE

All the fifteen lanthanides have atomic weights between those of barium (atomic number, $Z=56$) and hafnium ($Z=72$) and, therefore, must be placed between these two elements as was also proved by Moseley.

Barium has exactly the same outer electronic configuration as calcium and strontium and resembles them very closely. In a similar way hafnium is similar to zirconium ($Z=40$). Therefore Ba must be placed below Sr (Group II B) and Hf below Zr (Group IV B), thus leaving only one place between them, which lies exactly below Y ($Z=39$, Group III B).

Since all the fifteen lanthanides resemble one another in many respects, these must be placed in the same group. These elements also resemble Y_{39} because of the following additional similarities : (*a*) Owing to lanthanide contraction (to be discussed subsequently), the ionic radius of Y^{3+} ion is almost similar to that of Er^{3+} ($r_{Y^{3+}} = 0·93$ Å, $r_{Er^{3+}} = 0·96$ Å). (*b*) Y generally occurs in nature associated with the ores of heavier lanthanides and resembles Tb (III) and Dy(III) in its compounds. It, therefore, became necessary to accommodate all the fifteen lanthanides together at one place. This has been done by placing the first element *viz.* La_{57} below Y_{39} and remaining fourteen elements (*viz.* Ce_{58} to Lu_{71}) have been placed separately in the lower part of the periodic table.

OCCURRENCE OF LANTHANIDES

The lanthanides are not so scare in the earth's crust as the name rare-earths implies. Potentially their sources are unlimited. Each lanthanide mineral contains all lanthanides, although some in traces only, excepting Pm which is an unstable radioactive element.

Classification of Rare-Earth Minerals. The rare-earth minerals, like the earths themselves, fall into two distinct classes.

(1) *Cerium Group Minerals.* These are also called *cerite-earth minerals* or simply *cerium earths* and are rich in cerite-earths. This group of minerals contains largely elements of atomic numbers from 57 to 63 (*i.e* La_{57} —— Eu_{63}), the light lanthanide elements. These are thus light rare earths.

(2) *Yttrium Group Minerals.* These are also called *yttrium-earth minerals* or simply *yttrium earths* and are rich in gadolinite

Table 9·1. *Important Minerals of Lanthanides.*

Minerals	*Composition*	*Location of significant deposits*
	(1) **Cerium group minerals**	
(*i*) Monazite Sand—Mixture of orthophosphates of Ce-earths, (Ce) PO_4	50—70% Ce-earths (*i.e.* elements of at. no. 57 to 62 calculated as oxides)	Occurs in the sand breaches of Travancore (India)
	1—4% Y-earths (*i.e.* elements of at. no. 63 to 71 calculated as oxides)	
	4—10% ThO_2	Brazil
	1—2% SiO_2	South Africa
	22—30% P_2O_5	U.S.A.
	Traces of U	
(*ii*) Bastaesite-cerium earth fluoro-carbonate, (Ce) FCO_3	65—70% Ce-earths < 1% Y-earths	Sweden, California, New Mexico
(*iii*) Cerite—A hydrated silicate of the composition, $(Ce)_3 M^{II} H_3 Si_3 O_{11}$ (M—Ca, Fe)	Traces of Thorium	
	51—72% Ce-earths	Sweden
	7·6% Y-earths	Caucasus
	Traces of Th, U, Zr	

	(2) Yttrium group minerals	
(i) Gradolinite or Ytterbite—A ytterium-earth, iron and beryllium silicate, $(Fe, Be)_3 (Y_2) Si_2 O_{10}$	35—48% Y-earths (Calculated as oxides) 2—17% Ce-earths Upto 11·6% BeO Traces of ThO_2	Sweden, Norway USA (Texas and Colorado)
(ii) Xenotime—An orthophosphate of Y-earth (analogous to Monozite), $(Y) PO_4$	54—65% Y-earths ~ 0·1% Ce-earths Upto 3% ThO_2, upto 3·5% U_3O_8 2—3% ZrO_2	Norway Brazil
(iii) Euxenite—Mixture of titanates, niobates and tantalates of Y-earths, $(Y) (Nb, Te) TiO_6 \cdot x H_2O$	13—35% Y-earths (Calculated as Oxides) 2—8% Ce-earths (Calculated as Oxides) 20—23% TiO_2, 25—35% $(Nb, Ta)_2 O_5$	Australia, Idaho (U.S.A.)

earths. This group contains largely yttrium and lanthanides of atomic numbers from 64 to 71 (Gd_{64}——Lu_{71}), the heavier lanthanides. These are thus heavy rare-earths.

Some of the important minerals of these two groups, their composition and the places where their most important deposits are found are given in Table 9·1. In this table the symbols Ce and Y stand for any lanthanide atom of cerium group and ytterium group minerals respectively. Both Euxenite and Gadolinite are quite abundant and are the future sources of yttrium earths.

Besides rare-earth minerals proper, there are many others, particularly the phosphates, arsenates, molybdates and tungstates of Ca, Sr, Fe and Pb which contain small amounts of rare-earths. In some of these Sm, Gd and Eu are present in much larger quantities than in rare-earth minerals.

EXTRACTION OF LANTHANIDES FROM MONAZITE MINERAL

Lanthanides are mainly extracted from monazite mineral which is chiefly worked for thorium and the lanthanides are obtained as by-products. The operation consists of the following three steps :

(I) Concentration of the mineral.

The concentration of monazite sand is usually begun with gravity separation on Wilfley tables, such as those which are used for gold. Since monazite sand is much more heavier than quartz (sp. gravity of monazite=5·5, sp. gravity of quartz=2·6), the monazite sand gets caught up on the riffles and the quartz sand and other gangue material is washed off. The heavier material which contains monazite sand and other material sands (ilemenite and garnet) is dried and then passed through magnetic separator. The monazite, being much less magnetic than the other material sands, gets thereby separated from the rest. The refined monazite so obtained has an average composition $ThO_2=7·5$, $Ce_2O_3=30\%$, other rare earths=32%. $P_2O_5=29\%$ and $SiO_2=1·5\%$.

(II) Cracking of the mineral.

The concentrated monazite obtained as above is subjected to chemical treatment which is technically known as "*processing*", "*opening up*" or "*cracking*" of the mineral.

The chemical treatment of concentrated monazite is done either by conc. H_2SO_4 or by conc. NaOH solution.

(*i*) *Cracking of the mineral by H_2SO_4 and removal of thorium and cerium.* The finely powdered (ca 100 mesh) and concentrated monazite mineral is heated with 93% H_2SO_4 at 210°C in vessels constructed of cast iron, tantalum iron or high silicon iron and provided with mechanical stirrers. Gas or oil-fired furnace is used. The reaction is exothermic. At the end of about four hours, the viscous paste consisting of lanthanide sulphates and thorium sulphate is leached with water for about 12 to 15 hours when all the sulphates of Ln^{3+}, Th^{4+} and ZrO_2^{2+} (traces) *go into solution* leaving behind insoluble SiO_2, unreacted monazite, TiO_2, $ZrSiO_4$. The latter residue is crushed and returned for extraction. The acidic solution so obtained [the solution becomes acidic due to the formation of H_3PO_4 in the reaction of P_2O_5 with H_2O : $P_2O_5+3H_2O \rightarrow 2H_3PO_4 \rightarrow 2H^+ + 2H_2PO_4^-$] which contains the sulphates of Ln^{3+}, Th^{4+} and ZrO_2^{2+} (traces) is treated with sodium pyrophosphate, $Na_2P_2O_7$ to precipitate much of thorium as $Th(P_2O_7)_2$. The filtrate obtained is treated with oxalic acid ($H_2C_2O_4$) to get the precipitate-mixture containing $Ln_2(C_2O_4)_3$ and traces of $Th(C_2O_4)_2$ and $(ZrO)(C_2O_4)$. This mixture is boiled with $(NH_4)_2C_2O_4$ solution whereby traces of $Th(C_2O_4)_2$ and $(ZrO)(C_2O_4)$ remain in solution and $Ln_2(C_2O_4)_3$ oxalates are left behind as residue which is converted into the corresponding sulphates by igniting carefully with conc. H_2SO_4. Na_2SO_4 is added to the clear solution of sulphates of Ln^{3+} so obtained so that the *light lanthanides* (La_{57} to Eu_{63}) *precipitate out as double sulphates and the heavy lanthanides* (Gd_{64} to Lu_{71}) *remain in solution as simple sulphates.* Hot NaOH is added to the precipitated mixture containing double sulphates of light lanthanides to form a mixture of hydrated oxides. This mixture is dried in air at 100°C whereby we get the mixture of oxides whose approximate composition is $La_2O_3=17\%$, $CeO_2=5\%$, $Pr_2O_3=8\%$, $Nd_2O_3=20\%$ $Sm_2O_3=5\%$ and traces of Eu_2O_3. This mixture of oxides is treated with dil. HNO_3 when all the light lanthanide oxides (except CeO_2) get dissolved as nitrates and CeO_2 is obtained as crude residue by filtration. The crude CeO_2 is dissolved in 85% HNO_3 to convert it into crude $Ce(NO_3)_4$ which is converted into red basic nitrate, $Ce(OH)(NO_3)_3.3H_2O$ by the addition of dil. H_2SO_4. The solution of nitrates of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} obtained as above after the removal of CeO_2 is separated into individual components by different methods discussed below.

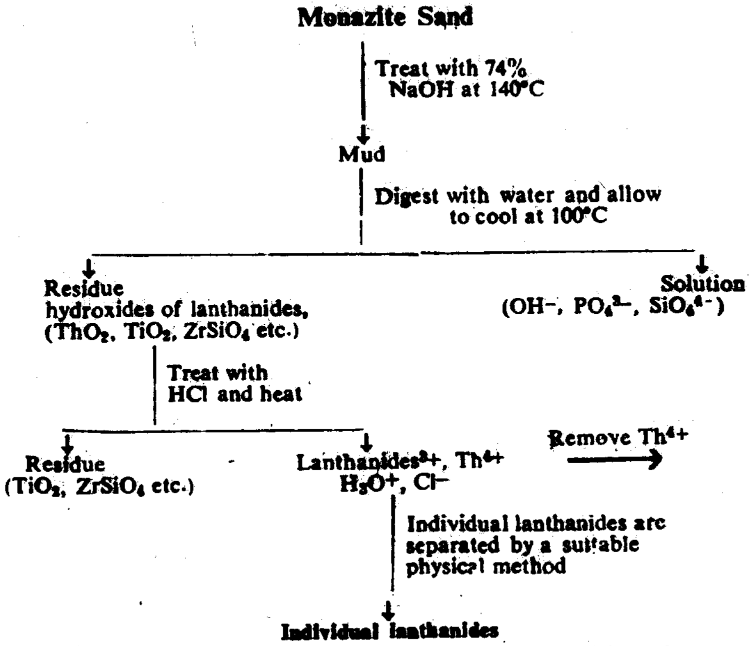
The solution containing the sulphates of heavy lanthanides can also be used to separate the individual components by the same methods as given below.

Thorium can also be removed by other methods like (i) selective precipitation method which consists of adding H_2F_2 to the acidic solution containing Ln^{3+} and Th^{4+} ions when Th^{4+} is precipitated as Th F_4 and that the fluorides of Ln^3 ions (LnF_3) go into the solution. Other selective precipitation methods include precipitation of Th^{4+} as ThO_2 with NaOH at $pH=5{\cdot}8$ to $6{\cdot}0$. *(ii) solvent extraction method* which is now widely used to get thorium to be used for nuclear purposes. Organic solvent *tri-n-butyl phosphate* in xylene is used which preferentially extracts thorium

Cerium can also be removed by various other methods, some of which are : (i) selected crystallisation of the double ammonium nitrate, $Ce(NO_3)_4.2NH_4NO_3$ from nitric acid solutions, but the recovery is not quantitative. *(ii) selective oxidation*, anodically or chemically, with bromate or permanganate results in the precipitation of Ce^{4+} from the buffered solution. *(iii) Selective hydrolysis* : the concentrated mixture of Ce^{4+} and nitrates of lanthanides (+3) or sulphates is diluted and boiled when Ce^{4+} separates out. (iv) *Solvent extraction* of Ce^{4+} with tri-n-butyl phosphate is similar to that of Th^{4+}. The Ce^{4+} is reduced to Ce^{3+} and extracted back into aqueous phase by treating the organic phase with aqueous sodium nitrite.

(ii) Cracking of the mineral by NaOH. This is shown below in Flow-sheet 1.

Flow-sheet 1. Cracking of the monazite mineral by Sodium hydroxide (due to C. de Rhoden and M. Peltier, 1957)



Sulphuric acid vs. caustic soda cracking. Although a greater variety of monazite sands can be processed by H_2SO_4 treatment than by the NaOH method, higher yields and cleaner separations are the main advantages of the latter process. However, the H_2SO_4 treatment method has the advantage over the NaOH process of being slightly cheaper to operate. In the NaOH cracking of monazite, concentration of the rare-earths is achieved at relatively early stage of the process.

(III) Separation of individual rare-earth elements.

The long story of the methods used for the separation of the individual rare-earths may broadly be divided into two classes :

(1) Old-classical methods.

The following classical methods were not only used by the early workers in the past, but still remain as very important methods for economical production of rare-earths on commercial scale.

(*i*) **Fractional Crystallisation.** This procedure depends on slight differences in the solubility of various salts. The chief salts (either simple or complex) utilised in this procedure are given in Table 9·2. The order of separation is indicated in the last column, the least soluble being placed first.

The mixed solution of rare-earth salts is evaporated to such an extent that, if it is allowed to cool, it would deposit about one-half of the dissolved salts as crystals.

The crystals obtained as a result of the first evaporation are re-dissolved in just sufficient amount of water and the solution is evaporated as before to such an extent that on cooling, it would deposit about one-half of the dissolved salts as crystals. Similarly, the liquor from the first crystallisation is also evaporated further so that about one-half of the dissolved salt may be obtained as crystals.

The crystals and mother liquors obtained from the second set of operations are separated from each other, and the mother liquor from the first crystallisation is combined with the crystals from the second evaporation of the original mother liquor. The starting solution thus gets separated, at this stage into three fractions, as shown in the third row of Fig. 9·1.

The three fractions are then submitted to crystallisation as before and the resulting liquors are combined with crystals from the adjacent solution, as indicated by arrow heads. The four fractions which thus result, on being processed in the same way as before, give rise to five fractions. Each series of operations, therefore, gives one more fraction.

As a result of the repetition of the above process, the components which are less soluble continuously pass on to the crop of crystals, while those which are soluble pass to the final mother liquor. The process is continued, until the desired degree of separation has been achieved. The systematic fractional crystallisation of any given mixture of rare-earths results in the separation into :

(*a*) the less soluble components that accumulate more and more in each successive crop of crystals as shown on the left-hand side of Fig. 9·1.

(*b*) the more soluble components that progressively accumulate in the mother liquor as shown on the right-hand side of Fig. 9·1.

(*c*) the intermediate components, distributed between the final crop of crystals and the end mother liquor, in the order of solubility, *i.e.*, from left to right as shown at the bottom row of Fig. 9·1.

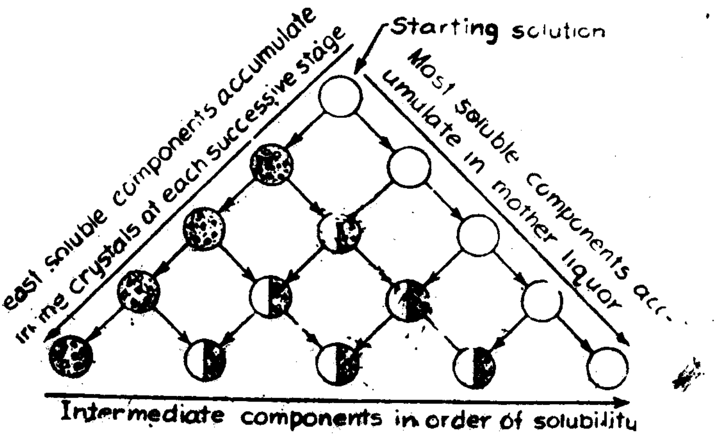


Fig. 9·1. Fractional crystallisation method for the separation of rare-earths.

(*ii*) **Fractional Precipitation Method.** We have already pointed out that the basic character of the hydroxides of lanthanide elements decreases from La_{57} to Lu_{71}. Thus, the hydroxides of cerium group lanthanide elements (La_{57}—Eu_{63}) are more basic than those of ytterbium group lanthanides (Gd_{64} - Lu_{71}). When pH of the solution containing mixture of the lanthanide elements is gradually increased by adding NH_3, amines or alkali etc., the hydroxides of the ytterbium group lanthanides being less basic get preferentially precipitated while those of the cerium group lanthanides which are more basic are left behind in the solution. From a given sub-group individual lanthanides are then separated by the further fractional precipitation of the hydroxides. Since the basicity differences in the hydroxides of lanthanide elements are small, complete separation of the adjacent members in a given sub-group by this method of fractional precipitation cannot be made

(*iii*) **Fractional Thermal Decomposition of Oxy-salts.** This method is based on the fact that the rate of thermal decomposition of oxysalts such as nitrates, sulphates and acetates of lanthanide elements at a given temperature decrease from La_{57} to Lu_{71}. This in other words means that the oxysalts of cerium group elements decompose more readily than those of the ytterbium group. Thus if a mixture containing the nitrates of lanthanide elements is fused and then leached with water, the ytterbium group lanthanides which are less basic are rapidly concentrated and their separation from the more basic cerium lanthanides is effected. The individual members of a given sub-group can be separated from each other by repeating the whole process several times.

Table 9·2. *Chief salts used in the fractional crystallisation procedures.*

Salts	*Composition*	*The order of separation*
(1) Double Nitrates		
Ammonium	$Ln(NO_3)_3.2NH_4NO_3\ 4HO_2$	La, (Ce), Pe, Nd
Sodium	$Ln(NO_3)_3.2NaNO_3.xH_2O$	La, Pa, Nd
Magnesium	$2Ln(NO_3)_3.3Mg(NO_3)_2.24H_2O$	La, Pr, Nd, Sm, Eu, Er Gd, Y
Manganese	$2Ln(N_3O)_3.3Mn(NO_3)_2.24H_2O$	For Nd from Pr, and for La from Sm
(2) Ethyl sulphates	$Ln(C_2H_5SO_4)_3.9H_2O$	(*i*) Nd, Pr, La
(3) Bromates	$Ln(BrO_3)_3.9H_2O$	(*ii*) Eu, Gd, Tb, Y, Dy, Ho, Er, Tm, Yb
(4) Nitrates	$Ln(NO_3)_3.5H_2O$	Nd, Pr, (Ce), La
(5) Metanitro-benzene Sulphonates	$Ln[C_6H_4(NO_2)SO_3]_3.6H_2O$	La, (Ce), Pr, Nd
(6) Oxalates	$Ln_2(C_2O_4)_3.xH_2O$	La
(7) Sulphates	$Ln_2(SO_4)_3.xH_2O$	La, Nd, Pr
(8) Double carbonates	$K_2CO_3.Ln_2(CO_3)_3.12H_2O$	La, Pr, (Ce), Nd

Since the differences in the basicity of the lanthanides are small, complete separation of the adjacent members of a given sub-group cannot be achieved by this method.

(*iv*) **Change of oxidation states by selective oxidation or reduction procedures.** As already discussed, some of the lanthanides show +2 and +4 oxidation states in addition to +3 state which is the most characteristic of all the elements of lanthanide series. The properties of Ln^{2+} and Ln^{4+} ions are different from those of the usual Ln^{3+} ions. A change in oxidation state results in a remarkable change in properties. Selective oxidation or reduction, therefore, provides a very effective method of separating specific lanthanides.

Examples : (*i*) Suppose we have to separate Ce from a mixture containing Ce^{3+} and other tripositive lanthanide cations. This mixture is treated with some strong oxidising agent such as bromate in neutral medium or chlorine or $KMnO_4$ in alkaline medium. By this treatment only Ce^{3+} ion is oxidised to Ce^{4+} ion while other lanthanide ions remain as Ln^{3+} ions. Since Ce^{4+} ion is smaller than Ce^{3+} ion, Ce^{4+} ion is less basic and less soluble. It (*i.e.* Ce^{4+} ion) can thus be precipitated as $Ce(OH)_4$ by the addition of a small amount of an alkali leaving all other Ln^{3+} ions in solution. By this method it has been possible to have 99% pure Ce from a mixture containing only 40% Ce.

(*ii*) Eu^{3+} can almost quantitatively be separated from a solution containing Eu^{3+} and other Ln^{3+} ions by reducing it to Eu^{2+} by means of Zn-amalgam and then precipitating it as $EuSO_4$ which is insoluble in water and hence can be separated. The sulphates of all the trivalent lanthanides, on the other hand, are soluble in water.

Zn-amalgam also brings about the reduction of Yb^{3+} to Yb^{2+} but not of Sm^{3+}.

(2) **Modern Methods.**

Following are the modern methods which are now used for separating individual lanthanides.

(*i*) **Ion-exchange method.** This is the most effective method now available for the separation of lanthanide elements. This method utilises synthetic cation-exchange resins which are usually organic compounds containing sulphonic ($-SO_3H$) or carboxylic acid ($-COOH$) groups, the hydrogens of which are replaced by other cations. Thus, if an aqueous solution containing a mixture of tripositive lanthanide ions, $Ln^{3+}(aq)$ is allowed to pass down a column packed with a cation exchange resin [abbreviated as HR (*solid*)], the $Lu^{3+}(aq)$ ions replace H^+ ions of $-SO_3H$ or $-COOH$ group of the resin and thus get fixed on the resin.

$$Ln^{3+}(aq) + 3HR\ (solid) \rightleftharpoons LnR_3\ (solid) + 3H^+(aq)$$

Thus all the Ln^{3+} (*aq*) ions are attached with the resin as LnR_3 (*solid*). Since Lu^{3+} (*aq*) is largest in size and La^{3+} (*aq*) is smallest, La^{3+} (*aq*) is attached to the resin in the column with *maximum* and Lu^{3+} (*aq*) with *minimum firmness*. In order to remove Ln^{3+} ions fixed as LuR_3 (*solid*) on the resin the column is *eluted* (*i.e. leached*) with a complexing agent in aqueous solution like a buffer solution of ammonium citrate-citric acid (*p*H = 4 to 7). Such complexing agents are called **eluants or eluates or eluting agents.** During eluation process NH_4^+ ions of the eluting agent replace Ln^{3+} ions from LnR_3 (*solid*) to give Ln^{3+} ions which react with citrate ion to form the Ln-citrate complex.

$$LnR_3 + NH_4^+ \longrightarrow NH_4R + Ln^{3+}$$

$$Ln^{3+} + \text{citrate ion} \longrightarrow \text{Ln-citrate complex}$$

We have seen that since $La^{3+}(aq)$ is attached to resin with maximum and $Lu^{3+}(aq)$ with minimum firmness, Lu-citrate complex comes out of the column *first* and La-citrate complex comes out *last*.

In actual practice the process of elution is to be repeated several times by careful control of concentration of ammonium citrate-citric acid solutions.

The yttrium group rare-earths have been separated by Ketelle and Boyd on a column of Dowex 50 (270—325 mesh) using 5% (0·25 M) citric acid at pH 3·28. Mixtures of Eu—Sm and Y—Tb took eight hours for complete separation with 0·5 M citrate at pH 3·04 (87°C) and with 0·24 M loctate at pH 5·0. Cunninghame *et. al.* reduced the separation time to four hours using 1M lactate (pH = 3·25) at 87°C for a mixture of Y-Pr-Nd-Pm-Sm-Eu with a Zeokarb 225.

Elution Curves. The elution behaviour of each of the constituent rare-earth ions is shown as an elution plot which is obtained by plotting volume of eluted portion against the concentration of the cation in eluate. The elution curves for the elements, Lu to Eu, present in a mixture are shown in Fig. 9·2. These elution curves follow one another, from left to right, in the order of decreasing atomic number.

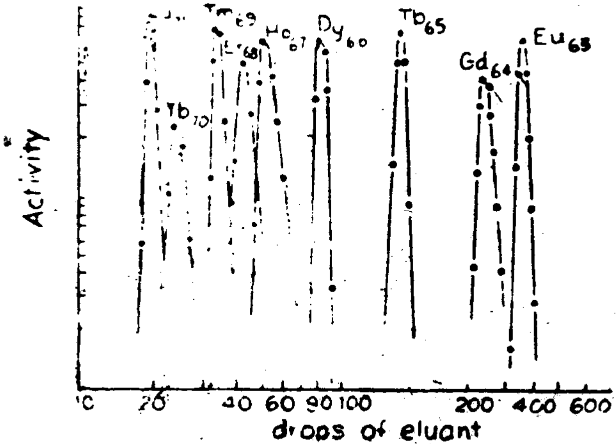


Fig. 9·2. A typical elution plot for the separation of rare-earths (Lu_{71} to Eu_{63})

(*ii*) **Solvent (liquid-liquid) extraction method.** The separation of lanthanides by this method was first reported by Fischer. The method is based on the differences in the solubility of lanthanide salts in water and an immiscible or partially miscible organic solvent. These organic solvents are called **extracting solvents** or **extractants**. This method has been used on both tracer and macroscales. The technique consists of passing the aqueous solution of lanthanide salts counter-current to the organic solution which extracts the lanthanides from water. The most widely used extracting solvent is tri-n-butyl phosphate, TBP in an inert medium like kerosene or xylene to extract the lanthanides from nitric acid solutions. TBP forms complexes with Ln^{3+} (*aq*) ions in presence of NO_3^- ions

$$Ln^{3+}(aq)+3NO_3^-(aq)+3TBP(org) \rightleftharpoons \underbrace{Ln(NO_3)_3(TBP)_3(org)}_{\text{Complex}},$$

where (*org*) represents the organic phase. The distribution between these two phases (*i.e.* solvents) is described by distribution ratio (also called extraction coefficient), λ, given by

$$\lambda = \frac{\text{Total concentration of solute in one solvent}}{\text{Total concentration of solute in the other solvent}}$$

$$= \frac{C_{Ln(NO_3)_3(TBP)_3(org)}}{C_{Ln^{3+}(aq)}} \qquad \ldots(9\cdot1)$$

For two tripositive lanthanide ions, Ln'^{3+} and Ln^{3+}, the separation factor, α, is given as,

$$\alpha = \frac{\lambda'}{\lambda} = \frac{C_{Ln(NO_3)_3(TBP)_3(org)} \cdot C_{Ln^{3+}(aq)}}{C_{Ln(NO_3)_3(TBP)_3(org)} \cdot C_{Ln'^{3+}(aq)}} \qquad \ldots(9\cdot2)$$

Peppard has reported that an average separation factor for adjacent lanthanides for 15·8 M nitric acid—100% TBP system is about 1·5.

Equilibrium constant, *K*, is given by :

$$K = \frac{C_{Ln(NO_3)_3(TBP)_3(org)}}{C_{Ln^{3+}(aq)} \cdot C^3_{NO_3^-(aq)} \cdot C^3_{TBP(org)}} \qquad \ldots(9\cdot3)$$

Combination of equation (9·3) with equation (9·1) gives equation (9·4), *viz.*

$$K = \frac{\lambda}{C^3_{NO_3^-(aq)} \cdot C^3_{TBP(org)}}$$

or $$\lambda = K \,.\, C^3_{NO_3^-(aq)} \cdot C^3_{TBP(org)} \qquad \ldots(9\cdot4)$$

Kilogram quantities of 95% pure lanthanides have been prepared by solvent extraction technique. Another organic solvent which is a better extractant than TBP is *Di (2-ethyl hexyl) phosphoric acid*. For this extractant the average separation factor of 2·5 for adjacent lanthanides has been reported. Other extractants used in the separation process are : monoalkylphosphoric acids : RP (O) $(OH)_2$ or RH_2PO_3, pyrophosphate esters : $(RO)_2$ P(O)—O—P(O) $(OR)_2$, phosphonates : $(RO)_2$ (R) PO and (RO) (R) P (O) (OH) and 1, 3-diketones or 8-quinolinols.

Present status of solvent extraction technique. Although solvent extraction technique is promising as a general technique, it cannot compete with ion exchange technique. The major uses of the solvent extraction process are that it can be used in separating the Ln^{3+} ions from Ln^{4+} ions such as Ce^{4+} and Th^{4+} and in the purification of Ce, Th and La. La is somewhat less readily extracted than other Ln^{3+} ions and it can thus be separated from them rather readily.

(*iii*) **Paper chromatography**. Cerrai and Testa separated some rare-earths by ascending paper chromatography, using CRL/I papers treated with 0·1M dil. (2-ethylhexyl) orthophosphoric acid (HDEHP). Under the same conditions an increase in R_F value is noted with decreasing atomic number, Z, of the rare-earths. For a given element the R_F value increases with the molarity of eluting acid (HCl) and with temperature, but decreases with the concentration of HDEHP. The following R_F values for 1 M HCl eluant have been reported:

$Ln^{3+} \longrightarrow$	La	Ce	Pr	Sm	Eu	Gd	Dy	Er	Yb	Y	Sc
$R_F \longrightarrow$	0·92	0·91	0·90	0·76	0·64	0·51	0·12	0·06	0·03	0·07	0·0

Later, Cerrai and Triulzi used a mixture of 3M HNO_3 and 80% CH_3OH as solvent on Whatman cellulose paper DE—20 to separate La, Ce, Pr, Nd, Sm and Gd. Whatman DE--20 is a cellulose anion exchanger, containing amine groups bonded to the cellulose matrix.

It has been found that a mixture of HCl and various aliphatic alcohols can successfully be used as eluant for the separation of rare-earths by paper chromatography (Whatman No. 1).

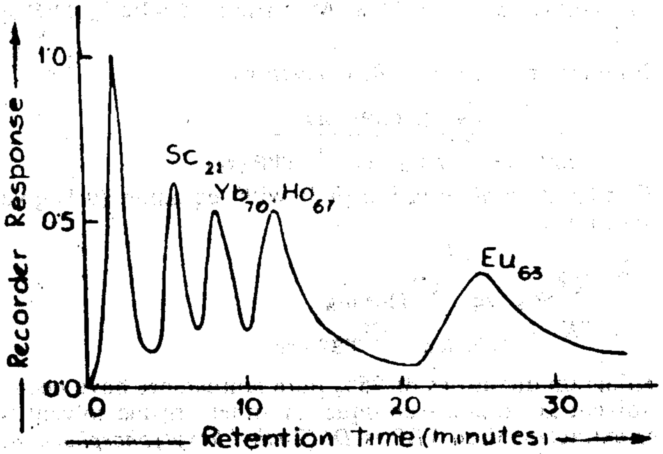


Fig. 9·3. Gas chromatographic separation of a mixture of $Ln(THD)_3$ complexes in benzene solution [Reproduced from Journal of the American Chemical Society, 87, 5254 (1965)].

(*iv*) **Gas Chromatography**. The 2, 2, 6, 6-tetra ethyl-3, 5-heptanedione complexes of Ln^{3+} ions, Ln $(THD)_3$ are quite stable, volatile and monomeric in C_6H_6. These complexes have appreciable and significant differences in the volatilities.

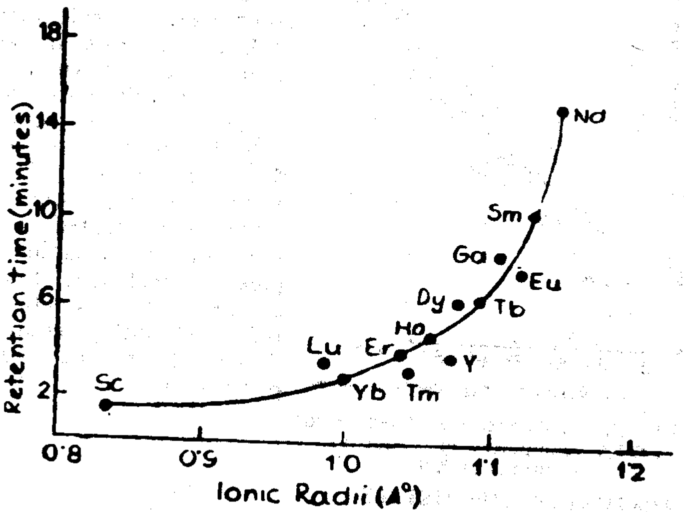


Fig. 9·4. Variation of the retention times (minutes) of the rare-earth tris-complexes with ionic radii (A°) showing the effect of lanthanide contraction.

Eisentraut and Sievers have recently separated these complexes by gas chromatographic technique. Fig. 9·3 shows a gas chromatographic separation of a mixture of Ln $(THD)_3$ complexes in C_6H_6 solution. It has been found that these complexes are eluted without decomposition.

The variation of the retention times (in minutes) of the rare-earth tris- complexes with ionic radii (in A°) shown in Fig. 9·4 exhibits the effect of lanthanide contraction.

(*v*) **Thin layer chromatography.** Daneels has separated Sm. Eu, Gd and Tb by this technique using Silica gel *H*. Radioactive traces were used to detect the rare-earths. The R_f values for Sm. Eu, Gd and Tb are 0·54, 0·29, 0·73 and 1·00 respectively.

(*vi*) **Complexe formation: oxalate precipitation in presence of EDTA.** In the presence of complexing reagent namely ethylene diamine tetra-acetic acid (EDTA), J.K, Marsh (1950-51) has been able to effect an efficient separation of rare-earths by precipitation as oxalates.

Lanthanide-oxalates are insoluble in water, but they can be dissolved by complexing with EDTA.

These lanthanide-EDTA complexes differ in their stabilities. The stability of these complexes, as a rule, increases with an increase in atomic number as shown in Fig. 9·5 The difference in stabilities of these complexes may be made the basis of the separation of rare-earths. Thus, if these complexes are treated with an acid, the least stable complex is destroyed first and changes to oxalate, while the most stable complex is destroyed on the addition of an acid.

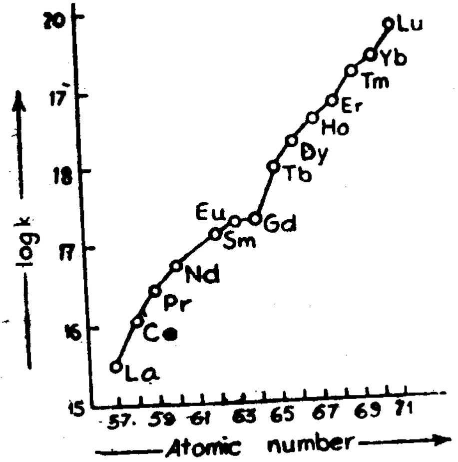


Fig. 9·5. Stability constants of lanthanide-EDTA complexes in aqueous solutions at 20°C.

PREPARATION OF THE METALS

Because of the ease of oxidation of these metals it is not a simple task to obtain the elements in the metallic state.

The following methods may be used for the preparation of metals :

(*i*) **Thermal decomposition of lanthanide-mercury amalgam.** Using a mercury cathode an amalgam of the lanthanides may be prepared by the electrolysis of aqueous solutions. The amalgam thus formed is thermally decomposed to get the metals in a finely divided state, but complete elimination of mercury is difficult.

(*ii*) **Electrolysis of fused chlorides.** The anhydrous lanthanide (+3) chlorides are fused with sodium, potassium or calcium chloride by external heating and the molten mass is electrolysed in an iron pot or in a refractory lined pot which serves as the anode. Graphite cathodes are used. The molten metal collects as a pool at the bottom of the pot from where it is withdrawn and cast into ingots.

This method does not give the metals in high degree of purity required in modern technology.

(*iii*) **Metallothermic reduction of the salts** In this method the anhydrous fluorides and chlorides of lanthanides are reduced with calcium in a tantalum container at about 1000°C. Calcium is volatilised from the lanthanide-calcium alloy. This method is successful for all the lanthanides except Sm, Eu and Yb, because these metals form stable divalent fluorides. However these metals can be prepared by reducing their oxides with lanthanum metal at 1400°C in vacuum and distilling out Sm, Eu and Yb. These metals are more volatile then lanthanum.

The metals can be purified by vacuum distillation (pressure $\simeq 10^{-5}$ mm Hg) in tantalum apparatus.

GENERAL PROPERTIES OF LANTHANIDES

Some of the important properties of lanthanides are discussed below.

(1) Electronic Configuration

We know that at Ba_{56} 6*s*-orbital is completely filled ($Ba_{56} \rightarrow$ [Xe] $6s^2$) and at La_{57} 5*d*-orbital is singly occupied ($La_{57} \rightarrow$ [Xe] $5d^1\ 6s^2$). But after La_{57} further filling of 5*d*-orbitals is discontinued. As the nuclear charge increases by one unit from La_{57} to Ce_{58}, 4*f*-orbitals which were higher in energy up to La_{57}, fall slightly below the 5*d* level. 4*f*-orbitals, therefore, begin to fill and are completely filled up to Lu_{71} before the filling of 5*d*-orbitals is resumed. Electronic configurations of lanthanides are shown in Table 9·3. From this table the following points may be noted :

Table 9·3. *Electronic configuration of the neutral gaseous atoms of lanthanides.*

Elements with atomic numbers	*Complete configurations*	*Valence-shell configurations*
La_{57}	*[Xe] $4f^0 5d^1 6s^2$	$4f^0\ 5d^1\ 6s^2$
Ce_{58}	[Xe] $4f^2\ 5d^0\ 6s^2$	$4f^2\ 5d^0\ 6s^2$
Pr_{59}	[Xe] $4f^3\ 5d^0\ 6s^2$	$4f^3\ 5d^0\ 6s^2$
Nd_{60}	[Xe] $4f^4\ 5d^0\ 6s^2$	$4f^4\ 5d^0\ 6s^2$
Pm_{61}	[Xe] $4f^5\ 5d^0\ 6s^2$	$4f^5\ 5d^0\ 6s^2$
Sm_{62}	[Xe] $4f^6\ 5d^0\ 6s^2$	$4f^6\ 5d^0\ 6s^2$
Eu_{63}	[Xe] $4f^7\ 5d^0\ 6s^2$	$4f^7\ 5d^0\ 6s^2$
Gd_{64}	[Xe] $4f^7\ 5d^1\ 6s^2$	$4f^7\ 5d^1\ 6s^2$
Tb_{65}	[Xe] $4f^9\ 5d^0\ 6s^2$	$4f^9\ 5d^0\ 6s^2$
Dy_{66}	[Xe] $4f^{10}\ 5d^0\ 6s^2$	$4f^{10}\ 5d^0\ 6s^2$
Ho_{67}	[Xe] $4f^{11}\ 5d^0\ 6s^2$	$4f^{11}\ 5d^0\ 6s^2$
Er_{68}	[Xe] $4f^{12}\ 5d^0\ 6s^2$	$4f^{12}\ 5d^0\ 6s^2$
Tm_{69}	[Xe] $4f^{13}\ 5d^0\ 6s^2$	$4f^{13}\ 5d^0\ 6s^2$
	[Xe] $4f^{14}\ 5d^0\ 6s^2$	$4f^{14}\ 5d^0\ 6s^2$
Lu_{71}	[Xe] $4f^{14}\ 5d^1\ 6s^2$	$4f^{14}\ 5d^1\ 6s^2$

*[Xe] indicates the complete configuration of Xe atom which is 2, 8, 18, 18, 8

(*i*) The complete electronic configuration of lanthanides can be represented by a general configuration *viz.*, 2, 8, 18, $4s^2p^6d^{10}f^{0,\ 2\ldots14}$

$5s^2p^6d^{0 \text{ or } 1}$, $6s^2$ (including La) which shows that the valence-shell configuration can be represented as $4f^{0, 2 \ldots 14} 5d^{0 \text{ or } 1} 6s^2$.

The valence-shell configuration indicates that the additional electron enters the 4 f-orbital without altering the electrons in the outermost 6s-orbital.

(ii) The filling of 4f-orbitals is not regular, *e.g.*, the additional electron in Gd_{64} does not enter 4 f-level but, instead, it goes to 5d-level. This is because the 4f and 5d orbitals in Gd *are at about the same energy level* and Gd atom has a tendency to retain the configuration with *half-filled 4f-orbitals which are relatively more stable.*

(2) Oxidation states and oxidation potentials.

Observed oxidation states of lanthanides noted either in solution or in insoluble compounds are given in Table 9·4 from which it may be noted that whatever the electronic configurations of the lanthanides in the ground state, all of the lanthanides form the tripositive lanthanide cations. This fact is not directly evident from the electronic configurations, it is actually due to the fact that the magnitudes of the energy required to remove an electron from the gaseous ion in its lower oxidation state (*i.e.*, ionisation energy) and of that released when two gaseous ions combine with water to form the aquated species (*i.e.*, hydration energy) are such that all the tetrapositive species (except possibly Ce^{4+}) and all the dipositive species (except Eu^{2+}) revert to the tripositive species. Thus this leads to the conclusion that *tripositive species are more stable than the di -and tetrapositive species in aqueous solutions.*

In the solid state too the combination of ionization energy and the energy released when gaseous ions combine to produce crystalline solids (*i.e.*, the lattice or crystal energy) is more negative for the tripositive species than for di- and tetrapositive species. Consequently, *the tripositive lanthanides are also the most common in the solid compounds.*

Stability of various oxidation states. It is possible to correlate the stability of various oxidation states of lanthanides with the electronic configuration of their ions. On the basis of general rule that empty, half-filled and completely filled 4f orbitals are highly stable, the formation of Ce^{4+}, La^{3+}, ($4f^0$), Tb^{4+}, Eu^{2+}, Gd^{3+} ($4f^7$) and Yb^{2+}, Lu^{3+} ($4f^{14}$) ions can be explained. It is, however, difficult to explain the stability of oxidation states of the cations other than those given above. It may thus be assumed that in addition to the special stability associated with $4f^0$, $4f^7$ and $4f^{14}$ configurations, there may be other factors such as thermodynamic and kinetic, in determining the stability of various oxidation states of lanthanides.

The stability order of +2 state is Eu > Yb > Sm > Tm ~ Nd. LnI_2 solids (Ln = La, Ce Pr and Gd) do not contain Ln^{2+} ions, but are metallic in nature. The stability order of +4 state is Ce > Tb ~ Pr > (Nd ~ Dy).

The ease of formation of the various oxidation states in solution is indicated by the values of the standard electrode potential, E°.

These values (in volts) for different couples of lanthanides such as $Ln^0 \rightarrow Ln^{3+} + 3e^-$, $Ln^{2+} \rightarrow Ln^{3+} + e^-$ and $Ln^{3+} \rightarrow Ln^{4+} + e^-$, for 1M perchloric acid at 25°C are tabulated in Table 9·4. Here Ln represents the elemental lanthanide. Ln^{2+}, Ln^{3+} and Ln^{4+} are the di-, tri- and tetrapositive lanthanide ions. From this table, we observe that :

(*i*) The high positive values of the oxidation electrode potentials for the couple $Ln^0\ (s) \rightleftharpoons Ln^{3+}(aq) + 3e^-$ indicate that the elemental lanthanides are powerful reducing agents, *i.e.* oxidation of the lanthanide metals to the tripositive state occurs readily and vigorously. The gradual decrease, though very slow, in the values of E° indicates very slight decrease in chemical activity from one element to the next one.

(*ii*) The enhanced stabilities associated with the empty, half-filled and completely filled $4f$-orbitals is also indicated by these values. Thus Ce^{4+} ($4f^0$) is much less readily reduced to the tripositive ion, Ce^{3+} ($4f^1$) than Pr^{4+} ion ($4f^1$). Furthermore, the $4f^7$ species (*e.g.* Eu^{2+} ion) and the $4f^{14}$ species (*e.g.* Yb^{2+} ion) are the weakest reducing agents of the dipositive species.

(*iii*) The values of E° for couple $Ln^0\ (s) \longrightarrow Ln^{3+}\ (aq) + 3e^-$ decreases with the increase of atomic number, as is evident from Table 9·4. The high values of E° are in accordance with the electropositive character of lanthanides. The decrease in the values of E° with the increase in atomic number (*i.e.* a decrease in the electropositive character) is evidently inconsistent with the corresponding decrease in the ionic radius, *i.e.* lanthanide contraction (to be described subsequently).

Chemistry of +3 state.

In general, the lanthanides behave as active metals. Their electrode potential values are comparable to those of alkaline earths. All the metals act as strong reducing agents. They are all attacked by acids with the liberation of hydrogen. The metals dissolve slowly in cold but more rapidly in warm water and liberate hydrogen. They absorb hydrogen to form interstitial hydrides.

Nearly all known anions form the compounds with Ln^{3+} cation. These compounds are stable in solid as well as in solution state. Compounds of Ln^{3+} cation with the anions such as OH^-, CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, NO_3^- etc. decompose on heating, give first basic salts and finally oxides. Hydrated salts that contain thermally stable anions such as F^-, Cl^-, Br^-, PO_4^{3-} etc. also give similar products on heating because of hydrolysis.

Compounds of Ln^{3+} cation with the anions Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, BO_3^{3-} are generally soluble in water while those with F^-, OH^-, O^{2-}, $C_2O_4^{2-}$, CO_3^{2-}, CrO_4^{2-}, PO_4^{3-} etc. are generally insoluble.

Oxides, Ln_2O_3. The oxides, Ln_2O_3, are formed by heating the metal in oxygen or by the thermal decomposition of the $Ln(OH)_3$ or oxy salts such as $Ln_2(CO_3)_3$ and $Ln(NO_3)_3$. The oxides resemble those of alkaline earth oxides. All the oxides are almost insoluble

Table 9·4. *Various oxidation states shown by lanthanides and standard oxidation potentials, E° (in volts) for various couples of lanthanide elements in 1 M perchloric acid at 25°C*

Lanthanide elements	*Oxidation states (Less stable states are shown in brackets)*	*E° values (in volts) for various couples (Estimated values are given in brackets)*
La_{57}	+3	$La^{\circ}/La^{3+} = 2{\cdot}52$ volts
Ce_{58}	+3, (+4)	$Ce^{\circ}/Ce^{3+} = 2{\cdot}48$
Pr_{59}	+3, +4	$Pr^{\circ}/Pr^{3+} = 2{\cdot}46$, $Pr^{3+}/Pr^{4+} = -1{\cdot}74$
Nd_{60}	+2, +3	$Nd^{\circ}/Nd^{3+} = 2{\cdot}43$, $Nd^{3+}/Nd^{4+} = (-2{\cdot}86)$
Pm_{61}	+3	$Pm^{\circ}/Pm^{3+} = (2{\cdot}42)$
Sm_{62}	(+2) +4	$Sm^{\circ}/Sm^{3+} = 2{\cdot}41$, $Sm^{2+}/Sm^{3+} = 1{\cdot}55$
Eu_{63}	(+2), +3	$Eu^{\circ}/Eu^{3+} = 2{\cdot}40$, $Eu^{2+}/Eu^{3+} = 0{\cdot}43$
Gd_{64}	+3	$Gd^{\circ}/Gd^{3+} = 2{\cdot}39$
Tb_{65}	+3, (+4)	$Tb^{\circ}/Tb^{3+} = 2{\cdot}39$
Dy_{66}	+3, +4	$Dy^{\circ}/Dy^{3+} = 2{\cdot}35$
Ho_{68}	+3	$Ho^{\circ}/Ho^{3+} = 2{\cdot}32$, $Ho^{2+}/Ho^{3+} = 0{\cdot}57$
Er_{69}	+3	$Er^{\circ}/Er^{3+} = 2{\cdot}30$
Tm_{69}	(+2), +3	$Tm^{\circ}/Tm^{3+} = 2{\cdot}28$
Yb_{70}	(+2), +3	$Yb^{\circ}/Yb^{3+} = 2{\cdot}27$, $Yb^{2+}/Yb^{3+} = 1{\cdot}15$
Lu_{71}	+3	$Lu^{\circ}/Lu^{3+} = 2{\cdot}25$

in water. They absorb CO_2 and H_2O from air to form carbonates and hydroxides respectively.

Hydroxides, $Ln(OH)_3$. The hydroxides are precipitated as gelatinous precipitates from aqueous solution by the addition of ammonia or dil. alkali to soluble salts of Ln^{3+} ion in solution. The precipitation of these hydroxides on the addition of an alkali or ammonia to their salts is as : Sc, Lu, Yb, Tm, Er, Ho, Dy, Tb, Sm, Gd, Eu, Y, Nd, Pr, Ce, La.

These hydroxides are not amphoteric. These are definite compounds with hexagonal structure and are not merely hydrous oxides. They absorb CO_2 to give normal carbonates.

The oxides and hydroxides are basic. The basicity decreases with increasing atomic number. Thus La_2O_3 and La $(OH)_3$ are the most basic while Lu_2O_3 and $Lu(OH)_3$ are least basic. La_2O_3 is a strong base and slakes like CaO on addition of water. The hydroxides are decomposed on heating to form oxides.

Oxy salts. Lanthanide salts of most oxy acids (called oxy salts) such as sulphates, nitrates, perchlorates, bromates etc. are also known. These are generally soluble and crystallise as hydrates. Soluble oxy salts such as sulphates, nitrates and perchlorates can be prepared by dissolving the oxides, hydroxides or carbonates in the appropriate oxyacids. From the solution, hydrated salts can be crystallised out. The nitrates are often deliquescent and crystallise with $6H_2O$. Solutions of oxy salts furnish hydrated cations, $[Ln(H_2O)_x]^{3+}$ which tend to undergo slight hydrolysis in aqueous solution :

$$[Ln(H_2O)_x]^{3+} + H_2O \longrightarrow [Ln(H_2O)_{x-1}(OH)]^{2+} + H_3O^+$$

The smaller the ionic radius of Ln^{3+} ion, the greater is the tendency of the ion, $[Ln(H_2O)_x]^{3+}$, to hydrolyse. Thus the tendency of the $[Ln(H_2O)_x]^{3+}$ ion to hydrolyse increases with increasing atomic number, since on passing from La^{3+} to Lu^{3+} there is a contraction in their ionic radii.

Double Salts. Lanthanide salts form a large number of double salts. The most important double salts are :

(*i*) Double nitrates such as $2[Ln(NO_3)_3 . 3M^{II}(NO_3)_2.24H_2O$ (M^{II} = Mg, Zn, Ni, Mn) and $Ln(NO_3)_3.2NH_4NO_3.4H_2O$.

(*ii*) Double sulphates such as $Ln_2(SO_4)_3 3M_2^I SO_4.12H_2O$ (M = alkali metal)

The double sulphates, $Ln_2(SO_4)_3.3Na_2SO_4.12H_2O$ where Ln=La—Eu are only sparingly soluble in Na_2SO_4, while those where Ln=Gd—Lu are appreciably soluble. Thus a separation of lanthanides into two groups : **Cerium group** having La_{57}—Eu_{63} lanthanides and **Yttrium group** having Gd_{64}—Lu_{71} lanthanides is possible. Since the double salts crystallise well, these are used to separate the rare-earths from one another.

Halides, LnX_3. Fluorides are precipitated by the addition of HF or a soluble fluoride to a Ln^{III} salts solution. The fluorides particularly of heavier lanthanides, are sparingly soluble in HF due to the formation of fluoro complexes.

The anhydrous chlorides can be prepared by the direct combination of the elements on heating. These are best prepared by heating the oxides with carbonyl chloride ($COCl_2$) or NH_4Cl

$$Ln_2O_3 + 3COCl_2 \longrightarrow 2LnCl_3 + 3CO_2$$

$$Ln_2O_3 + 6NH_4Cl \xrightarrow{300^\circ} 2LnCl_3 + 3H_2O + 6NH_3$$

The anhydrous chlorides cannot be obtained from the hydrated chlorides, since these lose HCl on heating to give the oxychlorides, (LnOCl), more easily than they lose H_2O. ($ScCl_3.3H_2O$ and $CeCl_4.2H_2O$, however, give Sc_2O_3 and CeO_2). The chlorides are non-volatile, deliquescent solids soluble in H_2O and alcohol. The hydrated chlorides are formed by dissolving the oxides or carbonates in HCl and concentrating the solution to crystallising point. They crystallise from solution usually as hexahydrates, $LnCl_3 . 6H_2O$

Bromides and iodides are rather similar to the chlorides. Iodides of the first few lanthanides are orthorhombic while those of the remaining lanthanides are hexagonal.

Carbonates, $Ln_2(CO_3)_3$: The normal carbonates can be prepared by passing CO_2 into an aqueous solution of $Ln(OH)_3$. They can also be prepared by adding Na_2CO_3 solution to Ln^{III} salt solution. The carbonates are insoluble in H_2O, but dissolve in acids with liberation of CO_2 and forming Ln^{III} salts.

Phosphates and Oxalates : These are also insoluble in water. All lanthanides are quantitatively precipitated as oxalates from Ln^{3+} solution containing $C_2O_4^{2-}$ ion. The precipitate on drying and ignition gives Ln_2O_3.

Compounds with non-metals and metalloids : The lanthanides also form well-defined compounds with non-metals and metalloids other than oxygen and halogens. These compounds can generally be prepared by the direct combination of the elements at elevated temperatures. Among these compounds are Ln_2S_3 (not of Eu), selenide (Ln_2Se_3) and oxy sulphides (Ln_2O_2S). Nitrides (LnN), phosphides (LnP), arsenides (LnAs), antimonides (LnSb) and bismuthides (LnBi) crystallise in the NaCl structure. The carbide (Ln_3C), is found for the lanthanides, Sm—Lu but not for La, Ce, Pr and Nd.

Chemistry of + 2 state.

This is an anomalous oxidation state. The lanthanides showing oxidation state can be divided into +2 two categories :

(*a*) Sm_{62}, Eu_{63} and Yb_{70}. The dipositive ions of these lanthanides (*i.e.* Sm^{2+}, Eu^{2+} and Yb^{2+}) exist in solution. The standard oxidation potentials at 25°C, in acid solution, of these cations are given below :

$$Sm^{3+}(aq) + e^- \rightleftharpoons Sm^{2+}(aq) - 1{\cdot}55 \text{ volts}$$

$$Eu^{3+}(aq) + e^- \rightleftharpoons Eu^{2+}(aq) - 0{\cdot}43 \text{ volt}$$

$$Yb^{3+}(aq) + e^- \rightleftharpoons Yb^{2+}(aq) - 1{\cdot}15 \text{ volts.}$$

These values indicate that Sm^{2+}, Eu^{2+}, and Yb^{2+} ions are strong reducing agents and their reducing strength is in the order :

$$Sm^{2+} > Yb^{2+} > Eu^{2+}.$$

Sm^{2+} and Yb^{2+} ions are rapidly oxidised by H_3O^+ ions (acidic solution), while Eu^{2+} ion is fairly stable and is only slowly oxidised by H_3O^+ ion.

$$2Sm^{2+} \text{ (or } Yb^{2+}) + 2H_3O^+ \longrightarrow 2Sm^{3+} \text{ (or } 2Yb^{3+}) + 2H_2O + H_2.$$

All these cations are rapidly oxidised in presence of oxygen, *e.g.*,

$4Ln^{2+} + 4H_3O^+ + O_2 \longrightarrow 4Ln^{3+} + 6H_2O$, where Ln^{2+} may be Sm^{2+}, Eu^{2+} or Yb^{2+}.

The compounds of Sm^{2+}, Eu^{2+} and Yb^{2+} which are insoluble in H_2O are not oxidised by H_2O, while hydrated water-soluble compounds of Sm^{2+} and Yb^{2+} are oxidised by their water. Hydrated water-soluble compounds of Eu^{2+} are more stable.

(*b*) **Ce_{58} (?), Nd_{60} and Tm_{69}.** The compounds having these elements in +2 oxidation state are known only as solid halides. These are immediately oxidised with air.

Of the divalent compounds of lanthanides, those of Eu^{2+} ion are most stable. The compounds of Ln^{2+} ion are not stable in solution. All the Ln^{2+} compounds decompose water with evolution of H_2.

$$2Ln^{2+} + 2H_2O \longrightarrow 2Ln^{3+} + 2OH^- + H_2\uparrow$$

The reaction is, however, sluggish ; with Eu the reaction is so retarded that Eu^{2+} compounds may be regarded as fairly stable in aqueous solutions at an ordinary temperature.

Chemistry of +4 state.

This oxidation state is also an anomalous oxidation state. Double salts like $Ce(NO_3)_4.2NH_4NO_3$ and $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$ have also been prepared.

The standard oxidation potentials at 25°C, in acid solution, of Ce^{4+} and Pr^{4+} ions are given as under ;

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} + 1{\cdot}74 \text{ volts}$$

$$Pr^{4+} + e^- \rightleftharpoons Pr^{3+} + 2{\cdot}86 \text{ volts}$$

These values show that Ce(IV) and Pr(IV) are strong oxidising agents, the latter being by far the stronger of the two. $Ce(SO_4)_2$ is generally used in volumetric analysis. Ce^{4+} ion is readily reduced to Ce^{3+} ion.

The tetravalent ions of Ce are stable in the solid state as well as in solution ; Pr^{IV} ; Nd^{IV} , Tb^{IV} and Dy^{IV} are stable only in solution.

(3) Atomic and Ionic Radii—Lanthanide Contraction

The atomic radii of the Ln atoms and the crystal or ionic radii of Ln^{2+}, Ln^{3+}, and Ln^{4+} ions are given in Table 9·5.

This table clearly shows that as we move along the lanthanide series, there is a decrease in atomic and ionic radii. This steady decrease in the atomic and ionic radii is called **lanthanide contraction.** This decrease in size is regular in ions (Fig. 9·6) but not so regular in case of atoms (Fig. 9·7).

Table 9·5. ***Atomic and Ionic (or crystal) Radii of lanthanides and allied elements in Å***

	Elements with atomic No.	Atomic Radius (r_{Ln})	Crystal or ionic radii of		
			Ln^{2+} ion	Ln^{3+} ion	Ln^{4+} ion
	Sc_{21}	1·64		0·68	
	Y_{39}	1·80		0·88	
Lanthanides	La_{57}	1·88		1·06	
	Ce_{58}	1·82		1·03	0·92
	r_{59}	1·83		1·01	0·90
	Nd_{60}	1·82		0·99	
	Pm_{61}	—		(0·98)	
	Sm_{62}	1·80	1·11	0·96	
	Eu_{63}	2·04	1·09	0·95	
	Gd_{64}	1·80		0·94	
	Tb_{65}	1·78		0·92	0·84
	Dy_{66}	1·77		0·91	
	Ho_{67}	1·77		0·89	
	Er_{68}	1·76		0·88	
	Tm_{69}	1·75	0·94	0·87	
	Yb_{70}	1·94	0·93	0·86	
	Lu_{71}	1·73		0·85	

Fig. 9·7 clearly shows that the graph has two peaks, one at Eu_{63} and the other at Yb_{70} which possess exceptionally high values for their atomic radii. This is regarded due to the difference in metallic bonding. Each of the lanthanides is assumed to contribute three electrons for the formation of metallic bond, excepting Eu and Yb. These two atoms contribute only two electrons towards bond formation, thus leaving behind half-filled and completely filled 4*f*-orbitals respectively. The three vertical lines shown in the figure have been drawn just to mark off the lanthanide part of the curve and to divide the lanthanides into two portions marked as 1 and 2. The dividing line passes through Gd_{64} which has half-filled 4*f*-shell (Gd $\longrightarrow$ $4f^7\ 5d^1\ 7s^2$). The right-hand half of the curve is obviously a duplicate pattern of left-hand half. The seven elements of portion 1 namely from Ce_{58} to Gd_{64} occupy a position corresponding to that occupied by the seven elements namely Tb_{65} to Lu_{71} of portion 2.

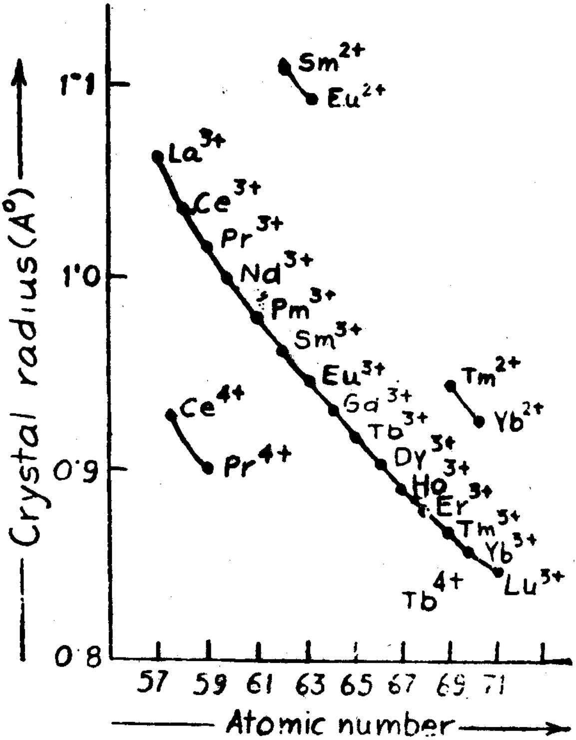


Fig. 9·6. Crystal radii of Ln^{3+}, Ln^{2+} and Ln^{4+} ions as a function of their atomic numbers.

Cause of lanthanide contraction.

We have already seen that in lanthanides the additional electron enters 4*f*-sub-shell but not in the valence-shell namely sixth shell. The shielding effect of one electron in 4*f*-sub-shell by another in the same sub-shell (*i.e.* mutual shielding effect of 4*f*-electrons) is very little, being even smaller than that of *d*-electrons, because the shape of *f*-sub-shell is very much diffused. The nuclear charge (*i.e.* atomic number), however, increases by unity at each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of 4*f*-electrons. This results in that electrons in the outermost shell experience increasing nuclear attraction from the growing nucleus. Consequently the atomic and ionic radii go on decreasing as we move from La_{57} to Lu_{71}.

Consequences of Lanthanide Contraction.

Some important consequences of the lanthanide contraction are summarised below :

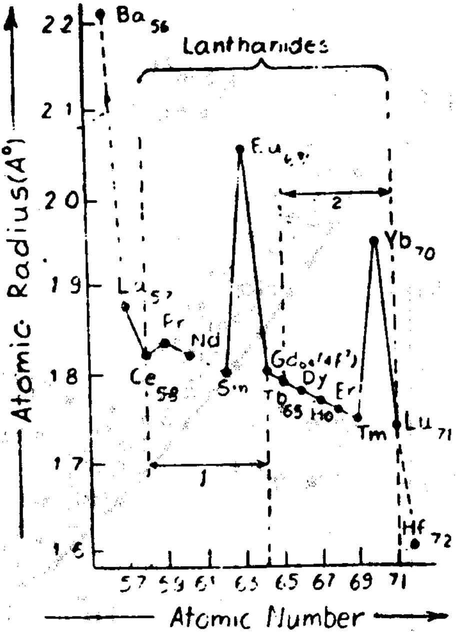


Fig. 9·1 Atomic radii of lanthanides, Ba and Hf as a function of their atomic numbers.

(*i*) **Anomalous behaviour of post-lanthanide elements.** The elements following lanthanides are called *post-lanthanide elements*. Thus these are the elements of third transition series. Lanthanide contraction effects the properties of post-lanthanide elements. The following examples illustrate this point.

(*a*) *Atomic and ionic radii of post-lanthanide elements.* Normally in the same sub-group, the covalent radii increase as the atomic number increases. This fact is evident when we compare the covalent radii values of the elements of the first and second transition series as given in Table 9·6.

If we compare the covalent radii values of the elements of the second transition series with those of the third series, we find that the normal increase in the covalent radii values from Sc_{21} to Y_{39} to La_{57} disappears after lanthanides and the pairs of elements : Zr—Hf, Nb—Ta, ..., Ag—Au, Cd—Hg possess almost same values. If the fourteen lanthanides had not been intervened between La_{57} and Hf_{72}, the value of covalent radius, for example, of Hf_{72} should have been greater than that of Zr_{40}, since Zr and Hf both are in the same subgroup IV B and Zr lies immediately above Hf. The occurrence of lanthanide contraction cancels the expected increase in the covalent radius value from Zr to Hf. This situation is also with other pairs of elements in the second and third series of transitional elements.

Table 9·6. *Atomic (covalent) Radii (in A°) of the elements preceding and following lanthanides.*

Transition series	*III B*	*IV B*	*V B*	*VI B*	*VII B*	*VIII*			*I B*	*II B*
First	Sc_{21} 1·44	Ti 1·32	V 1·22	Cr 1·18	Mn 1·17	Fe 1·17	Co 1·16	Ni 1·15	Cu 1·17	Zn_{30} 1·25
Second	Y_{39} 1·62	Zr_{40} 1·45	Nb 1·34	Mo 1·30	Tc 1·27	Ru 1·25	Rh 1·25	Pd 1·28	Ag 1·34	Cd_{48} 1·48
Third	La_{57} Ce_{58}—Lu_{71} 1·69 1·65 1·65 14 lanthanides	Hf_{72} 1·44	Ta 1·3	W 1·30	Re 1·28	Os 1·26	Ir 1·27	Pt 1·30	Au 1·34	Hg_{80} 1·49

Since the pairs of elements of second and third transition series, occurring after lanthanides, (*e.g.* Zr—Hf, Nb—Ta etc. pairs) have almost similar size (which is due to lanthanide contraction), they are much more close to one another in properties than do the pairs of elements of first and second transition series, *e.g.*, solubilities of their salts are very much similar to one another.

(*b*) *High density of post-lanthanide elements.* Because of lanthanide contraction the atomic sizes of the post-lanthanide elements become very small. Consequently the packing of atoms in their metallic crystals become so much compact that their densities are very high. Thus, while the densities of the elements of second transition series are only slightly higher than those of the elements of first series, the densities of the elements of third transition series are almost double to those of the elements of second transition series.

(*ii*) **Basic character of oxides, Ln_2O_3 and hydroxides, $Ln(OH)_3$.** The chemical properties of an element or an ion depend on the size of the atom or ion. The greater the atomic or ionic radius, greater is the ease with which the species (*i.e.* atom or ion) will lose electrons. Thus the ease with which a species loses electrons is the measure of the basicity of the species. Basicity decreases as the ionic radius decreases. Thus, basicity of Ln^{3+} ions may be expected to decrease in the order : $La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$.

These differences in basicity are reflected in (*a*) thermal decomposition of oxy-salts, *e.g.* more basic oxy-salts decompose less easily, (*i.e.* with difficulty) (*b*) hydrolysis of ions—more basic ions hydrolyse less readily (*c*) solubilities of salts (*d*) formation of complexes, and (*e*) decreasing ease of oxidation of the metals with increasing atomic number—oxidation potential for the couple $Ln \longrightarrow Ln^{3+} + 3e^-$ regularly goes on decreasing.

Due to lanthanide contraction the decrease in size of Ln^{3+} ions from La^{3+} to Lu^{3+} increases the covalent character (*i.e.* decreases the ionic character) between Ln^{3+} and OH^- ions in Ln(III) hydroxides (*Fajans rules*). Thus $La(OH)_3$ *is the most basic while* $Lu(OH)_3$ *is the best basic.*

Similarly there is a decrease in the basic strength of the oxides, Ln_2O_3 with the increase of atomic number of Ln atom.

(*iii*) Small variation in the properties on account of lanthanide contraction allows the separation of lanthanides by the methods based on fractional crystallisation and basicity differences.

(*iv*) **Occurrence of Y with heavy lanthanides.** The crystal radii of Y^{3+} and Er^{3+} are equal ($Y^{3+} = 0{\cdot}93$ Å and $Er^{3+} = 0{\cdot}96$ Å). This similarity in ionic size of these two cations coupled with the equality in ionic charge (= +3 in both the ions) accounts for the invariable occurrence of Y with heavier lanthanides. The marked similarities in the crystal structure, chemical properties and solubility between yttrium compounds and the corresponding ones of the heavier lanthanides make it difficult to separate yttrium from the heavier lanthanides. It is because of these similarities that yttrium is regarded for all practical purposes as a member of lanthanide series.

(4) Colour and Absorption Spectra of Ln^{3+} Ions

The striking colour characteristics of crystalline salts of a number of Ln^{3+} ions persist in aqueous and non-aqueous solutions and remain unaffected by the change of the anion present or by the addition of colourless complexing groups. Thus it can be said that the colours are characteristic of Ln^{3+} ions themselves. Colours of Ln^{3+} ions are given in Table 9·7.

From Table 9·7 the following points may be noted :

(*i*) Ln^{3+} ions having x electrons and $(14-x)$ electrons in $4f$ orbital have the same colour. For example Pr^{3+} and Tm^{3+} ions having 2 and $(14-2)=12$ electrons in the $4f$-orbital respectively have the same colour namely green. Thus we see that $4f$-orbitals are the source of colours of Ln^{3+} ions.

(*ii*) The colours of Ln^{3+} ions from La^{3+} to Gd^{3+} repeat themselves at least qualitatively, from Lu^{3+} back to Gd^{3+}. It can thus be concluded that the colours depend on the number of unpaired electrons in $4f$-orbitals, but the fact that Ln^{2+} (*e.g.* Sm^{2+}, Eu^{2+}, Yb^{2+} ions) and Ln^{4+} ions (*e.g.* Ce^{4+} ion) which are iso-electronic with Ln^{3+} ions have different colours suggests that the situation is somewhat more complex. For example, although both Eu^{3+} $(4f^6)$ and Sm^{2+} $(4f^6)$ ions have the same number of unpaired electrons in $4f$-orbitals $(=6)$, they have different colours (Eu^{3+}—colourless, Sm^{2+}—reddish). Other examples of pairs of cations having the same number of unpaired electrons in $4f$-orbitals but with different colours are :

(*a*) $La^{3+}(4f^0, n=0)$—colourless, $Ce^{4+}(4f^0, n=0)$—orange-red
(*b*) $Gd^{3+}(4f^7, n=7)$—colourless, $Eu^{2+}(4f^7, n=7)$—straw-yellow
(*c*) $Lu^{3+}(4f^{14}, n=0)$—colourless, $Yb^{2+}(4f^{14}, n=0)$—Green.

(*iii*) The colour of the Ln^{3+} cations can, to a large extent, be correlated with the electronic configuration of Ln^{3+} ions. Thus, as is evident from Table 9·7, the Ln^{3+} ions having no unpaired $4f$-electrons (*i.e.* having either $4f^0$ or $4f^{14}$ electronic configuration) or half-filled $4f$-orbital (*i.e.* $4f^7$ configuration) are colourless, *e.g.* all the cations *viz* $La^{3+}(4f^0)$, $Gd^{3+}(4f^7)$ and $Lu^{3+}(4f^{14})$ are colourless.

Origin of Colour

The colours are due to *Laporte-forbidden f-f transitions, i.e.*. transitions between the J states of $4f^n$ configuration. Hence the absorption bands of Ln^{3+} ions (except Ce^{3+} and Yb^{3+} ions) are *very weak* but *sharp* when compared to those of *d*-block elements. Many of these bands are *line-like* and *become even narrower as the temperature is lowered.* These narrow bands appear due to *f-f transition* and are independent of the nature of the anion present. As $4f$-electrons lie deep inside the atom, the colours of Ln^{3+} ions are not effected by changing the anion.

The colour one sees is the result of absorption of light of certain wavelengths and transmission of light of other wavelengths.

Table 9·7. *Colours and wavelengths (in Å) of the prominent light absorption bands of Ln^{3+} ions in aqueous solutions (n = No. of unpaired electrons in 4f-orbitals).*

Ln^{3+} ions with valence-shell configuration and number of unpaired electrons (n) in 4f-orbitals	*Colours and wavelengths (in A°)*	*Ln^{3+} ions with valence-shell configuration and number of unpaired electrons (n) in 4f-orbitals*	*Colours and wavelengths (in A°)*
$La^{3+}(4f^0, n=0)$	Colourless	Lu^{3+} $(4f^{14}, n=0)$	Colourless
	(No absorption in visible or infrared region)		(No absorption in visible, ultraviolet and infrared region)
Ce^{3+} $(4f^1, n=1)$	Colourless	$Yb^{3+}(4f^{13}, n=1)$	Colourless
	(No absorption in the visible region, strong bands in ultra violet region—2105, 2220, 2380, 2520)		(No absorption in visible region: strong bands in infrared-9750)
$Pr^{3+}(4f^2, n=2,$	Green	Tm^{3+} $(4f^{12}, n=2)$	Green
	(4445, 4690, 4822, 5885)		(3600, 6825, 7800)
$Nd^{3+}(4f^3, n=3)$	Reddish	$Er^{3+}(4f^{11}, n=3)$	- Reddish
	(3540, 5218, 5745, 7395, 7420, 7975, 8030, 8680)		(3642, 3792, 4870, 5228, 6525)
$Pm^{3+}(4f^4, n=4)$	Pink-yellow	$Ho^{3+}(4f^{10}, n=4)$	Pink-yellow
	(5485, 5680, 7025, 7355)		(2870, 3611, 4508, 5370, 6404)

$Sm^{3+}(4f^5, n=5)$	Pale-yellow	$Dy^{3+}(4f^9, n=5)$	Pale-yellow
	(3625, 3745, 4020)		(3504, 3650, 9100)
$Eu^{3+}(4f^6, n=6)$	Pale-pink (nearly colourless)	$Tb^{3+}(4f^8, n=6)$	Pale-pink (nearly colourless)
	(3755, 3941)		(3694, 3780, 4875)
$Gd^{3+}(4f^7, n=7)$	Colourless	$Gd^{3+}(4f^7, n=7)$	Colourless
	(No absorption in visible region, strong bands in ultraviolet region—2729, 2733, 2754, 2756)		(No absorption in visible region, strong bands in ultraviolet region—2729, 2733, 2754, 2756)

The coloured ions absorb in the visible region, and on occasion in the ultraviolet region. The colourless ions absorb either in the ultraviolet (Ce^{3+}, Gd^{3+} ions) or in the infrared region (Yb^{3+} ion). The Ln^{2+} ions absorb strongly in the ultraviolet. The only Ln^{4+} ion stable in aqueous solution, the Ce^{4+} ion, absorbs in the blue ultraviolet regions.

Laporte-permitted bands due to the transitions of $4f^n \longrightarrow 5d^1$ type have been observed in Ce^{3+}, Tb^{3+}, Sm^{2+}, Eu^{2+} and Yb^{2+}. These bands are *strong* and *broader*, since the transition is considerably influenced by the chemical environment. A charge transfer phenomena is also observed in certain lanthanide ions, *e.g.* the orange-red colour of Ce^{4+} is due to the *electronic transition from the ligand orbital to the f orbital of cerium.* Compounds of Eu^{3+} with reducing anions are yellow *due to electron transfer from the metal.*

(5) Magnetic Properties

The paramagnetic property of an ion or an atom is due to the presence of unpaired electrons in it. Thus, since both La^{3+} ($4f^0\,5d^0\,6s^0$) and Lu^{3+} ($4f^{14}\,5d^0\,6s^0$) ions have no unpaired electrons, these are not paramagnetic. All other Ln^{3+} ions show paramagnetic property.

Since for most of Ln^{3+} ions the energy difference between the two successive J levels of a multiplet (*i.e., multiplet width* is large compared to kT, k = Boltzman constant and T = absolute temperature), there is a strong L-S coupling (*see magnetic properties of transition elements*). In these ions the unpaired electrons in $(n-2)f$ orbitals are quite deeply seated and hence are well shielded by $5s$ and $5p$ electrons from the effects of other atoms in their compounds (*crystal field effect*). Consequently the effective magnetic moments of Ln^{3+} ions, with the exception of Sm^{3+} and Eu^{3+} ions, are given by the following equation provided that the ground state symbols of Ln^{3+} ions are known.

$$\mu_{eff} = \mu_J = g\sqrt{J(J+1)}\ \text{BM} \qquad \ldots(9{\cdot}5)$$

where g is the Lande splitting factor and is given by

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \qquad \ldots(9{\cdot}6)$$

S = resultant spin quantum number, L = resultant orbital quantum number and J = resultant inner quantum number which is obtained by coupling L and S.

Values of μ_{eff} of the sulphates of Ln^{3+} ions calculated from equation (9·5) and those found experimentally (*i.e.* μ_{exp} values) are given in Table 9·8. From this Table the following points may be noted :

(*i*) Although for most of Ln^{3+} ions there is an almost good agreement between the calculated and experimental values, for Sm^{3+} and Eu^{3+} ions the agreement is poor. This is due to the fact that in case of Sm^{3+} and Eu^{3+} ions the energy difference (*i.e.* multiplet width) between the successive J energy levels is *comparable* to kT and the J levels above the lowest energy J level are populated by atoms to some extent. The situation is actually not so simple as we have described here.

(*ii*) We know that for Ln^{3+} ions like $La^{3+}(4f^0)$, $Gd^{3+}(4f^7)$ and Lu^{3+} $(4f^{14})$ which have S term symbol, L$=$0, *i.e.* no orbit effect (L$=$0 shows S term symbol). For these ions when L$=$0, J$=$S and hence $g=2$. (From eqn. 9·6). Thus equation (9·5) reduces to

$$\mu_{eff}=\mu_S=2\sqrt{S(S+1)}$$

or
$$\mu_{eff}=\mu_{spin\ only}=2\sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)}=\sqrt{n(n+2)}$$

The values of μ_{eff} calculated from these two equations are also given in Table 9·8 which shows that μ_J and μ_S values for La^{3+}, Gd^{3+} and Lu^{3+} ions are the same.

(6) Complex Formation

The lanthanides are moderate in their complex forming ability which increases to the right in the periodic table. The 4*f*- electrons of lanthanides are too well shielded to interact. Consequently each lanthanide ion is effectively an inert gas-type ion, like those of the alkaline earth metals, that attracts ligands only by overall electrostatic forces. On this basis, we expect and also observe a general decrease in case of complex ion formation with a specific ligand in the series $Ln^{4+} > Ln^{3+} > Ln^{2+}$.

The tendency of the anhydrous Ln^{3+} ions to form complexes increases from La^{3+} to Lu^{3+}, whereas that of the hydrated Ln^{3+} ions, $Ln^{3+}(aq)$, decreases in the same order. The difference in complexation tendencies of the anhydrous and hydrated ions is due to the fact that while the size of the Ln^{3+} ions decreases, that of the Ln^{3+} (*aq*) increases with the increasing atomic number.

Lanthanides, owing to the unavailability of orbitals for bonding, high basicity and rather larger size of their common cation, Ln^{3+}, form few complexes which are mostly formed with oxygen or oxygen plus nitrogen containing chelating ligands such as β-diketones, hydroxo acids (*e.g.* tartaric acid or citric acid), various amino acids of the types $RN(CH_2OOH)_2$ and $N(CH_2COOH)_3$, EDTA, oxine. β-diketones form complexes of the type [Ln(β-diketone)$_3$]. H_2O.

Some non-chelated species such as : (*i*) ammines, $LnCl_3.x\ NH_3$ (*ii*) amine adducts, $LnCl_3.y\ RNH_2$ (*iii*) antipyrine adducts, $[Ln(ap)_6]X_3$, where $X = I^-$, IO_4^-, NCS^- and ap $=$ antipyrine, have also been prepared.

Since lanthanides are highly electropositive, they have little or no tendency to form complexes with π-bonding ligands. However, few complexes of 1, 10 phenothroline and α, α'-dipyridyl have been reported. Cyclopentadienides of the stoichiometry, $(C_6H_5)_3Ln$, also have been prepared. These complexes are ionic and have magnetic moments similar to Ln^{3+} ions themselves. A complete study of Ln $(C_6H_5)_3$ shows that these compounds are salts rather than complex compounds. Eu and Yb also form the cyclopentadienides of the type $(C_6H_5)_2Ln$ where Ln $=$ Eu or Yb. Most complexes are

Table 9·8. *Calculated and experimental values of magnetic moment, μ_{eff} (in BM) of the sulphates of Ln^{3+} ions. (n=No. of unpaired electrons in 4f-orbitals).*

$$g=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Ln^{3+} ions with configurations	*n*	*Term symbol*	*S=n/2*	*L*	*J*	*g*	$\mu_J=g\sqrt{J(J+1)}$ B.M.	$\mu_S=2\sqrt{S(S+1)}$ B.M. $=\sqrt{n(n+2)}$ B.M.	μ_{exp} (*in* B. M.)
La^{3+} $(4f^0)$	0	$^1S^0$	0	0	0	—	0·00	0·0	0·00 (Diamagnetic)
Ce^{3+} $(4f^1)$	1	$^2F_{5/2}$	1/2	3	5/2	6/7	2·54	1·7	2·3—2·5
Pr^{3+} $(4f^2)$	2	$^3H_4$	1	5	4	4/5	3·58	2·8	3·4—3·6
Nd^{3+} $(4f^3)$	3	$^4I_{9/2}$	3/2	6	9/2	8/11	3·62	3·9	3·5—3·6
Pm^{3+} $(4f^4)$	4	$^5I_4$	2	6	4	3/5	2·70	4·9	—
Sm^{3+} $(4f^5)$	5	$^6H_{5/2}$	5/2	5	5/2	2/7	0·84	5·9	1·5—1.6
Eu^{3+} $(4f^6)$	6	$^7F_0$	3	3	0	—	0·00	6·9	3·4—3·6
Gd^{3+} $(4f^7)$	7	$^8S_{7/2}$	7/2	0	7/2	2	7·94	7·94	7·8—8·0
Tb^{3+} $(4f^8)$	6	$^7F_6$	3	3	6	3/2	9·70	6·9	9·4—9·6
Dy^{3+} $(4f^9)$	5	$^6H_{15/2}$	5/2	5	15/2	4/3	10·60	5·9	10·4—10·5
Ho^{3+} $(4f^{10})$	4	$^5I_8$	2	6	8	5/4	10·60	4·9	10·3—10·5
Er^{3+} $(4f^{11})$	3	$^4I_{15/2}$	3/2	6	15/2	6/5	9·60	3·9	9·4—9·6
Tm^{3+} $(4f^{12})$	2	$^3H_6$	1	5	6	7/6	7·60	2·9	7·1—7·4
Yb^{3+} $(4f^{13})$	1	$^2F_{7/2}$	1/2	3	7/2	8/7	4·50	1·7	4·4—4·9
Lu^{3+} $(4f^{14})$	0	$^1S_0$	0	0	0	—	0·00	0·0	0·00 (Diamagnetic)

are octahedral. But some 8, 9 and 10 coordinated complexes have also been prepared.

Bonding between lanthanide ions and coordinating ligands depends primarily on the electronegativity of the bonding atom in the ligand. Bond formation follows the order F^-, OH^-, H_2O, NO_3^-, Cl etc., for monodentate ligands. Complex formation with bidentate ligands in the presence of water is usually successful only with ligands that form chelate rings through oxygen atoms.

USES OF LANTHANIDES AND THEIR COMPOUNDS

(A) Uses of the elements

(*i*) Lanthanides are used in *metallothermic reactions* due to their extraordinary reducing property (Ce is a stronger reducing agent than Al). Lanthanido-thermic processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, W, U, B and Si. These metals are also used as de-oxidising agents particularly in the manufacture of Cu and its alloys.

(*ii*) **Uses of mish-metals.** Alloys of lanthanides are known as *mish-metals*. The major constituents of mish-metals are Ce (45—50%), La (25%), Nd (5%) and small quantities of other lanthanide metals and Fe and Ca impurities.

Mish-metals are used for the production of different brands of steel like heat resistant, stainless and instrumental steels. The addition of 0·75% of mish-metal to steel raises its yield point and its workability in heated state and improves its resistance to oxidation. Misch metal is an excellent scavenger for adsorbed oxygen and sulphur in metallurgy.

Mg-alloys containing about 30% misch metal and 1% Zr are useful in making parts of jet engine. When alloyed with 30% iron, it is sufficiently pyrophoric to be useful in lighter flints.

(B) Uses of the Lanthanide Compounds

The uses of the compounds of lanthanides can broadly be classified as follows :

(*a*) **Non-nuclear applications.** The following uses are important.

(*i*) **Ceramic applications.** CeO_2, La_2O_3, Nd_2O_3 and Pr_2O_3 are widely used for decolorising glass. Approximately 1% CeO_2 is used in the manufacture of protective transparent glass blocks to be used in nuclear technology because these blocks are not affected by prolonged exposure to radiations. Because lanthanide oxides can absorb ultra-violet rays, these are used as additives in glasses for special purposes, *e.g.* for making (*i*) sun-glasses (by adding Nd_2O_3) (*ii*) goggles for glass blowing and welding work ($Nd_2O_3+Pr_2O_3$) (*iii*) glasses protecting eyes from neutron radiation ($Gd_2O_3+Sm_2O_3$) etc.

The addition of more than 1% CeO_2 to a glass gives it a brown colour. Nd_2O_3 and Pr_2O_3 give respectively red and green colours. ($Nd_2O_3+Pr_2O_3$) gives a blue colour.

(*ii*) **Refractories.** CeS (m.pt.$=2000°C$) is used in the manufacture of a special type of crucibles which are used for melting metals in a reducing atmosphere at temperatures up to 1800°C. Borides, carbides and nitrides of lanthanides are also used as refractories.

(*iii*) **Abrasives.** Lanthanide oxides are used as abrasives for polishing glasses, *e.g.* the mixture of oxides, CeO_2 (47%), $La_2O_3+Nd_2O_3+Pr_2O_3$ (51%)$+SiO_2$, CaO, Fe_2O_3 etc. ($\simeq$2%) which is called **polirite** has been used for polishing glasses.

(*iv*) **Paints.** Lanthanide compounds are used in the manufacture of lakes, dyes and paints for porcelain, *e.g.* cerium molybdate gives light yellow colour, cerium tungstate gives greenish blue colour and salts of Nd give red colour.

(*v*) **In textiles and leather industries.** Ceric salts are used for dying in textile industries and as tenning agents in leather industries. $Ce(NO_3)_4$ is used as a mordant for alizarin dyes. Chlorides and acetates of lanthanides make the fabrics water-proof and acid resistant.

(*vi*) **In medicine and agriculture.** **Dimals** which are salicylates of Pr and Nd are used as germicides. Cerium salts are used for the treatment of vomiting and sea-sickness. Salts of Er and Ce increase the red-blood corpuscles and haemoglobin content of blood.

In agriculture lanthanide compounds are used as insecto-fungicides and as trace elements in fertilisers.

(*vii*) **In lamps.** Salts of La, Ce, Eu and Sm are used as activators of luminophores. They are used in the manufacture of gas mantles, in the coatings of luminescent lamps and for painting the screens of cathode-ray tubes.

(*viii*) **In analytical chemistry.** $Ce(SO_4)_2$ is used as an oxidising agent in volumetric titrations.

Radio-isotopes of lanthanides (*e.g.* La^{140}, Ce^{142}, En^{152}, Tb^{160} etc.) are used in the study of co-precipitation, chromatographic separations etc.

(*ix*) **Catalytic applications.** Certain compounds of lanthanides are employed for the hydrogenation, dehydrogenation and oxidation of various organic compounds. Cerium phosphate finds use as a catalyst in petroleum cracking.

(*x*) **Electronic applications.** Ferrimagnetic garnets of the type $3Ln_2O_3.5Fe_2O_3$ are employed in microwave devices.

(*b*) **Nuclear applications**

Lanthanide elements and their compounds find many important nuclear uses, *e.g.*, in nuclear fuel control, shielding and fluxing devices. Pr^{147} is used in the production of atomic battery.

Comparison between *d*- and *f*-block elements (particularly between 3*d*- and 4*f*-block elements)

Since both *d*- and *f*-block elements have partly filled inner orbitals, these have many properties in common, but there are significant differences also. Some of the differences are given below :

(*i*) *d*-orbitals are five while *f*-orbitals are seven.

(*ii*) (*n*—1) *d*-orbitals have higher energy than (*n*—2) *f*-orbitals.

(*iii*) (*n*—2) *f*-orbitals lie closer to the nucleus than (*n*—1) *d*-orbitals and have accordingly greater screening effect on the outermost shell of electrons. *f*-block contraction, particularly with lanthanides (*i.e.*, lanthanide contraction), is much more pronounced than the *d*-block contraction,

(*iv*) (*n*—2) *f*-orbitals, particularly 4*f*-orbitals, participate in bonding with greater difficulty than (*n*—1) *d*-orbitals.

(*v*) **Magnetic moment.** The maximum magnetic moment of *f*-block element compounds corresponds to seven unpaired electrons, while for *d*-block elements it corresponds to five. Further, there is much greater orbital contribution in *f*-block elements as compared to *d*-block elements.

(*vi*) **Absorption bands.** The *f*-block elements usually give narrow absorption bands, whereas *d*-block elements give broad absorption bands in the visible region.

(*vii*) **Oxidation states.** *d*-block elements show much greater variability of oxidation states as compared to the *f*-block elements, particularly the lanthanides.

(*viii*) **Oxidation potentials.** The oxidation potentials of *f*-block elements (particularly of lanthanides) are comparatively much higher than those of the *d*-block elements.

(*ix*) **Metal ion-ligand bonding characteristics.** Unlike 3*d*-orbitals of the transition elements, the 4*f*-orbitals of the lanthanides do not contribute significantly to complex formation or to bonding of the lanthanide ions. Covalent contributions to bond formation have been invoked to explain certain effects of the extremely complicated spectra resulting from the *f*-*f* electronic transitions in the lanthanide ions. However, energy shifts in the lanthanide spectra between different compounds are only 10—20 cm^{-1} where complex formation with ions of the 3*d*-transition series elements in spectral shifts of the order of 1000 cm^{-1}.

A general comparison between the bonding and coordination properties of the 4*f*-metal ions (*i.e.* lanthanide ions) and the ions of the 3*d* transition elements is given in Table 9·9. The bonding between the ligands and the lanthanide ions is essentially electrostatic, with little, if any, interaction between the 4*f*-orbitals and ligand orbitals, while in the bonding of the ligands to transition metal ions there is strong interactions between the 3*d*-orbitals and the ligand orbitals. The interaction of 3*d*-orbitals and ligand orbitals in case of transition metal ions leads to strong directional bonding, but there is little directional influence in the electrostatic bonding of the lanthanide ion.

(*x*) **Coordination geometry.** Because of their larger size, lanthanide ions generally have higher coordination numbers than transitional metal ions. Coordinate numbers greater than 6 for transition metal ions are only formed with difficulty because of the strong ligand repulsion in the coordination spheres

Table 9·9. *Comparison of 4f- and 3d-Metal ions.*

Properties	*4f-metal ions (Lanthanide ions)*	*3d-metal ions (Transition metal ions)*
1. Metal orbitals	4*f*	3*d*
2. Ionic radii	La^{3+} (=1·06 A°), Lu^{3+} (=0·85 A°)	0·75–0·6 A°
3. Common coordination numbers	6, 7, 8, 9	4, 6
4. Bonding	No metal-ligand orbital interaction	Strong metal-ligand orbital interaction
5. Bond direction	Little preference in bond directions	Strong direction bonding
6. Bond strengths	Ligands bond in order of electronegativity F^-, OH^-, H_2O, NO_3^-, Cl^-	Bond strengths determined by orbital interaction normally in the following order : CN^-, NH_3, H_2O, OH^-, F^-
7. Solution complexes	Ionic, rapid ligand exchange	Often covalent, covalent complexes normally exchange slowly

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10

Actinides (5f-Block Elements)

DEFINITION

The elements in which the extra electron enters $5f$-orbitals of $(n-2)$th main shell are known as **$5f$-block elements, actinides** or **actinones.** Thus strictly according to this definition of actinides only *thirteen* elements from Th_{90} ($5f^0\ 6d^2\ 7s^2$) to No_{102} ($5f^{14}\ 6d^0\ 7s^2$) should be the members of actinide series. However, all the fifteen elements from Ac_{89} ($5f^0\ 6d^1\ 7s^2$) to Lw_{103} ($5f^{14}\ 6d^1 7s^2$) are considered as the members of actinide series, since all these fifteen elements have similar physical and chemical properties. In fact the name actinides has been derived from actinium which is *prototype* of actinides as lanthanum is the prototype of lanthanides.

POSITION OF ACTINIDES IN THE PERIODIC TABLE

The study of the position of the actinides in the periodic table can be made under the following two heads :

(*i*) **Prior to the discovery of the trans-uranium elements** (*i.e.* before 1940). The existence of the lanthanide series helped the discoverers to predict that another series of elements resulting from the addition of electrons to an $(n-2)$ f-shell (*i.e.* $5f$-shell) should occur somewhere in the heavy elements region. Prior to the discovery of transuranium elements, the naturally occurring heaviest known elements namely Th_{90}, Pa_{91}, and U_{92}, were placed below Hf_{72}, Ta_{73} and W_{74} in IV B, V B and VI B groups of the periodic table, because these elements showed +4, +5 and +6 oxidation states and resembled Hf, Ta and W respectively in many of their properties. The then undiscovered transuranium elements with atomic numbers 93 to 100 were thus expected to occupy the positions in the periodic table below Re_{75}, Os_{76}, Ir_{77}, Pt_{78}, Au_{79}, Hg_{80}, Tl_{81}, and Pb_{82} respectively as shown in Fig. 10·1.

(*ii*) **Following the discovery of the trans-uranium elements.** The discovery of the element neptunium (Np_{93}) came in 1940 and this discovery was followed shortly by the discovery of plutonium (Pu_{94}) in 1941. The tracer chemical experiments with Np_{93} and Pu_{94}

showed that the chemical properties of these two elements very much resemble those of U_{92}, and not at all those of Re_{75} and Os_{76}. On this basis in 1944, the position of U_{92}, Np_{93} and Pu_{94} was shown in the periodic table as given in Fig. 10·2. It was thought that the

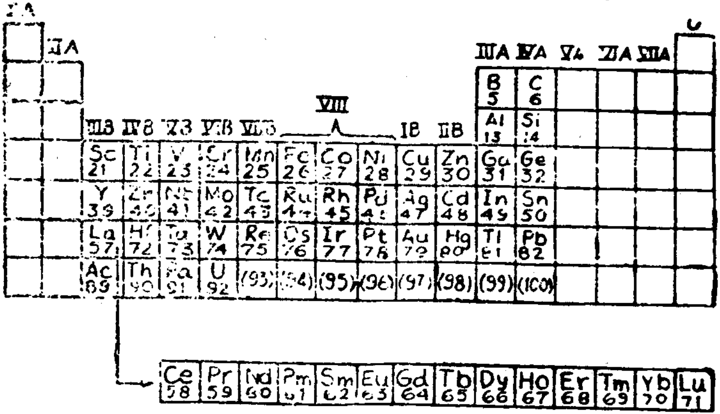


Fig. 10·1. Supposed position of actinides (before 1940)

undiscovered elements with atomic numbers 95 and 96 should be very much like U_{92}, Np_{93} and Pu_{94} in their chemical properties. This assumption, however, proved to be wrong, since the experiments directed towards the discovery of elements with atomic numbers 95 and 96 on the pattern of discovery of Np_{93} and Pu_{94} failed. Later on, in the same year (1944) Seaborg thought that all the known elements heavier than Ac_{89} were wrongly placed in the periodic table as shown in Fig. 10·2.

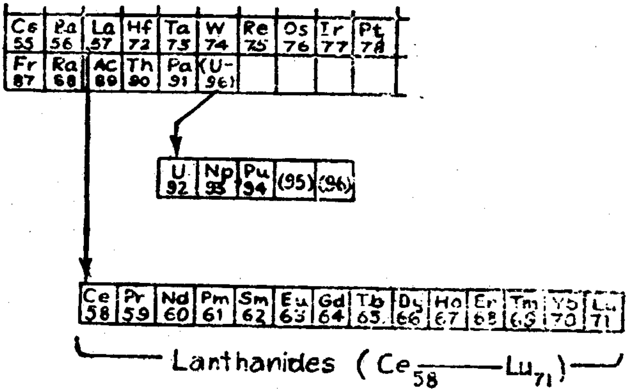


Fig. 10·2. The position of heavy elements in the periodic table as predicted in 1944. Atomic numbers of the then undiscovered elements are given in parentheses.

He advanced the idea that the elements having atomic numbers greater than that of Ac_{89} might constitute *a second series of inner-transition elements similar to the lanthanide series*. The revised periodic table thus included the elements after Ac_{89} as a second inner transition series and these elements with the name "*actinide*" elements, were paired off with those in the already known lanthanide elements outside the body of the periodic table as shown in Fig. 10·3.

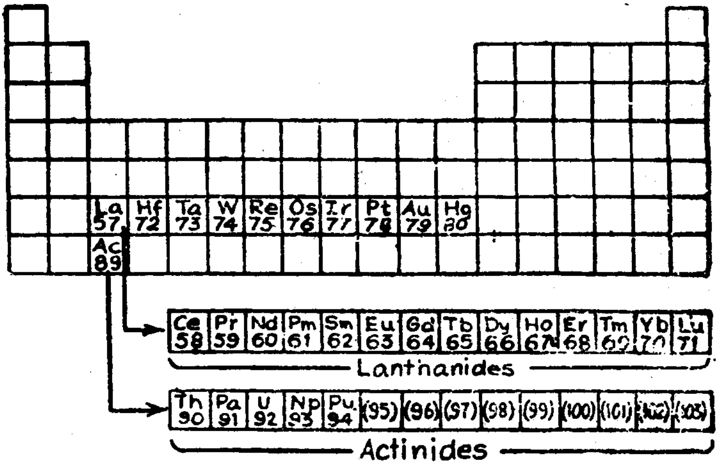


Fig. 10·3. Position of the actinide elements in the periodic table as predicted in 1944. Atomic numbers of the then undiscovered elements are given in parentheses.

The new position of the actinides was further confirmed by the fact that all the predicted elements up to 103 were discovered by 1961. The actinides now occupy the same position in the periodic table as suggested in 1944 and the periodic table, as it looks now, is shown in Fig. 10·4. The atomic nembers of the undiscovered "transactinide elements" (*i.e.*, the elements with atomic number greater than 103) have been shown in parentheses.

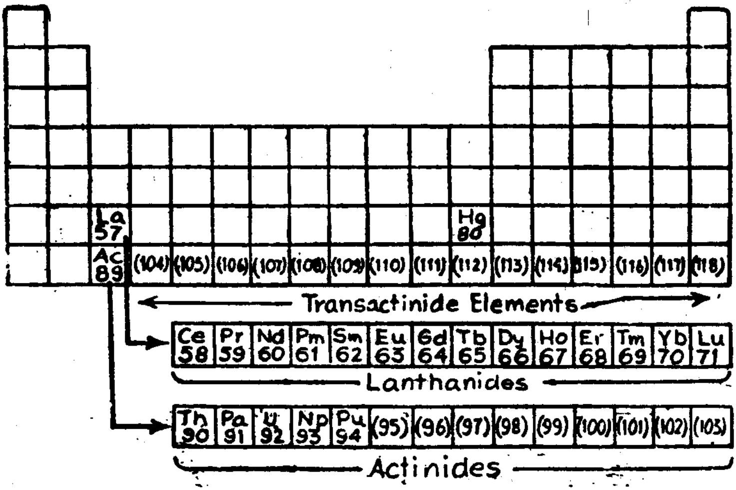


Fig. 10·4. The Periodic Table as it looks today.

IDENTIFICATION AND NUCLEAR SYNTHESIS OF TRANS-URANIUM ELEMENTS

Of all the naturally occurring elements, uranium has the highest atomic number equal to 92. For this reason this element continued to occupy the last position in the periodic table for a pretty long time. Since 1940 eleven elements with atomic numbers equal to 93, 94, 95, 96, 97, 98, 99, 100, 101, 102 and 103 respectively have been identified and synthesised by the transformation of naturally occurring elements by nuclear reactions. These man-made eleven elements are placed beyond uranium in the periodic table and are collectively called **trans-uranium elements.**

The year of identification of the first isotope, the names of the discoverers, the method of identification and synthesis of these trans-uranium elements are summarised in Table 10·1.

SEPARATION OF ACTINIDE ELEMENTS

Trasuranium elements, produced as a result of nuclear reactions, are isolated from the target materials and irradiated nuclear fuels by the following methods :

(1) Precipitation method

Tri-and tetrapositive actinides can be precipitated as fluorides or phosphates from acidic solutions. Actinides in higher oxidation states either do not give a precipitate or form complexes. This method is particularly useful for the separation of the actinide elements of U-Am group. When the quantity of the actinide ion is insufficient to precipitate by itself, co-precipitation with a *carrier* like LaF_3 or $BiPO_4$ is adopted. The LiF_3-coprecipitation method has been used for the separation of Np and Pu (obtained by neutron irradiation of uranium) from uranium and other fission products. The $BiPO_4$- coprecipitation method has been discovered by Thomson and Seaborg and is used for the large scale preparation of Pu from U and fission products. This is shown in Flow-sheet 1.

Flow-sheet 1. $BiPO_4$-coprecipitation method for the separation of Pu from U and fission products (FP's).

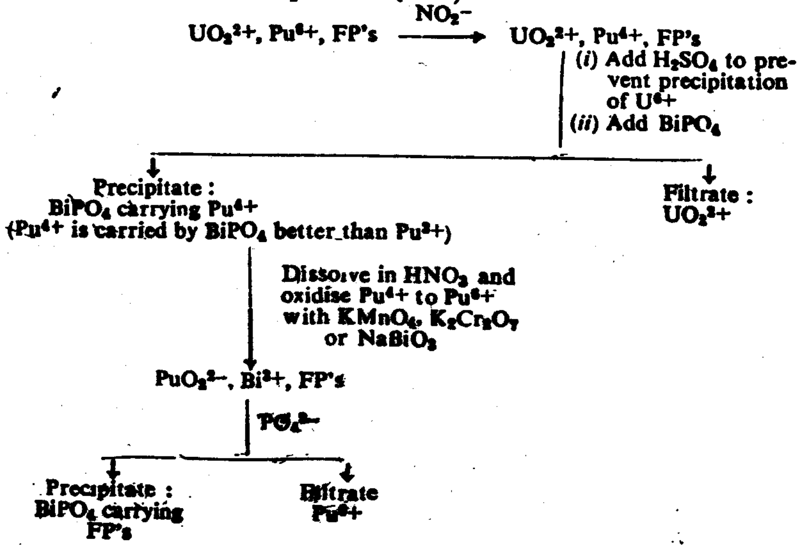


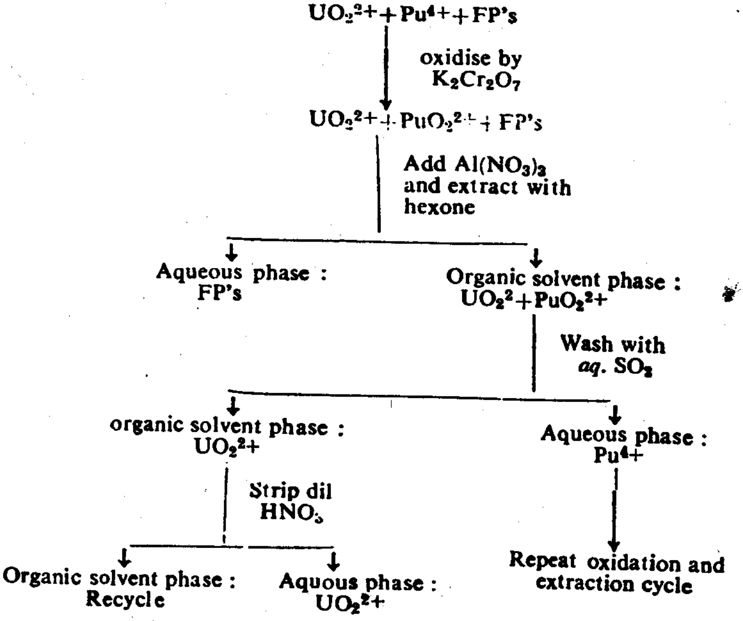
Table 10·1. *The year of identification of the first isotope, the names of the discoverers and the method of identification and synthesis of trans-uranium elements (Np_{93} to Lw_{103})*

Trans-uranium Elements	*First isotope identified*	*Year*	*Source of synthesis*	*Discoverers*
Neptunium ($_{93}Np$)	$_{93}Np^{239}$	1940	$_{92}U^{238}+{}_0n^1 \longrightarrow {}_{92}U^{239}$ $_{92}U^{239} \longrightarrow {}_{93}Np^{239}+{}_{-1}e^0$	McMillan and Abelson
Plutonium ($_{94}Pu$)	$_{94}Pu^{239}$	1941	$_{93}Np^{239} \longrightarrow {}_{94}Pu^{239}+{}_{-1}e^0$	Seaborg, McMillan, Keenedy and Wahl
Americium ($_{95}Am$)	$_{95}Am^{241}$	1945	$_{92}U^{238}+{}_2He^4 \longrightarrow {}_{94}Pu^{241}+{}_0n^1$ $_{94}Pu^{241} \longrightarrow {}_{95}Am^{241}+{}_{-1}e^0$	Seaborg, James, Morgan and Ghiorso
Curium ($_{96}Cm$)	$_{96}Cm^{242}$	1944	$_{94}Pu^{239}+{}_2He^4 \longrightarrow {}_{96}Cm^{242}+{}_0n^1$	Seaborg, James and Ghiorso
Berkelium ($_{97}Bk$)	$_{97}Bk^{243}$	1949	$_{95}Am^{241}+{}_2He^4 \longrightarrow {}_{97}Bk^{243}+2{}_0n^1$	Thomson, Ghiorso and Seaborg
Californium ($_{98}Cf$)	$_{98}Cf^{245}$	1950	$_{96}Cm^{242}+2_2He^4 \longrightarrow {}_{98}Cf^{245}+{}_0n^1$	Thomson, Stred, Ghiorso and Seaborg
Einstenium ($_{99}Es$)	$_{99}Es^{255}$	1952	$_{92}U^{238}+{}_{17}{}_0n^1 \longrightarrow {}_{92}U^{255}$ $_{92}U^{255} \longrightarrow {}_{99}Es^{255}+7{}_{-1}e^0$	Ghiorso and coworkers
Fermium ($_{100}Fm$)	$_{100}Fm^{255}$	1953	$_{92}U^{255} \longrightarrow {}_{100}Fm^{255}+8{}_{-1}e^0$	Ghiorso and coworkers
Mendelevium ($_{101}Md$)	$_{101}Md^{256}$	1955	$_{99}Es^{253}+{}_2He^4 \longrightarrow {}_{101}Md^{256}+{}_0n^1$	Ghiorso and coworkers
Nobelium ($_{102}No$)	$_{102}No^{252}$	1958	$_{96}Cm^{246}+{}_6C^{12} \longrightarrow {}_{102}No^{252}+6{}_0n^1$	Ghiorso, Sikkelaw, Walton and Seaborg
Lawrencium ($_{103}Lw$)	$_{103}Lw^{254}$	1961	$_{98}Cf^{245}+{}_5B^{10} \longrightarrow {}_{103}Lw^{254}+{}_0n^1$	Ghiorso and coworkers

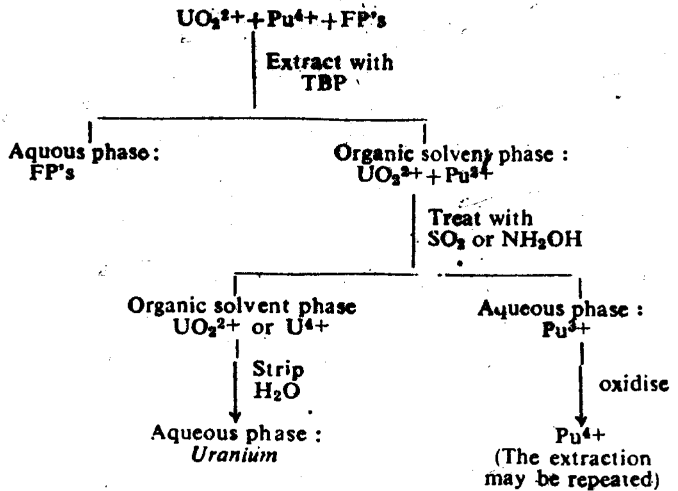
(2) Solvent extraction method

This method depends on the extractability of the various oxidation states of actinide elements. This technique finds extensive application in the recovery of U and Pu from used-up nuclear fuels. This process is based on the distribution of a metal between the aqueous solution and an organic solvent. Thus with *methyl isobutyl ketone* (*hexone*) Np^{4+}, Np^{5+}, Pu^{6+} and U^{6+} are extracted while Pu^{3+} is not extracted. *Diethyl ether* and *tri-n-butyl phosphate* (TBP) are other solvents which are used as extractants. Because of the high viscosity and density, TBP is used as 20% solution in kerosene. The method is preferentially applied to nitrate systems, because other ions like sulphate, perchlorate, fluoride etc. are strongly complexing and tend to retain the metal in aqueous solution. Hexone and diethyl ether require a high concentration of NO$_3^-$ ions in the aqueous phase and it is achieved by adding Al(NO$_3$)$_3$ which has a high salt-out action. TBP is resistant to nitric acid oxidation and acts by itself as a salt agent. Solvent extraction of Pu and U by hexone and TBP is shown in Flow-sheets 2 and 3 respectively.

Flow sheet 2. Separation of Pu and U from fission products (FP's) by solvent extraction with hexane (Redox process).



Flow sheet 3. Separation of Pu and U from fission products (FP's) by solvent extraction with tributyl phosphate TBP (Purex process).



(3) **Ion-exchange technique.** Although this technique can be used to separate the actinide ions, this is best suited for separation of the trans-americium elements and also for some of the preceding elements, particularly for small amounts of material.

This method involves the following two steps :

(*i*) *Lanthanide-actinide separation.* The actinides as a group are separated from lanthanides by cation-exchange resin. Strong HCl is used as the eluting agent. The actinide ions form chloride complexes more easily and hence are eluted first.

Separation of actinides from lanthanides is now done on an anion-exchange resin with 10 M LiCl as eluent at elevated temperatures up to ~ 90°. With the exceptions of Gd, Ho and of Cm, Es, the elution sequences proceed in the order of increasing atomic number. Thus La is absorbed least strongly.

(*ii*) *Separation of individual actinide elements.* The actinide ions, in general, can be separated from each other by removing from the cation exchange resin by elution with ammonium citrate, lactate, α-hydroxy isobutyrate and ethylene diamine tetracetate. If the activity is plotted against the number of drops of eluent, elution curves will be obtained as shown in Fig 10·5. Lw (atomic number, Z = 103) is predicted to leave the column first, to be followed by No (Z = 102), and so on down the scale of atomic numbers. Elution positions for Md (Z = 101), Fm (Z = 100), and down to Am (Z = 95) are shown in the typical elution curves. Elution curves for lanthanides are also shown in the same figure for comparison. It may be noted that a very striking similarity occurs in the spacings of the corresponding elements in the two series (*e.g.* Am and Eu, Cm and Gd, Bk and Tb etc). It is this similarity that made possible for scientists to predict the elution positions of the elements from Bk to Md before their discovery, and which also makes possible today to predict the elution positions of elements with Z = 102 and 103.

There is a distinct breakdown between Gd and Tb (lanthanide series) and between Cm and Bk (actinide series), which can be attributed to the small change in ionic radius occasioned by the half-filling of the 4*f* and 5*f* shells respectively. The elution order is not always as regular as shown in Fig. 10·5.

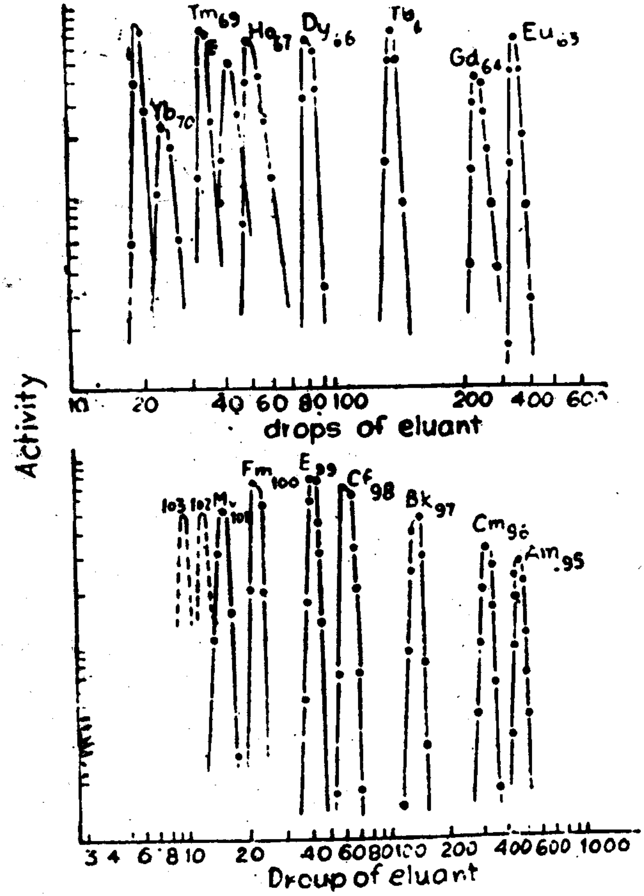


Fig. 10·5. Elution curves showing the elution positions of Ln^{3+} and An^{3+} ions eluted from Dowex-50 ion-exchange resin with ammonia alpha-hydroxy-isobutyrate. The dotted elution curves indicate the predicted elution positions of the then undiscovered elements with atomic numbers 102 and 103.

GENERAL PROPERTIES OF ACTINIDES AND THEIR COMPARISON WITH LANTHANIDES.

Some of the important properties of actinides are discussed below.

(1) **Electronic configuration and nature of bonding in actinide compounds.**

According to modern view 5*f*-orbitals in actinides start filling from protoactinium (Pa_{91}) and not from thorium (Th_{90}) as is evident from the valence-shell electronic configurations of actinides given in Table 10·2. For the sake of comparison the valence-shell configurations of lanthanides are also given in the same table.

Table 10·2. *Electronic configurations of the neutral gaseous atoms of lanthanides and actinides.*

Lanthanides		**Actinides**		
Elements with atomic number	*Valence shell configurations*	*Elements with atomic number*	*Complete configurations*	*Valence-shell configurations*
La_{57}	$4f^0\ 5d^1\ 6s^2$	Ac_{89}	*$[Rn]5f^0\ 6d^1\ 7s^2$	$5f^0\ 6d^1\ 7s^2$
Ce_{58}	$4f^2\ 5d^0\ 6s^2$	Th_{90}	$[Rn]5f^0\ 6d^2\ 7s^2$	$5f^0\ 6d^2\ 7s^2$
Pr_{59}	$4f^3\ 5d^0\ 6s^2$	Pa_{91}	$[Rn]5f^2\ 6d^1\ 7s^2$	$5f^2\ 6d^1\ 7s^2$
Nd_{60}	$4f^4\ 5d^0\ 6s^2$	U_{92}	$[Rn]5f^3\ 6d^1\ 7s^2$	$5f^3\ 6d^1\ 7s^2$
Pm_{61}	$4f^5\ 5d^0\ 6s^2$	Np_{93}	$[Rn]5f^4\ 6d^1\ 7s^2$	$5f^4\ 6d^1\ 7s^2$
Sm_{62}	$4f^6\ 5d^0\ 6s^2$	Pu_{94}	$[Rn]5f^6\ 6d^0\ 7s^2$	$5f^6\ 6d^0\ 7s^2$
Eu_{63}	$4f^7\ 5d^0\ 6s^2$	Am_{95}	$[Rn]5f^7\ 6d^0\ 7s^2$	$5f^7\ 6d^0\ 7s^2$
Gd_{64}	$4f^7\ 5d^1\ 6s^2$	Cm_{96}	$[Rn]5f^7\ 6d^1\ 7s^2$	$5f^7\ 6d^1\ 7s^2$
Tb_{65}	$4f^9\ 5d^0\ 6s^2$	Bk_{97}	$[Rn]5f^9\ 6d^0\ 7s^2$	$5f^9\ 6d^0\ 7s^2$
Dy_{66}	$4f^{10}\ 5d^0\ 6s^2$	Cf_{98}	$[Rn]5f^{10}\ 6d^0\ 7s^2$	$5f^{10}\ 6d^0\ 7s^2$
Ho_{67}	$4f^{11}\ 5d^0\ 6s^2$	Es_{99}	$[Rn]5f^{11}\ 6d^0\ 7s^2$	$5f^{11}\ 6d^0\ 7s^2$
Er_{68}	$4f^{12}\ 5d^0\ 6s^2$	Fm_{100}	$[Rn]5f^{12}\ 6d^0\ 7s^2$	$5f^{12}\ 6d^0\ 7s^2$
Tm_{69}	$4f^{13}\ 5d^0\ 6s^2$	Md_{101}	$[Rn]5f^{13}\ 6d^0\ 7s^2$	$5f^{13}\ 6d^0\ 7s^2$
Yb_{70}	$4f^{14}\ 5d^0\ 6s^2$	No_{102}	$[Rn]5f^{14}\ 6d^0\ 7s^2$	$5f^{14}\ 6d^0\ 7s^2$
Lu_{71}	$4f^{14}\ 5d^1\ 6s^2$	Lw_{103}	$[Rn]5f^{14}\ 6d^1\ 7s^2$	$5f^{14}\ 6d^1\ 7s^2$

*[Rn] indicates the complete configuration of Rn atom which is 2, 8, 18, 32, 18, 8.

Comparison of the electronic configurations of lanthanides and actinides shows both a substantial overall similarity and enhanced tendency for the lighter members, namely Ac_{89} to Np_{93} to retain 6*d* electrons. The latter tendency results both from the even smaller energy separation between the 5*f* and 6*d* orbitals in actinides than that between the 4*f* and 5*d* orbitals in lanthanides and from the difference in change in binding energy of the weakest bound (*i.e.* most readily removable) 6*d* and 5*f* electrons in actinides with atomic number as shown in Fig. 10·6 in which a rough quantitative picture for the binding energies of the weakest bound 5*f* and 6*d* electrons in actinides is shown. Spectroscopic chemical and other data tell that 5*f*-level becomes progressively lower in energy compared to the 6*d*-level with increasing atomic number. The relative point of change is thus different in the two series and also the fall in energy and shrinkage in size are not so precipitous for 5*f* orbitals as for 4*f*-orbitals. The spatial extension of 5*f* orbitals relative to 6*s* and 6*p* orbitals is thus greater than that of 4*f* orbitals relative to 5*s* and 5*p* orbitals. The greater spatial extension of 5*f* orbitals has also been shown experimentally.

Since *f* shell is being filled in lanthanides (4*f* shell) and actinides (5*f* shell), the elements of these two series have close relationship in properties with one another. Thus Ac_{89} and La_{57} occupy corresponding positions as prototypes for the two series.

Although important similarities exist between the elements of the two series, very important differences also occur. These differences are due mainly to the relatively lower binding energies and less effective shielding of the 5*f*-electrons (in actinides) than those of 4*f*-electrons (in lanthanides).

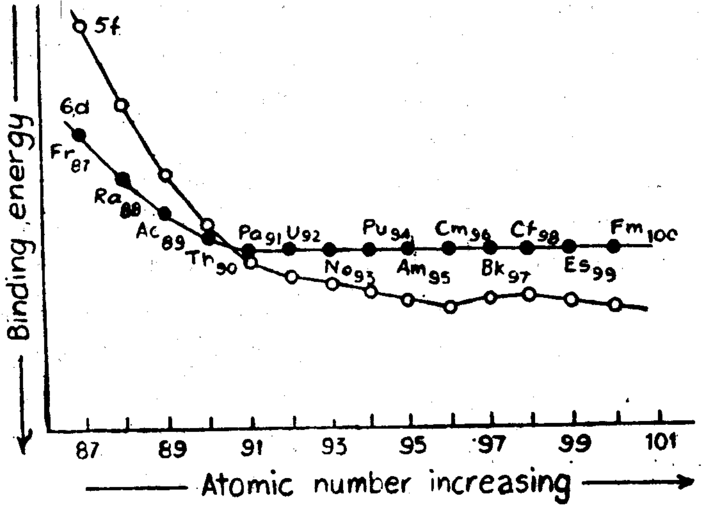


Fig. 10·6. Qualitative comparison of binding energies of 5*f*- and 6*d*-electrons. (Reproduced from Katz and Seaborg: "The Chemistry of the Actinide Elements," p. 465, Metheun, London, 1957).

The actinides have *deeply seated incomplete* 5*f*-orbitals compared to 4*f*-orbitals in lanthanides. 4*f* and 5*f* orbitals differ in their radial distribution functions. The radial distribution of 4*f*-orbitals shows a small [illegible] of electron density below the main 5*f*-orbital (compare, for example, 1*s* and 2*s* radial functions). Therefore 5*f*-orbitals are more penetrating than 4*f*-orbitals. In lanthanides 4*f*-orbitals are well within the 6*s* and 5*p* orbital. Therefore there is no question of an overlap between 4*f* and the surrounding ligands. The 5*f*-orbitals which are more penetrating than 4*f*-orbitals are little more diffuse at the periphery of the atom. Hence these orbitals are somewhat disturbed by ligands. It is well known that the energy difference between different levels and sub-levels decreases with increasing atomic number. Thus in the actinides the energies of 5*f*, 6*d*, 7*s* and 7*p* orbitals are but equal. This results in that unlike lanthanides, *the bonding in the compounds of actinides can involve any or all of these orbitals.* This fact is realised when we find that, while lanthanides virtually form no complexes or covalent compounds in which 4*f*-orbitals participate in bonding (*lanthanides form mostly ionic compounds*), the actinides form complexes not only with anions such as X^-, SO_4^{2-} etc., but also with π-bonding ligands such as alkyl phosphines, thioethers and cyclopentadiene by the use of 5*f*-orbitals.

(2) **Oxidation States and Oxidation Potentials.**

Observed oxidation states of actinide elements noted either in solution or in isolable compounds are summarised in Table 10·3.

Comparison of the oxidation states of lanthanides given in Table 9·4 p. 292 with those of actinides indicates that +3 oxidation state is the most common for both the series of elements. This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series. The increasing stability of +3 oxidation state is illustrated by the increasing difficulty of oxidation above +3 oxidation state. This is clearly shown by the values of oxidation potentials (E° values) listed in the same Table. E° values have been recorded in 1M per chloric acid at 25°C. The standard electrode potentials for the lanthanides couple, Ln°/Ln^{3+} *become steadily more positive with the increase of atomic number* (*due to lanthanide contraction*), while for the actinides couple An°/An^{3+} these values *become more positive from* Ac to U *and become less positive till* Am. Am^{4+} is thus a more powerful oxidising agent than Ce^{4+}, when Pu^{4+}, Np^{4+} and U^{4+} are less powerful. U^{3+} is a strong reducing agent.

As regards lanthanides, no definite rule can be given about whether or not the +3 oxidation state of lanthanides increases in stability with the increase of atomic number.

Actinides show a greater multiplicity of oxidation states. Since in the first half of the actinide series (*i e.* lower actinides), the energy required for the conversion $5f \longrightarrow 6d$ is less than that required for the conversion $4f \longrightarrow 5d$, the lower actinides should, on a comparative basis, show more higher oxidation states such as +4, +5, +6 and +7. Correspondingly, since in the second half of the actinide series (*i.e*, higher actinides), the energy required for the conversion $5f \longrightarrow 6d$ is more than that required for the conversion $4f \longrightarrow 5d$, the higher actinides should show more lower oxidation states such as +2. These expectations are in agreement with oxidation states given in Table 10·3. The second half of the series appears to parallel the lanthanides while the first halves of the two series are widely different from each other.

Table 10·2 *Various oxidation states shown by actinides and standard oxidation potentials, E° (in volts) for various couples in 1M per chloric acid at 25°C*

Actinides with atomic numbers	*Oxidation states (Less stable states are given in brackets)*	*E° values (in volts) for various couples (Estimated values are given in brackets)*
Ac_{89}	+3	$Ac^{\circ} \xrightarrow{2{\cdot}6 \text{ volts}} Ac^{3+}$
Th_{90}	+4	$Th^{\circ} \xrightarrow{1{\cdot}90} Th^{4+}$
Pa_{91}	(+4), +5	$Pa^{\circ} \xrightarrow{(0{\cdot}9)} Pa^{4+} \xrightarrow{0{\cdot}1} PaO_2^{+}$ $Pa^{\circ} \xrightarrow{1{\cdot}0} PaO_2^{+}$
U_{92}	(+3), (+4), (+5), +6	$U^{\circ} \xrightarrow{1{\cdot}80} U^{3+} \xrightarrow{0{\cdot}631} U^{4+} \xrightarrow{-0{\cdot}58} UO_2^{+} \xrightarrow{-0{\cdot}063} UO_2^{2+}$ $U^{4+} \xrightarrow{-0{\cdot}32} UO_2^{2+}$
Np_{93}	(+3), (+4), +5, (+6), (+7)	$Np^{\circ} \xrightarrow{1{\cdot}83} Np^{3+} \xrightarrow{-0{\cdot}155} Np^{4+} \xrightarrow{-0{\cdot}739} NpO_2^{+} \xrightarrow{-1{\cdot}137} NpO_2^{2+}$ $Np^{3+} \xrightarrow{0{\cdot}447} NpO_2^{+}$ $Np^{4+} \xrightarrow{-0{\cdot}938} NpO_2^{2+}$
Pu_{94}	(+3), +4, (+5), (+6), (+7)	$Pu^{\circ} \xrightarrow{2{\cdot}03} Pu^{3+} \xrightarrow{-0{\cdot}981} Pu^{4+} \xrightarrow{-1{\cdot}172} PuO_2^{+} \xrightarrow{-0{\cdot}913} PuO_2^{2+}$

Am_{95}	+2, (+3), (+4), (+5), (+6)	$Am^{\circ} \xrightarrow{(<2{\cdot}7)} Am^{2+} \xrightarrow{>1{\cdot}5} Am^{3+} \xrightarrow{-2{\cdot}4} Am^{4+} \xrightarrow{-1{\cdot}04}$ $AmO_2^{+} \xrightarrow{-1{\cdot}60} AmO_2^{2+}$
Cm_{96}	+3, (+4)	$Cm^{\circ} \xrightarrow{(>-2{\cdot}80)} Cm^{4+}$
Bk_{97}	+3, (+4)	$Bk^{\circ} \xrightarrow{(-1{\cdot}6)} Bk^{4+}$
Cf_{98}	+3	—
Es_{99}	+3	—
Fm_{100}	+3	—
Md_{101}	+3	$Md^{2+} \xrightarrow{(0{\cdot}2)} Md^{3+}$
No_{102}	+2	$No^{2+} \xrightarrow{(-1{\cdot}4)} No^{3+}$
Lw_{103}	+3	—

The tripositive oxidation state occurs widely in each series. The two groups of elements, however, are not entirely comparable in this respect. The +3 state characteristic of lanthanides does not appear in aqueous solution of Th and Pa and this oxidation state becomes the predominantly stable oxidation state in aqueous solution of the actinides only when we reach Am. The elements from U to Am have several oxidation states, while there is no analogous example among lanthanides. These differences can readily be explained on the basis of the assumption that 7*s*-, 6*d*- and 5*f*- levels have almost the same energies in this region.

Since 5*f*-electrons are more easily removed than the 4*f*-electrons, for the actinide metals the lower oxidation states are less and the higher ions are more important compared to the lanthanide metals ; *e.g.*, even Cm gives Cm (IV) oxidation state in solids CmO_2 and CmF_4, whereas only Gd(III) compounds are known. Cm^{4+} ion is also stable in solution.

+2 Oxidation state. Only americium (analogous to europium) is known to form a stable +2 state. This state is stable in CaF_2 only and has been studied by optical and electron spin resonance spectra +2 state is uncommon for other actinides. An^{2+} ions resemble Ln^{2+} ions in their general chemistry.

+3 Oxidation state. +3 state is a general oxidation state for most of the actinides. For Th and Pa, +4 and +5 states respectively are important. An^{4+} ions resemble Ln^{4+} ions in their properties. A large number of isomorphous salts are given by the elements of both the series Trichlorides and trifluorides of Ac, U, Np, Pn and Am are isomorphous. On hydrolysis all the halides give oxyhalides.

Ac, Pu and heavier elements give the oxides of An_2O_3 type which are isomorphous with Ln_2O_3 oxides.

Nitrates, perchlorates and sulphates are soluble while hydroxides, fluorides and carbonates are insoluble. Like lanthanides, actinides also form complexes with EDTA. Lanthanide-EDTA complexes are less stable than the corresponding actinide-EDTA complexes.

+4 Oxidation state. This is the principal oxidation state for Th and is a stable oxidation state upto Am. Am^{4+} and Cm^{4+} exist only as complexes in concentrated fluoride solution of low acidity. General chemistry of An^{4+} ions is similar to that of Ln^{4+} ions. The hydrated fluroides and phosphates of both An^{4+} and Ln^{4+} ions are insoluble. ThO_2, PaO_2, UO_2, NpO_2, AmO_2, CmO_2 and BkO_2 have fluorite structure. The tetrachlorides and tetrabromides of Th, Pa, U and Np are only known, while tetraiodides of Th. Pa and U have been isolated. Oxyhalides of Th, U and Np can be prepared by heating AnX_4 with Sb_2O_3. An^{4+} ions form complexes mostly with anionic ligands like HSO_4^-, NO_3^-, Cl^- etc.

+5 Oxidation state. This state is very important for Pa. Pa^{5+} resembles very much Na^{5+} and Ta^{5+}. U, Np, Pu and Am also exist in +5 states, but these are less characterised. The only known pentahalides are those of Pa^{5+} and U^{5+}.

Fluoro anions of Pa, U, Np and Pu of the types AnF$_6^-$, AnF$_7^{2-}$ and AnF$_8^{3-}$ are known to exist in the solid state. Oxychlorides, AnOCl$_3$ (An = Pa, U and Np) are also known.

AnO$_2^+$ is the most important ion which contains An^{5+} cation. It has linear structure both in solid and solution. This monovalent dioxo cation forms many complexes with anionic and neutral ligands.

+6 Oxidation state. U, Np, Pu and Am show +6 oxidation state in divalent dioxo cation, AnO$_2^{2+}$. This cation is linear both in solid and solution. The simple molecular halide, UO$_2$F$_2$ has the linear O—U—O group with fluorine bridges. The O—U bond distance is 1·75 to 2·00 A°. The overall structure is a *flattened octahedron*. Although AnO$_2^{2+}$ cation is linear in shape, it forms complexes with exceptional geometries, *e.g.* four, five and six coordinated complexes are given by this cation.

+7 Oxidation states. +7 oxidation state is shown only by Np and Pu. Electrolysis or ozone oxidation of Np^{5+} or Np^{6+} in NaOH gives a green solution of NpO$_5^{3-}$ which is slowly reduced to Np^{6+} at 25°C (E° for Np^{7+}/Np^{6+} = 0·58 volts in 1M NaOH). The existence of Np^{7+} ion has been confirmed by Mossbauer spectra.

Ph^{7+} ion is obtained by exposing a mixture of PuO$_2$ and Li$_2$O oxygen at 430°C when Li$_5$PuO$_6$ is formed. The chemistries of Np^{7+} and Pu^{7+} resemble those of Re^{7+} and Te^{7+}.

(3) Atomic and Ionic Radii—Actinide Contraction

Crystal structure data have provided the basis for ionic radii of the actinide elements. In Table 10·4 atomic and ionic radii of the tripositive and tetrapositive actinide ions (*i.e.* An^{3+} and An^{4+} ions) are summarised. The atomic radii of lanthanide atoms and ionic radii of Ln^{2+}, Ln^{3+} and Ln^{4+} ions are also included in the same table for comparison. It may be noted that for An^{3+} and An^{4+} ions there *is an actinide contraction* (*i.e.* decrease in ionic radii of An^{3+} and An^{4+} ions), *analogous to the lanthanide contraction*, with increasing positive charge on the nucleus. This actinide contraction is due to the addition of successive electrons to an inner *f*-shell (*i.e.* 5*f* shell), so that the imperfect screening of the increasing nuclear charge by the additional 5*f* electrons results in a contraction of the outer or valence orbital.

It may also be noted that the tripositive actinide ion (An^{3+} ion) is always somewhat larger than the formally analogous Ln^{3+} ion as shown in Fig. 10·7. The slight but readily detectable discontinuity at the Gd^{3+} ion does not have a parallel at the Cm^{3+} ion. Rather there is a continuing divergence in size among the An^{3+} ions as the nuclear charge increases. The ionic radii of Ln^{4+} and An^{4+} cations are shown together in Fig. 10·8.

The jumps in contraction between the consecutive elements in the actinides is greater than in the lanthanides. The greater contraction is *due to the lesser shielding of 5f-electrons which are there-*

Table 10·4. *Atomic and Ionic (or crystal) Radii*[a] *of lanthanides and actinides in A°*

Lanthanides					Actinides			
		Crystal or ionic radii of					Crystal or ionic radii of	
Elements with atomic number	*Atomic Radius*	Ln^{2+} ion	Ln^{3+} ion (Decreasing ↓)	Ln^{4+} ion	*Elements with atomic number*	*Atomic Radius*	An^{3+} ion (Decreasing ↓)	An^{4+} ion (Decreasing ↓)
La_{57}	1·88		1·06		Ac_{89}	1·88	1·11	0·99
Ce_{58}	1·82		1·03	0·92	Th_{90}	1·80	(1·08)	0·96
Pr_{59}	1·83		1·01	0·90	Pa_{91}	1·61	(1·05)	0·93
Nd_{60}	1·82		0·99		U_{92}	1·38	1·03	0·92
Pm_{61}	—		(0·98)		Np_{93}	1·30	1·01	0·92
Sm_{62}	1·80	1·11	0·96		Pu_{94}	1·51	1·00	0·90
Eu_{63}	2·04	1·09	0·95		Am_{95}	1·73	0·99	0·89
Gd_{64}	1·80		0·94		Cm_{96}		0·98	0·88
Tb_{65}	1·78		0·92	0·84				
Dy_{66}	1·77		0·91					
Ho_{67}	1·77		0·89					
Er_{68}	1·76		0·88					
Tm_{69}	1·75	0·94	0·87					
Yb_{70}	1·94	0·93	0·86					
Lu_{71}	1·73		0·85					

[a] Predicted values are given in parentheses, In the octahedral fluorides, AnF_6, the An—E bond distance also decreases with increasing atomic number, namely, U—F=1·99 A°, Np—F=1·98 A°, Pu—F=1·96 A° (Z for U, Np and Pu are 92, 93 and 94 respectively).

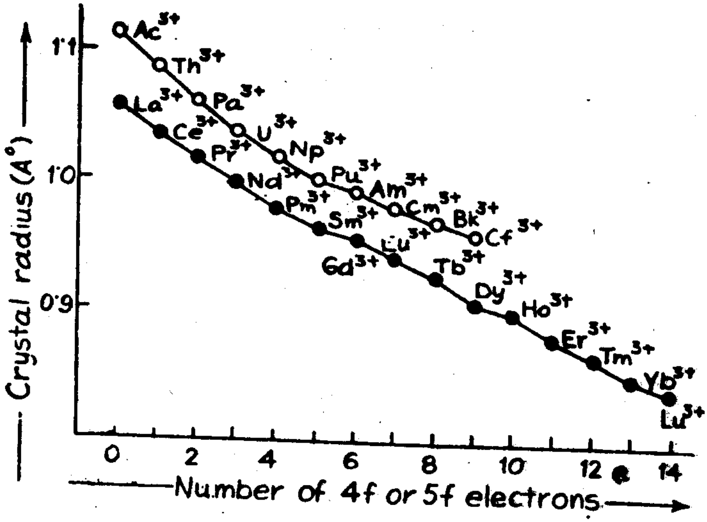


Fig. 10·7. Crystal radii of Ln^{3+} (shown by black circles) and An^{3+} ions (shown by white circles) [Reproduced from Journal of The American Chemical Society, 47, 421, 1970].

fore, pulled more strongly by the nucleus. The actinide contraction, as usual, leads to a decrease in the basicity of the elements with increasing atomic number.

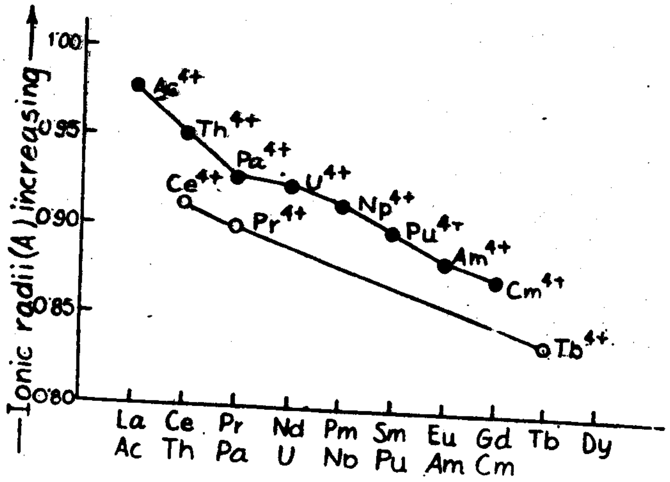


Fig. 10·8. Ionic Radii of Ln^{4+} (shown by white circles) and An^{4+} ions (shown by black circles).

(4) **Colours and Absorption Spectra of Actinide ions.**

Colours and the wavelengths of the more prominent light absorption bands of actinide ions like An^{3+}, An^{4+}, AnO_2^{+}, and AnO_2^{2+} are given in Table 10·5. It may be seen, by comparing the

Table 10·5. *Colours and wave-lengths (in A°) of more prominent light absorption bands of actinide ions (An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+}) in aqueous solution*

Elements	An^{3+} *ions*	An^{4+} *ions*	AnO_2^+ *ions*	AnO_2^{2+} *ions*
Ac	Colourlesss ($5f^0$) (No absorption)	—	—	—
Th		Colourless ($5f^0$) (No absorption)	—	—
Pa	—	Colourless ($5f^1$) (2240, 2550, 2760)	Colourless	—
U	Red ($5f^3$) (5200, 8800, 9000)	Green ($5f^2$) (5500, 6500)	—	Yellow (4000, 4110, 4250)
Np	Blue or purple ($5f^4$) (5520, 6610, 7875)	Yellow-green ($5f^3$) (5040, 7430, 8250)	Green	Pink to red (4760, 5570)
Pu	Blue or violet ($5f^5$) (5600, 6000, 6030)	Tan to orange brown ($5f^4$) (4700, 6550, 8150)	Reddish-purple	Yellow to pink-orange (8330, 9530, 9830
Am	Pink ($5f^6$) (5027, 8200)	Rose ($5f^7$)	Yellow (5131, 7151)	Run-coloured (6660, 9950)
Cm	Colourless ($5f^7$) (2368, 2680, 2774)	—	—	—

colours of Ln^{3+} and An^{3+} ions, that *the pairs of ions which have the same number of f-electrons (4f and 5f electrons) have roughly comparable colours.* The pairs *viz* (*i*) Nd^{3+} ($4f^3$—reddish) and U^{3+} ($5f^3$—red) and (*ii*) Gd^{3+} ($4f^7$—colourless) and Cm^{3+} ($5f^7$—colourless) illustrate this point. Ce^{3+} ($4f^1$) and Pa^{4+} ($5f^1$) ions are colourless.

The absorption spectra of actinide ions, in aqueous solution and in crystals, contain narrow bands in the visible, near-ultraviolet and near infrared regions of the spectrum. The bands seen in case of actinide ions arise from electronic transitions between energy states within the 5*f*-electron sub-shell. It has been found, in general, that the absorption bands seen in case of actinide ions are about ten times sharper than those seen in case of lanthanide ions. The absorption spectra of lanthanide ions are observed due to electronic transitions between energy states within the 4*f*-electron sub-shell.

Light absorption spectra of lanthanides are much more affected by environment.

Charge-transfer phenomena occur more frequently and the bands are more intense in the actinides because of lower energy involved in transitions. Moreover, the overlap of 5*f*-orbitals with the ligand orbitals increases the intensity of absorption bands.

5. Magnetic Properties

In the 5*f*-series, Pu^{3+} and Am^{3+} ions show the analogous behaviour as noted for Sm^{3+} and Eu^{3+} ions in 4*f*-series.

The magnetic properties of the actinide ions are considerably more difficult to explain than those of the lanthanide ions. The

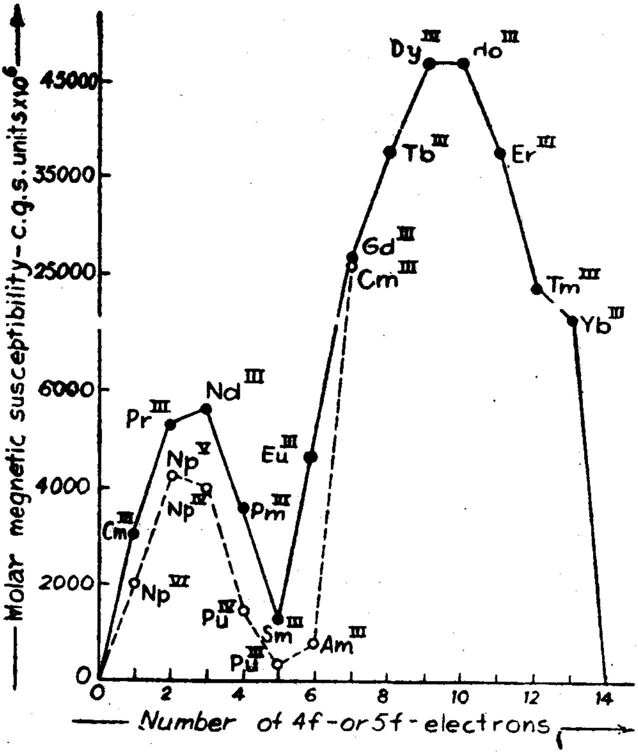


Fig. 10·9. Comparison of magnetic susceptibilities of lanthanide (shown by black circles) and actinide ions (shown by white circles).

values of magnetic moments found experimentally are usually lower than those calculated using Russell-Saunders coupling scheme. This is due perhaps to the inadequacy of the Russell-Saunders coupling scheme for $5f^n$ ions and also to more subtle ligand field effects which involve $5f$-orbitals to a greater extent than the $4f$-orbitals are involved in bonding in the lanthanide complexes.

An equation used for the calculation of molar susceptibility, χ_M, is given by

$$\chi_M = \frac{Ng^2\beta^2 J(J+1)}{3kT} + N\alpha$$

where N = Avogadro's number, g = Lande splitting factor which is given by :

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$$

$$\beta = \text{Bohr magneton} = \frac{eh}{2\pi mc} = 9{\cdot}27 \times 10^{-21} \text{ erg/gauss},$$

J = Total angular momentum of atom = | L+S |,
k = Boltzmann constant, T = absolute temperature,
and α = Small, temperature independent term due to second order Zeeman effect.

Strictly speaking the above equation can be applied only to gaseous ions in which the multiplet intervals are larger compared

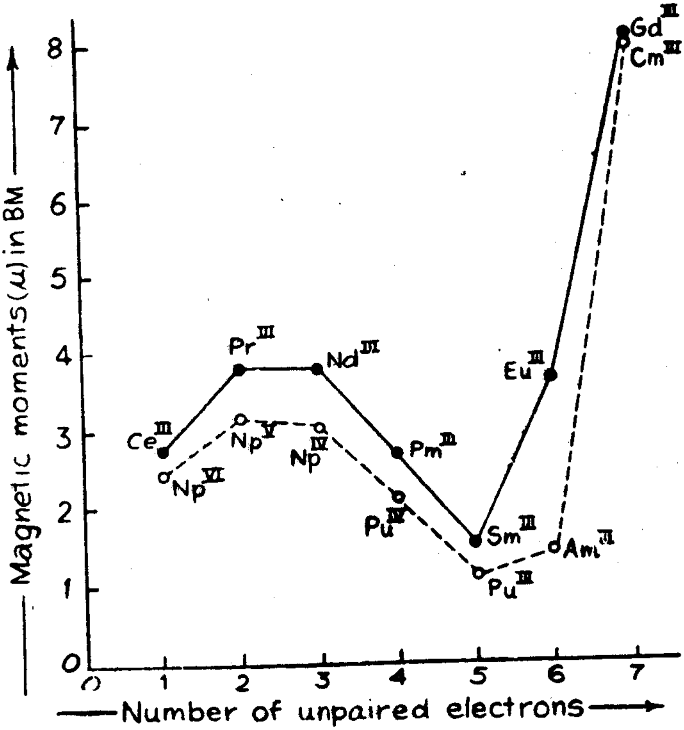


Fig. 10·10. Comparison of magnetic moments (in B.M.) of lanthanide (shown by black circles) and actinide ions (shown by white circles).

with kT and the valve of J to be used in it is taken from the ground state symbols of ions.

A comparison of the plots of molar magnetic susceptibilities of tripositive lanthanide and actinide ions against the number of 4f- or 5f-electrons (Fig. 10·9) reveals that there are remarkable similarities between the two plots. The plot of lanthanide ions has two humps while that of actinide ions has only one. In both the cases the first hump is, however, at the identical place. The moments of the lanthanide ions agree closely with theoretical predictions but those of the transuranic ions are somewhat lower than expected (Fig. 10·10). This is because the 5f-electrons of the transuranic ions are less effectively screened from the crystal field, which quenches the orbital contribution, than are the 4f-electrons of the lanthanide ions.

6. Complex Formation

The degree of complex formation decreases in the order :

$$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}$$

The complexing power of different singly-charged and doubly charged anions follows the order :

Singly-charged anions : $F^- > NO_3^- > Cl^-$

Doubly-charged anions : $CO_3^{2-} > Ox^{2-} > SO_4^{2-}$

Actinides also form complexes with a large number of organic substances.

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11

Basic Concepts of Co-ordination Chemistry

DEFINITION OF SOME TERMS

(1) **Simple Salts.** When an acid reacts with an alkali, neutralisation takes place and a simple salt is produced,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

When dissolved in water, these salts ionise and produce ions in solution. Depending upon the extent of neutralisation of the acid or base, these may be *normal, acid* or *basic* salts. *Mixed salts* contain more than one acidic or basic radicals, *e.g.*, $NaKSO_4$.

(2) **Molecular or Addition Compounds.** When solutions containing two or more salts in stoichiometric (*i.e.*, simple molecular) proportions are allowed to evaporate, we get crystals of compounds known as *molecular* or *addition compounds*. These are of two types depending on their behaviour in aqueous solution.

(*i*) **Double salts or Lattice compounds.** The addition compounds having the following characteristics are called double salts or lattice compounds.

(*a*) They exist as such in crystalline state.

(*b*) When dissolved in water, these dissociate into ions in the same way in which the individual components of the double salts do.

$$\underset{\text{Mohr's salt}}{FeSO_4.(NH_4)_2SO_4.6H_2O} \longrightarrow Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O$$

$$\underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O} \longrightarrow 2K^+(aq) + 2Al^{3+}(aq) + 4SO_4^{2-}(aq) + 24H_2O$$

In aqueous solution they give the test of all their constituent ions *i.e.* the individual components of a double salt do not lose their identity.

(*ii*) **Coordination (or complex) compounds.** It has been observed that when solutions of $Fe(CN)_2$ and KCN are mixed together and evaporated, potassium ferrocyanide, $Fe(CN)_2 4KCN$ is obtained which in aqueous solution does not give test for the Fe^{2+} and CN^- ions, but gives the test for K^+ ion and ferrocyanide ion, $Fe(CN)_6^{4-}$.

$$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4KCN \rightleftharpoons 4K^+ + Fe(CN)_6^{4-}$$

Thus we see that in the molecular compound like $Fe(CN)_2$. 4KCN, the individual compounds lose their identity. Such molecular compounds are called **coordination** (or **complex**) **compounds.** The difference between a double salt and a complex compound appears to be one of the degree rather than of a more fundamental nit.

A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and complex anion, *e.g.* $K_2[Pt^{IV}Cl_6]$, $[Pt^{IV}(NH_3)_4Br_2]Br_2$ and $[Co^{III}(NH_3)_6]$ $[Cr^{III}(C_2O_4)_3]$ are all complex compounds. The term complex compound is used synonymously with the term **coordination compound.**

In the above complex compounds the ions, $[Pt^{IV}Cl_6]^{2-}$, $[Pt^{IV}(NH_3)_4Br_2]^{2+}$, $[Co^{III}(NH_3)_6]^{3+}$ and $[Cr^{III}(C_2O_4)_3]^{3-}$ are called **complex ions.** Thus *a complex ion is an electrically charged radical which is formed by the union of a metal cation with one or more neutral molecules or anions.*

(3) **Ligands.** The neutral molecules or ions (usually anions) which are attached with the central metal ion are called **Ligands,** *e.g.* in the complex ion, $[Fe(CN)_6]^{3-}$ the six CN^- ions are the ligands. In most of complexes a ligand acts as a donor partner, *i.e.* it donates one (or more) electron pair (or pairs) to the central metal ion. Note that in metallic carbonyls the ligand *viz* CO molecule acts both as donor and acceptor, ($M \rightleftharpoons CO$).

The ligands are arranged round the metal ion inside the first sphere of attraction in preferred geometries. The common geometrics are : *linear, equilateral triangular, tetrahedral, square planar, trigonal bipyramidal, square pyramidal* and *octahedral.*

(4) **Coordination Number** (**C.N.**) or **Ligancy.** *It is the total number of the atoms of the ligands that can coordinate to the central metal ion.* Numerically coordination number *represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands.* Thus in $[Fe^{III}(CN)_6]^{3-}$, **C.N.** of Fe^{3+} is *six* while in $[Ni^{II}(NH_2-CH_2-CH_2-H_2N)_3]^{2+}$ C.N. of Ni^{2+} is

also *six*, since each ethylene diamine molecule, $\dot{N}H_2-CH_2-CH_2-H_2\dot{N}$

has two donor atoms viz. nitrogen atoms denoted by asterisks. Note that the number of ligands in $[Ni^{II}(NH_2-CH_2-CH_2-H_2N)_3]^{2+}$ is only three. Coordination number is usually considered to be a fixed number for a particular metal but now a large number of complexes is known in which the metal ion has more than one C.N.

Familiar C.N's of some common metal ions are tabulated in Table 11·1.

Table 11·1. *Fimiliar C.N.'s of some common metal ions.*

Univalent ions	*C.N.*	*Divalent ions*	*C. N.*	*Trivalent ions*	*C. N.*	*Tetravalent ions*	*C.N.*
Ag^+	2	V^{2+}	6	Sc^{3+}	6	Pt^{4+}	6
Au^+	2, 4	Fe^{2+}	6	Cr^{3+}	6	Pd^{4+}	6
Tl^+	2	Co^{2+}	4, 6	Fe^{3+}	6		
Cu^+	2, 4	Ni^{2+}	4, 6	Co^{3+}	6		
		Cu^{2+}	4, 6	Os^{3+}	6		
		Zn^{2+}	4	Ir^{3+}	6		
		Pd^{2+}	4	Au^{3+}	4		
		Pt^{2+}	4				
		Ag^{2+}	4				

(5) **Coordination sphere.** The central metal ion and the ligands that are directly attached to it are enclosed in a square bracket, which Werner has called **coordination sphere** or **first sphere of attraction**. The anions being outside the square bracket form the **second sphere of attraction.**

CLASSIFICATION OF LIGANDS

The following two ways have been used to classify the ligands :

(1) **Classification based on donor and acceptor properties of the ligands.**

(*i*) *Ligands having one (or more) lone pair (or pairs) of electrons.*

Such ligands are further classified as :

(*a*) Ligands which contain *vacant π-type orbitals that can receive back donated π-electrons from the metal ion in low oxidation state.* Important examples of such ligands are : CO, NO, CN , isocyanides, R—N=C, R_3P, R_3As, α, α-dipyridyl, o-phenanthroline and unsaturated organic molecules. All these ligands also have filled donor orbitals in addition to vacant π-type acceptor orbitals. *Thus in the complexes formed by these ligands both metal and the ligand function both as donors and acceptors* $(M \underset{\pi}{\overset{\sigma}{\leftrightarrows}} L)$

(*b*) Ligands which do not have vacant orbitals to receive back donated electrons from the metal, *e.g.* H_2O, NH_3, F .

(*ii*) *Ligands having no lone pairs of electrons but have π-bonding electrons, e.g., ethylene, benzene, cyclopentadenyl ion.*

(2) **Classification based on the number of donor atoms present in the ligands.**

The ligands of this class may be of the following types :

(*i*) **Monodentate or unidentate ligands.** The ligands which have only one donor atom and hence can coordinate to the central metal ion at one site only are called **monodentate** or **unidentate ligands.**

These ligands may be neutral molecules, negatively charged ions (anions) or positively charged ions (cations), *e.g.*

(*a*) **Neutral monodentate ligands.** The names of neutral ligands are not systematic. Some examples are : H_2O (aquo), NH_3 (ammine), CO (carbonyl), CS (thiocarbonyl), NO (nitrosyl), NS (thionitrosyl).

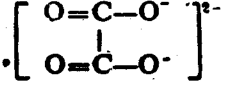
(*b*) **Negative monodentate ligands.** If the names of the anions end in *-ide, -ite* or *-ate,* the endings of the names of the ligands used are *-ido, -ito,* and *-ato* respectively. Some examples of negative ligands are : CH_3COO^-(*acetato*), F^-(*fluoro*), Cl^- (*chloro*), Br^-(*bromo*), I^- (*iodo*), CN^- (*cyano*), OCN^- (*cyanato*), SCN^- (*thiocyanato*), when S-atom of the ligand coordinates with the metal ion), NCS^- (*isothiocyanato,* when N-atom coordinates with the central metal ion), NO_2^- (*nitro,* when the ligand coordinates with the metal ion through N-atom), NO_2^- (*nitrito,* coordination through O-atom), OH^- (*hydroxo* or sometimes *hydroxy*), H^- (*hydrido*) etc.

(*c*) **Positive monodentate ligands.** Examples of positively charged monodentate ligands are NO^+ (*nitrosylium*) and $NH_2NH_3^+$ (*hydrazium*). Quite obviously the names of these ligands have the suffix *-ium.*

Bridging ligands. It is also possible that a manodentate ligand may have more than one free electron pairs and thus may simultaneously coordinate with two or more atoms, *i.e.* the ligand forms two σ-bonds with two metal atoms and thus acts a bridge between the metal atoms. Such a ligand is called a **bridging ligand** and the resulting complex is known as **bridged complex.** Examples of bridging ligands are : OH^-, F^-, Cl^-, NH_2^-, CO, O^{2-}, SO_4^{2-} etc.

(*ii*) **Bidentate, tridentate.....polydentate ligands.** The ligands having two, three, four, five or six donor atoms are called, bi, tri- (or ter-), tetra- (or quadri-), penta-, and hexa- (or sexi-) dentate ligands respectively. The bidentate, tridentate. etc. are called **polydentate** or **multidentate ligands** (literally dentate means **toothed**).

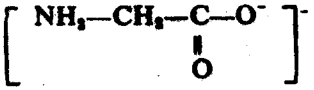
The polydentate ligands may further be subdivided according to the nature of their donor atoms. For example ethylene diamine, $NH_2—(CH_2)_2—NH_2$ is a bidentate ligand with *two neutral donors viz.* N-atoms, whereas oxalate ion,



$$\left[\begin{array}{c} O{=}C{-}O^- \\ | \\ O{=}C{-}O^- \end{array}\right]^{2-}$$

is bidentate

having *two acidic* (anionic) *donors viz* O⁻. Glycinato ion,



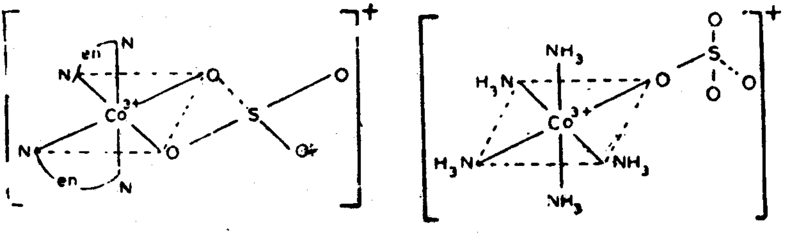
$$\left[\begin{array}{c} NH_2\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{C}\text{—}O^- \end{array}\right]^-$$

is again a bidentate with *one neutral donor viz* N-atom and an *acidic donor viz* O⁻.

Symmetrical and unsymmetric bidentate ligands. Bidentate ligands may be symmetrical or unsymmetrical ligands. In symmetrical bidentate ligands the two coordinating atoms are the same, while in unsymmetrical bidentate ligands the two coordinating atoms (*i.e.*, donor atoms) are different. Thus symmetrical and unsymmetrical bidentate ligands are generally represented as (AA) and (AB) respectively, where A and B are the two donor atoms.

Some of the common polydentate ligands are listed in Table 11·2.

Flexidentate character of polydentate ligands. Polydentate ligands have flexidentate character, *i.e.* a polydentate ligand may not necessarily use all its donor atoms to get coordinated to the metal ion, *e.g.* ethylene diamine tetracetic acid which usually acts as a hexadentate ligand functions as a *pentadentate ligand* in$[Cr^{III}(OH)(HEDTA)]^{2-}$ and $[CO^{III}(Br)(HEDTA)]^{2-}$ and as a *tetradentate ligand* in $[Pd^{II}(H_2EDTA)]^0$. In $[Co^{III}(NH_3)_5SO_4]^+$ and $[Co^{III}(en)_2SO_4]^+$ sulphate group acts as a monodentate and bidentate ligand respectively. This has been confirmed by infrared spectrocopy. In the spectrum of $[Co^{III}(NH_3)_5SO_4]^+$ six separate absorption bands due to S—O vibrations are observed. Thus an oxygen atom of the sulphate group is covalently bonded to Co^{3+} and the structure of the complex is as shown in Fig. 11.1 (*b*). In the spectrum $[Co^{III}(en)_2SO_4]^+$ eight bands which are due to S—O vibrations are observed. This indicates that in this complex the sulphate group acts as a bidentate group [Fig. 11.1 (*a*)].

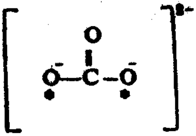
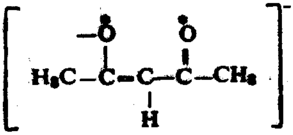
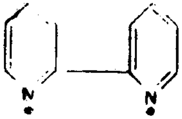
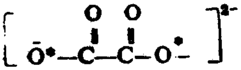
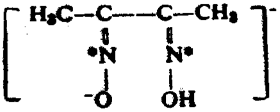
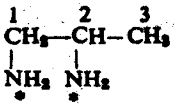
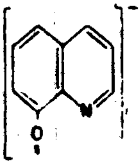


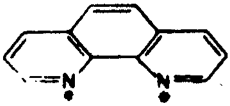
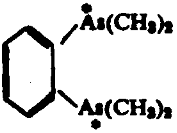
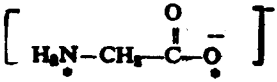
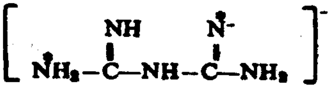
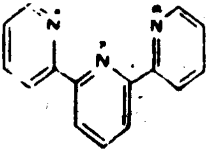
(*a*) $[Co^{III}(en)_2SO_4]^+$ ion

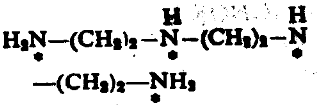
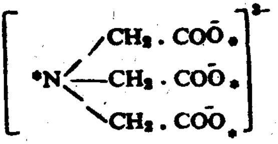
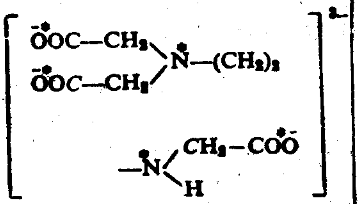
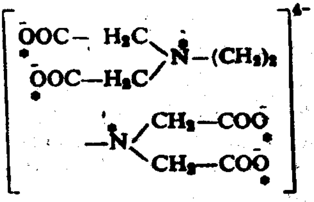
(*b*) $[Co^{III}(NH_3)_5SO_4]^+$ ion

Fig. 11·1. Structures of $[Co^{III}(NH_3)_5SO_4]^+$ and $[Co^{III}(en)_2SO_4]^+$ showing the flexidentate character of SO_4^{2-} ion.

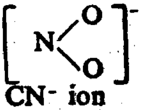
Table 11·2. *Some Common Polydentate Ligands.*
(Donor atoms having the lone pairs are indicated by asterisks)

Type of Ligand	*Name of Ligand*	*Structure of Ligand*	*Abbreviation*
Bi-dentate	**Carbonato**		CO_3^{2-}
	Acetylacetonato		$(acac)^-$
	2 : 2′-Dipyridyl or 2, 2′-dipyridine		**dipy**
	Oxalato		$(ox)^{2-}$
	Dimethyl glyoximato		$(dmg)^-$ or $(DMG)^-$
	Ethylene diamine	$H_2\overset{*}{N}-CH_2-CH_2-\overset{*}{N}H_2$	**en**
	Propylene diamine or 1, 2-diamino propane		**pn**
	Isobutylene diamine	$H_2\overset{*}{N}-C\,(CH_3)_2-\overset{*}{N}H_2$	**i-bn**
	butylene diamine	$H_2\overset{*}{N}-CH\,(CH_3)-CH\,(CH_3)-\overset{*}{N}H_2$	**bn**
	Tetra methyl-ethylene diamine	$H_2\overset{*}{N}-C\,(CH_3)_2-C\,(CH_3)_2-\overset{*}{N}H_2$	**tetra. meen**
	8-hydroxyquinolinato		$(oxin)^-$ or $(oxinate)^-$

Type of Ligand	Name of Ligand	Structure of Ligand	Abbreviation
	1, 10 phenanthroline or *o*-phenathroline		o-phen
	o-phenylene *bis* dimethyl arsine		diars or D
	Glycinato	 $\left[H_2N-CH_2-\overset{\overset{O}{\Vert}}{C}-\overset{-}{O}\right]^-$	$(gly)^-$
	Biguanido	 $\left[NH_2-\overset{\overset{NH}{\Vert}}{C}-NH-\overset{\overset{N^-}{\Vert}}{C}-NH_2\right]^-$	$(Big)^-$
Tridentate	Diethylene triamine	$H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$	dien
	Imino-di-acetato	$\left[\overset{-}{O}OC-H_2C-NH-CH_2-CO\overset{-}{O}\right]^{2-}$	$(IDA)^{2-}$
	2, 2′, 2″-terpyridine		terpy

Type of Ligand	*Name of Ligand*	*Structure of Ligand*	*Abrevia-tion*
Tetra-denate	**Triethylene tetramine**	 $H_2\underset{\bullet}{N}-(CH_2)_2-\overset{H}{\underset{\bullet}{N}}-(CH_2)_2-\overset{H}{\underset{\bullet}{N}}-(CH_2)_2-\underset{\bullet}{N}H_2$	**trien**
	Nitrilo triacetato		$(NTA)^{3-}$
Penta-dentate	Ethylene diamine triacetato		—
Hexa-dentate	Ethylene diamine tetracetato		$(EDTA)^{4-}$ Y^{4-}

Ambidentate ligands. These are the ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time. Such ligands are called **ambidentate ligands.** Some examples of such type of ligands are given below :

 ion	Nitro ($M-NO_2$) Nitrito ($M-ON=O$)
CN^- ion	Cyano (MCN) Isocyano (MNC)
NCS^- ion	Thiocyanate (MSCN) Isothiocyanate (MNCS)
NCO^- ion	MOCN, MNCO
$SeCN^-$ ion	MSeCN, MNCSe
R_2SO	S-bonded or O-bonded
$S_2O_3^{2-}$ ion	Thiosulphato—S ($MSSO_3$) Thiosulphato—O ($MOSO_2S$)

In few cases ambidentate ligands give rise to linkage isomers, *i.e.* complexes that differ only in the manner in which one or more ambidentate ligands are attached to the metal ion. For example, the complex, $[Co(NH_3)_5 NO_2]Cl_2$ exists in two linkage isomers *viz* $[Co(NH_3)_5ONO]Cl_2$ (nitrito isomer) and $[Co(NH_3)_5NO_2]Cl_2$ (nitro isomer).

CHELATION

Polydentate ligands whose structures permit the attachment of their two or more donor atoms (or sites) to the same metal ion simultaneously and thus produce one or more rings are called *chelate* or *chelating ligands* (from the Greek for claw) or *chelating groups*. However, it should be noted here that every multidentate ligand is not necessarily a chelating ligand—the coordinating atoms of the ligand may be so arranged that they cannot be coordinated to the same metal atom to produce a ring structure. Thus $\ddot{N}H_2-CH_2-CH_2-\ddot{N}H_2$ is a chelating ligand, while

is not, although both are diamines. The formation of such rings is termed *chelation* and the resulting ring structures have been called *chelate rings* or simply *chelates* by Morgan and Drew. These are also called chelated complexes or cyclic complexes and the term chelation is also called *cyclisation*.

Classification of Chelates

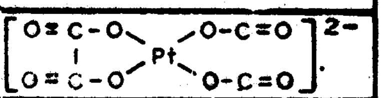
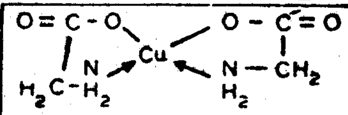
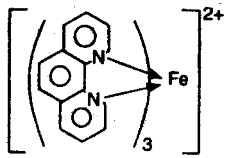
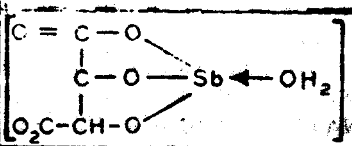
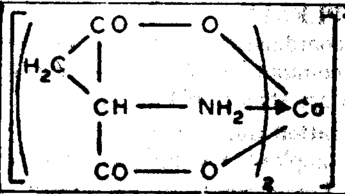
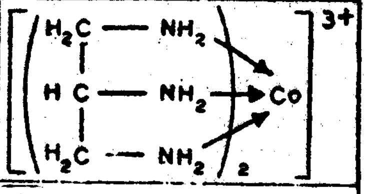
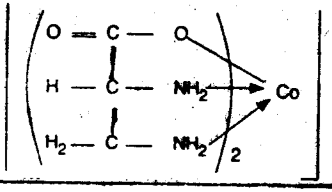
Since the polydentate ligands may be attached to the central metal ion through two kinds of functional groups namely acidic and coordinating groups to form covalent and coordinate linkages respectively, the classification of chelates follows the number and kind of linkages by which the metal ion is attached with the ligands. The covalent bonds are formed by the replacement of one or more H-atoms from the acidic groups present in the ligand by the metal atom. The examples of most common groups of this type are $-COOH$ (carboxyl), $-SO_3H$ (sulphonic), $-OH$ (enolic hydroxyl) and $=NOH$ (oxime). Coordinating linkages, without the replacement of H, are formed by the donation of an electron pair from the ligands. The examples of most common groups of this type are $-NH_2$ (primary, secondary and tertiary amines), $=NOH$ (oxime), $-OH$ (alcoholic hydroxyl), $=CO$ (carbonyl) and $-S-$ (thio ether). Some of the chelates classified on this basis are summarised below in Table 11·3.

Ordinarily such chelate rings as mentioned above are most stable, because of reduced strain, when they have 5 or 6 members including the metal ion. The enhanced stability of complexes containing chelated ligads (*i.e.*, multidentate ligands) is known as the *chelate effect*.

Uses of Chelates

(*i*) **In Analytical Chemistry**. Al^{3+}, Ni^{2+} and Mg^{2+} ions can quantitatively be identified by the formation of stable and highly

Table 11·3. *Types of chelates*

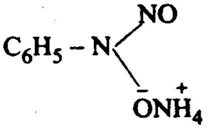
Type of Chelates	Type of Linkages	Examples of Chelates
1. BIDENTATE CHELATES	TWO COVALENT LINKAGES	
	ONE COVALENT AND ONE COORDINATE LINKAGE	 Cu-glycinate
	TWO COORDINATING LINKAGES	 Ferrous - orthophenothroline Complex ion
2. TRITENTATE CHELATES	THREE COVALENT LINKAGES	
	TWO COVALENT AND ONE COORDINATE LINKAGE	
	THREE COORDINATING LINKAGES	
	ONE COVALENT AND TWO COORDINATING LINKAGES	

coloured chelates of these ions. Nickel and magnesium can also be determined quantitatively by their precipitation. Chelate agents are also used as indicators in the titration of certain metal ions.

(*ii*) **In water softening.** The suppression of the precipitation reactions of Ca^{2+} and Mg^{2+} which are responsible for the hardening of water is known as sequestration. By complexing the metal ions, it is possible to prevent the precipitation of soaps as their Ca^{2+} and Mg^{2+} salts by hard water. In the presence of the excess of the complexing agents such as polyphosphates and polydentate amino acids soaps give no precipitate with hard water. Thus hard water is effectively softened.

(*ii*) **In the elimination of harmful radioactive metals from the body.** Some of the chelating agents such as EDTA are used in the elimination of harmful radioactive metals from the body.

(*iv*) **In solvent Extraction.** The neutral chelate (inner complexes have usually low solubility in water but their solubility in organic solvents is appreciable. Thus in presence of ligands that are capable of forming inner complexes, many metals can be extracted into water-immiscible organic phase. Trifluoroacetylacetone, for example, has been used for the separation of Zr and Hf. Cupferron,



$$C_6H_5-N\begin{matrix}NO\\ \overset{-}{O}\overset{+}{N}H_4\end{matrix}$$

has also been used in the refinement of a number of metals by the solvent extraction metod.

(*v*) **In food preservation.** Fruit, fruit juices, food stuffs etc. are now preserved with the help of chelating compounds.

COORDINATION NUMBER AND STEREOCHEMISTRY OF COMPLEXES

The coordination numbers shown by metals in complexe are 2 to 9. The most common are 2, 3 and 6. Geometries correponding to C.N's = 2, 3, 4 and 5 are shown in Fig. 11.2.

1. Coordination number 2

The complexes having CN = 2 are *linear*, since this geometry provides minimum ligand repulsion. Cu^+, Ag^+, Au^+ and in some cases Hg^{2+} from such complexes e.g. $Cu(CN)_2^-$, $Cu(NH_3)_2{}^+$, $Ag(NH_3)_2{}^+$, AG $(CN)_2^-$, Au $(CN)_2^-$, Hg $(NH_3)_2{}^{2+}$, $Hg(CN)_2$.

2. Coordination number 3

Two possible geometries exhibited by the complexes with CN = 3 are (*i*) *equilateral triangular* as in $[HgI_3]^-$ in which I^- ions are arranged at the corners of a slightly distorted equilateral triangle with Hg^{2+} at its centre, and (*ii*) *trigonal pyramidal* as in $[H_3O]^+$.

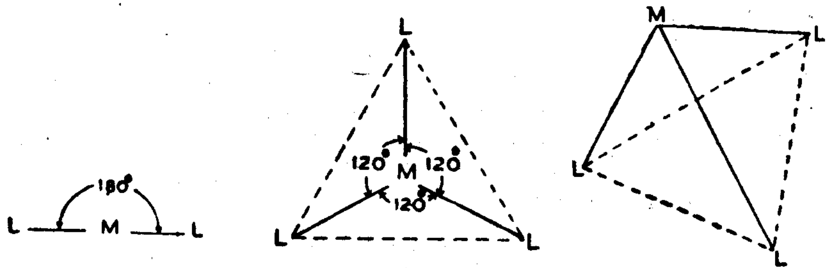
3. Coordination number 4

Complexes with CN = 4 may be *tetrahedral* or *square planar* in geometry. Complexes like

$ZnCl_4^{2-}$
$ZnBr_4{}^{2-}$
$Zn(CN)_4{}^{2-}$
$Zn(NH_3)_4{}^{2-}$

$Cu(CN)_4^{2-}$
$CuX_4{}^{2-}$
($X = Cl^-, Br^-, I^-, CNS^-$)

$Hg(CN)_4^{2-}$, $[Ni(CO)_4]^0$; $FeCl_4^-$

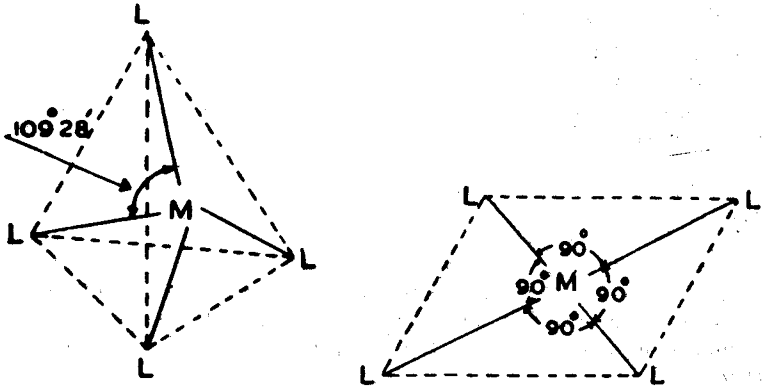


Linear ML$_2$
(C.N.=2)

Equilateral triangular ML$_3$

Trigonal pyramidal ML$_3$

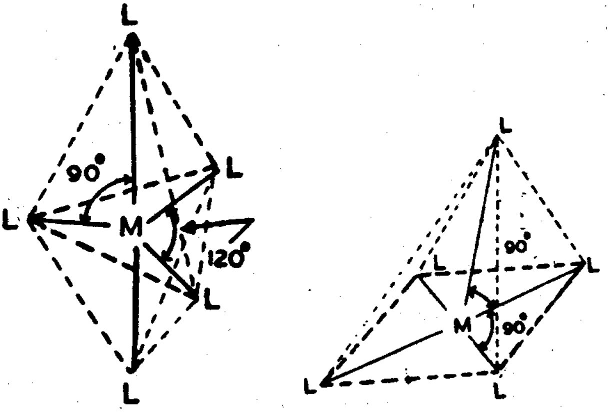
(C.N.=3)



Tetrahedral ML$_4$

Square planar ML$_4$

(C.N.=4)



Trigonal bipyramidal ML$_5$ **Square pyramidal ML$_5$**

(C.N.=5)

Fig. 11·2. Geometries of complexes with coordination numbers of 2, 3, 4 and 5. M and L stand for metal atom and ligands respectively.

are tetrahedral. Oxyanions such as VO_4^{3-}, CrO_4^{2-}, FeO_4^{2-} and MnO_4^- are also tetrahedral.

Square planar geometry is found in complexes of Cu^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+} etc. ions, e.g. $[Cu(en)_2]^{2+}$, $Cu(NH_3)_4^{2+}$, $Ni(NH_3)_4^{2+}$, $Ni(CN)_4^{2-}$, $[Ni(dmg)_2]^0$, $Pt(NH_3)_4^{2+}$, $PdCl_4^{2-}$, $AuCl_4^-$ etc.

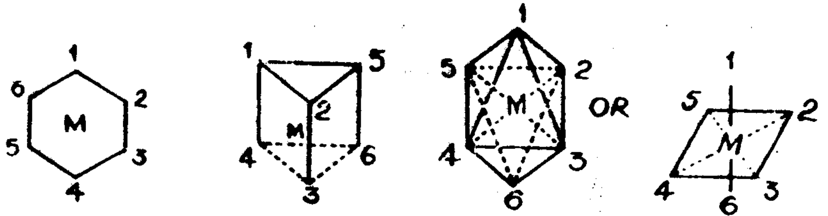
4. Coordination number 5

Complexes with C.N. 5 may be *trigonal bipyramidal* or *square pyramidal*. $Fe(CO)_5$, $Fe(CO)_4(R_3P)$, $Fe(CO)_3(R_3P)_2$, $[Mn(CO)_5]^-$, $CuCl_5^{3-}$, $SnCl_5^-$, $[Cu(dipy)_2I]^+$ etc. possess trigonal bipyramidal geometry while $[VO(acac)_2]$, $NiBr_3[(C_2H_5)_3P]_2$ have square pyramidal structure.

5. Coordination number 6

Complexes with C.N. = 6 are the most common ones formed by transition metal ions.

Six ligands in a 6-coordination compound may be arranged round the central metal ion, M, either at the corners of hexagonal plane or at the apices of a trigonal prism or at the apices of a regular octahedron. These arrangements together with numbers designating substitution positions may be depicted as shown in Fig. 11·3. An extensive study of the geometrical and optical isomers of complexes with C.N. = 6 has, however, shown that arrangement of six ligands in a 6-coordination compound is always octahedral and that the arguments concerning other possible geometries (*i.e.* hexagonal planar and trigonal prismatic geometries) are of historical interest only.



Hexagonal planar geometry **Trigonal prismatic geometry** **Regular octahedral geometry**

Fig. 11·3. Possible arrangements of six ligands of a 6-coordinated complex round the central metal ion, M.

In order to show that other geometries *viz.* hexagonal planar and trigonal prismatic are not preferred geometries for 6-coordination complex, Werner worked out the theoretical number of geometrical isomers that each of these geometries could give for the complexes *viz.* ML_6, ML_5L', ML_4L_2', ML_3L_3' and then compared with the number of isomers experimentally isolated (*See* Tabla 11·4). A single form is predicted by each geometry for the complexes ML_6 and ML_5L'. But for the complexes ML_4L_2' both hexagonal planar and trigonal prismatic geometries predict three isomers *viz.* (1, 2), (1, 3) and (1, 4) but regular octahedral geometry predicts only two geometrical isomers namely (1, 2) and (1, 6). The number of isomers isolated experimentally for ML_4L_2' complexes is also two. Similarly for ML_3L_3' complexes the octahedral geometry predicts two geometrical isomers and experiments confirm this number.

Tahle 11·4. *Comparison of the number of experimentally isolated geometrical isomess of 6-coordinated complexes with the theoretically predicted for hxagonal planar, trigonal prismatic and regnlar actahedral arrangement of six ligands round the central metal ion, M.*

Complexes	*No. of geometrical isomers experimentally isolated*	*No. of geometrical isomers predicted theoretically for*		
		Hexagonal geometry	*Trigonal prismatic geometry*	*Regular octahedral geometry*
ML_6	1	1	1	1
ML_5L'	1	1	1	1
ML_4L_2'	2	3	3	2
		(1, 2), (1, 3) (1, 4)	(1, 2), (1, 3), (1, 4)	(1, 2), (1, 6)
ML_3L_3'	2	3	3	2
		(1, 2, 3) (1, 2, 4) (1, 3, 5)	(1, 2, 3), (1, 2, 5) (1, 2, 6)	(1, 2, 3), (1, 2, 6)

Further the hexagonal and trigonal prismatic geometries donot predict any optical isomers for the complex, $[M(AA)_3]$ where (AA) is a symmetrical bidentate ligand, but octahedral shape predicts two isomers *viz.* mirror-image isomers. Werner, therefore, concluded that for a 6-coordinate complex octahedral geometry is the preferred geometry. However, octahedral geometry of some 6-coordinate complexes like $[Cu(NH_3)_4(H_2O)_2]^{2+}$ gets distorted and thus becomes *tetragonal* which arises due to the elongation of the ligands along *z*-axis.

NOMENCLATURE OF COORDINATION COMPOUNDS

The first comprehensive system of nomenclature was suggested by A. Werner. Though this has been modified by the Inorganic Nomenclature Committee of the *International Union of Pure and Applied Chemistry* (IUPAC), the fundamental rules suggested by Werner essentially remain the same. Trivial names for certain coordination compounds still persist, e.g., many authors still prefer to call the ions *viz.* $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ ferrocyanide and ferricyanide instead of hexacyanoferrate (II) and hexacyanoferrate (III) ions respectively as suggested by IUPAC system.

On the basis of the nature of the cation and anion of the complexes, these are classified as :

(*i*) *cationic complexes*, e.g. $[Cr(H_2O)_4Cl_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Ni(en)_2Cl_2]^{2+}$ etc.

(*ii*) *anionic complexes*, e.g. $[Cr(en)I_4]^-$, $[Pt(NH_3)Cl_5]^-$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ etc.

(*iii*) *ionic complexes*. These contain simple or complex cation and simple or complex anion, e.g., $K_2^+ [PtCl_6]^{2-}$, $[Pt(NH_3)_4Br_2]^{2+}Br_2^-$, $[Pt(py)_4]^{2+} [PtCl_4]^{2-}$ etc.

(*iv*) *neutral complexes*. These are *non-ionic* (*non-electrolyte*) or *molecular complexes*, *e.g.* $[Ni(CO)_4]^0$, $[Co(NO_2)_3(NH_3)_3]^0$, etc.

For naming all the types of complexes mentioned above the following rules are observed :

1. **Naming of the ligands.**

In all the types of complexes mentioned above *the ligands are named first and the central atom is named last*. The ligands are named according to the following rules :

(*i*) **Order of naming ligands.** If the coordination sphere of a given complex compound contains various types of ligands. The ligands are named in alphabetical order. The prefixes di, tri etc are not to be considered while determining this alphabetical order. For example $[Co(NH_3)_4(NO_2)Cl]^+$ ion is named as tetramminechloronitro cobalt (III) ion.

(*ii*) **Naming of the negative ligands.** In general, if the anion name ends in *-ide*, *-ite*, or *-ate*, the final *-e* is replaced by *o*, giving *-ido*, *-ito* and -ato respectively, *e.g.* SO_3^{2-} (*sulphito*), SO_4^{2} (*sulphato*), CH_3COO^- (*acetato*), S^{2-} (*thio* or *sulphido*), NO_3^- (*nitrato*), NH^{2-} (*imido*), NH_2^- (*amino* or *amine*), N_3^- (*azido*), $NHOH^-$ (*hydroxylamido*), $HON=C(CH_3)C(CH_3)=NO^-$ (*dimethylglyoximato*).

Some exceptions to this rule are : F^- (*fluoro*), Cl^- (*chloro*), CN^- (*cyano*), O^{2-} (*oxo*), OH^- (*hydroxo*), O_2^{2-} (*peroxo*), O_2H^- (*perhydroxo*).

Thus we see that the names of the negative ligands end in *-o*.

The negative ligands are named in the order : H^-, O^{2-}, OH^-, other simple monoatomic anionic ligands, polyatomic anionic ligands and finally organic anions in *alphabetical order*. Where the two ligands have the same number of atoms, the order is that of decreasing atomic number of the central metal species in the ligand, e.g. CrO_4^{2-} first and then SO_4^{2-}

(*iii*) **Naming of the neutral ligands.** For neutral ligands, the names are not systematic. For less common neutral ligands (*e.g.*

PH_3), the names of free molecules is used as such. For some of the more common neutral ligands, special names are used, *e.g.*, H_2O (*aquo*), NH_3 (*ammine*), CO (*carbonyl*), NO (*nitrosyl*), CS (*thiocarbonyl*), NS (*thionitrosyl*).

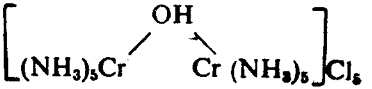
Neutral ligands are named in the following order : *first* : H_2O (*aquo*), then NH_3 (*ammine*), *second* : other neutral coordinated ligands in the order in which the coordinated atom falls in the series: B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F, *third* : neutral organic ligands in alphabetical order.

(*iv*) **Naming of the positive ligands.** Positively charged ligands have suffix *-ium*, *e.g.* $NH_2NH_3^+$ is called hydrazinium, and NO^+ is nitrosylium.

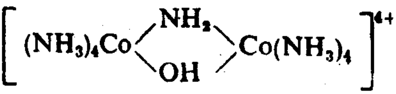
(*v*) **Indication of the number of ligands.** The number of simple ligands such as Cl^-, CH_3COO^-, $C_2O_4^{2-}$ etc. is indicated by using before them the Greek prefixes : *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* etc. In case of chelating ligands like ethylenediamine, trialkyl phosphine which contain the prefixes *di-*, *tri-*, etc. in their ligand names, the prefixes *bis-* (for two), *tris-*, (for three), *tetrakis-* (for four), *pentakis-* (for five), *hexakis-* (for six) etc. are used before their names. The ligands to which these prefixes refer are often placed in parentheses. For example : $[Co^{III}(NH_3)_2(en)_2]Cl_3$—diammine *-bis* (ethylene diamine) cobalt (III) chloride, $[Co^{III}(en)_3]_2(SO_4)_3$—*tris* (ethylene diamine) cobalt (III) sulphate, $[Fe^{II}(CN)_2(CH_3NC)_4]$—dicyano *tetrakis* (methylisocyanide) iron (II).

(*vi*) **Naming of the bridging ligands of the bridged polynuclear complexes.** The complexes having two or more metal atoms are called polynuclear complexes. In these complexes the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens and by adding the prefix μ before its name. The Greek letter μ should be repeated before the name of each different bridging group. Two or more bridging groups of the same kind are indicated by *di-μ-*, *t i-μ-*, ...etc.

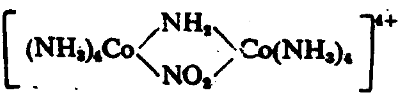
Examples :



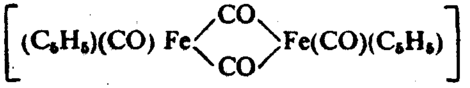
μ-hydroxo-bis {penta-ammine chromium (III)} chloride



μ-amido μ-hydroxoocta-ammine dicobalt (III) ion



μ-amido-μ-nitro octa-ammine dicobalt (III) ion



$[(C_5H_5)(CO)Fe(CO)_2Fe(CO)(C_5H_5)]$ Di-μ-carbonyl-bis (carbonyl cyclopentadienyl iron)

$[(CO)_3Fe(CO)_3Fe(CO)_3]$ Tri-μ-carbonyl-bis (tricarbonyl iron)

If a bridging group bridges more than two metals, use of μ_3, μ_4......etc. should be made to indicate the number of central atoms bridged by a given ligand, *e.g.* $[Be_4O(CH_3COO)_6]$ is called μ_4-oxo-hexa-μ-acetatotetra beryllium (II). The common name of this compound is basic beryllium acetate.

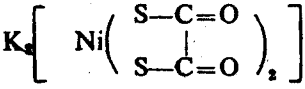
(*vii*) **Naming of ambidentate ligands.** The ligands which can be coordinated to the central metal ion through either of the two donor atoms are called ambidentate ligands. Such ligands are either named by special names such as *thiocyanate* for —SCN and *isothiocyanate* for —NCS, *nitro* for $—NO_2$ and *nitrito* for —ONO or the symbol of the element coordinated with the metal ion is written after the name of the ligand, *e.g.* *thiooxalate*-S for a thio-oxalate group coordinated to the metal ion through sulphur atom and *thio-oxalato*-O for a thio-oxalate group coordinated through oxygen atom. The following examples will illustrate this point :

$[Co(NH_3)_5—ONO]Cl_2$ ⟶ Nitro-O or Nitrito complex

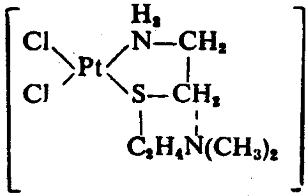
$[Co(NH_3)_5—NO_2]Cl_2$ ⟶ Nitro-N or Nitrato complex

$[Pd(diph)(SCN)_2]$ ⟶ Thiocynate-S complex

$[Pd(diph)(NCS)_2]$ ⟶ Thiocynate-N complex



⟶ Potassium bis (dithiooxalato S, S′) nickelate (II)



⟶ Dichloro (N, N-dimethylamino ethylamino ethyl sulphide-N′, S)-platinum (II)

2. **Naming of the central metal ion and mononuclear complexes**

Different rules are used for naming different complexes.

(*i*) **Anionic complexes.** In naming anionic complexes like $[Pt(NH_3)Cl_5]^-$, $[Cr(en)I_4]^-$ etc. ***ligands are named first and then the central metal ion.*** To name the cental metal ion the suffi "*ate*" is attached to its name and in order to indicate the oxidation state of the metal ion this suffix is followed by Roman numeral (such as I, II, III etc.) in the parentheses at the end of the name of the complex without a space between the two. (o) is used for an oxidation state of zero. For negative oxidation state the negative sign is placed before the Roman numeral. In some cases the metal name is derived from the Latin name, *e.g.* plumbate, argentate, ferrate, aurate, cuprate are used for lead, silver, iron, gold and copper respectively.

Examples :

$[Cr^{III}(en)\,I_4]^-$	Tetra iodo (ethylene diamine) chromate (III) ion
$[Pt^{IV}(NH_3)\,Cl_5]^-$	Pentachloro mono-ammine platinate (IV) ion
$[Zn^{II}\,(OH)_4]^{2-}$	Tetrahydroxo zincate (II) ion
$[Ag^{I}\,Cl_2]^{1-}$	Dichloro argentate (I) ion
$[Fe^{II}\,(CN)_6]^{4-}$	Hexacyanoferrate (II) ion (generally known as ferricyanide ion)
$[Fe^{III}\,(CN)_6]^{8-}$	Hexacyanoferrate (III) ion (generally known as ferricyanide ion)
$[Ni^{0}\,(CN)_4]^{4-}$	Tetracyanonicklate (0)
$[Co^{-I}\,(CO)_4]^-$	Tetracarbonylcobaltate (–I)

(*ii*) **Cationic and neutral complexes.** In case of cationic and neutral complexes like $[Cr(H_2O)_4Cl_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CO)_4]$, $[Co(NO_3)_3(NH_3)_3]^0$ etc. the ligands are named first and then the central metal ion followed by a Roman numeral in parentheses to indicate its oxidation state. The suffix *ate* is *not* attached to the name of the metal in case of these complexes.

Examples :

$[Cr^{III}(H_2O)_4\,Cl_2]^+$	Dichloro-tetra-aquo chromium (III) ion	Cationic complexes
$[Ag^{I}\,(NH_3)_2]^+$	Diammine silver (I) ion	
$[Cu^{II}\,(NH_3)_4]^{2+}$	Tetra-ammine copper (I) ion	
$[Al^{III}(OH)\,(H_2O)_5]^{2+}$	Hodroxo pentaaquo aluminium (III) ion	
$[Ni^{IV}(en)_2\,Cl_2]^{2+}$	Dichlorabis (ethylene diamine) nickel (IV) ion	
$[Ni^{0}\,(CO)_4]^0$	Tetra carbonyl Nickel (0)	Neutral complexes
$[Co^{III}(NO_2)_3\,(NH_3)_3]^0$	Trinitro triammine cobalt (III)	

(*iii*) **Ionic complexes.** In ionic complexes like $K_2^+\,[Pt^{IV}\,Cl_6]^{2-}$, $[Pt^{IV}\,(NH_3)_4Br_2]^{2+}Br_2^-$, $[Pt^{II}\,(py)_4]^{2+}$, $[Pt^{II}\,Cl_4]^{2-}$ etc. *the cation is named first and then the anion* as we do in naming a simple salt like

NaCl. The rules for naming the anionic and cationic parts of ionic complexes are the same as mentioned above at (*i*) and (*ii*) respectively.

Examples. The names of some mononuclear ionic complex compounds are given in Table 11·5 below :

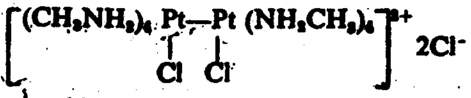
Table 11·5. *Names of some mononuclear ionic complex compounds*

Composition	*Cation and anion type*	*Name*
$K_2[Pt^{IV}Cl_6]$	Simple cation, K+ and complex anion, $[Pt^{IV}Cl_6]^{2-}$	Potassium hexa chloro platinate (IV)
$NH_4[Cr^{III}(SCN)_4(NH_3)_2]$	Simple cation, NH_4^+ and complex anion, $[Cr^{III}(SCN)_4(NH_3)_2]^-$	Ammonium tetra-thiocyanato diammine chromate (III)
$[Pt^{II}(py)_4][Pt^{II}Cl_4]$	Complex cation, $[Pt^{II}(py)_4]^{2+}$ and complex anion, $[Pt^{II}Cl_4]^{2-}$	Tetrapyridine platinum (II) tetrachloroplatinate (II)
$[Co^{III}(NH_3)_6][Cr^{III}(C_2O_4)_3]$	Complex cation, $[Co^{III}(NH_3)_6]^{3+}$ and complex anion, $[Cr^{III}(C_2O_4)_3]^{3-}$	Hexa-ammine cobalt (III) trioxalato chromate (III)
$[Pt^{IV}(NH_3)_4Br_2]Br_2$	Complex cation, $[Pt^{IV}(NH_3)_4Br_2]^{2+}$ and simple anion, Br^-	Dibromo-tetra ammine platinum (IV) bromide
$[Fe^{III}(H_2O)_4(C_2O_4)]_2SO_4$	Complex cation, $Fe^{III}(H_2O)_4C_2O_4)]^+$ ano simple anion, SO_4^{2-}	Oxalato-tetra aquo-iron (III) sulphate

It should be noted that the names of cation and anion are separated by a space and the number of each type of ion is not indicated.

3. Metal-to-metal bonding

In complexes containing metal-to-metal bonds, the prefix bi- is used before the name of the metals forming a metal-to-metal bond e.g., the name of the complex having the formula,

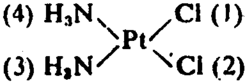


$$\left[(CH_3NH_2)_4\underset{\underset{Cl}{|}}{Pt}-\underset{\underset{Cl}{|}}{Pt}(NH_2CH_3)_4\right]^{2+}2Cl^-$$

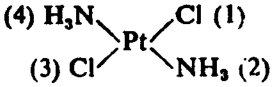
is *sym*-dichloro octakis (methyl-amine) *bi*-platinum (II) chloride.

4. Geometrical isomers

Geometrical isomers are named either by using the prefixes *cis* for adjascent (90° apart) positions and *trans* for opposite (180° apart) positions before the name of the ligands or by numbering system. In square planar complexes the groups at positions (1, 2) and (3, 4) are *cis* to each other while those at positions (1, 3) and (2, 4) are *trans* to each other. Thus :



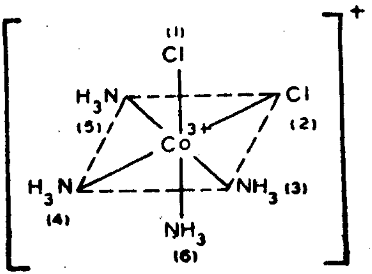
cis-diamminedichloroplatinum (II) or 1, 2-dichlorodiammineplatinum (II)



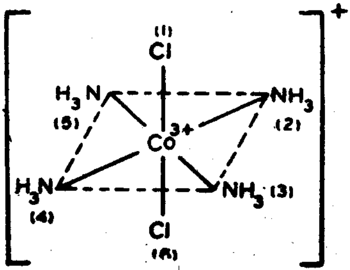
trans-diamminedichloroplatinum (II) or diammine 1,2-dischloroplatinum (II)

F. Basolo and R.G. Pearson in their book **Mechanism of Inorganic Reactions** have described the numbering system for naming the mono-nuclear, bi-nuclear bridged and bi-nuclear planar octahedral complexes.

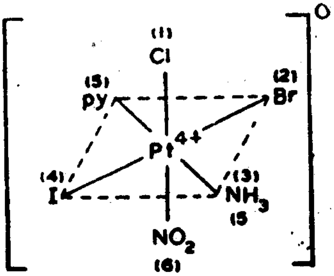
In mono-nuclear octahedral complexes of Ma$_2$b$_4$ type (1, 2), (1, 3), (1, 4), (1, 5), (6, 2), (6, 3), (6, 4), (6, 5), (2, 3), (3, 4), (4, 5) and (5, 2) are *cis* positions and (1, 6), (2, 4) and (3, 5) are *trans* positions. In mono-nuclear complexs of Ma$_3$b$_3$ type (1, 2, 3) are *cis* and (1, 2, 6) are *trans* positions. Thus :



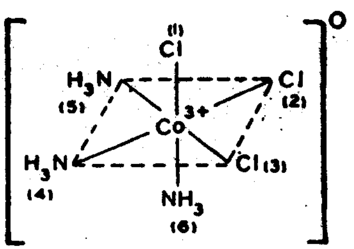
Cis-dichlorotetraammine cobalt (III) ion or 1, 2-dichlorotetra-ammine cobalt (III) ion



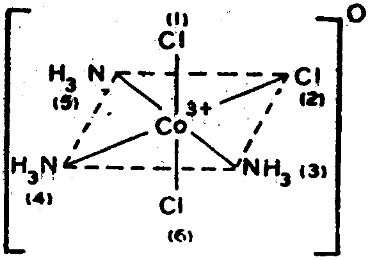
Trans-dichlorotetra-ammine cobalt (III) ion or 1, 6-dichlorotetra-ammine cobalt (III) ion



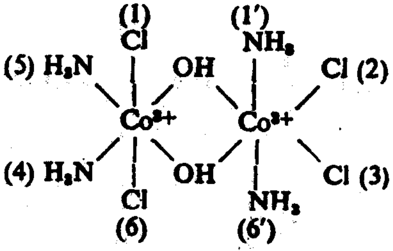
1-chloro-2-bromo-4-iodo-6-nitro-ammine-pyridineplatinum (IV), [py = pyridine = C_5H_5N]



Cis-trichlorotriammine-cobalt (III) or 1, 2, 3-trichlorotriammine cobalt (III)



Trans-trichloroammine cobalt (III) or 1, 2, 6-trichlorotriammine cobalt (III)



Di-μ-hyhroxo-1, 2, 3, 6-tetrachloro-tetra ammine dicobalt (III) or di-μ-hydroxo-*cis*-dichloro-*trans*-dichloro-tetra ammine dicobalt (III) ion (Bi-nuclear bridged octahedral complex)

5. Optical isomers

Dextro and *levorotatory* complexes are respectively designated either by (+) or (−) or by *d* or *l*, *e.g.*

(+), or *d*-$K_3[Ir(C_2O_4)_3]$—potassium (+), or *d*-trioxalatoiridate (III).

If the ligand molecules of a complex are optically active, the configuration of the whole ion is represented by D or L and that of the ligand molecules by *d* or *l*, *e.g*,

$$\text{D-}[Co(l\text{-}pn)_3]^{3+},\ \text{D-}[Co(l\text{-}pn)_2(d\text{-}pn)]^{3+},\ \text{L-}[Co(l\text{-}pn)_3]^{3+},$$
$$\text{L-}[Co(l\text{-}pn)_2(d\text{-}pn)]^{3+}\ \text{etc.}$$

DETECTION AND STRUCTURE DETERMINATION OF COMPLEXES

Some of the simpler methods are given below :

(1) Solubility.

Complex formation is often indicated by the fact the solubility of a sparingly soluble salt is increased when one of its ions forms a complex in solution, *e.g.*

(*i*) When KCN is added to a solution of AgCN which is sparingly soluble, the solubility of AgCN is increased due to the formation of a soluble complex ion, $[Ag(CN)_2]^-$.

$$\underset{\text{sparingly soluble}}{AgCN + KCN} \rightleftharpoons \underset{\text{soluble}}{K[Ag(CN)_2]} \rightleftharpoons K^+ + \underset{\substack{\text{complex ion}\\ \text{(soluble)}}}{[Ag(CN)_2]^-}$$

(*ii*) Addition of NH_3 to insoluble AgCl gives very soluble $[Ag(NH_3)_2]^+$.

$$\underset{\text{insoluble}}{AgCl + 2NH_3} \rightleftharpoons [Ag(NH_3)_2]Cl \rightleftharpoons \underset{\text{soluble}}{[Ag(NH_3)_2]^+} + Cl^-$$

(2) **Change in Colour.**

Sometimes a change in colour is an indication of complex formation, *e.g.* addition of NH_3 to $[Cu(H_2O)_4]^{2+}$ ion leads to an intense blue colour due to the formation of the complex ion, $[Cu(NH_3)_4]^{2+}$.

(3) **pH measurements.**

Generally ligands are either weak bases or acids. The formation of a complex is accompanied by the displacement of one or more, usually weak, acidic protons of the ligand by the metal ion. This increases the concentration of H^+, $[H^+]$ in the complex formation and hence causes a drop in the value of *p*H. Thus the change in *p*H value can be used as an indication of the extent of complex formation.

(4) **Visible absorption spectral studies.**

The absorption of light in the visible region (400—800 mμ) by a metal ion depends on the electron transitions within the ion and also on the type and strength of ligand-to-metal bonding. Thus, the metal ions containing *d*-electrons (except those having 10 electrons in *d*-orbitals) give variable colours depending on the nature of the ligands attached with the metal ion. In many cases the intensity of absorption is increased and the absorption shifts to higher energies (lower *m*μ), when coordinated water molecules are replaced by ligands more basic than water.

The extent to which a spectrum can change is illustrated in Fig. 11·4. In this figure the visible spectrum shown by dotted lines

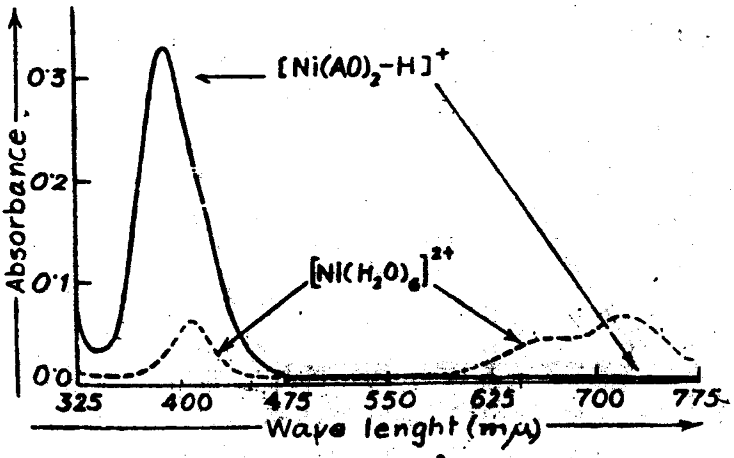


Fig. 11·4. Visible spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(AO)_2—H]^+$ ions is that of $[Ni(H_2O)_6]^{2+}$ ion while that shown by solid lines is that of α-amino oxime complex of Ni^{2+}, represented as $[Ni(AO)_2—H]^+$. The absorption has shifted to higher energies (*i.e.*, lower mμ) and has become more intense.

(5) Change in chemical properties.

When a metal ion combines with a ligand to form a complex, its usual chemical properties are lost in the solution. Thus the loss of the normal chemical properties of the metal ion in solution is an indication of the complex formation, *e.g.* when $CuSO_4$ is treated with excess of KCN, the complex, $K_3[Cu^+(CN)_4]$ (soluble complex) is formed. This complex gives none of the tests of Cu^+.

Limitations of the technique. Usually the formation of complexes of low thermodynamic stability cannot be demonstrated by this technique, since an appreciable amount of simple metal ion is left uncomplexed, *e.g.*, the complexes formed between NH_3 and Ca^{2+}, Zn^{2+} or Al^{3+} give all the usual precipitation reactions of the free metal ion.

(6) Polarographic Method.

Polarographic measurements provide certain information which can be used for the detection of complex formation, determination of coordination number and stability constant. This method is based on the fact that when a ligand is added to a metal ion, the characteristic half-wave potential of the metal ion is shifted which indicates the formation of the complex between the metal and the ligand.

(7) Change in oxidation potential.

There is a decrease in ionic activity of the metal and hence an increase in its oxidation potential, when it combines with a ligand to form a complex *e.g.*,

(*i*) (*a*) $Co^{2+} \longrightarrow Co^{3+} + e^-, \; E^\circ = -1{\cdot}85$ volts

(*b*) $[Co^{2+}(NH_3)_6]^{2+} \longrightarrow [Co^{3+}(NH_3)_6]^{3+} + e^-,$ $E^\circ = -0{\cdot}10$ volts

(*ii*) (*a*) $Fe^{2+} \longrightarrow Fe^{3+} + e^-,$ $E^\circ = -0{\cdot}77$ volts

(*b*) $[Fe^{2+}(CN)_6]^{4-} \longrightarrow [Fe^{3+}(CN)_6]^{3-} + e^-,$ $E^\circ = -0{\cdot}36$ volts

(8) Magnetic Susceptibility.

A measurement of the magnetic susceptibility sometimes indicates the formation of a complex, nature of bonding and stereochemistry, e.g. Ni(II) square-planar complexes like $[Ni(Big)_2]^0$ (*dsp*^{2} hybridisation) are *diamagnetic* due to the absence of unpaired electrons while Ni(II) tetrahedral complexes like $[NiCl_4]^{2-}$ (*sp*^{3} hybridisation) are paramagnetic due to the presence of two unpaired electrons.

(9) Conductance measurements.

There is a decrease or increase in the value of electrical conductance of the solution in which complex formation occurs. This is due to the disappearance or production of ions of comparatively higher mobility, *e.g.* the addition of two moles of glycine, NH_2CH_2COOH to one mole of aqueous copper acetate solution decreases the solution conductivity because of the formation of a non-ionic chelated complex, $[Cu^{2+}(NH_2CH_2COO)_2]^{\circ}$

$$[Cu(H_2O)_x]^{2+} + 2CH_3COO^- + 2NH_2CH_2COOH \longrightarrow \underset{\text{Non-chelated complex}}{[Cu(NH_2CH_2COO)_2]^0} + 2CH_3COOH$$

Note that NH_2CH_2COO is acting as a bidentate ligand in $[Cu(NH_2CH_2COO)_2]^0$, hence the coordination number of Cu^{2+} in the complex is four.

This method can also be used to give useful information about the total number of ions (complex ions and simple ions both) given by a complex in solution and charge type on each ion. This point has been discussed for Co(III) ammines under Werner's Theory.

(10) Dipole moment measurements.

Dipole moment measurements are often used to distinguish between *cis-* and *trans-*isomers of a complex, *e.g.*, $[Pt^{II}(R_3P)_2Cl_2]^{\circ}$ has been isolated in α- and β- forms. The α- form has *zero* dipole moment and must, therefore, have collinear Pt—Cl and Pt—P bonds, *i.e.* it should be *trans-* form. The β- form has high dipole moment and is, therefore *cis-* form.

There are many other techniques such as infra-red spectra, nuclear magnetic resonance, electron-spin resonance etc. which also furnish valuable information on the structure of the complex. The discussion of these techniques is out of the scope of this book.

POLYNUCLEAR OR BRIDGED COMPLEXES

Definition

An atom of some of the ligands may have more than one free electron pairs and hence it may co-ordinate simultaneously with two or more metal atoms, *i.e.*, the ligand atom serves as a bridging atom between the two metal atoms. A ligand containing such an atom is called **bridging ligand** and the resulting complex is known as **bridged** or **polynuclear** (or **multinuclear**) **complex**. The term bridged complex is a better name, since the prefix *poly* usually denotes a high molecular weight, whereas these complexes are often only dimers or trimers. The bridged complexes may be *binuclear* (or *dinuclear*), *trinuclear*, etc. depending on the number of metal atoms with which the bridging ligand is linked.

Types and preparation of polynuclear complexes

There are numerous types of these complexes and their structures have been determined by X-ray diffraction. Some of the common types are .

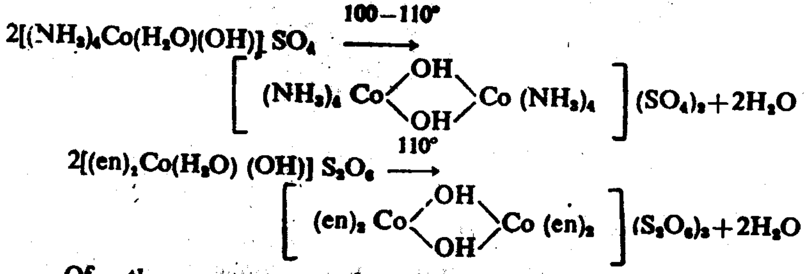
(1) **Complexes with —OH or —O— bridges** A typical example of this class is seen in the hydrolysis reactions of Th^{4+}.

$$2Th^{4+} + 2H_2O \rightleftharpoons [Th_2(OH)_2]^{6+} + 2H^+$$

$$2Th^{4+} + H_2O \rightleftharpoons [Th_2(OH)]^{7+} + H^+$$

In these polynuclear complexes of Th^{4+} the OH groups are shared by Th^{4+} ions.

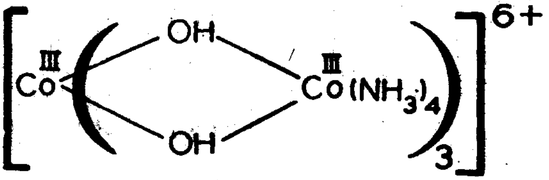
It has been shown that binuclear complex of Co (III) is obtained during the hydrolytic reaction of Co(III) compound in solution, *e.g.*



$$2[(NH_3)_4Co(H_2O)(OH)]SO_4 \xrightarrow{100-110°} \left[(NH_3)_4Co{<}\begin{matrix}OH\\OH\end{matrix}{>}Co(NH_3)_4\right](SO_4)_2+2H_2O$$

$$2[(en)_2Co(H_2O)(OH)]S_2O_6 \xrightarrow{110°} \left[(en)_2Co{<}\begin{matrix}OH\\OH\end{matrix}{>}Co(en)_2\right](S_2O_6)_2+2H_2O$$

Of the many polynuclear complexes of Co(III) containing OH bridges, the tetranuclear complex *viz*



$$\left[\overset{III}{Co}\left({<}\begin{matrix}OH\\OH\end{matrix}{>}\overset{III}{Co}(NH_3)_4\right)_3\right]^{6+}$$

is the most important and is prepared by the treatment of $[Co^{III}(NH_3)_4(H_2O)(Cl)]SO_4$ with cold alkali. This complex is

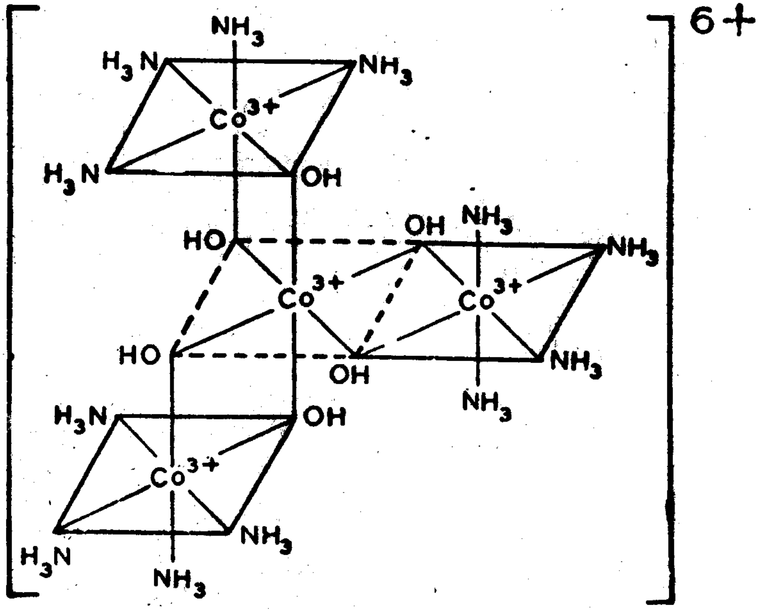


Fig. 11·5. An asymmetric tetranuclear complex of Co(III) asymmetric and one of the enantiomorphs is shown in Fig. 11·5. From this figure it may be noted that there are three pairs of OH^- groups around the central octahedron (shown by dotted lines). Each pair forms a bridge to a peripheral octahedron.

The complex shown in Fig. 11·6 is a good example of trinuclear complex of Co (III).

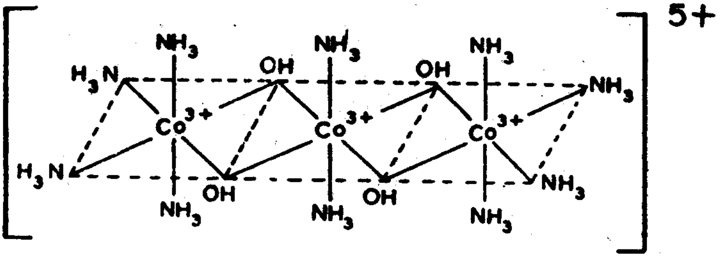


Fig. 11·6. Tetra-μ-hydroxo-decaammine tricobalt (III) cation.

A dinuclear Cr (III) complex which contains both chelating groups like ethylene diamine, $NH_2-CH_2-CH_2-NH_2$, (en) and bridging OH groups has been prepared. It is formulated as $[(en)_2\,Cr^{III}-(OH)_2-Cr^{III}(en)_2]^{4+}$ and its structure is shown below in Fig. 11·7.

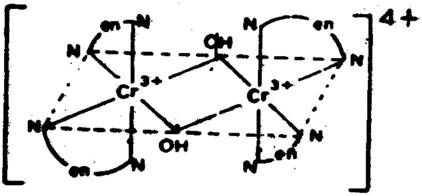
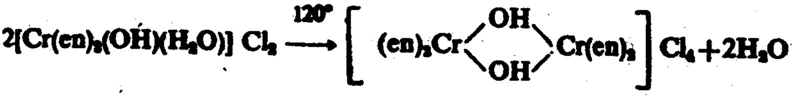


Fig. 11·7. Structure of $[(en)_2\,Cr^{III}-(OH)_2-Cr^{III}(en)_2]^{4+}$

It is prepared by heating $[Cr(en)_2\,(OH)\,(H_2O)]\,Cl_2$.



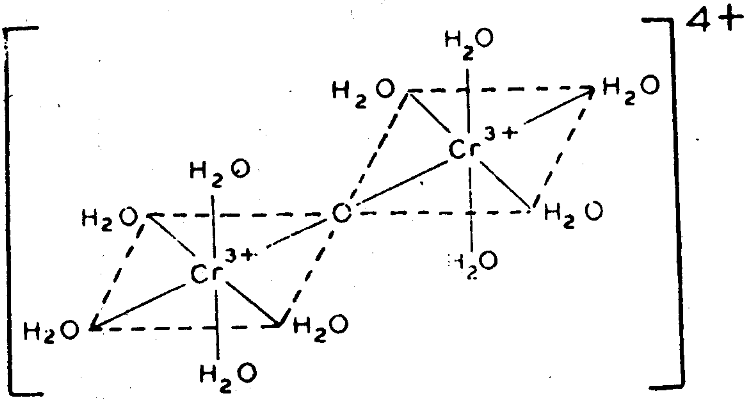
$$2[Cr(en)_2(OH)(H_2O)]\,Cl_2 \xrightarrow{120^\circ} \left[(en)_2Cr\begin{matrix}OH\\ \\OH\end{matrix}Cr(en)_2\right]Cl_4+2H_2O$$

It has recently been shown that oxidation of Cr^{2+} by two electron-oxidising agents like HClO or H_2O_2 gives dinuclear chromium complex, probably $[(H_2O)_5Cr^{III}-O-Cr^{III}(H_2O)_5]^{4+}$. The two electron oxidation occurs in steps with Cr^{4+} intervening.

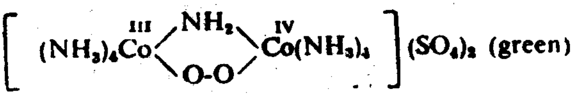
$$\underset{(Cr=+2)}{Cr^{2+}} + ClO^- \longrightarrow \underset{(Cr=+4)}{CrO^{2+}} + Cl^-$$

$$CrO^{2+} + Cr^{2+} \longrightarrow \underset{\text{dinuclear species}}{[Cr^{3+}\text{—}O\text{—}Cr^{3+}]^{4+}}$$

The structure of $[(H_2O)_5Cr\text{—}O\text{—}Cr(H_2O)_5]^{4+}$ is :

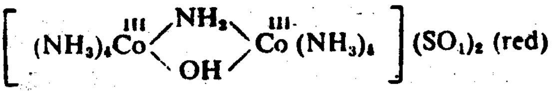


(2) **Complexes with —NH₂— or —NH— bridging groups.** Such complexes are common among the polynuclear complexes of Co(III). The complex mixture designated as Vortmann's sulphate is an example of such complexes. This is prepared by the air oxidation of ammoniacal solution of $Co(NO_3)_2$ followed by subsequent neutralisation with dil. H_2SO_4 in the cold. The chief constituents of the brown product produced in the above reaction are :



$$\left[(NH_3)_4\overset{III}{Co}\begin{matrix}NH_2\\ O\text{-}O\end{matrix}\overset{IV}{Co}(NH_3)_4\right](SO_4)_2 \text{ (green)}$$

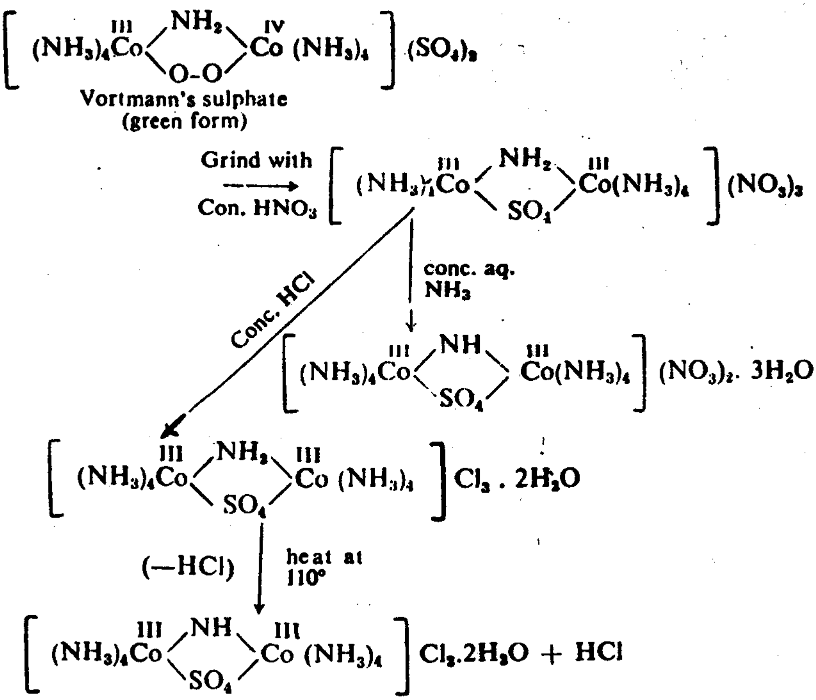
and



$$\left[(NH_3)_4\overset{III}{Co}\begin{matrix}NH_2\\ OH\end{matrix}\overset{III}{Co}(NH_3)_4\right](SO_4)_2 \text{ (red)}$$

The electron spin resonance studies of the green complex have shown that *one unpaired electron is spread* over the area between the two cobalt atoms, rather than being confined to just one of the cobalts. Thus it is impossible to assign integral oxidation numbers to two cobalt atoms in such complexes.

Co(III) complexes with bridging amido groups (—NH—) may sometimes be prepared by treating those containing bringing amino groups (—NH₂—) with base or by driving off acid by heating. The preparation of such complexes by using Vortmann's sulphate can be illustrated by the following reactions :



(3) **Complexes with peroxo bridges, —O—O—.** Complexes containing peroxo bridges between cobalt atoms are quite remarkable. The simplest of these is the brown ion, pentammino cobalt(III) μ-peroxo pentammino cobalt (III), $[(NH_3)_5Co-O-O-Co(NH_3)_5]^{4+}$ which is formed by the careful air oxidation of ammoniacal solutions of Co(II) salts.

$$2[Co(NH_3)_6]^{2+} + O_2 \longrightarrow \underset{\text{brown ions}}{[(NH_3)_5Co-O-O-Co(NH_3)_5]^{4+}} + 2NH_3$$

If the solution containing these brown ions is further oxidised (still carefully) by warming with dil. (1 : 1) HNO_3, a green complex, $[(NH_3)_5Co^{III}-O-O-Co^{IV}(NH_3)_5]^{5+}$ is obtained.

(4) **Complexes containing the anions like X_2 SO_4^{2-}, CH_3COO^- or CN^- as bridging groups.** Complexes containing the halide ions as bridging groups are known in the solid state but such bridges are often destroyed on solution in water. Some examples of such complexes are :

(*a*) Ferric chloride which is dimeric in the gaseous state, $(FeCl_3)_2$ in which each iron is at the centre of a tetrahedron and two tetrahedra share an edge and correspondingly two Cl ions.

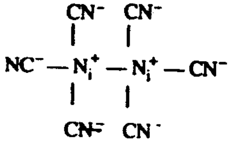
(*b*) Aluminium chloride which is also dimeric, $(AlCl_3)_2$ and has a similar structure in the gaseous state.

(*c*) Palladium (II) chloride in the solid state consists of infinite chains of square planar $PdCl_4$ groups in which each Cl^- ion is shared by adjacent Pd(II) species.

Often the structure of such compounds in the solid state is different from that in the gaseous state, *e.g.* in the gaseous state of Fe(III) chloride four chlorine atoms surround each iron while in the solid state six chlorine atoms surround each iron octahedrally.

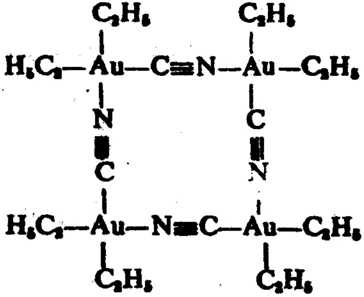
Complexes containing CH_3COO^- groups as bridging groups are those of Fe(III), *e.g.* in ferric acetate the composition corresponds to $Fe(CH_3COO)_3$, while the properties correspond to $[Fe_3(CH_3COO)_6](CH_3COO)_3$.

The complex $[Ni^{II}(CN_4]^{2-}$ can be reduced by solidum amalgam to red ion, $(N^{iI}(CN)_3]^{2-}$. This ion is readily oxidised and X-ray and magnetic studies have shown that it is dimeric in its crystalline potassium salt it contains cyano bridges as shown below :



$$\begin{array}{ccccccc} & & CN^- & & CN^- & & \\ & & | & & | & & \\ NC^- & - & N_i^+ & - & N_i^+ & - & CN^- \\ & & | & & | & & \\ & & CN^- & & CN^- & & \end{array}$$

Another example of the complex containing the CN^- bridging groups is R_2AuCN which is probably tetrameric, $(R_2AuCN)_4$:

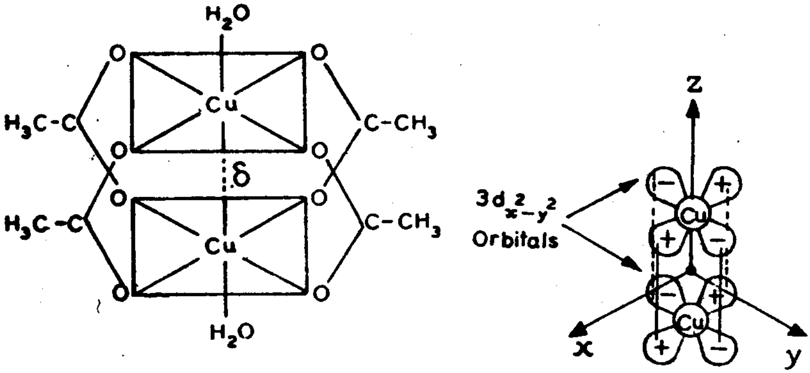


Cyanides of Pd (II), Pt (II), Ni (II) and Cu(I) have similar bridging CN^- groups.

(5) **Complexes with metal-to-metal bonds.** The examples of complexes in which metal-to-metal bonds are present are given below. Their structures are also mentioned.

Complex	*Structure*
$Mo_2Cl_8^{4+}$	An octahedron with Mo atoms on each apex and 8 Cl's on the 8 vertical edges of the octahedron.
$Nb_6Cl_{12}^{2+}$	An octahedron with Nb atoms on each apex and 12 Cl's on the 12 edges of the octahedron.
$Ta_6Cl_{12}^{2+}$	Same as $Nb_6Cl_{12}^{2+}$
$W_2Cl_9^{3-}$	Two WCl_6 octahedra share a face and hence three bridging Cl's ; W in centre of each octahedron.

Cu(II) acetate is dimeric in both solid and solution state: $[Cu(CH_3COO)_2]_2.2H_2O$. Each Cu(II) is coordinated in a square plane by four oxygens of the bridging acetato groups. The two H_2O molecules are attached one each to Cu(II). The copper-copper distance is short [Fig. 11·8 (*a*)] and this bond results from a lateral overlap of singly-filled $d_{x^2-y^2}$ orbitals of two Cu(II) ions ($Cu^{2+} \longrightarrow 3d_{xy}^2\, 3d_{yz}^2\, 3d_{xz}^2\, 3d_{z^2}^2\, 3d_{x^2-y^2}^1$) [see Fig. 11·8 (*b*)].



(*a*) Structure of dimeric copper acetate, $[Cu(CH_3COO)_2]_2 2H_2O$

(*b*) Schematic representation of the formation of a δ-bond between two Cu(II) ions in $[Cu(CH_3COO)_2]_2$ by the lateral overlap of $3d_{x^2-y^2}$ orbitals

Fig. 11·8. Structure of dimeric Cu (II) acetate, $[Cu(CH_3COO)_2]_2 \cdot 2H_2O$

Such type of metal-metal bond is called δ-bond and is different from a σ- and a π-bond. Such overlap leads to a partial quenching of the magnetic moment in copper acetate ($\mu = 1{\cdot}43$ B.M.).

(6) **Polynuclear carbonyls.** All transition metals with *odd atomic number* which form carbonyls give only polynuclear carbonyls. These may be prepared from simple carbonyls by photochemical reaction or by thermal decomposition, *e.g.*

$$2\,Re + 10\,CO \xrightarrow[\Delta]{\text{Pressure}} Re_2(CO)_{10}$$

$$\begin{array}{l} \quad \xrightarrow{h\nu} Fe_2(CO)_9 + CO \\ Fe(CO)_5 \\ \quad \xrightarrow{h\nu} Fe_3(CO)_{12} + 3CO \end{array}$$

Binuclear carbonyls of Mn (0) and Fe (0) are also important. These are formulated as $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$ and have carbonyl bridges. In these molecules there is also significant metal-to-metal bonding interaction. (*See* Figs. 11·9 and 11·10).

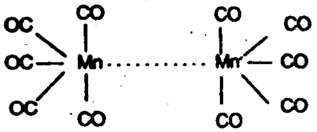


Fig. 11·9. Structure of binuclear $Mn_2(CO)_{10}$ carbonyl.

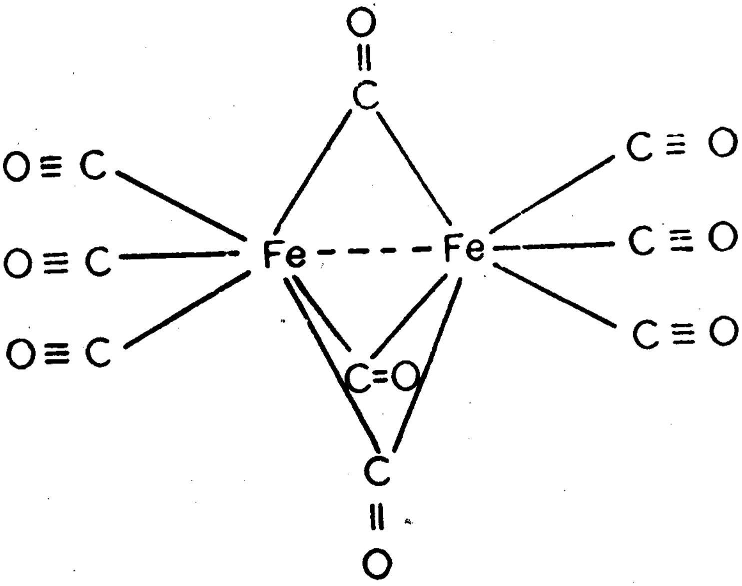
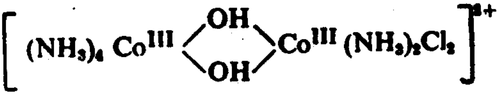


Fig. 11·10. Structure of binuclear $Fe_2(CO)_9$ carbonyl.

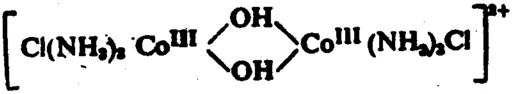
Coordination position isomerism in polynuclear complexes

In some polynuclear complexes to interchange the ligands between the metal nuclei which are present as a part of the complex is possible. This type of interchange of ligands gives rise to *coordination position isomerism, e.g.*



$$\left[(NH_3)_4\,Co^{III}\begin{smallmatrix}OH\\OH\end{smallmatrix}Co^{III}\,(NH_3)_2Cl_2\right]^{2+}$$

and



$$\left[Cl(NH_3)_3\,Co^{III}\begin{smallmatrix}OH\\OH\end{smallmatrix}Co^{III}\,(NH_3)_3Cl\right]^{2+}$$

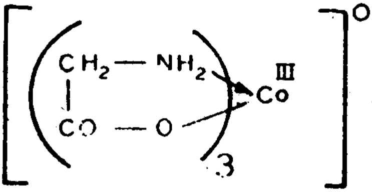
are coordination position isomers.

INNER METALLIC COMPLEXES

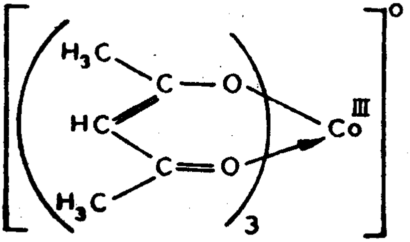
Definition

When the ligands like acetyl acetonato, glycinato etc. which have both neutral (donor) and anionic (acidic) groups coordinate with metallic cation, they form complexes in which both the coordination number and charge of the cation are satisfied simultaneously. Such complexes are called *inner-metallic complexes* or simply *inner complexes.*

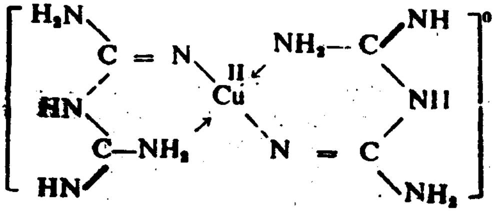
$[Co^{III}(gly)_3]^0$, $[Co^{III}(acac)_3]^0$, $[Cr^{III}(acac)_3]^0$, $[Cu^{II}(Big)_2]^0$, $[Cu^{II}(gly)_2]^0$ etc. are the important examples of such complexes. In these complexes the ligands gly^- (glycinato), $acac^-$ (acetylacetonato) and *Big* (biguanido) function as monobasic bidentate ligands, one of the groups being acidic and one being donor group. These complexes have the following formulae.



OR $[Co^{III}(gly)_3]^0$



OR $[Co^{III}(acac)_3]^0$



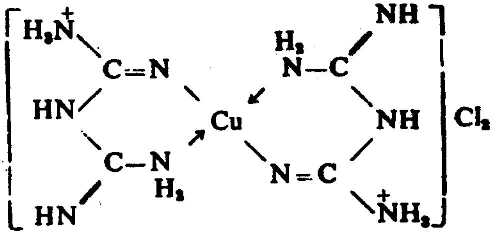
OR $[Cu^{II}(Big)_2]^0$

Since in these complexes both the coordination number and the charge of the metallic cation are satisfied by the complexing ligands in the coordination sphere, these complexes are non-electrolyte and are called *inner-metallic complexes of the first order.* On the other hand the complexes like $[Si^{IV}(acac)_3]Cl$ in which three $(acac)^-$-ligands satisfy only the coordination number of six of Si^{4+} but not the charge of +4 are ionic in nature and are termed as *inner-metallic complexes of the second order.* Other examples of such complexes are :

$$Na[Co^{II}(acac)_3],\ [B^{III}(acac)_2][Fe^{III}Cl_4]^-$$

$$Na[Co^{III}(NO_2)_2(acac)_2]\ \text{etc.}$$

Interestingly the coordinated ligand, *Big*⁻ in $[Cu(Big)_2]^0$ has one-NH_2 group which remains uncoordinated gets protonated with dilute acid (say HCl) to give a soluble, red-rose complex, $[Cu(Big\ H)_2]\ Cl_2$(I). Thus a first order complex gives a soluble inner complex when its uncoordinated group is protonoted



Soluble, red-rose complexes (I)

Properties of inner complexes

Main properties are :

(*i*) Many of them are insoluble in water but may be extracted into organic solvents immiscible with water. Their extractability is often a function of pH of the aqueous phase so that selective extraction and subsequent return to a new aqueous phase are possible.

(*ii*) There is sometimes pronounced colour changes during the formation of inner complexes. This permits colorimetric measurements.

(*iii*) Most of the inner complexes have low melting points and are volatile.

Applications

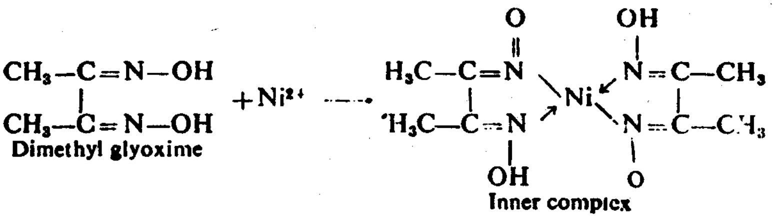
(*i*) Due to the electrical neutrality of these complexes they can be extracted into water-immiscible organic phase. This property is used in both analytical and industrial separations, *e.g.* α-theonyltrifluoroacetone (TTA) is used for the separation of hafnium and zirconium. This process is of great importance in nuclear reactor. Beryllium and scandium which are nuclear engineering metals have also been refined by solvent extraction in the preparation of TTA.

(*ii*) Inner complexes are also used in analytical chemistry for the estimation of several cations, e.g.

(*a*) The 8-hydroxyquinoline (oxin) coordinates with a number of cations to form inner complex. For each cation there is a definite pH range in which the formation of inner complex occurs :

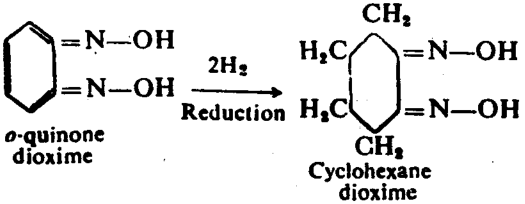
Cation	Cu^{2+}	Fe^{2+}	Al^{3+}	Th^{4+}	Mn^{2+}	Mg^{2+}
pH range	$\sim$2·7	2·8—11·2	4·2—9·8	4·8—8·8	5·9—10·0	$>$8·2

(*b*) Organic substances like dimethyl glyoxime are capable of forming inner complexes with a number of metallic ions, *e g.*


Dimethyl glyoxime

Inner complex

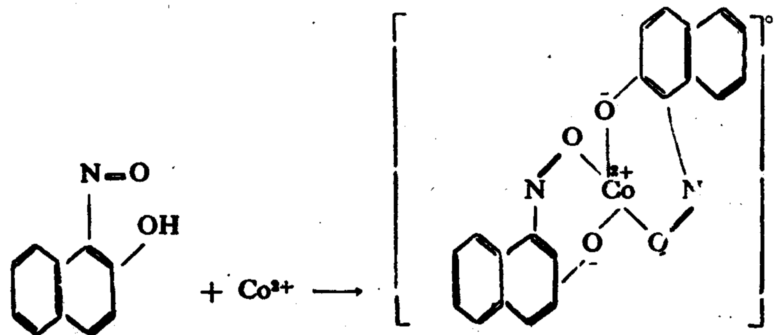
It may be noted that the compounds like *o*-quinone dioxime do not form inner complexes. However, it on being reduced, gives cyclohexane dioxime which forms a stable inner complex.



o-quinone dioxime

Cyclohexane dioxime

(*c*) α-nitroso-β-naphthol is commonly used as a reagent for Co^{2+} which forms red inner complex even in the acetic acid solution.


α-nitroso-β-naphthol

Inner complex

WERNER'S COORDINATION THEORY

Historical Development

It is difficult to state exactly when the first metal complex was discovered. Perhaps the earliest recorded coordination compound is Prussian blue, $KCN.Fe^{II}(CN)_2.Fe^{III}(CN)_3$, an artist colour. It was prepared accidentally in 1704 by a Berlin colour maker, Diesbach, by strongly heating animal wastes and Na_2CO_3 in an iron container. However the accidental discovery of hexaammine cobalt (III) chloride, $CoCl_3.6NH_3$ by Tassaert in 1799 marks the real beginning of coordination chemistry. Tassaert obtained it by mixing $CoCl_3$ and aqueous NH_3. He was unable to understand how $CoCl_3$ and NH_3, each of which is a stable compound, could combine to give yet another very stable compound, $CoCl_3.6NH_3$. No satisfactory answer could be given by chemists to explain the Tassaert's experimental observations until approximately 100 years later. During that time many coordination compounds of $CoCl_3$ with NH_3 were prepared and their properties studied. These compounds which were called metal ammines differed in their Cl^- ion reactivity, *i.e.* they gave different number of Cl^- ions as AgCl when treated with Ag^+ ions, *e.g.* the addition of a solution of $AgNO_3$ to a freshly prepared solution of $CoCl_3.6NH_3$ results in the immediate precipitation of all the three Cl^- ions as AgCl. The same experiment with $CoCl_3.5NH_3$ precipitates only two Cl^- ions. The results of such studies on the complete series of Co(III) ammines are summarised in Table 11·6.

Table 11·6. *Characteristics of Co(III) ammines*

Ammines (i.e. complexes)	*No. of Cl^- ions precipitated as AgCl by $AgNO_3$ solution*	*Molar conductivity range (ohm^{-1})*	*Total No. of ions given by complex in soln.*	*Charge type on ions*	*Ionic Formulation*
$CoCl_3.6NH_3$	3	430	4	(3+, 1−)	$[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$
$CoCl_3.5NH_3.H_2O$	3	430	4	(3+, 1−)	$[Co^{III}(NH_3)_5(H_2O)]^{3+}(Cl^-)_3$
$CoCl_3.5NH_3$	2	250	3	(2+, 1−)	$[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$
$CoCl_3.4NH_3$	1	100	2	(1+, 1−)	$[Co^{III}(NH_3)_4Cl_2]^+Cl^-$
$CoCl_3.3NH_3$	0	0	— (Non-electrolyte)	—	$[Co^{III}(NH_3)_3Cl_3]^0$ (Non-electrolyte)

Another property that was studied was the molar conductivities of their solutions at infinite dilution. This property gave useful information about the total number of ions given by the complex compound in solution and charge type on each ion. The results of this study for Co(III) ammines are also given in the same Table.

It may be seen from the Table that :

(*i*) The number of Cl^- ions given by the ammines as AgCl on the addition of $AgNO_3$ solution is 3, 3, 2, 1 and 0 respectively. This fact has been utilised while writing the ionic formulae of the ammines as given in the last column of the Table.

(*ii*) *The greater is the molar conductivity of the solution of the complex compound, the greater is the total number of ions (complex ions and simple ions both) given by it in solution.* Since the compounds give different number of ions in solution, it must be concluded that in some of the ammines the Cl^- ions exist in coordination sphere, [ ], while others exist as free ions outside the coordination sphere. The Cl^- ions in the coordination sphere behave differently from the Cl^- ions outside the coordination sphere on treatment with $AgNO_3$ solution.

(*iii*) The molar conductivity in the range of 430 ohm^{-1} for $CoCl_3 . 6NH_3$ is characteristic of (3+, 1−) charge type while that in the range (less than 10 ohm^{-1}) for $CoCl_3 . 3NH_3$ shows that this compound is non-electrolyte.

Werner's Theory

Several theories were proposed to explain the observed properties of Co(III) ammines and of other similar compounds like Pt(IV) ammines which had been prepared by then. It was only in 1893, that Werner presented a theory known as Werner's **coordination theory** which could explain all the observed properties of complex compounds. More important postulates of this theory are :

(*i*) Most elements exhibit two types of valencies : (*a*) *primary valency* and (*b*) *secondary valency.*

(*a*) **Primary valency.** This corresponds to oxidation state of the metal ion. This is also called *principal, ionisable* or *ionic valency.* It is satisfied by negative ions and its attachment with the central metal ion is shown by *dotted lines.*

(*b*) **Secondary or auxiliary valency.** It is also termed as **coordination number** (usually abbreviated as CN) of the central metal ion. It is *non-ionic* or *non-ionisable* (*i.e.* coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules. The ligands which satisfy the coordination number are directly attached to the metal atom or ion and shown by *thick lines.* While writing down the formulae these are placed in the coordination sphere along with the metal ion. These are directed towards fixed positions in space about the central metal ion, *e.g.* six ligands are arranged at the six corners of a regular octahedron with the metal ion at its centre. This postulate predicted the existence of different types of isomerism in coordination complexes and after 19 years Werner actually succeeded in resolving various coordination examples into optically active isomers.

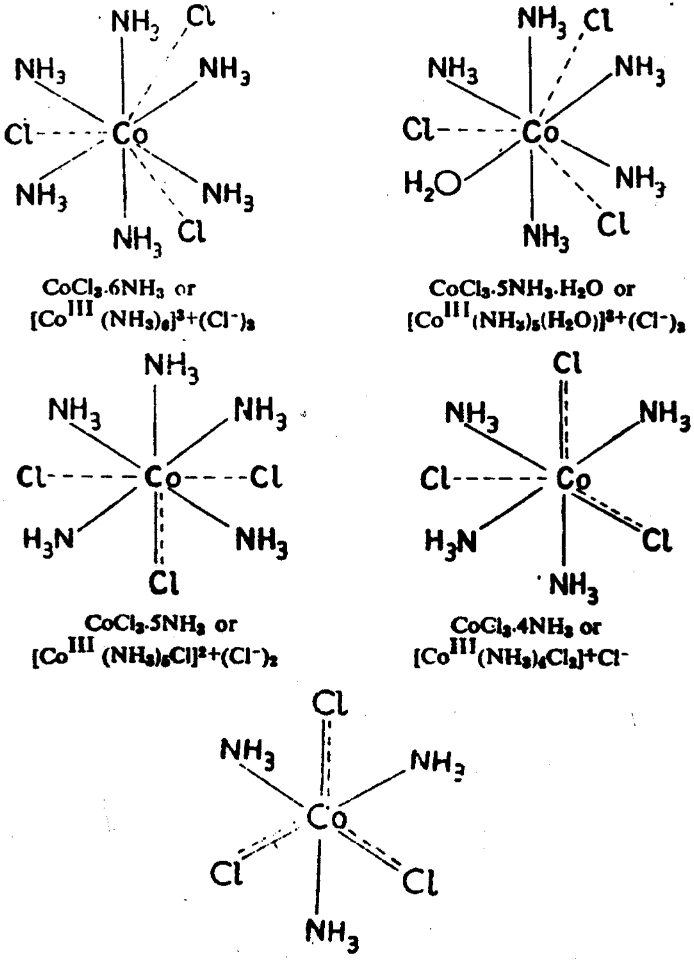
(*ii*) Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, *i.e.* it may satisfy both primary and secondary valencies since in every case the fulfilment of coordination number of the central metal ion appears essential (*see* the designations of $CoCl_3.5NH_3$, $CoCl_3 . 4NH_3$ and $CoCl_3.3NH_3$ as given in Fig. 11·11.

The properties of Co (III) ammines mentioned in Table 11·6 can be explained on the basis of the postulates mentioned above.

In all the ammines cobalt shows secondary valency (*i.e. coordination number*) of *six* and primary valency (*i.e* , *oxidation state*) of *three.*

Designation and Formation of Co (III) ammines. On the basis of postulates of his theory Werner designated the ammines as given in Fig. 11·11 · and formulated them as : $[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$, $[Co^{III}(NH_3)_5(H_2O)]^{3+}(Cl^-)_3$, $[Co^{III}(NH_3]_5Cl]^{2+}(Cl^-)_2$, $[Co^{III}(NH_3)_4\ Cl_2]^+Cl^-$ and $[Co^{III}(NH_3)_3Cl_3]^0$.

The molecule, $CoCl_3.6NH_3$ which is formulated as $[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$ has six NH_3 molecules that satisfy the secondary valency of the metal ion, *viz.*, Co^{3+} ion and their attachment with the central metal ion is shown by thick lines. The primary valency



$CoCl_3.6NH_3$ or $[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$

$CoCl_3.5NH_3.H_2O$ or $[Co^{III}(NH_3)_5(H_2O)]^{3+}(Cl^-)_3$

$CoCl_3.5NH_3$ or $[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$

$CoCl_3.4NH_3$ or $[Co^{III}(NH_3)_4Cl_2]^+Cl^-$

$CoCl_3.3NH_3$ or $[Co^{III}(NH_3)_3Cl_3]^0$

Fig. 11·11. Designations and formulations of Co(III) ammines on the basis of Werner's theory.

(*i.e.*, oxidation state of +3) is satisfied by three Cl^- ions which have been shown by dotted lines and are kept outside the coordination sphere. As all the three Cl^- ions are loosely bound, they are immediately precipitated as AgCl on the addition of $AgNO_3$ solution. Thus the solution of this compound should conduct current to give four ions in all *viz.* $[Co(NH_3)_6]^{3+}$ and $3Cl^-$ which has been confirmed by conductivity measurements.

In the molecule, $CoCl_3.5NH_3.H_2O$ which is formulated as $[Co^{III}(NH_3)_5(H_2O)]Cl_3$, five NH_3 molecules and one H_2O molecule satisfy the secondary valency (shown by thick lines in the designation). Primary valency is satisfied by three Cl^- ions. The solution of this compound also conducts current and gives in all four ions : one complex ion, $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ and three simple ions, $3Cl^-$.

In the molecule $CoCl_3.5NH_3$ which is formulated as $[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$ on the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both primary and secondary valency. Werner, therefore, showed its attachment with the central metal ion by a combined dashed-solid line, ———. This Cl^- ion, being non-ionic, is not precipitated as AgCl by Ag^+ ions and hence it is different from the other two Cl^- ions and has been placed along with five NH_3 molecules and central metal ion in the coordination sphere as shown in its formulation. The other two Cl^- ions, being ionic, are precipitated as AgCl by Ag^+ ions and the total number of ions obtained is three : one complex ion, $[Co^{III}(NH_3)_5Cl]^{2+}$ and two simple ions, $2Cl^-$. Thus the formulation, $[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$ satisfies both primary (=+3) and secondary (=C.N.=6) of Co^{3+}.

The formulation $[Co^{III}(NH_3)_4Cl_2]^+Cl^-$ of $CoCl_3.4NH_3$ shows that it has only one ionic Cl^- ion which gets precipitated as AgCl by $AgNO_3$ solution. The conductivity measurements show that it has two ions in solution *viz.* $[Co^{III}(NH_3)_4Cl_2]^+$ and Cl^-.

The formulation $[Co^{III}(NH_3)_3Cl_3]^0$ of $CoCl_3.3NH_3$ has no ionic Cl^- ions and hence it behaves as a non-electrolyte.

Example. The substance $CoBr_3.4NH_3.2H_2O$ has a molar conductivity of 420 ohm^{-1} at infinite dilution. Formulate the substance.

Solution. Since the conductivity value of 420 ohm^{-1} corresponds to (3+, 1−) charge type (see Table 11·6), the substance is formulated as

$[Co^{III}(NH_3)_4(H_2O)_2]^{3+}(Br^-)_3$ or simply as $[Co^{III}(NH_3)_4(H_2O)_2]Br_3$.

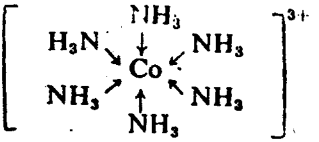
Sidgwick's Electronic Interpretation of Coordination

Until the advent of electronic theory of valency, Werner's theory was regarded as satisfactory. But with the advent of electronic theory of valency, it was considered necessary to make some modifications in it. Sidgwick accepted the Lewis concept of the two-electron covalent bond between two atoms in a molecule and introduced a new concept of coordinate bond (sometimes called the *semipolar* or *dative bond*) which, in fact, is an extension of Lewis concept of covalent bond. According to Sidgwick's concept the ligands attached with the central metal ion have atoms which have at least one unshared electron pair. He further says that when the ligands are attached with the central metal ion, they donate the electron pair to the central metal ion. The atoms which donate the electron pair to the central metal ion are called **donors** and the central metal ion which accepts the electron pair is called an **acceptor.**

According to Sidgwick the bond thus established between the ligands and the central metal ion is a *coordinate* or *dative* or *semi-polar bond.* This bond is not very different from a covalent bond.

The only difference lies in the mode of its formation. The bond formed is usually represented as M ⟵ L which indicates that the donor group, L (*i.e.* ligand) has donoted an electron pair to the metal ion, M (*i.e.* acceptor).

Thus on the basis of Sidgwick's concept, the structure of the complex ion, $[Co(NH_3)_6]^{3+}$, can be shown as



Evidently, in the formation of the bonds between the six
ds (which are NH_3 molecules) and the central metal Co^{3+} ion,
atom of each NH_3 molecule donates an electron pair to Co^{3+}
hus in all twelve electrons (*i.e.* six electron pairs) are
by six ligands to Co^{3+} ion. The donation of an electron
H_3 molecule has been represented by an arrow.

•

ncept of Effective Atomic Number—EAN concept (also
oble Gas Rule).

uggested that after the ligands have donated a cer-
ections to the central metal ion through bonding,
f electrons on the central atom, including those
in the bonding is called the **effective atomic**
central metal ion and in many cases this total
e. EAN) surrounding the coordinated metal
ic number of the inert gas.

Co(III) in $[Co(NH_3)_6]^{3+}$ can be calculated

=atomic number of Co $=27$ electrons
7 − 3 $=24$ electrons
$H_3)=2\times6$ $=12$ electrons
in $[Co(NH_3)_6]^{3+}$ $=24+12=36$

ly equal to the atomic number

Exceptions to EAN Rule.

Though in many cases the EAN is the same as the atomic number of the next inert gas, yet it is not always so—this total number of electrons *i.e.* EAN may be a few units more or less than the atomic number of the next inert gas. Complexes of Ni(II), Co(II), Ag(I) etc. which have more than one coordination number depending on the nature of the ligand, generally do not follow the EAN rule. Some metal atoms such as Fe(III) which has its coordination number equal to 4 in $[Fe^{III}Cl_4]^-$ and equal to 6 in $[Fe^{III}(CN)_6]^{3-}$ never follow this rule. The validity and exception of EAN concept is shown in Table 11.7.

EAN rule as applied to carbonyls

Metal carbonyls and its derivatives frequently obey EAN rule. By using this rule to metal carbonyls it is possible to predict whether a given carbonyl is a monomer.

Examples. The EAN of the central metal ion in the compounds *viz.* $Ni^0(CO)_4$, $Fe^0(CO)_5$, $Cr^0(CO)_6$, $Fe^{2+}(CO)_4Cl_2$, $Mn^+(CO)_5Br$, $Co^0(NO)(CO)_3$ and $Fe^0(NO)_2(CO)_2$ is 36. To estimate the EAN in these complexes it has been assumed that CO, Cl^- and Br^- contribute two electrons and NO, three electrons to the central metal ion.

$V(CO)_6$ is the only monomeric carbonyl which does not obey EAN rule.

Metal carbonyls of $M_x(CO)_y$ type also obey this rule, *e.g.* the EAN of Mn in $Mn_2(CO)_{10}$ is 36 as shown below :

This compound has the formula $(CO)_5Mn—Mn(CO)_5$ which shows that each Mn atom donates one electron to the formation of Mn—Mn bond and thus each metal atom shares two electrons :

Electrons from each Mn atom = atomic number of Mn	= 25
Electrons from 5 (: CO) = 5 × 2	= 10
Electron from Mn—Mn bond	= 1
EAN of Mn in $Mn_2(CO)_{10}$ = 25 + 10 + 1	= 36

Objections against Sidgwick's electronic interpretation of coordination and the electro-neutrality principle.

The concept of valency introduced by Sidgwick suffers from a number of defects such as those given below :

(*i*) The donation of electron pair or pairs by the ligand to the central cation would cause a reduction in the positive charge of the central cation. Due to the creation of a negative charge on the metal ion, a partial ionic character is developed in the complex, making it less stable.

How a negative charge is developed on the central metal ion can be explained for $[Fe(H_2O)_6]^{3+}$ ion by studying two cases as follows :

Table 11·7. *Illustration of the validity and exception of EAN concept.*

Complex ion	*Oxidation state (= x) of the central metal ion*	*No. of electrons in the central metal ion before combination = At. No. (Z) of the central metal ion*	*No. of electrons donated by ligands (n_L)*	*EAN of the central metal ion = [(Z−x)+n_L]*	*Next inert gas with its atomic number*
$[Pt^{IV}(NH_3)_6]^{4+}$	+4	78	2×6=12	(78−4)+12=86	Rn_{86}
$[Fe^{II}(CN)_6]^{4-}$	+2	26	2×6=12	(26−2)+12=36	Kr_{36}
$[Fe^{III}Cl_4]^{-}$	+3	26	2×4=8	(26−3)+8=31	Kr_{36}
$[Fe^{III}(CN)_6]^{4-}$	+3	26	2×6=12	(26−3)+12=35	Kr_{36}
$[Cr^{III}(NH_3)_6]^{3+}$	+3	24	2×6=12	(24−3)+12=33	Kr_{36}
$[Ni^{II}(NH_3)_6]^{2+}$	+2	28	2×6=12	(28−2)+12=38	Kr_{36}
$[Pd^{II}Cl_4]^{2-}$	+2	46	2×4=8	(46−2)+8 =52	Xe_{54}
$[Pt^{II}(NH_3)_4]^{2+}$	+2	78	2×4=8	(78−2)+8 =84	Rn_{86}
$[Ag^{I}(NH_3)_2]^{+}$	+1	47	2×2=4	(47−1)+4 =50	Xe_{54}
$[Ni^{II}(en)_3]^{2+}$	+2	28	4×3=12	(28−2)+12=38	Kr_{36}

(*a*) *Each of the six Fe—O bonds is 100 per cent covalent.* If it is assumed that the Fe—O bonds in $[Fe(H_2O)_6]^{3+}$ ion are 100 per cent covalent (*i.e.* equal sharing of each electron pair between the Fe- and O-atoms) Fe-atom and O-atom would each 'own' one half of each electron pair. Thus each O-atom in effect would lose one electron and the Fe-atom would gain in all six electrons. Thus a formal charge of —3 would exist on Fe-atom and each of the six O-atoms would bear a positive charge of unity.

(*b*) *Each of the six Fe—O bonds is 50% covalent and 50% ionic.* If it is assumed that each of the six Fe—O bonds is 50% covalent and 50% ionic, Fe-atom would 'own' one quarter of each electron (*i.e.* ¼ electron). Now since there are six electron pairs (*i.e.* 12 electrons), the Fe-atom virtually gains a total of three electrons ($\frac{1}{4} \times 12 = 3$) and Fe-atom is thus rendered exactly neutral (+3 charges on Fe^{3+} ion are neutralised by the three negative charges of 3 electrons). Each O-atom which 'owns' three-quarters of an electron ($1 - \frac{1}{4} = \frac{3}{4}$) would have a $+\frac{1}{4}$ charge. This is shown below in Fig. 11·12.

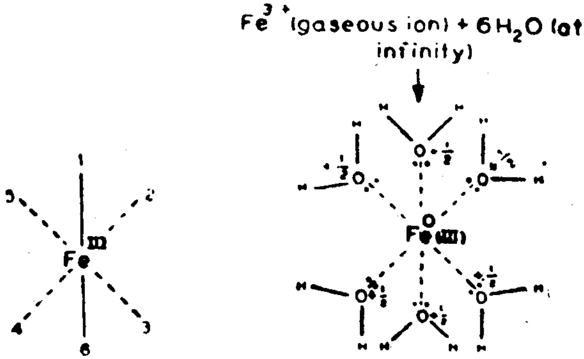


Fig. 11·12. +3 charges on Fe^{3+} ion in $[Fe^{III}(H_2O)_6]^{3+}$ are neutralised by the three negative charges of 3 electrons gained by Fe-atom. Water molecules shown at 1 and 6 positions are lying on an axis at right-angles to the plane having the four H_2O molecules shown at 2, 3, 4 and 5 positions.

Now the O-atoms that are reluctant to bear a positive charge would cause a displacement of the electrons in the O—H bonds towards the O-atoms. The net effect would be that a positive charge on each H-atoms would be developed. If in this process the O-atoms become exactly neutral, each of the twelve H-atoms would bear a charge of $+\frac{1}{4}$. This is shown in Fig. 11·13. Total positive charge borne by twelve H-atoms would thus be equal to $+\frac{1}{4} \times 12 = +3$. The charge of +3 on the complex ion, $[Fe(H_2O)_6]^{3+}$ would be that borne by twelve H-atoms.

According to Pauling's *electoneutrality principle, the overall* charge distribution on each atom in species like $[Fe(H_2O)_6]^{3+}$ would depend on the relative electronegativity values of iron and oxygen atoms. Electroneutrality principle requires that the bonds in

$[Fe(H_2O)_6]^{3+}$ have some ionic character. In other words the electron pair is not equally shared between Fe- and O-atoms but is attracted more strongly to the O-atom. This prevents the accumulation of negative charge on the Fe-atom and is in keeping with the greater electronegativity value of O-atom as compared to Fe-atom.

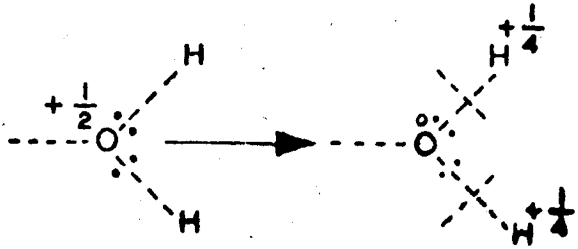


Fig. 11·13. Dissipation of the $+\frac{1}{2}$ charge from the oxygen atom to two hydrogen atoms by the displacement of the bonding electron pairs towards the oxygen atom.

(*ii*) Another objection is that electron pair used by H_2O, NH_3 and many other neutral molecules for donation purpose is $2s^2$ electron pair. This $2s^2$ electron pair has no bonding characteristics, and if these electrons, in order to make them useful for bonding purpose, are excited to higher energy level, there is required more energy than what is actually available in the bond formation. The answer to this objection may lie in the re-organisation of energy levels in the bonding atom to form hybrid bonds.

(*iii*) Finally, there are complexes which are predominantly ionic in character and hence the forces acting between the central atom and the ligands may be regarded as essentially electrostatic. Fluoro complexes of metals provide examples of such type of complexes.

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12

Nature of Metal-Ligand Bonding In Complexes

To explain the nature of bonding in transition metal complexes, three different theories are generally used.

(*i*) *Valence Bond Theory*, VBT (due to L. Pauling and J. L. Slater, 1935).

(*ii*) *Crystal Field Theory*, CFT (due to H. Brethe, 1929 and J. Van Vleck, 1932).

(*iii*) *Ligand Field Theory*, LFT or *Molecular Orbital Theory*, MOT (due to J. Van Vleck, 1935).

These are discussed below :

VALENCE BOND THEORY (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of central metal ion in its ground state, kind of bonding, geometry (*i.e.*, shape) and magnetic properties of the complexes. This is based on the following assumptions :

(*i*) *The central metal atom or ion* (as the case may be) *makes available a number of empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These are vacant, equivalent in energy and have definite geometry.* The most commonly encountered hybridisations in complexes are given in Table 12·1.

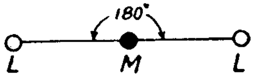
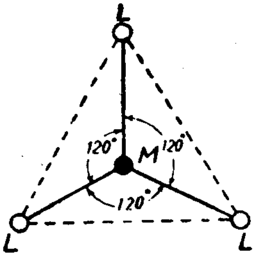
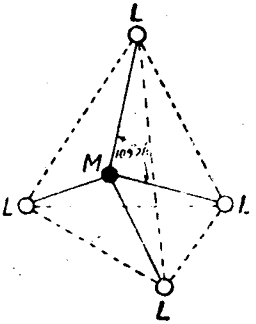
(*ii*) The ligands have at least one σ-orbital containing *a lone pair of electrons.*

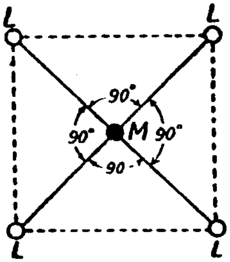
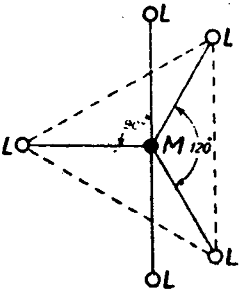
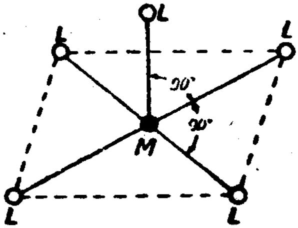
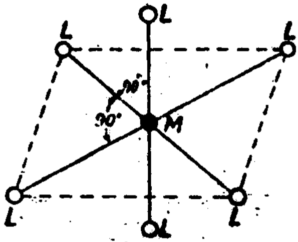
(*iii*) Vacant hybrid orbitals of the metal atom or ion *overlap with the filled* (containing lone pair of electrons) σ-orbitals of the ligands to form ligand → metal σ-bond (represented as $M \overset{\sigma}{\rightarrow} L$). This bond which is generally known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.

Table 12·1. *Important types of hybridisation occurring in the first row transition metal complexes.*

Notes. (*i*) C. N. = Coordination number of the central metal, M indicated by black circles

(*ii*) L = Ligands indicated by white circles. These may be the same or different.

C.N.	*Type of hybridisation*	*Geometry of the hybrid orbitals or complex*	*Examples of complexes*
2	*sp* ($4s\ 4p$)	Linear or diagonal  	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2 ($4s\ 4p^2$)	Trigonal planar  	$[HgI_3]^-$
4	sp^3 ($4s\ 4p^3$)	**Tetrahedral**  	$[Ni(CO)_4]^0$, $[Zn(NH_3)_4]^{2+}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, $[MnX_4]^{2-}$, $[NiX_4]^{2-}$, $X = Cl^-, Br^-, I^-$

C.N.	*Type of hybridisation*	*Geometry of the hybrid orbitals or complex*	*Examples of complexes*
4	dsp^2 $(3d_{x^2-y^2}$ $4s\ 4p_x\ 4p_y)$	Square planar 	$[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$ $[Cu(NH_3)_4]^{2+}$
5	dsp^3 $(3d_{z^2}4s4p^3)$	Trigonal bipyramidal 	$[CuCl_5]^{3-}$, $[Fe(CO)_5]^0$
5	sp^3d $(4s\ 4p^3$ $4d_{x^2-y^2})$	Square pyramidal 	$[SbF_5]^{2-}$, IF_5
6	d^2sp^3 $(3d_{x^2-y^2}$ $3d_{z^2}\ 4s\ 4p^3)$	Inner-orbital octahedral	$[Cr(NH_3)_6]^{3+}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ etc.
	sp^3d^2 $(4s\ 4p^3$ $4d_{x^2-y^2}$ $4d_{z^2})$	Outer-orbital octahedral 	$[FeF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ etc.

Pauling has made a use of magnetic measurements to find out the number of unpaired electrons (*n*) in a complex. According to him the number of unpaired electrons (*n*) and the geometries of the complex ions having the central metal ion with configurations d^1 to d^9 are related to each other as shown in Table 12·2.

Table 12·2. *No. of unpaired electrons (n) and geometry of complexes.*

d^x-Configuration	*Number of unpaired electrons (n) for different geometries*			
	Octahedral		*Tetrahedral* (sp^3)	*Square planar* ($d_{x^2-y^2}\,s.p_x.p_y$)
	Inner-orbital [$(n-1)d^2.ns.np^3$]	*Outer-arbital* ($ns.np^3.nd^2$)		
d^1	1	1	1	1
d^2	2	2	2	2
d^3	3	3	3	3
d^4	2	4	4	4
d^5	1	5	5	3
d^6	0	4	4	2
d^7	1	3	3	1
d^8	0	2	2	0
d^9	1	1	1	1

Now let us apply the assumptions of VBT to the formation of the following types of complexes :

(A) **Octahedral complexes.** [$(n-1)d^2.ns.np^3$ or $ns.np^3.nd^2$-hybridisation] :

Since d_{z^2} and $d_{x^2-y^2}$ orbitals lie directly in the path of the ligands, it is these orbitals which are used in the $(n-1)d^2.ns.np^3$ or $ns.np^3.nd^2$-octahedral hybridisation. These orbitals are generally referred to as e_g-set of orbitals.

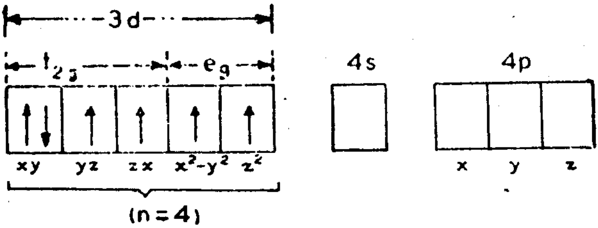
Let us consider the formation of $[Co^{III}(NH_3)_6]^{3+}$ and $[Co^{III}F_6]^{3-}$ ions. Both of these ions are octahedral ions, since the C.N. of the central metal ion is 6 in each case, and are of the same metal ion, Co^{3+}. $[Co(NH_3)_6]^{3+}$ contains strong (er) ligands while $[CoF_6]^{3-}$ has weak (er) ligands.

(*i*) **$[(Co^{III}(NH_3)_6]^{3+}$ ion.** Pauling originally called such complexes **covalent complexes,** since according to him the metal-ligand bonds in such complexes are primarily covalent. He further says that in covalent complexes electrons in the 3*d*-orbitals of the metal ion are paired to vacate two 3*d*-orbitals (namele $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals) which are occupied by the ligand electrons to form six $(3d)^2$ $(4s)$ $(4p)^3$ hybrids.

On the basis of VBT the formation of this complex ion has been explained as follows :

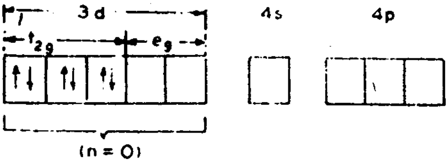
In this complex ion Co is present as Co^{3+} ion whose electronic configuration $(3d^6 4s^0 4p^0)$ is shown at (*a*) : (*n*=No. of unpaired electrons).

(*a*) Co^{3+} $(3d^6)$ (Ground state)



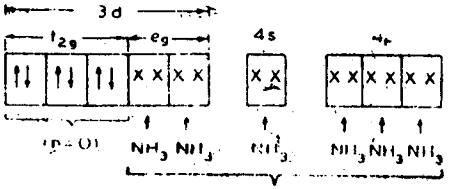
In order to accomodate the six electron pairs donated by six ligands (6 : NH_3 molecules), six vacant hybrid orbitals namely $e_g^2sp^3$ must be made available. It can be done by transferring the two unpaired electrons (one being in $3d_{x^2-y^2}$ and the other in $3d_{z^2}$ orbital) to the $3d_{yz}$ and $3d_{zx}$ orbitals. Thus in $[Co^{III}(NH_3)_6]^{3+}$ ion Co^{3+} has the configuration shown at (*b*).

(*b*) Co^{3+} in $[Co(NH_3)_6]^{3+}$ ion



The six electron pairs donated by six NH_3 molecules will be entering the hybrid orbitals formed by combining two 3*d*-orbitals (namely $3d^2_{x^2-y^2}$ and $3d_{z^2}$ orbitals), one 4*s* and three 4*p*- (*i.e.* $4p_x$, $4p_y$ and $4p_z$-orbitals) orbitals. Thus the configuration of $[Co(NH_3)_6]^{3+}$ ion will be as shown at (*c*). × × represents an electron pair denoted by each NH_3 molecule. The two electrons of this pair have opposite spins.

(*c*) $[Co(NH_3)_6]^{3+}$ ion



six $(3d)^2$ $(4s)^1$ $(4p)^3$ hybrids having 12 electrons donated by six ligands, 6: NH_3 molecules–inner orbital complex

Evidently, since $[Co(NH_3)_6]^{3+}$ ion has no unpaired electron, it should be diamagnetic. Actually this ion has been found diamagnetic.

Here it may be noted that the *d*-orbitals used in the formation of octahedral d^2sp^3 hybrids (six hybrids) are from a lower shell than the *s*- and *p*-orbitals, since *d*-orbitals are 3*d*-orbitals while *s*- and *p*-orbitals are 4*s*- and 4*p*-orbitals *i.e.* for 3*d*-orbitals, $n=3$ and for 4*s*- and 4*p*-orbitals, $n = 4$ (n = Principal quantum number). Complexes using the inner *d*-orbitals (which are 3*d*-orbitals for the first row transition elements) are called **"inner orbital' complexes** by Huggin. Thus, in general, the complexes which use two $(n-1)d$ [namely $(n-1)d_{z^2}$ and $(n-1)d_{x^2-y^2}$-orbitals], one *ns*-and three *np*-orbitals in their octahedral hybridisation scheme are the "inner orbital" complexes. In our present case the scheme of octahedral hybridisation is $(3d)^2\,(4s)\,(4p)^3$.

The formation of the inner-orbital (*i e.*, covalent) octahedral complexes of d^4, d^5, d^6, d^7 and d^8 ions of 3*d*-series elements on the basis of VBT has been explained by the scheme shown in Table 12·3. In this table (*i*) the electronic configuration shown at (*a*) is that of the free metal ion while that shown at (*b*) is that of the same metal ion in the complex (*ii*) n_1 and n_2 are the number of unpaired electrons in the free metal ion and the complex respectively. (*iii*) crosses represent the electrons donated by the ligands which have been denoted by L.

It will be seen from the table that the number of unpaired electrons, n_2, in the complex is less than that in the free-metal ion, *i.e.* $n_2 < n_1$ in each case. It is for this reason (namely $n_2 < n_1$) that the value of the experimental magnetic moment, μ_{exp}, for these complexes is less than μ_S value of the free metal ion calculated from "spin-only" formula ;

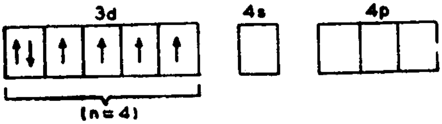
$$\mu_S = \sqrt{n(n+2)}\ \text{B.M}\ ,$$

i.e.

$$\mu_{exp} < \mu_S.$$

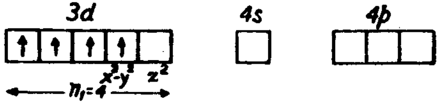
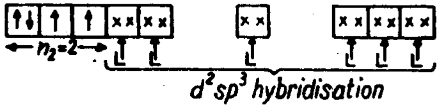
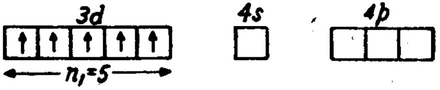
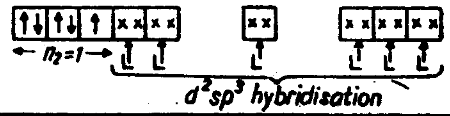
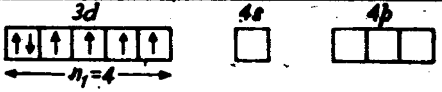
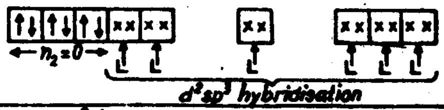
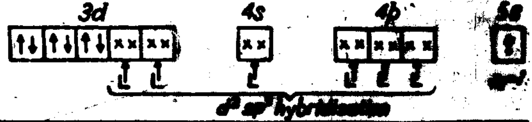
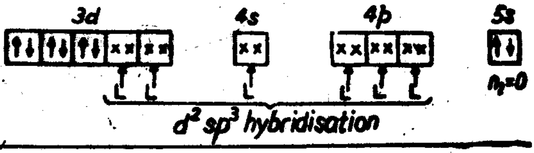
(*ii*) **$[Co^{III}F_6]^{3-}$ ion.** Electronic configuration of Co^{3+} ion is shown at (*a*) below :

(*a*) $Co^{3+}(3d^6)$
(Ground state)



Physical measurements have shown that $[CoF_6]^3$ ion has paramagnetic character corresponding to the presence of four unpaired electrons in 3*d*-orbital. Thus, to get six d^2sp^3 hybrid orbitals none of the five electrons in 3*d*-orbitals should be disturbed but should be allowed to remain unpaired as they are in the free Fe^{3+} ion.

Table 12·3. *Formation of inner-orbital octahedral complexes (d^2sp^3-bonding) of d^4, d^5, d^6, d^7, and d^8 ions of 3d-series elements on the basis of VBT.*

d^x ion		Inner-orbital octahedral complexes (d^2sp^3 hybridisation)
d^4	(a)	
	(b)	
d^5	(a)	
	(b)	
d^6	(a)	
	(b)	
d^7	(a)	
	(b)	
d^8	(a)	
	(b)	

That $\mu_{exp} < \mu_s$ is quite evident from Table 12·4.

Table 12·4. *Comparison of μ_{exp} and μ_s values for some typical inner-orbital octahedral complexes.*

Inner-orbital complex ion	*d^n-configuration*	n_1	n_2	μ_s (*in BM*)	μ_{exp} (*in BM*)
$[Cr^{II}(dipy)_3]^{2+}$	d^4	4	2	4·90	3·3
$[Mn^{II}(CN)_6]^{4-}$	d^5	5	1	5·92	1·8
$[Mn^{III}(CN)_6]^{3-}$	d^4	4	2	4·90	3·2
$[Fe^{II}(dipy)_3]^{2+}$	d^6	4	0	4·90	0·0
$[Fe^{III}(phen)_3]^{3+}$	d^5	5	1	5·92	2·5
$[Co^{II}(NO_2)_6]^{4-}$	d^7	3	1	3·87	1·8
$[Co^{III}(NH_3)_6]^{3+}$	d^6	4	0	4·90	0·0

In Table 12·4 *dipy* = 2, 2′-dipyridyl and *phen* = *o*-phenanthroline.

How to explain then the formation of this complex ion ? To explain its formation two suggestions have been put forward :

(*i*) **Pauling's suggestion.**

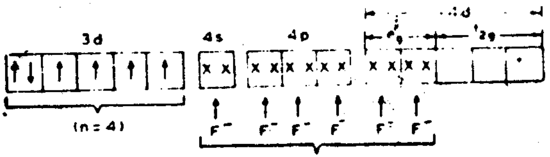
Pauling originally suggested that in the complex ions such as $[CoF_6]^{3-}$ ion the metal-ligand bonds are primarily "ionic" and not covalent (as in the inner-orbital complexes) and the *d*-electrons in the complex ion are, therefore, not required to pair but are allowed to remain unpaired just as they are in the free Co^{3+} ion. Thus he assumed that the metal ion *d*-orbitals are left free to accommodate only the metal ion electrons and the ligand electrons are contained in separated orbitals located primarily on the ligand. According to him when electronegative ligands are involved, the electrostatic bonding takes place which does not disturb the electrons of the *d*-orbitals. The use of the term "ionic" for such strongly paramagnetic complexes was abandoned, when it became known that many of such paramagnetic complexes such as Fe $(acac)_3$, behave like typical covalent compounds.

(*ii*) **Huggin's suggestion (1937)—Outer-orbital octahedral complexes**

To account for the paramagnetic nature of the complexes like $[CoF_6]^{3-}$ Huggin assumed that the *d*-orbitals involved in the hybridisation process to form six hybrid orbitals are not 3*d*-orbitals (as in case of inner-orbital octahedral complexes) but are 4*d*-orbitals so that the four 3*d*-orbital electrons remain unpaired which explain the paramagnetic character of $[CoF_6]^{3-}$ ion.

Thus $[CoF_6]^{3-}$ ion can be represented as shown at (*b*) below :

(*b*) $[Co^{III}F_6]^{3-}$ ion



six $(4s)^1 (4p)^3 (4d)^2$ hybrids having 12 electrons donated by six ligands, $6F^-$; outer-orbital complex.

Complexes such as $[CoF_6]^{3-}$ are called "outer-orbital" complexes, since the *d*-orbitals involved in the octahedral hybridisation scheme are from the same shell as the *s*-and *p*-orbitals as is evident from the fact that in the present case the principal quantum number, *n* for all the three orbitals (*s*-, *p*- and *d*-orbitals) being used in the formation of six hybrids is four. In general, complexes which use one *ns*-, three *np*-and two *nd*-orbitals (nd_{z^2} and $nd_{x^2-y^2}$ orbitals) to form the six sp^3d^2 hybrids are called outer-orbital complexes. Thus, in the outer-orbital complexes of the cations derived from the elements of the first row of transition series elements the *d*-orbitals are 4*d*-orbitals while in the inner-orbital complexes of the same cations the *d*-orbitals are 3*d*-orbitals. In both types of complexes *d*-orbitals are d_{z^2}- and $d_{x^2-y^2}$-orbitals which are called e_g-set of orbitals.

In $[Co^{III}F_6]^{3-}$ ion, the six hybrid orbitals are formed from one 4*s*-, three 4*p*- (*i.e.* $4p_x$-, $4p_y$- and $4p_z$-orbitals) and two 4*d*- (*i.e.* $4d_{x^2-y^2}$ and $4d_{z^2}$-orbitals) orbitals.

At present it has become usual to call the "ionic complexes" as "outer-orbital complexes" and the "covalent complexes" as "inner-orbital complexes". These two classes of complexes are also called *spin-free* and *spin-paired* (by Nyholom), *high-spin* (abbreviated as HS) and *low-spin* (abbreviated as LS) (by Orgel) and *hypo-ligated* and *hyper-ligated* (by Pauling) complexes.

The formation of outer-orbital octahedral complexes (*i.e.* ionic complexes) of d^4, d^5, d^6, d^7 and d^8 ions of 3*d*-series elements is explained in Table 12·5. From this table it may be seen that the metal ion in these complexes has the same electronic configuration as it has in the free metal ion (*i.e.* ground state). Thus, in case of these complexes $n_1 = n_2$ and consequently μ_S values are comparable with μ_{exp} values (Table 12·6).

Generally it is seen that the outer-orbital complexes are formed with more electronegative ligands (*e g.* oxygen, fluorine, etc.), while inner-orbital complexes are formed with ligands of low electronegativity (*e.g.* phosphorus and arsenic) especially when $d\pi$-$d\pi$ bonding is possible.

Table 12·5. *Formation of outer-orbital octahedral complexes (sp^3d^2-bonding) of d^4, d^5, d^6, d^7 and d^8 ions of 3d-series elements on the basis of VBT.*

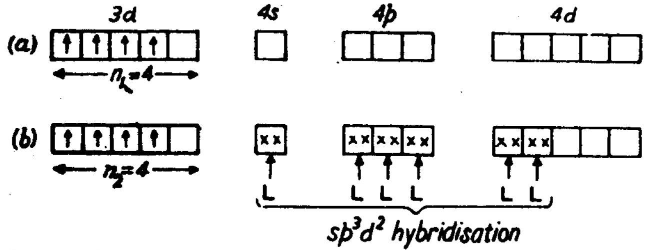
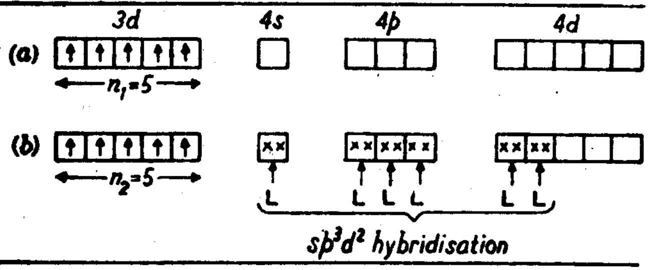
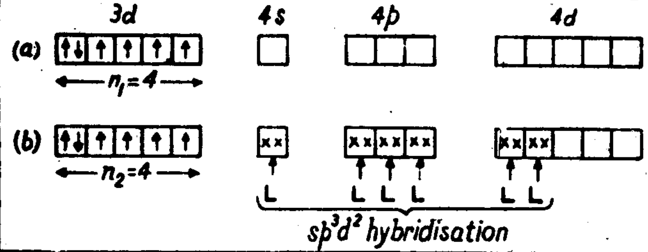
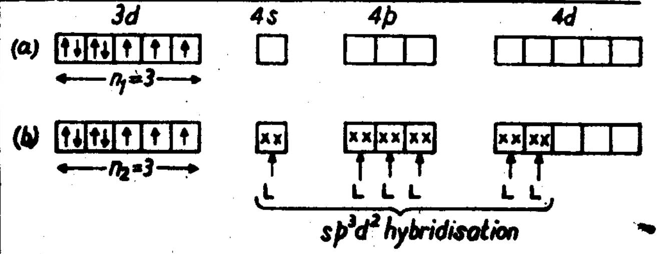
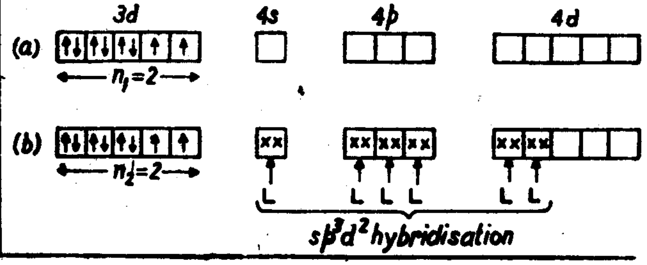
d^x ion	Outer-orbital octahedral complexes (sp^3d^2 hybridisation)
d^4	
d^5	
d^6	
d^7	
d^8	

Table 12·6. *Comparison of μ_{exp} and μ_s values for some outer-orbital octahedral complexes.*

Outer-orbital complexes ions	*d^n-configuration*	n_1	n_2	μ_s *(in BM)*	μ_{exp} *(in BM)*
$[Mn^{II}(CNS)_6]^{4-}$	d^5	5	5	5·92	5·1
$[Mn^{III}(acac)_3]^0$	d^4	4	4	4·90	5·0
$[Fe^{II}(en)_3]^{2+}$	d^6	4	4	4·90	5·5
$[Co^{III}F_6]^{3-}$	d^6	4	4	4·90	5·3

Following ions give both inner-and outer-orbital complexes :

Mn^{2+}, Mn^{3+} ; Fe^{2+}, Fe^{3+} ; Co^{2+} and Co^{3+}

Outer orbital complexes include high-spin complexes of d^4, d^5 and d^6 ions and complexes of d^7, d^8, d^9 and d^{10} ions.

Examples of inner-and outer-orbital octahedral complexes are given below :

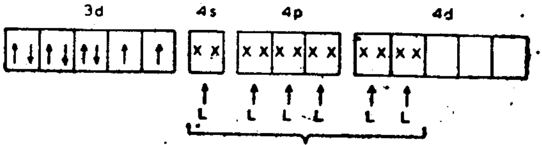
Inner-orbital complexes : $d^3 \longrightarrow [Cr^{III}(NH_3)_6]^{3+}$; $d^4 \longrightarrow [Cr^{II}(CN)_6]^{4-}$, $[Mn^{III}(CN)_6]^{3-}$; $d^5 \longrightarrow [Fe^{III}(CN)_6]^{3-}$; $d^6 \longrightarrow [Fe^{II}(CN)_6]^{4-}$, $[Co^{III}(NO_2)_6]^{3-}$, $[Co^{III}(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$ $[Pt^{IV}(NH_3)_6]^{4+}$; $d^7 \longrightarrow [Co^{II}(NO_2)_6]^{4-}$.

Outer-orbital complexes : $d^3 \longrightarrow [Cr^{III}(H_2O)_6]^{3+}$, $[Cr^{III}(NH_3)_6]^{3+}$; $d^4 \longrightarrow [Cr^{II}(H_2O)_6]^{2+}$, $[Mn^{III}(H_2O)_6]^{3+}$; $d^5 \longrightarrow [Mn^{II}(H_2O)_6]^{2+}$, $[Fe^{III}(H_2O)_6]^{3+}$, $[Fe^{III}F_6]^{3-}$; $d^6 \longrightarrow [Fe^{II}(H_2O)_6]^{2+}$, $[Fe^{II}(NH_3)_6]^{2+}$; $d^7 \longrightarrow [Co^{II}(H_2O)_6]^{2+}$; $d^8 \longrightarrow [Ni^{II}(NH_3)_6]^{2+}$, $[Ni^{II}(H_2O)_6]^{2+}$; $d^9 \longrightarrow [Cu^{II}(NH_3)_6]^{2+}$; $d^{10} \longrightarrow [Cu^{I}(NH_3)_6]^{+}$.

Example. *Show that all octahedral complexes of Ni^{2+} must be outer-orbital complexes.*

Solution. The electronic configuration of Ni^{2+} ion $(3d^8)$ indicates that two inner *d*-orbitals (3*d*-orbitals) cannot be made available to allow d^2sp^3 hybridisation. However by using two 4*d*-orbitals, sp^3d^2 hybridisation may be possible.

$[Ni^{II}L_6]^{2+}$ ion

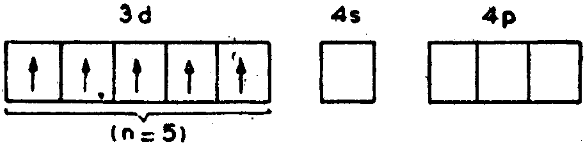


sp^3d^2 hybridisation—outer orbital octahedral complex

(B) Tetrahedral Complexes (sp^3-hybridisation).

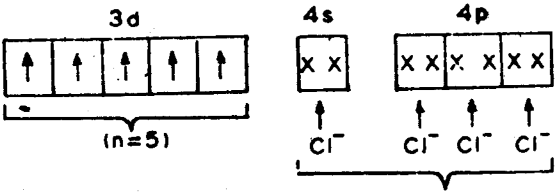
The formation of tetrahedral complexes can be explained by considering the formation of $[Mn^{II}Cl_4]^{2-}$ complex ion. The configuration of Mn^{2+} ion is :

(a) Mn^{2+} ($3d^5$)
(Ground state)



and that of $[Mn^{II}Cl_4]^{2+}$ ion is :

(b) $[Mn^{II}Cl_4]^{2-}$ ion



Four sp^3 hybrids having eight electrons donated from four ligands, 4Cl−

The hybridisation scheme given at (b) above clearly shows the presence of five unpaired electrons in $[MnCl_4]^{2-}$ ion. Experiments also show that this ion is paramagnetic corresponding to five unpaired electrons ($\mu_S = 5{\cdot}92$ BM, $\mu_{exp} = 5{\cdot}95$ BM).

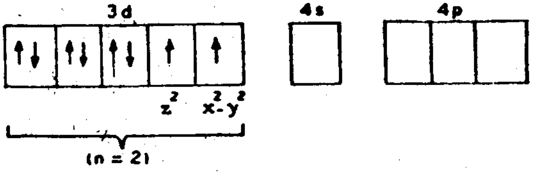
(C) Square planar complexes [$(n-1)\ d_{x^2-y^2}.\ ns\ .\ np^2$-hybridisation.]

In the formation of four dsp^2- hybrid orbitals, $d_{x^2-y^2}$ orbital should be of lower shell than the s-and p orbitals. If these four hybrid orbitals are in the xy-plane, the two p-orbitals involved in the formation of four dsp^2-hybrids should be p_x and p_y orbitals.

The formation of square planar complexes by VBT can be explained by considering the complexes such as $[Ni(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$.

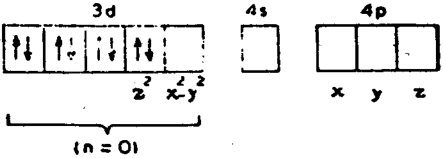
(i) $[Ni^{II}(CN)_4]^{2-}$ **ion.** Evidently in this complex ion Ni is present as Ni^{2+} whose electronic configuration is shown at (a) given below :

(a) Ni^{2+} ion ($3d^8$)
Ground state)



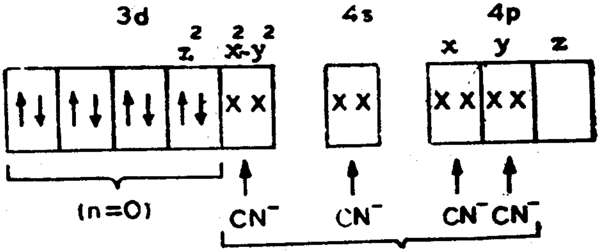
Since the coordination number of Ni in $[Ni(CN)_4]^{2-}$ ion [illegible], it can also be assumed that the complex ion is formed by sp^3-hybridisation $[(4s)(4p)^3]$. This type of hybridisation will give two unpaired electrons to this complex ion and consequently the ion should be paramagnetic corresponding ~~to~~ two unpaired electrons having μ_S value equal to 2·83 BM. Actually the complex ion has $\mu_{exp}=0$ which indicates that it is diamagnetic *i.e.* it has no unpaired electron. This situation can be obtained by sending one $3d_{x^2-y^2}$ orbital electron to $3d_{z^2}$-orbital so that all the electrons get paired and we get the electronic configuration of Ni^{2+} ion as shown at (*b*).

(*b*) Ni^{2+} ion in $[Ni(CN)_4]^{2-}$ ion
(Excited state)



Now $3d_{x^2-y^2}$, 4*s*-and two 4*p*-orbitals (namely $4p_x$ -and $4p_y$-orbitals) on hybridising give four $(3d_{x^2-y^2})$ (4*s*) $(4p_x)$ $(4p_y)$ hybrid orbitals which are used in the formation of $[Ni(CN)_4]^{2-}$ ion as shown at (*c*) below :

(*c*) $[Ni(CN)_4]^{2-}$ ion

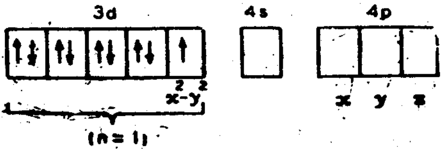


Four $(3d_{x^2-y^2})$ (4*s*) $(4p_x)$ $(4p_y)$ hybrids having 8 electrons donated by four ligands, 4 CN^- ions.

Evidently the complex ion, $[Ni(CN)_4]^{2-}$, has no unpaired electrons and the value of μ_S should be zero. Actually the value of μ_{exp} has been found to be equal to zero.

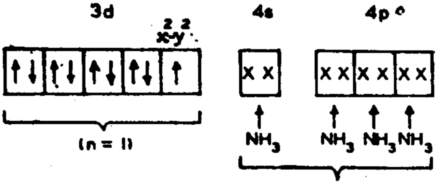
(*ii*) $[Cu^{II}(NH_3)_4]^{2+}$ **ion.** In this ion Cu is present as Cu^{2+} ($3d^9$ ion) whose configuration is shown at (*a*) given below :

(*a*) Cu^{2+} ion (d^9)



Configuration of Cu^{2+} ion ($3d^9$) shown at (*a*) and the fact that coordination number of Cu^{2+} ion in $[Cu(NH_3)_4]^{2+}$ is 4 indicates that it can also be formed by sp^3-hybridisation as shown at (*b*) given below :

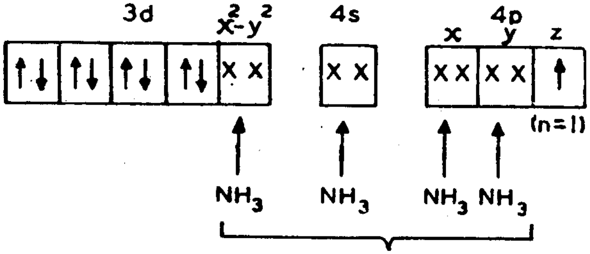
(*b*) $[Cu^{II}(NH_3)_4]^{2+}$ ion according to sp^3 hybridisation (tetrahedral)



sp^3 hybridisation
(Tetrahedral)

Now if the formation of the complex ion, $[Cu(NH_3)_4]^{2+}$ ion, is to be explained in terms of dsp^2-hybridisation, then the $d_{x^2-y^2}$-orbital should be vacated in the electronic configuration of Cu^{2+} ion shown as above at (*a*). This can be done by promoting one electron in the $3d_{x^2-y^2}$-orbital to $4p_z$-orbital and then the formation of $[Cu(NH_3)_4]^{2+}$ will be as shown at (*c*) given as follows :

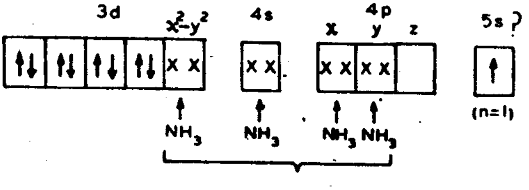
(*c*) $[Cu^{II}(NH_3)_4]^{2+}$ ion according to dsp^2 hybridisation (square planar)



Four dsp^2 hybrids having eight electrons
(squaré planar)

Some authors suggest that the unpaired electron resides in the 5*s*-orbital as shown below : (still doubtful)

(*d*) $[Cu^{II}(NH_3)_4]^{2+}$ ion



dsp^2-hybrids
(square planar)

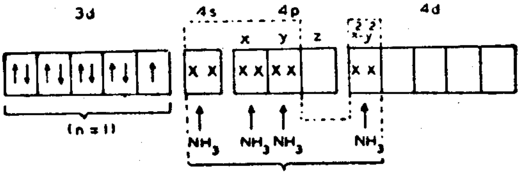
Evidently both the configurations of $[Cu(NH_3)_4]^{2+}$ shown at (*b*) (in terms of sp^3 hybridisation) and at (*c*) or (*d*) in terms of dsp^2-hybridisation) have one unpaired electron and consequently the magnetic character of this ion cannot be used to predict the geometry of the ion. However, physical measurements have indicated the non-existence of tetrahedral geometry for the ion. Now, if the square planar structure for this ion is supposed to be correct, the

$4p_z$-electron shown at (*c*) and $5s$ electron shown at (*d*) which is in a higher energy level would be expected to be easily lost which would mean that the complex ion, $[Cu^{II}(NH_3)_4]^{2+}$, could be easily oxidised to $[Cu^{III}(NH_3)_4]^{3+}$, but this is not so, *i.e.* the reaction,

$$\underset{(Cu^{2+}=3d^9)}{[Cu^{II}(NH_3)_4]^{2+}} \xrightarrow[(-e^-)]{\text{oxidisation}} \underset{(Cu^{3+}=3d^8)}{[Cu^{III}(NH_3)_4]^{3+}} \text{ does not occur.}$$

How to explain then the geometry of $[Cu^{II}(NH_3)_4]^{2+}$ ion ? It is now suggested by Huggin that it has square planar shape corresponding to sp^2d-hybridisation $[(4s)(4p)^2(4d)$- hybridisation] as shown at (*e*) below :

(*e*) $[Cu^{II}(NH_3)_4]^{2+}$ ion



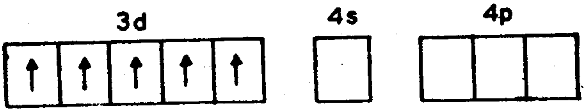
$(4s)(4p_x)(4p_y)(4d_{x^2-y^2})$ hybrids having eight electrons from four : NH_3 molecules (ligands (square planar)

This difficulty is avoided in the crystal field and molecular orbital theories when applied to this ion. According to these theories the unpaired electron is accommodated in an e_g-orbital or an anti-bonding orbital respectively. According to the modern view the $[Cu(NH_3)_4]^{2+}$ ion has a **distorted octahedral geometry.**

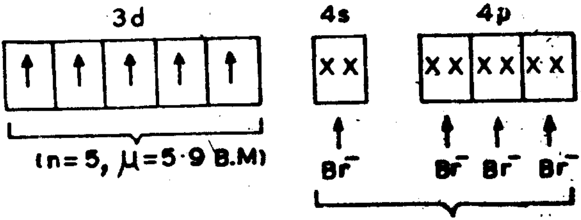
Example. *The magnetic moment of* $[MnBr_4]^{2-}$ *is 5·9 B.M. What is the geometry of this complex ion ?*

Solution. Since the coordination number of Mn^{2+} ion in this complex ion is 4, it may be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation) as shown below at (*b*) and (*c*). But the fact that the magnetic moment of the complex ion is 5·9 B.M. shows that it should be tetrahedral in shape rather than square-planar.

(*a*) Mn^{2+} ion ($3d^5$)

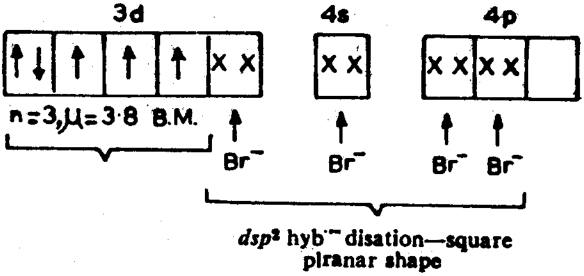


(*b*) $(MnBr_4)^{2-}$ (sp^3 hybridisation—tetrahedral shape)



sp^3 hybridisation—tetrahedral shape

(c) [MnBr$_4$]$^{2-}$
(dsp^2 hybridisation
square – planar
shape)



Limitations of VBT

(*i*) Table 12·2 shows that (*a*) octahedral (d^2sp^3 or sp^3d^2 hybridisation), tetrahedral (sp^3 hybridisation) and square planar (dsp^2 hybridisation) complexes of d^1, d^2, d^3 and d^9 ions have the same number of unpaired electrons and hence cannot be distinguished from each other merely on the basis of the number of unpaired electrons (*b*) similarly outer-orbital octahedral and tetrahedral complexes of all the ions *viz*. d^1 to d^9 which have the same number of unpaired electrons cannot be distinguished from each other.

(*ii*) It is firmly established that both the colour and the magnetic moments of transition metal complexes are due to their possessing *d*-orbital electrons. Therefore there must be a quantitative connection between spectra and magnetic moment. Unfortunately this connection is not revealed by the VBT which does not consider the splittings of the *d*-orbitals of the central metal ion and consequently these properties (*i.e*. magnetic and spectral properties) could not be explained by this theory.

(*iii*) VBT does not explain the behaviour of complexes having d^8 central ion (*e.g.* Ni^{2+}, Pb^{2+}, Au^{3+} etc.) in forming the expected 5-coordinated complexes. Moreover, it is also not clear why this theory prefers only square planar geometry of complexes to other possible geometries such as tetrahedral and trigonal bipyramidal with co-ordination five (C.N.=5).

(*iv*) VBT cannot explain why square planar complexes of Cu^{2+} ion (d^9 system) like [Cu(NH$_3$)$_4$]$^{2+}$ are not reducing agents like inner-orbital octahedral complexes of Co^{2+} (d^7 system), although in both the cases promotion of a non-bonding *d*-electron to some higher-energy level (presumeably to 5*s* level) is required.

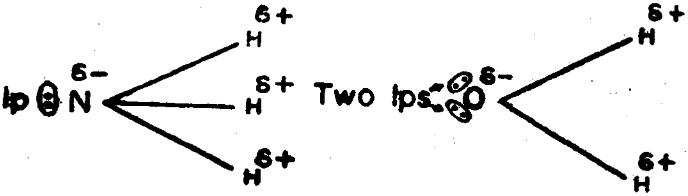
(*v*) Too much stress has been laid on the metal ion while the importance of ligand is not properly stressed.

(*vi*) VBT cannot explain reaction rates and mechanism of reactions.

CRYSTAL FIELD THEORY (CFT)

This theory advanced by Brethe and Van Vleck was originally applied mainly to ionic crystals and is, therefore called **Crystal Field Theory** (CFT). It was not until 1952 that Orgel popularised its use for **Inorganic** Chemist.

This theory regards the ligand atoms of ionic ligands such as F^-, Cl^- or CN^- as *negative point charges* (also called *point charges*), and if the ligands are neutral molecules, these are regarded as *point dipoles* or *simply dipoles*, since such ligands are dipolar, *e.g.* NH_3 and H_2O shown below :



Such ligands approach the central metal ion with negative poles (*i.e.* ends) closest to the central metal ion. Actually, even if the ligands are not negatively charged (*i.e.* neutral ligands), they are polarised by the positive charge of the cation and thus appear negatively charged. Thus in octahedral complexes having neutral molecules as ligands, the central metal ion is sorrounded by dipoles.

Here it should be clearly understood that to regard the ligand atoms as simply points is a sheer formalism which is devoid of physical meaning. Actually the ligand atoms are not points but are bodies with about the same size and structure as the metal atom itself. Thus, it can be said that CFT regards the ligand atoms as negative point charges or dipoles aligned with their most negative regions towards the central metal ion. This considers only those complexes which are having a central metal ion surrounded by the ionic or dipolar ligands and with partially filled *d*-orbitals. The theory also considers the effects of ligands on the energies of the *d*-orbitals of the central metal cation.

Important Features of CFT

(*i*) CFT regards a complex as a combination of a central ion surrounded by other ions or molecules with electrical dipoles (*i.e.*, ligands). It considers these ligands as point charges or as point dipoles.

(*ii*) In its simplest treatment CFT does not consider covalent bonding in complexes, but the bonding between the metal cation and ligands arises from the electrostatic attraction between the nucleus of the metal cation and the partial negative charge invariably present on the ligands. The interaction between the electrons of cation and those of the ligands is entirely repulsive. It is these repulsive forces that are responsible for causing the splitting of the *d*-orbitals of the metal cation. The bonds between the metal and the surrounding ligands are thus purely ionic.

(*iii*) The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons *i.e.*, it does not consider any orbital overlap.

(*iv*) CFT gives a representation of bonding that is purely an electrostatic or coulombic interaction between positively charged (*i.e.*, cation) and negatively charged (*i.e.*, anions or dipole molecules which act as ligands) species. Complexes are thus presumed to form when centrally situated cations electrically attract ligands which may be either anions or dipole molecules. The attraction between the cations and the ligands is because the cations are positively charged and the anions are negatively charged and the dipole molecules, as well, can offer their negatively incremented ends for such electrostatic attractions.

Crystal Field Splitting of d-Orbitals

We shall confine our attention to the splitting of *d*-orbitals in octahedral, tetragonal, square planar and tetrahedral complexes.

(A) Splitting of d-orbitals in octahedral complexes.

On the basis of the orientation of the lobes of the five-*d*-orbitals with respect to coordinates these have been divided into two groups :

(*i*) This group has the orbitals *which have their lobes along the axes* and hence are called *axial orbitals*. Quite obviously these are d_{z^2} and $d_{x^2-y^2}$ orbitals. Group theory calls these e_g orbitals in which *e* refers to doubly degenerate set.

(*ii*) This group includes the orbitals *whose lobes lie between the axes* and are called *non-axial orbitals*. Group theory calls these t_{2g} orbitals wherein *t* refers to triply degenerate set.

In case of free metal ion all the five *d*-orbitals are degenerate, *i.e.* these have the same energy. Now let us consider an octahedral complex, $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in Fig. 12·1.

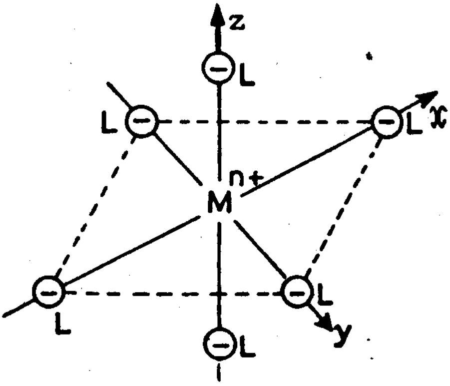
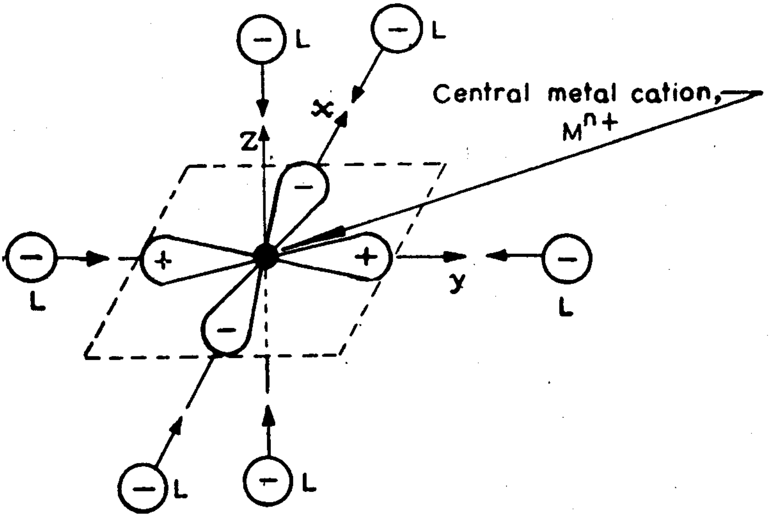
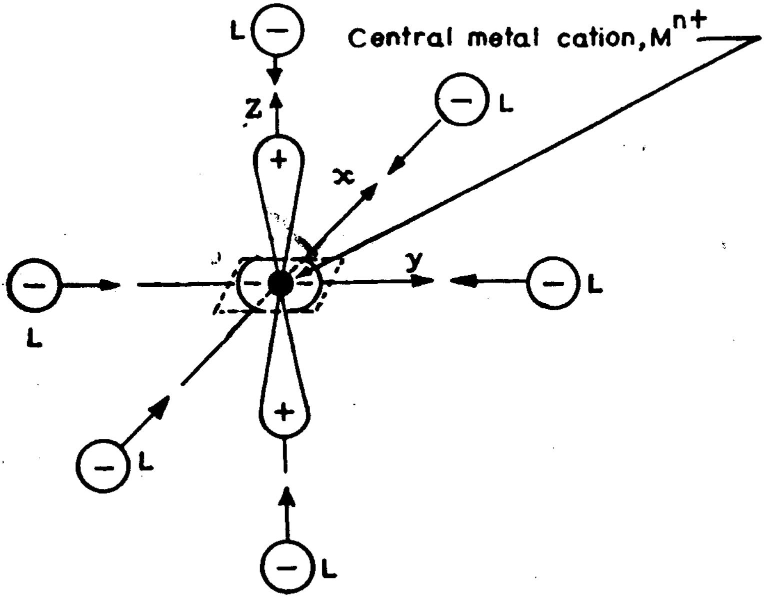


Fig. 12·1. Position of the centre metal cation, M^{n+} and six ligands, L's in an octahedral complex, $[ML_6]^{n+}$

The three axes *viz.* *x*-, *y*-, and *z*-axes which point along the corners have also been shown.



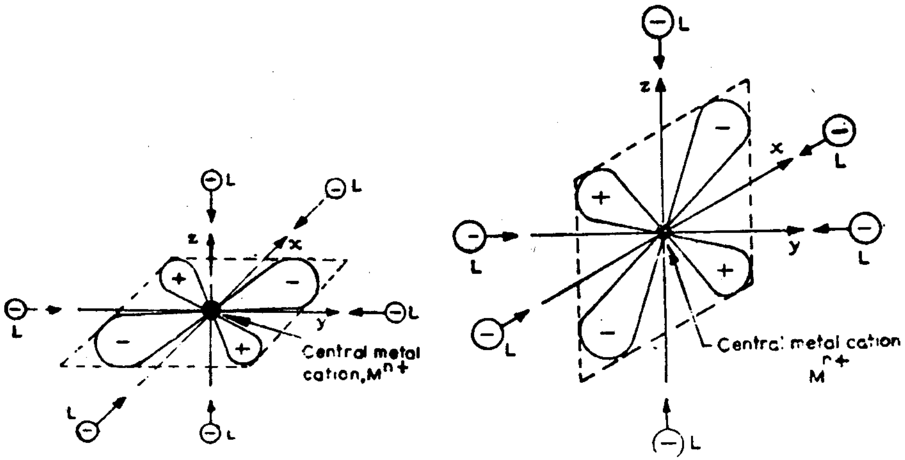
$d_{x^2-y^2}$ orbital



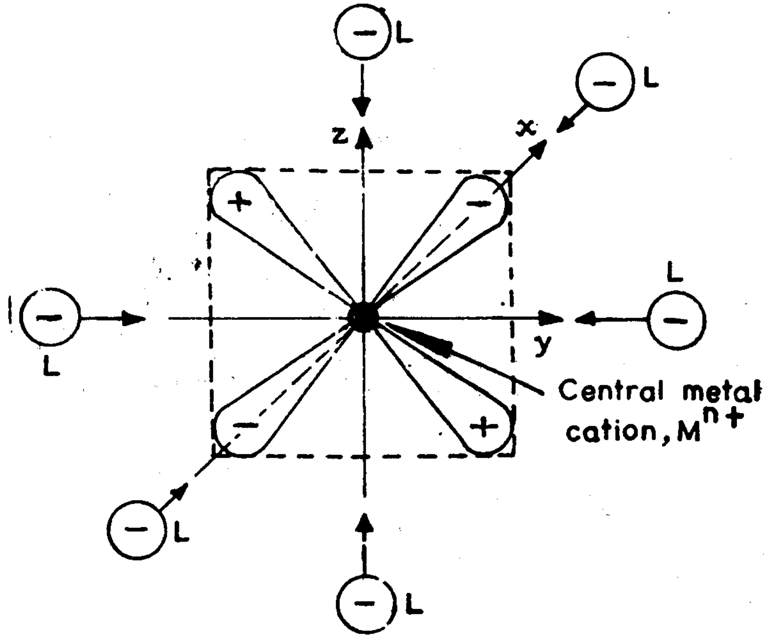
d_{z^2} orbital

Fig. 12·2. Six ligands approaching the $d_{x^2-y^2}$ and d_{z^2} orbitals (e_g set) along *x*, *y* and *z* axes in an octahedral complex

Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M^{n+} from both the



d_{xy} orbital d_{xz} orbital



d_{yz} orbital

Fig. 12·3. Six ligands approaching the d_{xy}, d_{xz} and d_{yz} orbitals (t_{2g} set) along the x, y and z axes in an octahedral complex

ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. (Remember CFT regards the ionic ligands as negative point charges and neutral ligands as dipoles). This repulsion will raise the energy of all the five *d*-orbitals. If all the ligands approaching the central cation are at an equal distance from each of the *d*-orbitals (*i.e.* the ligand field is spherically symmetrical), the energy of each of five *d*-orbitals will raise by the same amount, *i.e.* all the *d*-orbitals will still remain degenerate, although they will have now higher energy than before. This is only a *hypothetical situation. Since the lobes of the two e_g orbitals* (*i.e.* d_{z^2} and $d_{x^2-y^2}$ orbitals) *lie directly in the path of the approaching ligands* (*see Fig. 12·2*), *the electrons in these orbitals experience greater force of repulsion than those in three t_{2g} orbitals* (*i.e.* d_{xy}, d_{yz} and d_{xz} orbitals) *whose lobes are directed in space between the path of the approaching ligands* (*see* Fig. 12·3), *i.e.* the energy of e_g orbitals is increased while that of t_{2g} is decreased (Remember : *greater is the repulsion, greater the increase in energy*). Thus we find that under the influence of approaching ligands the five *d*-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels *viz.* (*i*) t_{2g} level which is triply degenerate and is of lower energy, and (*ii*) e_g level which is doubly degenerate and is of higher energy (*see* Fig. 12 4). In other words the degeneracy of the five *d*-orbitals is removed under the influence of the ligands. *The separation of five d-orbitals of the metal ion into two sets having different energies is called* **crystal field splitting** or **energy level splitting**. This concept of crytal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by $\triangle_0$ or 10 Dq where *o* in $\triangle_0$ indicates an octahedral arrangement of the ligands round the central metal cation. This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation. $\triangle_0$ or 10 Dq is called **crystal field splitting energy**. With the help of simple geometry it can be shown that the energy of t_{2g} orbitals is $0{\cdot}4\ \triangle_0$ (=4 Dq) *less* than that of hypothetical degenerate *d*-orbitals (No splitting state shown by dotted line in Fig. 12·4) and, hence, that of e_g orbitals is $0{\cdot}6\triangle_0$ (=6 Dq) *above* that of the hypothetical degenerate *d*-orbitals. Thus, we find that t_{2g} set *loses* an energy equal to $0{\cdot}4\triangle_0$ (=4 Dq) while e_g set *gains* an energy equal to $0{\cdot}6\ \triangle_0$ (=6 Dq). In Fig. 12·4 the loss and gain in energies of t_{2g} and e_g orbitals is shown by negative and positive signs respectively.

(B) Splitting of d-orbitals in tetragonal, square planar and tetrahedral complexes

If the two *trans* ligands lying on the z-axis of an octahedron are moved away from the central cation so that their distance from the metal cation is slightly greater than it is for the other four ligands lying in the *xy* plane, we get a **tetragonally distorted octahedron.** Such a structure is called **tetragonal structure.**

In order to consider the splitting of *d*-orbitals in tetragonal structure, it is convenient to start with the splitting in octahedral complexes. In a tetragonal geometry since the distance of the two ligands on *z*-axis is increased from the central metal cation by removing them away, *d*-orbitals along the *z*-axis (*i.e.* d_{z^2} orbital) and in *xz*

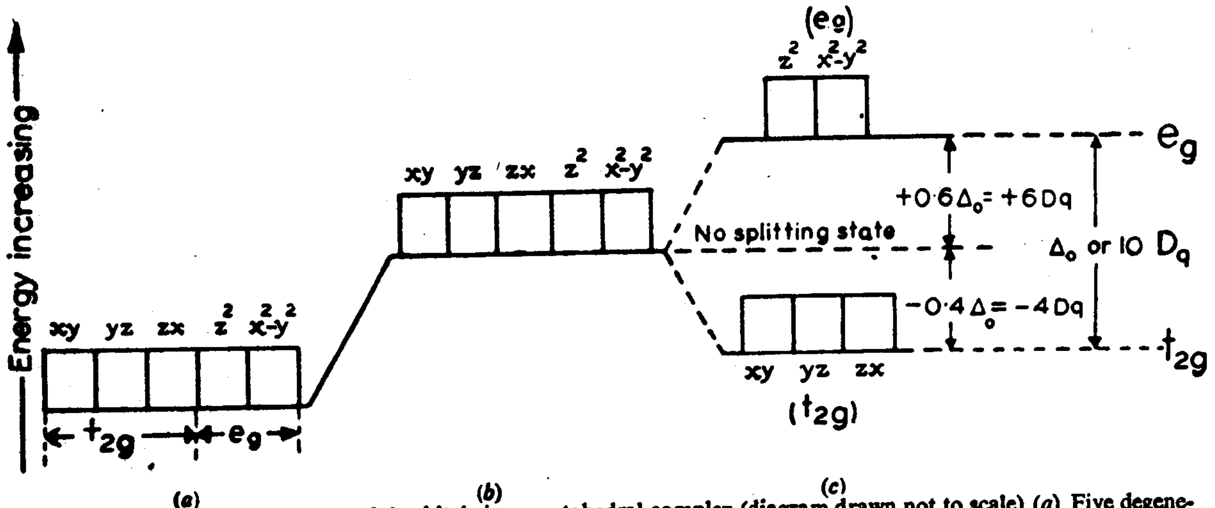


Fig. 12·4. Crystal field splitting of *d*-orbitals in an octahedral complex (diagram drawn not to scale) (*a*) Five degenerate *d*-orbitals of free metal cation which are free from any ligand field. (*b*) Hypothetical degenerate *d*-orbitals at a higher energy level under spherically symmetrical ligand field (*c*) Splitting of *d*-orbitals under the influence of approaching ligands into t_{2g} and e_g sets.

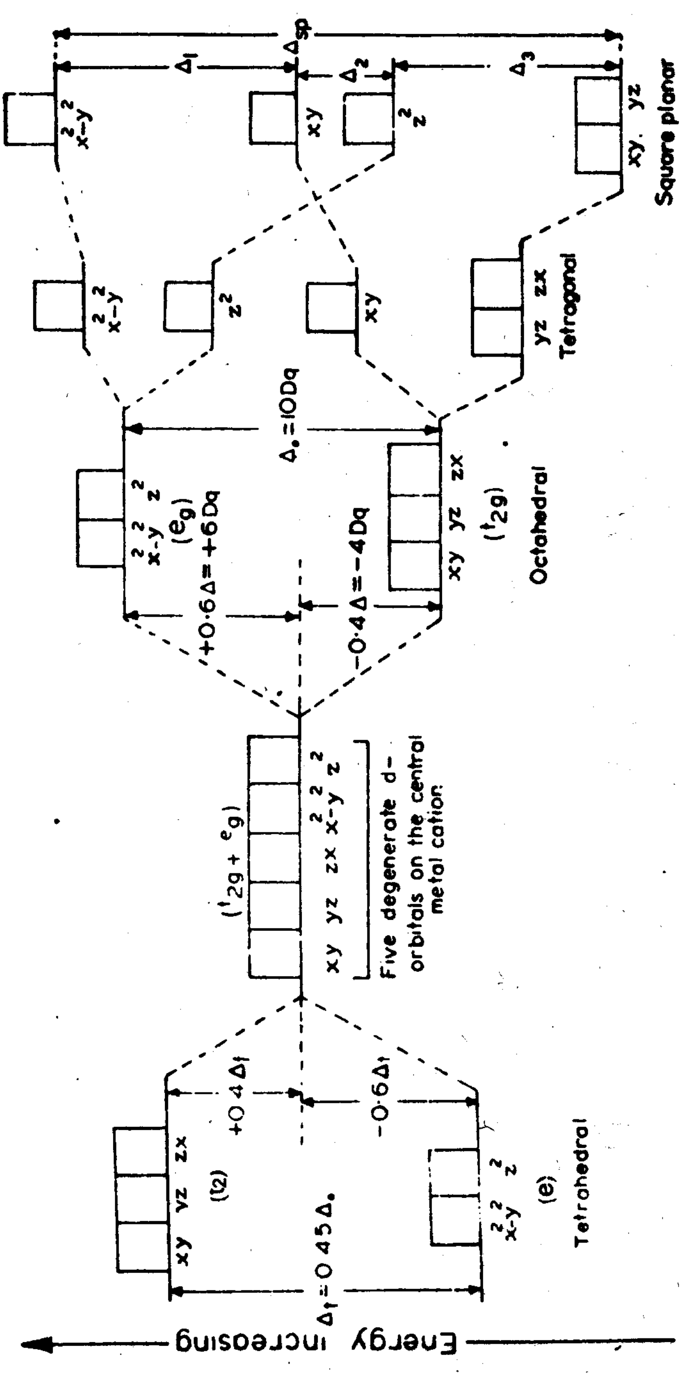


Fig. 12·5. Crystal field splitting of *d*-orbitals of the central metal cation of tetrahedral, tetragonal and square planar complexes. Splitting in octahedral complexes is also given for comparison.

(*i.e.* d_{xz}) and yz (*i.e.* d_{yz}) planes experience less repulsion from the ligands than they do in an octahedral geometry and those in the xy plane (*i.e.* d_{xy} and $d_{x^2-y^2}$ orbitals) experience relatively greater repulsion. Consequently the energy of the orbitals experiencing less repulsion decreases while that of the orbitals experiencing greater repulsion increases (*see* Fig. 12·5).

Note that d_{xz} and d_{yz} orbitals are degenerate. Thus under the influence of the ligands in tetragonal complex the order of energy of various d-orbitals is :

$$d_{yz}=d_{xz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$$

If the two *trans* ligands on the z-axis are completely removed, we get a **square planar geometry**. This is accompanied by a further rise in the energies of $d_{x^2-y^2}$ and d_{xy} orbitals and a further fall in the energies of d_{z^2}, d_{xz} and d_{yz} orbitals as shown in Fig. 12·5. Thus in square planar geometry the order of energy of different d-orbitals is :

$$d_{yz}=d_{xz} < d_{z^2} < d_{xy} < d_{x^2-y^2}.$$

From this order we can see that planar complexes of d^7, d^8 and d^9 (the only ones at present known) should have 1, 0 and 1 unpaired electrons respectively. The crystal field splitting in square planar complex is denoted by Δ_{sp} which represents the total square planar splitting from the lowest d_{xz}, d_{yz} pair to the highest $d_{x^2-y^2}$ and is given by

$$\begin{aligned}\Delta_{sp}&=[E(d_{x^2-y^2})-E(d_{xz}, d_{yz})]\\&=[E(d_{x^2-y^2})-E(d_{xy})]+[E(d_{xy})-E(d_{z^2})]\\&\qquad+[E(d_{z^2}-E(d_{zx}, d_{yz})]\\&=\Delta_1+\Delta_2+\Delta_3\end{aligned}$$

The value of Δ_{sp} has been found larger than Δ_0 because of the reason that d_{xz}- and d_{yz}-orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to 1·3 Δ_0. Thus :

$$\Delta_{sp}=(\Delta_1+\Delta_2+\Delta_3) > \Delta_0$$

and

$$\Delta_{sp}=1{\cdot}3\ \Delta_0$$

In order to understand the splitting of d-orbitals in **tetrahedral complexes** it is convenient to picture a tetrahedron placed inside a cube (*see* Fig. 12·6). We may note from this Fig. that the four negative ligands (represented by circles with negative signs) placed at the four corners of the tetrahedron are located at the four corners of the cube. Thus these four ligands are lying between the three axes *viz.* x, y and z axes which protrude from the centres of the six faces of the cube and thus go through the centre of the cube. Now since the lobes of t_{2g} orbitals (d_{xy}, d_{yz} and d_{zx}) are lying between the axes, *i.e.* are lying directly in the path of the ligands, these orbitals will experience greater force of repulsion from the ligands than those of e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) whose lobes are lying along the axes, *i.e.* are lying in space between the ligands. Thus the energy of t_{2g} orbitals will be *increased* while that of e_g orbitals will be *decreased*. Consequently the d orbitals are again split into two sets as shown in Fig. 12·5 from which it may be seen that the order of energy of t_{2g} and e_g sets is the reverse of that seen in octahedral complexes.

The energy difference between t_{2g} and e_g-sets for tetrahedral complex is represented as Δ_t. It has been shown that

$$\Delta_t < \Delta_o,$$

the cause of which is that t_{2g}-orbitals, although now closest to the ligands, do not point directly at the ligands *i.e.* in an octahedral complex there is a ligand along each axis and in a tetrahedral complex, no ligand lies directly along any axis. For this reason and also because there are only four ligands in the tetrahedral complex, while in an octahedral complex there are six ligands, the tetrahedral orbital splitting, Δ_t is less than Δ_o, for the same metal and ligands and the same internuclear distances.

It has been shown that $\Delta_t = 0{\cdot}45\ \Delta_o$

Thus the energy level of the t_{2g}-set is raised by $0{\cdot}4\ \Delta_t = 0{\cdot}18 \Delta_o$ while that of e_g-set is lowered by $0{\cdot}6\ \Delta_t = 0{\cdot}27\ \Delta_o$. The relation namely $\Delta_t = 0{\cdot}45\ \Delta_o$ also shows that, other things being about equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex. Since Δ_t is relatively small orbital splitting, spin-pairing in tetrahedral complexes is rather unlikely.

Since $\Delta_t < \Delta_o$, *crystal field splitting favours the formation of octahedral complexes.*

Factors influencing the magnitude of Δ_o

A mass of experimental data show that the magnitude of Δ_o depends on the following factors :

1. Nature of the metal cation

The influence of this factor can be studied under the following four headings :

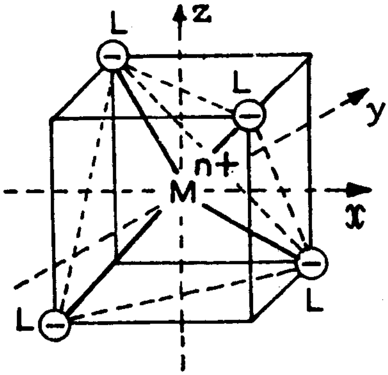


Fig. 12·6. A tetrahedron placed in a cube. The centre of the cube is the centre of the tetrahedron at which is placed central metallic cation, M^{n+}. Four corners of the cube are the four corners of the tetrahedron at which are placed the four negative ligands which have been shown by circles with negative signs.

(*i*) *Different charges on the cation of the same metal.* The cations from atoms of the same transition series and having the same oxidation state have almost the same value of Δ_o but the cation with a higher oxidation state has a larger value of Δ_o than that with lower oxidation state, *e.g.*,

(*a*) Δ_o for $[Fe^{II}(H_2O)_6]^{2+} = 10,400\ cm^{-1}$ ......$3d^6$
Δ_o for $[Fe^{III}(H_2O)_6]^{3+} = 13,700\ cm^{-1}$ ......$3d^5$

(*b*) Δ_o for $[Co^{II}(H_2O)_6]^{2} = 9,300\ cm^{-1}$ ...... $3d^7$
Δ_o for $[Co^{III}(H_2O)_6]^{3+} = 18,200\ cm^{-1}$ ...... $3d^6$

This effect is probably due to the fact that the central ion with higher oxidation state (*i.e.* with higher charge) will polarise the ligands more effectively and thus the ligands would approach such a cation more closely than they can do the cation of lower oxidation state, resulting in larger splitting.

(*ii*) *Different charges on the cation of different metals.* Two different cations having the same number of *d*-electrons and the same geometry of the complex but with different charge can also be compared. The cation with a higher oxidation state has a larger value of Δ_o than that with a lower oxidation state. For example, the behaviour towards the same ligand of V (II) and Cr (III), which are both d^3 ions can be compared. It is observed that the value of Δ_o in $[V^{II}(H_2O)_6]^{2+}$ is less than that in $[Cr^{III}(H_2O)_6]^{3+}$, as is shown below :

Δ_o for $[V^{II}(H_2O)_6]^{2+} = 12,400\ cm^{-1}$ ......$3d^3$
and Δ_o for $[Cr^{III}(H_2O)_6]^{3+} = 17,400\ cm^{-1}$ ......$3d^3$

This fact can be explained in terms of the charge on the cation. The Cr^{3+} ion, which has greater positive charge than V^{2+} ion, exerts a greater attraction for water molecules (ligands) than does the ion. Hence the water molecules approach the Cr^{3+} ion more closely than they approach the V^{2+} ion and so exert a stronger crystal field effect on the *d*-electrons of Cr^{3+} ion.

(*iii*) *Same charges on the cation but the number of d-electrons is different.* In case of complexes having the cations with the same charges but with different number of *d*-electrons in the central metal cation the magnitude of Δ_o decreases with the increase of the number of *d*-electrons, *e.g.*

Δ_o for $[Co^{II}(H_2O)_6]^{2+} = 9,300\ cm^{-1}$ ......$3d^7$
Δ_o for $[Ni^{II}(H_2O)_6]^{2+} = 8,500\ cm^{-1}$ ......$3d^8$

From the combination of (*i*), (*ii*) and (*iii*) mentioned above it can be concluded that (*a*) for the complexes having the same geometry and the same ligands but having different number of *d*-electrons, *the magnitude of Δ_o decreases with the increase of the number of d-electrons in the central metal cation* (No. of *d*-electrons $\propto \frac{1}{\Delta_o}$) (*b*) In case of complexes having the same number of *d*-electrons the *magnitude of Δ_o increases with the increase of the charges* (*i.e. oxidation state*) *on the central metal cation* (oxidation state $\propto \Delta_o$).

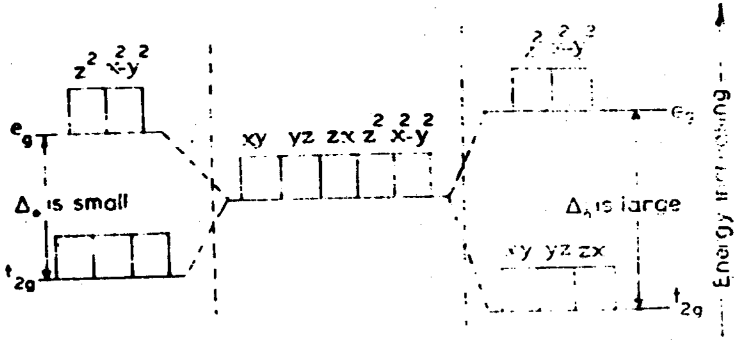
(*iv*) *Quantum number* (*n*) *of the d-orbitals of the central metal ion.* Δ_o *increases about* 30% to 50% from $3d^n$ to $4d^n$ and by about the same amount again from $4d^n$ to $5d^n$ complexes; *e.g.*,

Δ_o for $[\mathrm{Co^{III}(NH_3)_6}]^{3+} = 23{,}000\ \mathrm{cm^{-1}}$......$3d^6$
Δ_o for $[\mathrm{Rh^{III}(NH_3)_6}]^{3+} = 34{,}000\ \mathrm{cm^{-1}}$......$4d^6$
Δ_o for $[\mathrm{Ir^{III}(NH_3)_6}]^{3+} = 41{,}000\ \mathrm{cm^{-1}}$......$5d^6$

Presumably the *5d* and *4d* valence orbitals of the central ion are better than the *3d*-orbitals in σ-bonding with the ligands.

2. Strong(er) and Weak(er) Ligands and Spectrochemical Series.

The magnitude of Δ_o varies from strong(er) to weak(er) ligands. Strong (er) ligands are those which exert a strong (er) field on the central metal ion and hence have higher splitting power while the weak (er) ligands are those which have a weak(er) field on the central metal cation and consequently relatively lower splitting power. Thus strong (er) ligands (*e.g.* $\mathrm{CN^-}$) give larger value of Δ_o and weak (er) ligands (*e.g.* $\mathrm{F^-}$) yield a smaller value of Δ_o (*see* Fig. 12·7).



Splitting of *d*-orbitals in presence of weak(er) ligands (*e.g.* $\mathrm{F^-}$)   Five degenerate *d*-orbitals in the free metal ion.   Splitting of *d*-orbitals in presence of strong (er) ligands (*e.g.* $\mathrm{CN^-}$)

Fig. 12·7. CFT splitting of five *d*-orbitals in strong (er) and weak (er) octahedral field (diagram drawn not to scale).

Fig. 12·7 shows that not only Δ_o, which represents the energy difference between the t_{2g} and e_g-sets of orbitals, is smaller in the weak (er) field complex than in the strong (er) field, but also that both the t_{2g} and e_g-levels of the weak (er) field are correspondingly closer to the level of the degenerate five *d*-orbitals of the free isolated metallic ion than are those, respectively, of the strong (er) field.

The common ligands can be arranged in the order of their increasing splitting power to cause *d*-orbitals splitting. This series is called **spectrochemical series** and is given below :

$\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} \sim \mathrm{SCN^-} \sim \mathrm{N_3^-} < \mathrm{(C_2H_5O)_2PS_2^-} < \mathrm{F^-} < \mathrm{(NH_2)_2CO} < \mathrm{OH^-} < \mathrm{C_2O_4^{2-}} \sim \mathrm{H_2O} < \mathrm{NCS^-} \sim \mathrm{H^-} < \mathrm{CN^-} < \mathrm{NH_2CH_2CO_2^-} < \mathrm{NH_3} \sim \mathrm{C_5H_5N} < \mathrm{en} \sim \mathrm{SO_3^{2-}} < \mathrm{NH_2OH} < \mathrm{NO_2^-} < \mathrm{phen} < \mathrm{H^-} < \mathrm{CH_3^-} < \mathrm{CN^-}, \mathrm{CO}$. (The binding atoms are in thick type and two positions have been given for $\mathrm{H^-}$ ion).

This series shows that the value, of Δ_o in the series also increases in the same order, *i.e.* from left to right.

The order of field strength of the common ligands shown above is, in fact, independent of the nature of the central metal ion and the geometry of the complex.

The increase in the value of Δ_0 on proceeding from left to right in the spectro-chemical series is quite evident from the values of Δ_0 for some octahedral complexes given in Table 12·7 which clearly shows that since on proceeding from $6Br^- \longrightarrow 3\,en$ the field strength of the ligands increases, the value of Δ_0 also correspondingly increases.

Table 12·7. *Δ_0 values (i.e. energy difference between t_{2g} and e_g levels) in cm^{-1} for some octahedral complexes (Δ_0 values in thick type are for low-spin octahedral complexes).*

Ligands →	6 Br^-	< 6 Cl^-	< 6 H_2O	< 6 NH_3	< 3 en
	Field strength increasing →				
Metal Ion					
Ni (II)	7,000 cm^{-1}	< 7,200 cm^{-1}	< 8500 cm^{-1}	< 10,800 cm^{-1}	< 11,500 cm^{-1}
Cr (III)	—	13,800	< 17,400	< 21,600	< 21,900
Co (III)	—	—	**18,200**	**< 23,000**	**< 23,200**
Rh (III)	**19,000**	**< 20,300**	**< 27,000**	**< 34,100**	**< 34,600**
	Δ_0 values (in cm^{-1}) also increasing →				

Example. *Which complex of the following pairs has the larger value of* Δ_0 (*i*) $[Co^{III}(CN_6]^{3-}$ and $[Co^{III}(NH_3)_6]^{3+}$ (*ii*) $[Co^{III}(NH_3)_6]^{3+}$ and $[Co^{III}F_6]^{3-}$ (*iii*) $[Co^{III}(H_2O)_6]^{3+}$ and $[Rh^{III}(H_2O)_6]^{3+}$ (*iv*) $[Co\ (H_2O)_6]^{2+}$ and $[Co^{III}(H_2O)_6]^{3+}$?

Solution. (*i*) Since CN^- is stronger than NH_3 (*i.e.* CN^- ion has greater field strength than NH_3), Δ_0 for $[Co(CN)_6]^{3-}$ is greater than Δ_0 for $[Co(NH_3)_6]^{3+}$.

(*ii*) $[Co\ (NH_3)_6]^{3+}$ ion has greater value of Δ_0 than that for $[CoF_6]^{3-}$.

(*iii*) Rh is a member of 4*d*-series while Co is a member of 3*d*-series. Thus principal quantum number, *n*, for Rh is greater than that of Co and consequently Δ_0 for $[Rh(H_2O_6)]^{3+}$ is greater.

(*iv*) The charge on Co in $[Co(H_2O)_6]^{3+}$ is higher than that on Co in $[Co(H_2O)_6]^{2+}$. Thus Δ_0 for $[Co(H_2O)_6]^{3+}$ is higher.

3. Geometry of the complex.

We have already seen that with the change of the geometry of the complex the value of Δ also changes. It has already been seen that

$$\begin{array}{ccccc} \Delta_{sp} & > & \Delta_0 & > & \Delta_t \\ 1{\cdot}3\,\Delta_0 & & \Delta_0 & & 0{\cdot}45\,\Delta_0 \end{array}$$

Distribution of d-electrons in t_{2g} and e_g orbitals in octahedral complexes

The distribution of *d*-electrons in t_{2g} and e_g orbitals takes place on the basis of the nature of the ligands, *i.e.* whether the ligands are weak (er) or strong (er). Thus two cases arise.

(*i*) **When the ligands are weak (er)**

We have seen that under the influence of weak (er) ligands the energy difference, $\triangle_0$ between t_{2g} and e_g sets is relatively small and hence all the five *d*-orbitals of these two sets may be supposed to be degenerate, *i.e.* in presence of weak (er) ligands all the *d*-orbitals have the same energy and consequently the distribution of *d*-electrons in t_{2g} and e_g sets *takes place according to Hund's rule which states that electrons will pair up only when each of the five d-orbitals is at least singly filled.* Thus in weak (er) field the first three electrons numbered as 1, 2, 3 go to t_{2g}-level, those numbered as 4 and 5 (two electrons) go to e_g-set, those numbered as 6, 7, 8 (three electrons) go to t_{2g}-set and the remaining two electrons numbered as 9 and 10 will occupy e_g-set. This can be shown as :

$$t_{2g}^{1,2,3} \longrightarrow e_g^{4,5} \longrightarrow {}^{6,7,8} \longrightarrow e_g^{9,10}$$ (*see* Table 12·8).

As an example, if we consider the octahedral complex *viz.* $[CoF_6]^{3-}$ which contains weak (er) ligands, the distribution of six *d*-electrons of Co^{3+} ion ($Co^{3+} \longrightarrow 3d^6$) in t_{2g} and e_g sets will be $t_{2g}^4 e_g^2$ (see Fig. 12·8 (*a*)]. The complexes like $[CoF_6]^{3-}$ which contain weak (er) ligands are called **weak field** or **low field** complexes.

In the formation of such complexes $\triangle_0 < P$ where P = average (or mean) pairing energy which is the energy required to pair two electrons in the same orbital, and $\triangle_0$ = octahedral crystal field splitting energy. $\triangle_0$ tends to force as many electrons to t_{2g} set while P tends to prevent the electrons to pair in the t_{2g} level.

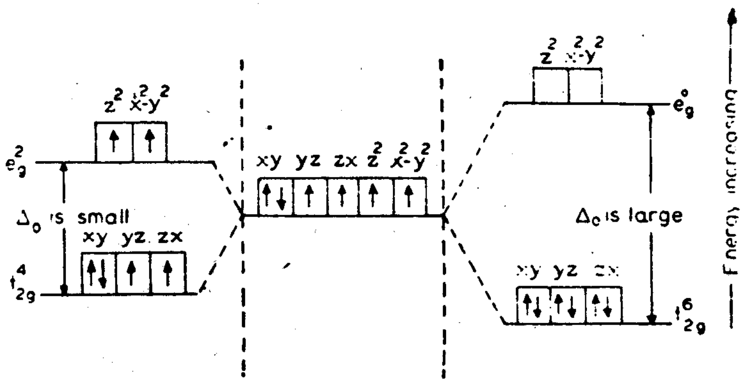
(*ii*) **When the ligands are strong (er).**

In octahedral complexes containing strong (er) ligands distribution of *d*-electrons in t_{2g} and e_g sets *does not obey Hund's rule.* Thus in strong (er) field the first six electrons numbered as 1, 2, 3, 4, 5 and 6 will go to t_{2g}-set and the remaining four electrons numbered as 7, 8, 9, and 10 enter e_g-set. This can be shown as :

$$t_{2g}^{1,2,3,4,5,6} \longrightarrow e_g^{7,8,9,10}$$ (*see* Table 12·8).

Consider the distribution of six *d*-electrons of Co^{3+} ion ($Co^{3+} \longrightarrow 3d^6$) in the complex ion, $[Co(NH_3)_6]^{3+}$ which contains strong (er) ligands. Quite obviously this distribution is $t_{2g}^6 e_g^0$ [*see* Fig. 12·8 (*b*)]. Complexes like $[Co(NH_3)_6]^{3+}$ which contain strong (er) ligands are called **strong field** or **high field complexes.**

For these complexes $\triangle_0 > P$.



d-orbitals in weak (er) ligand field (Hund's rule is followed), $[CoF_6]^{3-}$ ($t_{2g}^4 e_g^2$) (weak-field complex).
(*a*)

Degenerate five *d*-orbitals of Co^{3+} ion ($Co^{3+} \longrightarrow 3d^6$) under no ligand field (Hund's rule is applied)

d-orbitals under strong(er) ligand field (Hund's rule is not followed), $[Co(NH_3)_6]^{3+}$ ($t_{2g}^6 e_g^0$) (strong-field complex)
(*b*)

Fig. 12·8. Formation of $[CoF_6]^{3-}$ which contains weak(er) ligands (*i.e.*, weak field complex) and $[Co(NH_3)_6]^{3+}$ which contains strong(er) ligands (*i.e.* strong-field complex).

Table 12·8. *Distribution of d-electrons in t_{2g}- and e_g-sets in strong (er) and weak (er) octahedral ligand fields.*

n = No. of unpaired electrons

S = Resultant spin = $\frac{1}{2} \times n$

$p + q = x = 1, 2, 3 \ldots\ldots, 8, 9$ or 10

[illegible]	*Strong (er) field (low-spin or spin-paired complexes) ($\Delta_0 > P$)*			*Weak (er) field (high-spin or spin-free complexes) ($\Delta_0 < P$)*		
	$t_{2g}^p e_g^q$ configuration	*n*	*S*	*$t_{2g}^p e_g^q$ configuration*	*n*	*S*
d^1	$t_{2g}^1 e_g^0$	1	1/2	$t_{2g}^1 e_g^0$	1	1/2
d^2	$t_{2g}^2 e_g^0$	2	1	$t_{2g}^2 e_g^0$	2	1
d^3	$t_{2g}^3 e_g^0$	3	3/2	$t_{2g}^3 e_g^0$	3	3/2
d^4	$t_{2g}^4 e_g^0$	2	1	$t_{2g}^3 e_g^1$	4	2
d^5	$t_{2g}^5 e_g^0$	1	1/2	$t_{2g}^3 e_g^2$	5	5/2
d^6	$t_{2g}^6 e_g^0$	0	0	$t_{2g}^4 e_g^2$	4	2
d^7	$t_{2g}^6 e_g^1$	1	1/2	$t_{2g}^5 e_g^2$	3	3/2
d^8	$t_{g2}^6 e_g^2$	2	1	$t_{2g}^6 e_g^2$	2	1
d^9	$t_{2g}^6 e_g^3$	1	1/2	$t_{2g}^6 e_g^3$	1	1/2
d^{10}	$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0

Table 12·8 in which the distribution of various *d*-electrons of the central metal cation in strong (er) and weak (er) octahedral ligand field is shown discloses the following facts:

(*i*) Whether the ligand field is strong (er) or weak (er), for d^1, d^2 and d^3 configurations, the electrons go to the lower energy t_{2g}-level (more stable), for d^8, d^9 and d^{10} configurations, the first six electrons go to the t_{2g}-level and the remaining two (in case of d^8 ion), three (in case of d^9 ion) and four (in case of d^{10} ion) electrons occupy the e_g-level. Thus, the distribution of electrons of d^1, d^2, d^3, d^8, d^9 and d^{10} configurations in t_{2g}- and e_g-levels for both strong (er) and weak (er) octahedral ligand field is the same.

(*ii*) For each of d^4, d^5, d^6 and d^7 configurations there is a difference in the arrangement of electrons in weak(er) and strong(er) ligand fields.

(*iii*) **Number of unpaired electrons** (*n*)—**high-spin and low-spin complexes.** Weak-field complexes of d^4, d^5, d^6 and d^7 ions have greater number of unpaired electrons (*n*) than those of (same ions) strong-field complexes and are thus with a higher value of resultant spin (S). It is for this reason that the weak-field and strong-field complexes are also called **spin-free** or **high-spin** (abbreviated as HS) and **spin-paired** or **low-spin** (LS) complexes respectively. Recall that VBT has called these complexes as *ionic* (*Pauling*) or *outer-orbital* (Huggin) and *covalent* (*Pauling*) or *inner-orbital* (*Huggin*) complexes respectively.

Different names used for octahedral complexes by different theories such as VBT, CFT and LFT (**Ligand Field Theory**—to be discussed later on) are summarised below. Note that the names given in the first column are equivalent to each other (*i.e.* convey the same meaning). Similarly those given in the second column are equivalent. The parenthes contain the names of the chemists who have used these names.

Theory	*Names used for complexes*	
VBT	**Outer-orbital (Huggin), ionic (Pauling)** **[$(4s)(4p)^3(4d)^2$ hybridisation]**	**Inner-orbital (Huggin), covalent (Pauling)** **[$(3d)^3(4s)(4p)^3$ hybridisation]**
CFT and **LFT**	**Spin-free (Nyholom)), Low-field or weak-field (Brethe and Vanvleck), High-spin (Orgel), Hypo-ligated (Pauling)**	**Spin-paired (Nyholom), High-field or strong-field (Brethe and Vanvleck), Low-spin (Orgel). Hyper-ligated (Pauling)**

The number of unpaired electrons (*i.e.* the value of the resultant spin, S) in the cases namely d^1 to d^3 and d^8 to d^{10} is the same in both the fields, and it is due to this reason that for these configurations the question of the formation of HS- and LS-complexes does not arise. The question does arise for the system d^4 to d^7.

The paramagnetism of HS-complexes is larger than that of LS-complexes, since, as is evident from Tables 12·8, HS-complexes have more unpaired electrons (*i.e.* larger value of S) than the LS-complexes (*i.e.* smaller value of S).

Examples of some HS- and LS-octahedral complexes are given in Table 12·9. In this table the value of P (in cm^{-1}) of the central metal ion of the corresponding complex determined from spectroscopic data and that of Δ_o (in cm^{-1}) for the complexes are also listed. From this table it may be seen that the spin-state of the complexes predicted by CFT is the same as that observed experimentally. In every case where $\Delta_o < P$, HS-complex is formed and in case where $\Delta_o > P$ LS-complex is formed.

Table 12·9. *Examples of some LS- and HS- Octahedral complexes*

d^x configuration	Examples of complexes	Value of P (cm^{-1})	Value of Δ_0 (cm^{-1})	spin-state		Relative magnitudes of Δ_0 and P
				Predicted by CFT	Observed experimentally	
d^4	$[Cr(H_2O)_6]^{2+}$	23,500	13,900	HS	HS	$\Delta_0 < P$
	$[Mn(H_2O)_6]^{3+}$	28,000	21,000	HS	HS	$\Delta_0 < P$
d^5	$[Mn(H_2O)_6]^{2+}$	25,500	7,800	HS	HS	$\Delta_0 < P$
	$[Fe(H_2O)_6]^{3+}$	30,000	13,700	HS	HS	$\Delta_0 < P$
d^6	$[Fe(H_2O)_6]^{2+}$	17,600	10,400	HS	HS	$\Delta_0 < P$
	$[Fe(CN)_6]^{4-}$	17,600	33,000	LS	LS	$\Delta_0 > P$
	$[Co(NH_3)_6]^{3+}$	21,000	23,000	LS	LS	$\Delta_0 > P$
	$[CoF_6]^{3-}$	21,000	13,000	HS	HS	$\Delta_0 < P$
d^7	$[Co(H_2O)_6]^{2+}$	22,500	9,300	HS	HS	$\Delta_0 < P$

Example (*i*) For Mn^{3+} ion, the electron pairing energy, P is about 28,000 cm^{-1}. Δ_o values for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 21,000 cm^{-1} and 38,500 cm^{-1} respectively. Do these complexes have high-spin or low-spin configurations? Also write down the configurations corresponding to these states.

Solution. For the complex ion, $[Mn(H_2O)_6]^{3+}$, since $P > \triangle_o$ ($P=28,000$ cm^{-1} and $\triangle_o=21,000$ cm^{-1}), this complex ion is a high-spin complex and its configuration is $t_{2g}^3\, e_g^1$. Note that Mn^{3+} ion is d^4 system.

For the complex ion, $]Mn(CN)_6]^{3-}$, since $P < \triangle_o$ ($P=28.000$ cm^{-1} and $\triangle_o=38,500$ cm^{-1}), the complex is a low-spin complex and its configuration is $t_{2g}^4\, e_g^0$.

Example (*ii*). Given the following three conditions with respect to the magnitudes of $\triangle_o$ and P for an octahedral complex, (1) $\triangle_o > P$ (2) $\triangle_o = P$ (3) $\triangle_o < P$, predict the spin states for the following types of ions : (*a*) d^8 (*b*) d^4 (*c*) d^6.

Example (*iii*). Give the number of unpaired electrons for the following complexes :

(*a*) $[V^{III} F_6]^{3-}$ (*b*) $[Fe^{II} (CN)_6]^{4-}$ (*c*) $[Fe^{III} (CN)_6]^{3-}$

(*d*) $[Rh^{III} Cl_6]^{3-}$

Solution. (*a*) In $[VF_6]^{3-}$ vanadium is present as V^{3+} ion which is a $3d^2$ system. Thus, in this case the question of the formation of HS- or LS- complex does not arise and the distribution of two $3d$ electrons in t_{2g}- and e_g-sets is as :

$V^{3+} (3d^2) \longrightarrow t_{2g}^2\, e_g^0$, which gives the number of unpaired electrons, n, equal to two, *i.e.* $n = 2$.

(*b*) In $[Fe(CN)_6]^{4-}$ ion, Fe is present as Fe^{2+} with $3d^6$ configuration. Since CN^- ion is a strong ligand. $[Fe(CN)_6[^{4-}$ ion is a LS-complex and hence the distribution of six $3d$-electrons in t_{2g}- and e_g-sets is as :

$$Fe^{2+} (3d^6) \longrightarrow t_{2g}^6\, e_g^0, \text{ giving } n=0.$$

(*c*) In this case :

$$Fe^{3+} (3d^5) \longrightarrow t_{2g}^5\, e_g^0, \text{ giving } n=1$$

(*d*) Cl^- ion is a weak ligand. Thus $[RhCl_6]^{3-}$ is a HS-complex and consequently

$$Rh^{3+} (4d^6) \longrightarrow t_{2g}^4\, e_g^2, \text{ giving } n=4.$$

Distribution of d-electrons in t_{2g} and e_g orbitals in tetrahedral complexes.

The distribution of d-electrons in the t_{2g}- and e_g- levels in a central ion surrounded by tetrahedral ligands exerting weak (er) and strong (er) fields is shown in Table 12·10.

Table 12·10 shows that HS- and LS-complex may be formed by d^3, d^4, d^5 and d^6 ions, but, in fact, LS-complexes are extremely rare, and, possibly non-existent. $ReCl_4$ is diamagnetic which suggests no paired electrons in it, but the geometrical shape of the complex has not been established.

Table 12·10. *Distribution of d-electrons in weak (er) and strong (er) tetrahedral ligand field. (n = number of unpaired electrons).*

The sum $(p+q)$ is equal to the number of electrons in the *d*-orbitals of the metal ion, *i.e.* $(p+q)=x=1, 2, 3, \ldots\ldots, 8, 9,$ or 10.

d^x configuration	*Weak field (HS-complexes)*		*Strong Field (LS-complexes)*	
	$t_{2g}{}^p\ e_g{}^q$ configuration	*n*	*$t_{2g}{}^p\ e_g{}^q$ configuration*	*n*
d^1	$t_{2g}{}^0\ e_g{}^1$	1	$t_{2g}{}^0\ e_g{}^1$	1
d^2	$t_{2g}{}^0\ e_g{}^2$	2	$t_{2g}{}^0\ e_g{}^2$	2
d^3	$t_{2g}{}^1\ e_g{}^2$	3	$t_{2g}{}^0\ e_g{}^3$	1
d^4	$t_{2g}{}^2\ e_g{}^2$	4	$t_{2g}{}^0\ e_g{}^4$	0
d^5	$t_{2g}{}^3\ e_g{}^2$	5	$t_{2g}{}^1\ e_g{}^4$	1
d^6	$t_{2g}{}^3\ e_g{}^3$	4	$t_{2g}{}^2\ e_g{}^4$	2
d^7	$t_{2g}{}^3\ e_g{}^4$	3	$t_{2g}{}^3\ e_g{}^4$	3
d^8	$t_{2g}{}^4\ e_g{}^4$	2	$t_{2g}{}^4\ e_g{}^4$	2
d^9	$t_{2g}{}^5\ e_g{}^4$	1	$t_{2g}{}^5\ e_g{}^4$	1
d^{10}	$t_{2g}{}^6\ e_g{}^4$	0	$t_{2g}{}^6\ e_g{}^4$	0

Some Applications of CFT

(1) Colour of transition metal complexes.

One of the major successes of the CFT is that it can provide an explanation for the observed colours of transition metal complexes.

When white light is allowed to full on a complex. the following things may occur :

(*i*) The complex may absorb the whole of white light. In this case complex appears black.

(*ii*) The complex may reflect (or transmit) the whole light. In this case it appears white.

(*iii*) The complex may absorb some of it and may reflect (or transmit) the remaining light. In this case the complex has some colour, *i.e.* it is coloured. The absorption of light by the coloured complexes takes place in the visible region of the spectrum which extends from 4000A° to 7000A° in wavelength. The colour of the absorbed light is different from that of the transmitted light.

The relation between the colours of the absorbed and reflected light is shown in Fig. 12·9. The colour of the transmitted light is called the *complementary colour* of that of the absorbed light and is, in fact, the colour of the complex.

Thus :

(*i*) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is *blue* (*colour of the transmitted light*) because it absorbs *yellow* light.

(*ii*) Cuprammonium sulphate containing $[Cu(NH_3)_4]^{2+}$ ions is *violet*, because it absorbs *yellow green* light.

(*iii*) $[Ti(H_2O)_6]^{3+}$ absorbs *green* light in the visible region and hence it is *purple* which is the colour of the transmitted light.

The complex ions which absorb light in the infra-red ($\lambda >$ 7000 A°) or ultra-violet ($\lambda <$ 4000 A°) regions of the spectrum are colourless, *e.g.*, (*i*) anhydrous cupric sulphate is *colourless*, since it absorbs light in the infra-red region. (*ii*) $[Cu(CN)_4]^{2-}$ ion absorbs light in the ultra-violet region and hence is *colourless*.

High —————— Decreasing Energy —————— → Low

Colour absorbed	Violet	Blue	Green-blue	Blue-green	Green	Yellow-green	Yellow	Orange	Red

Wave length of the absorbed light — 4000 Å 4350 4800 4900 5000 5600 5800 5900 6050 7000

Low —————— Increasing wavelength —————— → High

Colour transmitted (observed or reflected) which is the colour of the complex	Yellow-green	Yellow	Orange	Red	Purple	Violet	Blue	Green	Blue-green

Fig. 12·9. Relation between the colours of the absorbed light (Visible spectrum) and those of the transmitted light.

With the help of *visible absorption spectrum* of a complex ion it is possible to predict the colour of the complex. For example $[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000Å° (Fig. 12·10) which corresponds to the wave number, $\bar{\nu}$ = 20000 cm^{-1} as shown below :

Since 1 A° $= 10^{-8}$ cm, wave length, $\lambda = 5000$ Å $= 5000 \times 10^{-8}$ cm.

Consequently wave number,

$$\bar{\nu} = \frac{1}{\lambda \text{ (in cm)}} = \frac{1}{5000 \times 10^{-8}\text{ cm}}$$

$$= \frac{1}{5 \times 10^{-5}}\text{cm}^{-1} = 0{\cdot}2 \times 10^{5}\text{ cm}^{-1}$$

$$= 20000\text{ cm}^{-1}$$

Light of this wavelength (= 5000 Å) is *green* (*see* Fig. 12·9) and is absorbed by the complex ion. Thus the transmitted light is *purple* which is, in fact, the colour of the ion.

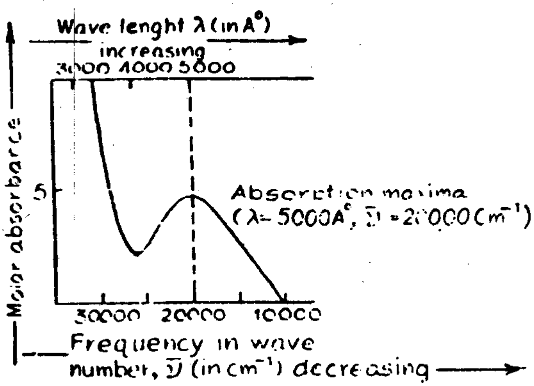
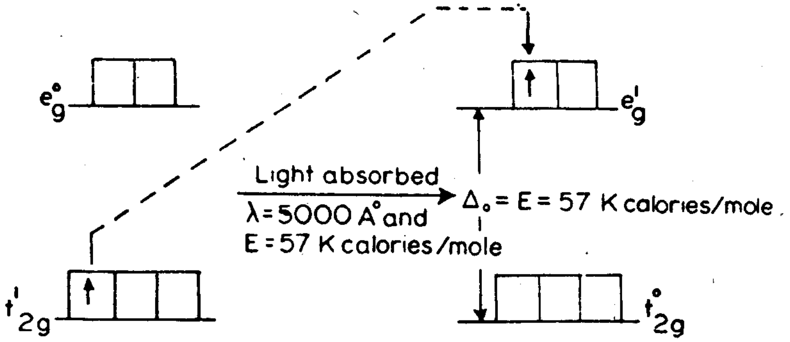


Fig. 12·10. Visible absorption spectrum of $[Ti^{III}(H_2O)_6]^{3+}$ ion. Peak of the curve shows the maximum absorption

Now let us see what happens to the single *d*-electron of Ti^{3+} ion in t_{2g} orbital ($Ti^{3+} \longrightarrow t_{2g}^{1}e_g^{0}$), when the complex ion absorbs light in the visible region at 5000 Å. The energy (in Kcal/mole) associated with this absorbed light of wave number, $\bar{\nu}$ of 20000 cm^{-1} is equal to $20000 \times 2{\cdot}85 \times 10^{-3} = 57$ Kcal/mole, since 1 cm^{-1} $= 2{\cdot}85 \times 10^{-3}$ Kcal/mole.

This energy (= 57 Kcalories/mole) is equal to the energy difference, $\triangle_0$ between t_{2g} and e_g levels and hence is sufficient to excite the single *d*-electron in t_{2g} orbital to e_g orbital. This type of electronic transition from t_{2g} to e_g level is called *d-d or ligand field transition* and is shown in Fig. 12·11.

Thus the colour of $[Ti(H_2O)_6]^{3+}$ is attributed to *d-d* electro-transition.



Ground state of $[Ti(H_2O)_6]^{3+}$ $(t_{2g}^1\, e_g^0)$

Excited state of $[Ti(H_2O)_6]^{3+}$ $(t_{2g}^0\, e_g^1)$

Fig. 12·11. Absorption of light by $[Ti^{III}(H_2O)_6]^{3+}$ ion involving a shift of an electron from t_{2g} level to e_g level. This transition : $t_{2g}^1\, e_g^0 \longrightarrow t_{2g}^0\, e_g^1$, gives the $[Ti^{III}(H_2O)_6]^{3+}$ ion its purple colour.

(2) Number of unpaired electrons and magnetic properties of octahedral complexes

CFT is helpful in determining the number of unpaired electrons in a given HS- and LS-octahedral complex, and consequently, with the help of "spin-only" formula, $\mu_S = \sqrt{n(n+2)}$ BM, we can find the value of "spin-only" moment, μ_S, of a given HS- and LS-octahedral complex.

Value of μ_S calculated from the spin-only formula given above and those of μ_J and μ_{S+L} calculated from the following equations for HS-octahedral complexes of some of the di- and trivalent ions of the 3*d*-series elements are given in Table 12·11.

$$\mu_J = g\sqrt{J(J+1)}\ \text{BM}$$

where *g* which is Lande splitting factor is given by

$$g = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

$$\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}\ \text{BM}$$

Table 12·12 contains μ_S values for LS-octahedral complexes.

For comparison, values of magnetic moment found experimentally (*i.e.* μ_{exp} values) are also included in both the tables.

Tables 12·11 and 12·12 make the following points clear : (In these tables n_1 indicates the number of unpaired electrons in the free metal ion and n_2 represents those in the metal ion when it is complexed).

(*i*) According to crystal field theory of complex compounds, since the number of unpaired electrons in the central metal ion with

d^4 to d^7 configuration (*i.e.* d^4, d^5, d^6 and d^7 configurations) in high-spin and low-spin octahedral complexes is different (see Table 12·8), the values of μ_{exp} for these ions in HS- and LS-complexes are also different.

(*ii*) For many of the ions of the series, particularly for the first half of the series, μ_S values for the HS-complexes agree with μ_{exp} values.

(*iii*) In case of the HS-complexes, μ_{exp} values frequently exceed μ_S, but seldom are as high as μ_{S+L} values. This is due to the whole or partial quenching of orbital moments.

(*iv*) For the ions such as Mn^{2+} and Fe^{3+} (d^5 ions) which are with S ground states (*i.e.* L = 0), the μ_S, μ_{S+L} and μ_J values are all equal (for HS-complexes).

(*v*) *Use of the table—Importance of magnetic moments.* From the tables it is obvious that from a knowledge of the number of unpaired electrons and of the magnetic moment values it is possible to find :

(*a*) the valence state of the metal ion in a given octahedral complex, and

(*b*) the nature of the bonding in the complex (*i.e.* whether the complex is of spin-free or spin-paired type), if there are more than three *d*-electrons.

These two points may be explained by considering the following examples :

(*i*) If an octahedral complex of cobalt is found to possess a moment of 4·5 M.B. (*e.g.* $Hg[Co(CNS)_4]$), it would be concluded (*a*) that the cobalt is in the bivalent state ($Co^{2+} \longrightarrow d^7$), and (*b*) that the bonding is of the spin-free type corresponding to $n = 3$.

(*ii*) If an octahedral complex of Fe is found to possess a moment of 2·2 B.M. (*e.g.* $[Fe(diph)_3](ClO_4)_3$), it would be concluded (*a*) that the iron is in the trivalent state ($Fe^{3+} \longrightarrow d^5$), and (*b*) that the bonding is of the spin-paired type corresponding to $n = 1$.

Now consider a Cr complex with magnetic moment equal to 3·72 B·M. (*e.g.* $K_3[Cr(CNS)_6]$). From the magnetic moment value, although it is obvious that Cr is in the trivalent state, it is not possible to say whether the bonding is of spin-paired or spin-free type.

Occasionally some confusion may arise regarding a definite evaluation of valence state of the metallic ion from the magnetic moment value, *e.g.*, see the cases of Fe^{2+} and Fe^{3+} spin-free complexes.

In low-spin octahedral complexes, the value of experimental magnetic moment, μ_{exp}, is less than the μ_S value calculated from the "spin-only" formula for the free metal ion. This fact can be used to answer whether a given octahedral complex is a high-spin or a low-spin complex. Thus when μ_{exp} value for the complex is less than the μ_S value for the free metal ion, the complex is of low-spin type, otherwise it is of high-spin type.

Table 12·11. *Values of μ_S, μ_{S+L}, μ_J and μ_{exp} in B. M. for d^x configuration of the first row transition series in HS-octahedral complexes (sp^3d^2 bonding : outer-orbital octahedral complexes)*

d^x configuration	*Ions*	*Ground state free ion term*	*n_1 and n_2 ($n_1 = n_2$)*	μ_S	μ_{S+L}	μ_J	μ_{exp}
d^1	Ti^{3+}	$^2D_{3/2}$	1	1·73	3·00	1·55	1·73—1·85
d^2	V^{3+}, Ti^{2+}	$^3F_2$	2	2·83	4·47	1·63	2·75—2·85
d^3	V^{2+}	$^4F_{3/2}$	3	3·87	5·20	0·70	3·80—3·90
	Cr^{3+}	$^4F_{3/2}$		3·87	5·20	0·70	3·70—3·90
d^4	Cr^{2+}	$^5D_0$	4	4·90	5·48	0·0	4·75—4·90
	Mn^{3+}	$^5D_0$	4	4·90	5·48	0·0	4·90—5·00
d^5	Mn^{2+}	$^6S_{5/2}$	5	5·92	5·92	5·92	5·65—6·10
	Fe^{3+}	$^6S_{5/2}$	5	5·92	5·92	5·92	5·70—6·00
d^6	Fe^{2+}	$^5D_4$	4	4·90	5·48	6·71	5·10—5·70
	Co^{3+}	$^5D_4$	4	4·90	5·48	6·71	~ 5·4
d^7	Co^{2+}	$^4F_{9/2}$	3	3·87	5·20	6·63	4·30—5·20
d^8	Ni^{2+}	$^3F_4$	2	2·83	4·47	5·59	2·80—4·00
d^9	Cu^{2+}	$^2D_{5/2}$	1	1·73	3·00	3·55	1·70—2·20

Table 12·12. *Values of μ_S and μ_{exp} (in B.M.) for d^x configuration of the first row transition series in LS-octahedral complexes (d^2sp^3 bonding : inner-orbital octahedral complexes)*

d^x configuration	*Ions*	*Ground state free ion term*	n_1	n_2	μ_S	μ_{exp}
d^4	Cr^{2+}	$^5D_0$	4	2	4·90	3·20—3·30
	Mn^{3+}	$^5D_0$	4	2	4·90	3·18
d^5	Mn^{2+}	$^6S_{5/2}$	5	1	5·92	1·80—2·10
	Fe^{3+}	$^6S_{5/2}$	5	1	5·92	2·00—2·50
d^6	Fe^{2+}	$^5D_4$	4	0	4·90	~ 0·00
	Co^{3+}	$^5D_4$	4	0	4·90	—
d^7	Co^{2+}	$^4F_{9/2}$	3	1	3·87	1·80—2·00

(3) Distortion of octahedral complexes and Jahn-Teller Theorem

The six-coordinated complexes in which all the six distances between the ligand electron clouds and central metal ion are the same are said to be **regular** (*i.e.*, **symmetrical**) **octahedral complexes.** On the other hand the six-coordinated complexes in which the distances are not equal are said to be **distorted octahedral complexes.** since their shape is changed (*i.e.* distorted). The change in shape is called **distortion.**

Distorted octahedral complexes may be of the following *three types* :

(*i*) *Diagonally distorted octahedral complexes* which are obtained when the distortion of a regular octahedron takes place along a *two-fold axis.*

(*ii*) *Trigonally distorted octahedral complexes* in which the distortion takes place along a *three-fold axis.*

(*iii*) *Tetragonally distorted octahedral complexes* which are also known as **tetragonal complexes.** These are obtained when the distortion of a regular octahedron takes place along a *four-fold axis.*

Tetragonal complexes may be obtained by any of the following two ways :

(*a*) If the two *trans* ligands lying on the *z*-axis in an octahedron are moved away from the central metal cation so that their distance from the metal cation is slightly greater than it is for the other four ligands lying in the *xy* plane, we get a tetragonal structure. Quite obviously this structure has *two long* bonds along the *z*-axis and *four short bonds in xy plane.*

Example (*i*) It has been shown that in tetraammine of Cn^{2+} ion in aqueons solution, $[Cn(NH_3)_4(H_2O)_6]^{2+}$ two water molecules are at larger distance from **the central Cu^{2+} ion than the four** coplanar NH_3 molecules and consequently **the complex has a *tetragonal* shape**. The two water molecules are in a **plane at right angles to that containing** Cu^{2+} ion and four NH_3 molecules which **are at equal distances** from Cu^{2+} ion.

(*ii*) Low-spin octahedral complexes of Ni^{2+}, Pd^{2+} and Pt^{2+} (all d^8 ion) undergo strong distortion and assume *square planar geometry* in which the two ligands along the *z*-axis are at larger distance and four ligands in the *xy*-plane are at shorter distance from M^{2+} ion. M^{III} $(diars)_2I_2$ is an example of such complexes.

(*iii*) In $CuCl_2$ crystal each Cu^{2+} ion is surrounded by six Cl^- ions ; four are at a distance of 2·30 A° and the other two are 2·95 A° away.

(*iv*) In CuF_2 crystal four F^- ions are 1·93 Å away from Cu^{2+} ion, while the two F^- ions are 2·27 Å apart.

(*b*) If the two *trans* ligands located at the *z*-axis are brought near the central metal cation so that their distance from the metal cation is smaller than it is for the other four ligands in the *xy* plane, we again get a tetragonal structure. This structure has *two short bonds* along the *z* axis and *four long bonds in xy plane.*

Examples. (*i*) In K_2CuF_4 the Cu^{2+} ion has two F^- at 1·95 Å and four at 2·08 Å.

(*ii*) In FeF_2 the Fe^{2+} ion has two F^- at 1·99 Å and four at 3·12 Å.

In 1937 Jahn-Teller put forward a theorem known as **Jahn-Teller theorem** which can explain why certain six-coordinated complexes undergo distortion to assume distorted octahedral (*i.e.*, tetragonal) geometry. This theorem states that *any non-linear molecular system possessing degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy and thus will remove digeneracy.* It should be noted that Jahn-Teller theorem only predicts the occurrence of a distortion; it does not predict its nature or its magnitude. If the undistorted configuration has a centre of symmetry, the distorted equilibirium configuration must have one too.

Symmetrical and unsymmetrical t_{2g}-and e_g-orbital. The t_{2g} and e_g-orbitals which are empty (t_{2g}^0 and e_g^0), half-filled (t_{2g}^3 and e_g^2) or completely filled (t_{2g}^6 and e_g^4) are said to be symmetrical orbitals. Here it should be noted that in the strong field (i.e., LS-complexes) e_g-set having two electrons (i.e., e_g^2-set) is unsymmetrical orbital. Orbitals other than those mentioned above are called unsymmetrical orbitals. Thus the symmetrical and unsymmetrical t_{2g} and e_g orbital can be written as :

$$t_{2g} \text{ orbitals} \left\{ \begin{array}{l} t_{2g}^0,\ t_{2g}^3,\ t_{2g}^6 \longrightarrow \text{symmetrical} \\ t_{2g}^1,\ t_{2g}^2,\ t_{2g}^4,\ t_{2g}^5 \longrightarrow \text{unsymmetrical} \end{array} \right.$$

$$e_g \text{ orbitals} \left\{ \begin{array}{l} e_g^0,\ e_g^4 \longrightarrow \text{symmetrical} \\ e_g^1,\ e_g^3 \longrightarrow \text{unsymmetrical} \\ e_g^2 \begin{array}{l} \nearrow \text{symmetrical in HS-complexes } [(d_{x^2-y^2})^1\,(d_{z^2})^1] \\ \searrow \text{unsymmetrical in LS-complexes } [(d_{x^2-y^2})^0\,(d_{z^2})^2] \end{array} \end{array} \right.$$

In Table 12·13 symmetrical [abbreviated as (sym)] and unsymmetrical [abbreviated as (unsym)] t_{2g}- and e_g-orbitals are listed. It will be seen that $t_{2g}-e_g$ pairs of orbitals that can exist are :

(*a*) t_{2g} (sym)—e_g (sym) pair (*b*) t_{2g} (sym)—e_g (unsym) pair (*c*) t_{2g} (unsym)—e_g (sym) pair and that the pair that cannot exist is t_{2g} (unsym)—e_g (unsym) pair.

No Distortion Condition. The *d*-orbitals which have both t_{2g} and e_g-sets as symmetrical orbitals lead to perfectly symmetrical (*i.e.*, regular) octahedral complexes. (*See* Table 12·13). Thus it may be seen from Table 12·13 that the *d*-orbitals : $d^0(t_{2g}^0\ e_g^0)$, d^3 $(t_{2g}^3\ e_g^0)$, d^5 $(t_{2g}^3\ e_g^2)$, d^8 $(t_{2g}^6\ e_g^2)$ and d^{10} $(t_{2g}^6\ e_g^4)$ of HS-octahedral complexes and d^0 $(t_{2g}^0\ e_g^0)$, d^3 $(t_{2g}^3\ e_g^0)$, d^6 $(t_{2g}^6\ e_g^0)$ and $d^{10}(t_{2g}^6\ e_g^4)$ of [illegible]-octahedral complexes give perfectly regular octahedral complexes. Thus in these cases there is no distortion.

Condition for slight distortion. When *d*-orbitals of the central metal ion of an octahedral complex have t_{2g}-orbitals as unsymmetrical orbitals, there occurs slight distortion in the complex, *i.e.* whenever the t_{2g}-orbitals, which do not come direct in the path of the ligands disposed octahedrally around the central metal ion, but point between the ligands contain 1, 2, 4 or 5 electrons, we shall expect only slight distortions from the regular octahedron. Thus, as is evident from Table 12·13, the HS-complexes of d^1 $(t_{2g}^1\ e_g^0)$, d^2 $(t_{2g}^2\ e_g^0)$, d^6 $(t_{2g}^4\ e_c^2)$ and d^7 $(t_{2g}^5\ e_g^2)$ ions and LS-complexes of d^1 $(t_{2g}^1\ e_g^0)$, d^2 $(t_{2g}^2\ e_g^0)$, d^4 $(t_{2g}^4\ e_g^0)$ and d^5 $(t_{2g}^5\ e_g^0)$ ions undergo slight distortion (often not experimentally detectable) from the octahedral shape.

Condition for strong distortion. Whenever the e_g orbitals which point directly towards the ligands, are unsymmetrical *i.e.* contain 1, 3 or 2 (only in LS-complexes) electrons, we shall strong distortions, leading to tetragonal and even to square planar complexes. Distortion produced in an octahedral complex due to the presence of unsymmetrical e_g-orbitals is due to the fact that, since the directions of the e_g-orbitals of the central metal ion correspond with the directions of the ligands disposed octahedrally around the metal ion, the octahedral arrangement of the ligands is likely to be more severely distorted by the dissymmetry of the e_g-orbitals than that of the t_{2g}-orbitals.

Thus from Table 12·13 it can be seen that the configuration : d^4 $(t_{2g}^3\ e_g^1)$, d^9 $(t_{2g}^6\ e_g^3)$ of HS-complexes and d^7 $(t_{2g}^6,\ e_g^1)$, d^8 $(t_{2g}^6\ e_g^2)$, d^9 $(t_{2g}^6\ e_g^3)$ of LS-complexes lead to strong distortion in octahedral complexes.

Conditions for various types of distortions can be summarised as

t_{2g} (*sym*) + e_g (*sym*) ⟶ No distortion

t_{2g} (*unsym*) ⟶ Slight distortion

$$\left.\begin{matrix} e_g\ (unsym) \\ e_g^3\ [(d_{x^2-y^2})^1\ (d_{z^2})^2 \text{ in LS-complexes} \end{matrix}\right\} \longrightarrow \text{Strong distortion}$$

Cause of distortion with some complexes

(*i*) High-spin octahedral complexes of d^4 ion have any of the following configurations :

$$\text{I} \longrightarrow t_{2g}^3 .\ (d_{z^2})^1 .\ (d_{x^2-y^2})^0 : \text{II} \longrightarrow t_{2g}^3 .\ (d_{z^2})^0 .\ (d_{x^2-y^2})^1 .$$

Table 12·13. *Showing* (*i*) *Distribution of electrons in t_{2g}- and e_g-orbitals in HS- and LS-octahedral complexes*
(*ii*) *Symmetrical* [*abbreviated as (sym)*] *and unsymmetrical* [*abbreviated as (unsym)*] *t_{2g}- and e_g-orbitals.*
(*iii*) *Predicted distortion in octahedral complexes.*

Note. The orbitals that are unsymmetrical produce distortion.

No. of d-electrons	*HS-octahedral complexes : weak ligand field (spin-free)*		*LS-octahedral complexes : strong ligand field (spin-paired)*	
	Distribution of electrons in t_{2g} and e_g-orbitals and symmetrical and unsymmetrical orbitals	*Predicted Distortion*	*Distribution of electrons in t_{2g}- and e_g-orbitals and symmetrical and unsymmetrical orbitals*	*Predicted Distortion*
d^0	t_{2g}^0 (*sym*) e_g^0 (*sym*)	No distortion	t_{2g}^0 (*sym*) e_g^0 (*sym*)	No distortion
d^1	t_{2g}^1 (unsym) e_g^0 (*sym*)	Slight distortion	t_{2g}^1 (unsym) e_g^0 (*sym*)	Slight distartion
d^2	t_{2g}^2 (unsym) e_g^0 (*sym*)	Slight distortion	t_{2g}^2 (unsym) e_g^0 (*sym*)	Slight distortion
d^3	t_{2g}^3 (*sym*) e_g^0 (*sym*)	No distortion	t_{2g}^3 (*sym*) e_g^0 (*sym*)	No distortion
d^4	t_{2g}^3 (*sym*) e_g^1 (unsym)	Strong distortion	t_{2g}^4 (unsym) e_g^0 (*sym*)	Slight distortion
d^5	t_{2g}^3 (*sym*) e_g^2 (*sym*)	No distortion	t_{2g}^5 (unsym) e_g^0 (*sym*)	Slight distortion
d^6	t_{2g}^4 (unsym) e_g^2 (*sym*)	Slight distortion	t_{2g}^6 (*sym*) e_g^0 (*sym*)	No distortion
d^7	t_{2g}^5 (unsym) e_g^2 (*sym*)	Slight distortion	t_{2g}^6 (*sym*) e_g^1 (unsym)	Strong distortion
d^8	t_{2g}^6 (*sym*) e_g^2 (*sym*)	No distortion	t_{2g}^6 (*sym*) e_g^2 (unsym)	Strong distortion leading to square planar
d^9	t_{2g}^6 (*sym*) e_g^3 (unsym)	Strong distortion	t_{2g}^6 (*sym*) e_g^3 (unsym)	Strong distortion
d^{10}	t_{2g}^6 (*sym*) e_g^4 (*sym*)	No distortion	t_{2g}^6 (*sym*) e_g^4 (*sym*)	No distortion

When the configuration has one electron in d_{z^2} orbital and the $d_{x^2-y^2}$ orbital is empty (structure I), cation-anion interaction along the *z*-axis is less than that along the *x*-and *y*-axes, leading to a larger interionic distance along the *z*-axis and hence to a tetragonal structure.

(*ii*) Complexes of Cu^{2+} ion (d^9 ion) such as aqueous solution of $[Cu(NH_3)_4]^{2+}$ in which the tetragonal distortion is so marked that a square planar complex results. This ion has the configuration $t_{2g}^6\ e_g^3$ in both the fields. Evidently in this ion the two possible arrangement of electrons in t_{2g}- and e_g- orbitals are :

Configuration I $\longrightarrow t_{2g}^6.(d_{z^2})^2\ (d_{x^2-y^2})^1$ and Configuration II $\longrightarrow t_{2g}^6.(d_{z^2})^1\ (d_{x^2-y^2})^2$.

Since in both the configurations t_{2g}-orbitals are completely filled, asymmetry (*i.e.* distortion) is caused by incomplete filling of e_g-orbitals.

Distortion arises mainly from the repulsion of ligands by the electrons occupying e_g-orbitals. If we consider configuration I namely, $t_{2g}^6.(d_{z^2})^2(d_{x^2-y^2})^1$, the d_{z^2}-orbital, which is completely filled and points at the ligands on the *z*-axis, offers greater shielding of the Cu^{2+} nucleus than the half-filled $d_{x^2-y^2}$-orbital, which points towards the ligands in the *xy*-plane. Thus the ligands on the *x*- and *y*-axes experience a higher effective nuclear charge, while those on the *z*-axis experience a lower effective nuclear charge. Consequently the ligands on the *x*- and *y*- axes are drawn in closer to the Cu^{2+} nucleus and those on the *z*-axis move further out. We thus observe *four short and two long bonds*, *i.e.* the ligands L_5 and L_6 existing along the *z*-axis would be at a greater distance from the central metal ion (Cu^{2+} ion) and the remaining four coplanar ligands : L_1, L_2, L_3 and L_4 (coplanar with the centralised metal ion, Cu^{2+}, in *xy*-plane) would be at a shorter distance from Cu^{2+} ion. Thus :

$$ML_5 = ML_6 > ML_1 = ML_2 = ML_3 = ML_4$$

where ML_1.........etc. indicate the metal ion – ligand distances [Fig. 12·12 (*a*)]. Ligands L_5 and L_6 are trans ligands while the ligands, L_1, L_2, L_3 and L_4 are equatorial ligands.

If, on the other hand, we consider configuration II $\longrightarrow (d_{z^2})^1\ (d_{x^2-y^2})^2\ t_{2g}^6$, we shall expect an exactly opposite distortion *i.e.* the ligands in the *xy*-plane (*i.e.* L_1, L_2, L_3 and L_4 ligands) would move and those (*i.e.* L_5 and L_6 ligands) on the *z*-axis would move out in from their equilibrium positions in the hypothetical regular octahedron and we would expect *two short bonds* (along the *z*-axis) *and four long bonds* (along *x*- and *y*- axes in the *xy*-plane). Thus :

$$ML_1 = ML_2 = ML_3 = ML_4 > ML_5 = ML_6 \text{ [Fig. 12·12(}b\text{)]}$$

How then to decide which of the two possible octahedral distortion configurations : I $\longrightarrow (d_{z^2})^2\ (d_{x^2-y^2})^1.\ t_{2g}^6$ and II $\longrightarrow t_{2g}^6.\ (d_{z^2})^1\ (d_{x^2-y^2})^2$ would yield the more stable complex. *CFT offers no way of deciding it*. Experimental results, however, show that it is I octahedral distortion configuration namely $(d_{z^2})^2\ (d_{x^2-y^2})^1\ .\ t_{2g}^6$ with *two long and* *four short bonds* which is more stable. There is no theoretical explanation for the instability of structure corresponding to II configuration namely $(d_{z^2})^1\ (d_{x^2-y^2})^2 . t_{2g}^6$ having *four long and two short bonds*.

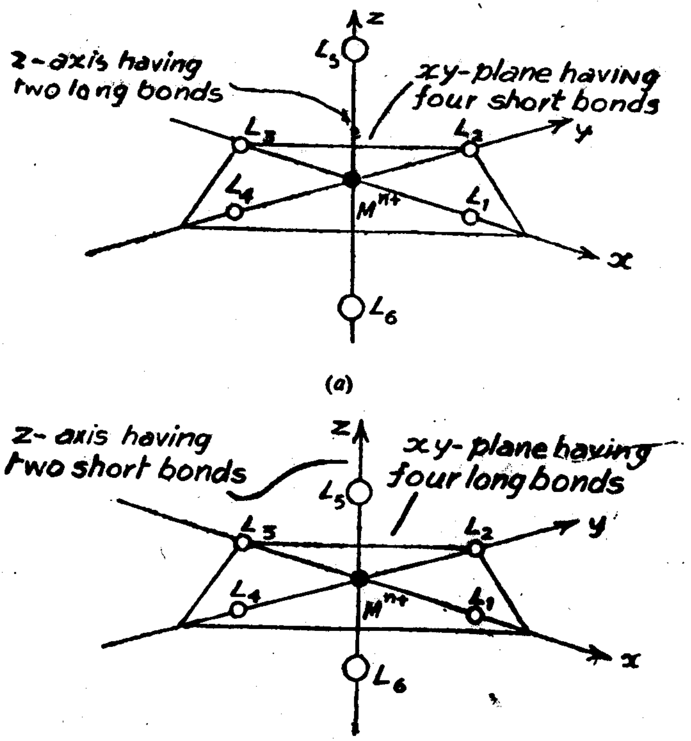


Fig. 12·12. Distortion in an octahedral complex.
(*a*) Configuration I $\longrightarrow (d_{z^2})^2\ (d_{x^2-y^2})^1 . t_{2g}^6$ having two long (along the z-axis) and four short (in the *xy*-plane) bonds, *i.e.* $ML_5 = ML_6 > ML_1 = ML_2 = ML_3 = ML_4$. This configuration is more stable.
(*b*) Configuration II $\longrightarrow (d_{z^2})^1\ (d_{x^2-y^2})^2 . t_{2g}^6$ having four long (coplanar in *xy* plane) and two short (along the z-axis) bonds. Two short bonds are prependicular to the *xy*-plane. Here $ML_1 = ML_2 = ML_3 = ML_4 > ML_5 = ML_6$.

How the d orbital energy levels change in Cu²+ (d⁹ ion) ion when the regular octahedron distorts. Let us consider the manner in which the *d*-orbital energy levels change in the Cu^{2+} ion (d^9 ion) when there occurs a small distortion of the type in which the regular octahedron becomes stretched along *z*-axis. The splitting and energy level diagram caused by such type of distortion are shown in Fig. 12·13.

In this diagram the various splittings are not drawn to scale in the interest of clarity. Here the splitting of the more stable octahedral distortion corresponding to configuration I $\longrightarrow t_{2g}^6\ (d_{z^2})^2\ (d_{x^2-y^2})^1$ has been considered, δ_1 and δ_2, which represent the splitting

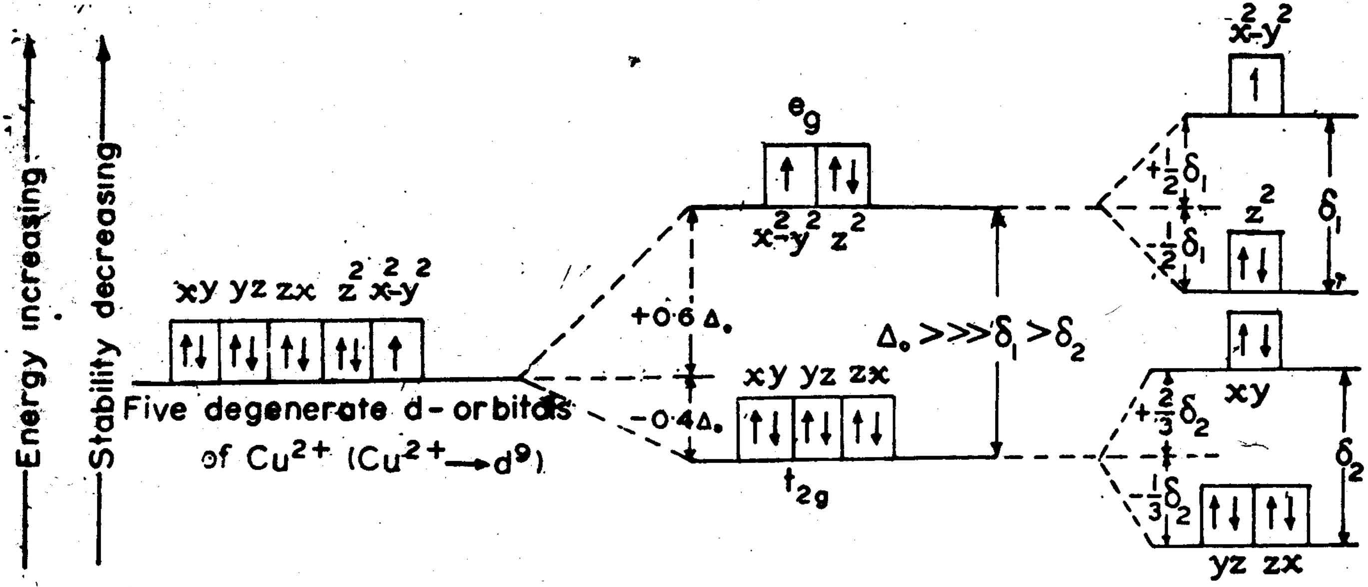


Fig. 12·13. Splitting and energy level diagram of *d*-orbitals of d^9 ion (Cu^{2+} ion) in an octahedral complex caused by Jahn-Teller effect.

of the e_g^2- and t_{2g}^6-levels respectively, both are much smaller than Δ_o and δ_2 is much smaller than δ_1, *i.e.* $\Delta_o >>> \delta_1 > \delta_2$.

The two e_g-orbitals separate so that one (namely $d_{x^2-y^2}$) goes up as much as the other (namely d_{z^2}) goes down ; the t_{2g}-orbitals separate so that doubly degenerate pair (*i.e.* d_{yz} and d_{zx}) goes down only half as far as the single orbital (namely d_{xy}) goes up.

Hence it can be seen that for t_{2g}-electrons there is no net energy change, since four electrons (namely d_{yz} and d_{zx} electrons) are stabilised by $4\times\left(-\frac{1}{3}\delta_2\right)=-\frac{4}{3}\delta_2$, while two electrons (namely d_{xy} electrons) are destabilised by $2\times\left(+\frac{2}{3}\delta_2\right)=+\frac{4}{3}\delta_2$. Thus in the splitting of t_{2g}-levels :

$$\begin{aligned}\text{Net energy gain} &= \text{energy gain}+\text{energy loss}\\ &= +\frac{4}{3}\delta_2+\left(-\frac{4}{3}\delta_2\right)=0\end{aligned}$$

However, in the splitting of e_g levels :

$$\begin{aligned}\text{Net energy gain} &= \text{energy gain}+\text{energy loss}\\ &= 1\times\left(+\frac{1}{2}\delta_1\right)+2\left(-\frac{1}{2}\delta_1\right)\\ &= +\frac{1}{2}\delta_1-\delta_1=-\frac{1}{2}\delta_1\end{aligned}$$

Thus the net lowering of the electronic energy in case of e_g-level is $\delta_1/2$. This net energy equal to $-\delta_1/2$, might be called the Jahn-Teller stabilisation energy and provides the driving force for the distortion.

(*iii*) We have already seen that the *high-spin octahedral complexes* of d^8 ion such as $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(N_2H_4)_3]^{2+}$ etc. are not expected to show distortion, since both t_{2g} and e_g orbitals in these complexes are symmetrically filled as is evident from the arrangement of eight electrons in these orbitals given below :

$$d^8 \text{ (high-spin state)} \longrightarrow t_{2g}^6\, e_g^2 \text{ or } t_{2g}^6\, (d_{x^2-y^2})^1\, (d_{z^2})^1.$$

However, *low-spin octahedral complexes* of d^8 ion (*e.g.* Ni^{2+}, Pd^{2+} and Pt^{2+} ions) undergo strong distortion and assume square planar geometry (*see* Table 12·13). $M^{II}((diars)_2I_2$ is a typical example of such complexes. Under the influence of strong ligand field of diarsine, (*diars*), the two electrons in e_g level pair up in d_{z^2} orbital, leaving $d_{x^2-y^2}$ orbital empty. Thus the arrangement of two electrons in e_g orbitals is *unsymmetrical* as shown below :

$$\left.\begin{array}{l} d^8 \text{ ion in low-spin state} \\ \text{(under the influence of strong} \\ \text{ligand field of } \textit{diarsine} \end{array}\right\} \longrightarrow t_{2g}^6\, (d_{z^2})^2\, (d_{x^2-y^2})^0,$$

and due to the operation of Jahn-Teller effect these orbitals split into a lower energy d_{z^2} orbital and a higher energy $d_{x^2-y^2}$ orbital. The two ligands along z-axis move away from Ni^{2+} ion while the four ligands in the xy plane move closer and as a result, the octahedral complex is *considerably distorted* and *assumes almost square planar geometry.*

4. Crystal field Stabilisation energies CFSE's and their uses

We have seen that, according to CFT, under the influence of the six ligands approaching towards the central metal ion during the formation of an octahedral complex, the d-orbitals of the central metal ion are split into two sets *viz.* t_{2g} (*lower energy set*) and e_g (*higher energy set*) sets. The energy gap between these two sets is equal to Δ_0 (or 10Dq). The energy of t_{2g} set is lowered by $2/5\Delta_0$ ($= 0{\cdot}4\ \Delta_0$) or 4Dq while that of e_g set is raised by $3/5\ \Delta_0$ ($= 0{\cdot}6\ \Delta_0$) or 6 Dq relative to the energy of hypothetical degenerate d-orbitals. Thus each electron occupying t_{2g} orbitals decreases the energy of d-orbitals by $-0{\cdot}4\ \Delta_0 (= -4$ Dq) while that going into e_g orbitals increases its energy by $+0{\cdot}6\ \Delta_0 (= +6$ Dq). $-$ and $+$ signs indicate respectively the decrease and increase in the energy of d-orbitals caused by their splitting under the influence of six ligands.

Now consider a d^{p+q} ion with p electrons in t_{2g} and q electrons in e_g orbitals. Quite obviously :

$$\left.\begin{array}{l}\text{Gain in energy due to}\\ q \text{ electrons in } e_g \text{ orbitals}\\ \text{(in terms of } \Delta_0)\end{array}\right\} = +0{\cdot}6\ \Delta_0 \times q$$

$$\left.\begin{array}{l}\text{and loss in energy due to}\\ p \text{ electrons in } t_{2g} \text{ electrons}\\ \text{(in terms of } \Delta_0)\end{array}\right\} = -0{\cdot}4\ \Delta_0 \times p$$

Thus :

$$\left.\begin{array}{l}\text{Net change in energy}\\ \text{for } d^{p+q}\text{-ion}\\ \text{(in terms of } \Delta_0)\end{array}\right\} = [-0{\cdot}4\,p + 0{\cdot}6\,q]\ \Delta_0 \qquad ...(i)$$

This change in energy in terms of Dq will be given by utilising the relation :

$\Delta_0 = 10$ Dq. Thus :

$$\text{Change in energy (in terms of Dq)} = [-0{\cdot}4\,p + 0{\cdot}6\,q] \times 10 \text{ Dq}$$
$$= [-4\,p + 6\,q] \text{ Dq} \qquad ...(ii)$$

This change in energy is called crystal field stabilisation energy (CFSE), since it stabilises d-orbitals by lowering their energy which results from their splitting into t_{2g} and e_g orbitals.

It may be seen from equations (*i*) and (*ii*) that for d^0 (low-spin and high-spin), d^5 (high-spin) and d^{10} (low-spin and high-spin) ions of an octahedral complex there is no net change in their energy due to their splitting into t_{2g} and e_g orbitals, *i.e.* no stabilisation results from the splitting of d-orbitals of these ions, *e.g.*

(*i*) for a d^{10} ion with $t_{2g}^6\ e_g^4$ configuration, the net change in energy ($p = 6$, $q = 4$)

$$= [-0{\cdot}4 \times 6 + 0{\cdot}6 \times 4]\ \Delta_0 = 0$$

(*ii*) for d^5 (high-spin) ion with $t_{2g}^3\,e_g^2$ configuration, the net change in energy ($p = 3$, $q = 2$)

$$= [-0{\cdot}4\times3+0{\cdot}6\times2]\,\Delta_o = 0$$

If P = mean pairing energy which is the energy required to pair two electrons against electron-electron repulsion in the same orbital and m = No. of paired electrons, then

$$\text{CFSE for } d^{p+q} \text{ ion (in terms of } \Delta_o)$$
$$= [-0{\cdot}4\,p+0{\cdot}6\,q]\,\Delta_o+mP \qquad \ldots(iii)$$

As an illustration let us use equation (*iii*) to calculate CFSE values for d^3, d^4 and d^7 ions in octahedral complexes :

(*i*) **d^3 ion.** We know that the distribution of three *d*-electrons in t_{2g} and e_g levels in both the fields (*i.e.* strong and weak) is $t_{2g}^3\,e_g^0$ and $m = 0$. Thus $p = 3$, $q = 0$ and $m = 0$ and hence

$$\left.\begin{array}{l}\text{CFSE for both the fields}\\ \text{(low spin and high spin}\end{array}\right\} = [-0{\cdot}4\times3+0{\cdot}6\times0]\,\Delta_o+0\times P$$
$$= -1{\cdot}2\,\Delta_o = -12\,Dq$$

(*ii*) **d^4 ion.** (*a*) For *weak field* (*high spin complex*) $d^4 = t_{2g}^3\,e_g^1$. Thus $p = 3$, $q = 1$ and $m = 0$ and hence

$$\text{CFSE for weak field} = [-0{\cdot}4\times3+0{\cdot}6\times1]\,\Delta_o+0\times P$$
$$= -0{\cdot}6\,\Delta_o = -6\,Dq$$

(*b*) For *strong field* (*low spin complex*) $d^4 = t_{2g}^4\,e_g^0$. Thus $p = 4$, $q = 0$ and $m = 1$ and hence

$$\text{CFSE for strong field} = [-0{\cdot}4\times4+0{\cdot}6\times0]\,\Delta_o+1\times P$$
$$= -1{\cdot}6\,\Delta_o+P = -16\,Dq+P$$

(*iii*) **d^7 ion.** (*a*) For weak field (high spin complex) $d^7 = t_{2g}^5 e_g^2$. Thus $p = 5$, $q = 2$ and $m = 2$ and hence

$$\text{CFSE for weak field} = [-0{\cdot}4\times5+0{\cdot}6\times2]\,\Delta_o+2P$$
$$= -0{\cdot}8\,\Delta_o+2P = -8Dq+2P$$

(*b*) For *strong field* (*low spin complex*) $d^7 = t_{2g}^6\,e_g^1$. Thus $p = 6$, $q = 1$ and $m = 3$, and hence

$$\text{CFSE for strong field} = [-0{\cdot}4\times6+0{\cdot}6\times1]\,\Delta_o+3P$$
$$= -1{\cdot}8\,\Delta_o+3P = -18\,Dq+3P$$

On these lines CFSE values for high spin and low spin octahedral complexes have been calculated and are listed (in terms of Δ_o and Dq) in Table 12·14.

Example. *For the* $[Cr(H_2O)_6]^{2+}$ *ion, the mean pairing energy,* P, *is found to be* 23,500 cm^{-1}. *The magnitude of* Δ_o *is* 13,900 cm^{-1}. *Calculate the CFSE for this complex ion corresponding to high spin and low spin state. Which state is more stable?*

Solution. Quite evidently in the given complex ion Cr is present as Cr^{2+} ion which is a d^4 ion.

For a d^4 ion in a high spin state,

$$\text{CFSE} = -0{\cdot}6\,\Delta_o$$

Table 12·14. *CFSE values (in the units of Δ_0 and Dq) for d^0 to d^{10} configuration of metal ion in high-spin (weak field) and low-spin (strong field) octahedral complexes. m = Total number of paired electrons in t_{2g} and e_g orbitals, P = Mean pairing energy.*

d^{p+q}	$t_{2g}^p e_g^q$ configuration in weak field (high-spin)	m	CFSE = $[-0{\cdot}4\,p+0{\cdot}6\,q]\ \Delta_0+mP$ $=[-4\,p+6q]\ Dq+mP$	$t_{2g}^p e_g^q$ configuration in strong field (low-spin)	m	CFSE = $[-0{\cdot}4\,p+0{\cdot}6\,q]\ \Delta_0+mP$ $=[-4\,p+6q]\ Dq+mP$
d^0	$t_{2g}^0 e_g^0$	0	0	$t_{2g}^0 e_g^0$	0	0
d^1	$t_{2g}^1 e_g^0$	0	$-0{\cdot}4\ \Delta_0\ (-4\ Dq)$	$t_{2g}^1 e_g^0$	0	$-0{\cdot}4\ \Delta_0\ (-4\ Dq)$
d^2	$t_{2g}^2 e_g^0$	0	$-0{\cdot}8\ \Delta_0\ (-8\ Dq)$	$t_{2g}^2 e_g^0$	0	$-0{\cdot}8\ \Delta_0\ (-8\ Dq)$
d^3	$t_{2g}^3 e_g^0$	0	$-1{\cdot}2\ \Delta_0\ (-12\ Dq)$	$t_{2g}^3 e_g^0$	0	$-1{\cdot}2\ \Delta_0\ (-12\ Dq)$
d^4	$t_{2g}^3 e_g^1$	0	$-0{\cdot}6\ \Delta_0\ (-6\ Dq)$	$t_{2g}^4 e_g^0$	1	$-1{\cdot}6\ \Delta_0$ (or -16 Dq)+P
d^5	$t_{2g}^3 e_g^1$	0	$0{\cdot}0\ \Delta_0\ (0{\cdot}0\ Dq)$	$t_{2g}^5 e_g^0$	2	$-2{\cdot}0\ \Delta_0$ (or -20 Dq)+2P
d^6	$t_{2g}^4 e_g$	1	$-0{\cdot}4\ \Delta_0$ (or -4 Dq)+P	$t_{2g}^6 e_g^0$	3	$-2{\cdot}4\ \Delta_0$ (or -24 Dq)+3P
d^7	$t_{2g}^5 e_g^2$	2	$-0{\cdot}8\ \Delta_0$ (or -8 Dq)+2P	$t_{2g}^6 e_g^1$	3	$-1{\cdot}8\ \Delta_0$ (or -18 Dq)+3P
d^8	$t_{2g}^6 e_g^2$	3	$-1{\cdot}2\ \Delta_0$ (or -12 Dq)+3P	$t_{2g}^6 e_g^2$	3	$-1{\cdot}2\ \Delta_0$ (or -12 Dq)+3P
d^9	$t_{2g}^6 e_g^3$	4	$-0{\cdot}6\ \Delta_0$ (or -6 Dq)+4P	$t_{2g}^6 e_g^3$	4	$-0{\cdot}6\ \Delta_0$ (or -6 Dq)+4P
d^{10}	$t_{2g}^6 e_g^4$	5	$0{\cdot}0\ \Delta_0$ (or $0{\cdot}0$ Dq)+5P	$t_{2g}^6 e_g^4$	5	$0{\cdot}0\ \Delta_0$ (or $0{\cdot}0$ Dq)+5P

$$= -0{\cdot}6\times(13{,}900\ \text{cm}^{-1}) = -8{,}340\ \text{cm}^{-1}$$

For a d^4 ion in a low spin state,

$$\begin{aligned} \text{CFSE} &= -1{\cdot}6\ \Delta_o + P \\ &= -1{\cdot}6\times(13{,}900\ \text{cm}^{-1}) + 23{,}500\ \text{cm}^{-1} \\ &= +1{,}260\ \text{cm}^{-1} \end{aligned}$$

Since $\Delta_o\ (= 13{,}900\ \text{cm}^{-1}) < P\ (= 23{,}500\ \text{cm}^{-1})$, the high spin configuration would be more stable.

CFSE values (in the units of Δ_o and Dq) for octahedral, tetrahedral and square planar complexes (in both the fields) are collectively given in Table 12·15. In this Table -ive sign has been omitted and mean pairing energy, P, has not been considered.

Uses of CFSE values

Following are the important uses of CFSE values :

(*i*) **Crystal structure of spinels.** Mixed oxides of the general formula $A^{2+}B_2^{3+}O_4^{2}$ are called spinels after the name of the mineral spinel, $MgAl_2O_4$. A^{2+} and B^{3+} are divalent and trivalent metallic cations which may be different or the same. In spinels oxygen atoms are arranged in a *cubic close-packed lattice.* In such lattices each oxygen atom has 12 other oxygen atoms equidistant from it and the holes between oxygen atoms are of two types : (*i*) *octahedral holes* which are so called because these are surrounded by six oxygen atoms. There is one of such holes for each oxygen atom. (*ii*) *tetrahedral holes* which are so called since these are surrounded by four oxygen atoms. There are two such holes for each oxygen atom. These are smaller than the octahedral holes. There are twice as many tetrahedral holes as there are octahedral holes. The cations occupy the octahedral and tetrahedral holes, since these are large enough to be filled by cations.

There are two main types of spinels : (*i*) *normal* and (*ii*) *inverse.* In normal spinels all the A^{2+} cations occupy one of the eight available tetrahedral holes (positions where a cation can be surrounded by four anions) and all B^{3+} cations occupy half of the available octahedral holes. In inverse spinels all the A^{2+}-and half of the B^{3+} cations are in octahedral and the other half of the B^{3+} cations are in tetrahedral holes. These inverse spinels are, therefore, represented as $B^{3+}[A^{2+}B^{3+})O_4^{2-}$ to distinguish them from the normal spinels which are represented as $A^{2+}[B_2^{3+}]O_4^{2-}$. The species enclosed in square brackets occupy the octahedral holes.

Spinels of general formula $A^{4+}B_2^{2+}O_4^{2}$ have also been obtained. Examples are : $Ti^{4+}Zn_2^{2+}O_4^{2-}$ $Sn^{4+}Co_2^{2+}O_4^{2-}$ etc. These are inverse spinels. Examples of simple and inverse spinels of $A^{2+}B_2^{3+}O_4^{2+}$ formula are given below :

Simple spinels : $M^{2+}[Al_2^{3+}]O_4$ where $M^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$; $Mg^{2+}[Cr_2^{3+}]O_4$, $Ni^{2+}[Cr_2^{3+}]O_4$, Mn_3O_4 or $Mn^{2+}[Mn_2^{3+}]O_4$, Co_3O_4 or $Co^{2+}[Co_2^{3+}]O_4$ etc.

Table 12·15. *Crystal field stabilisation energies (CFSE) in terms of Δ_0 and Dq for d^0 to d^{10} configurations of metal ions in high-spin and low-spin octahedral, tetrahedral and square planar complexes.*

No. of d- electrons ⟶		d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
High-spin (weak field)	**Octahedral**	0 Δ_0	0·4	0·8	1·2	0·6	0	0·4	0·8	1·2	0·6	0
		0 Dq	4	8	12	6	0	4	8	12	6	0
	Tetrahedral	0 Δ_0	0·27	0·54	0·36	0·18	0	0·27	0·54	0·36	0 18	0
		0 Dq	2·67	5·34	3·56	1·78	0	2 67	5·34	3 56	1·78	0
	Square planar	0 Δ_0	0·51	1·02	1·45	1·22	0	0·51	1·02	1·45	1·22	0
		0 Dq	5·14	10·28	14 56	12·28	0	5 14	10·28	14·54	12·28	0
Low-spin (strong field	**Octahedral**	0 Δ_0	0·4	0·8	1·2	1 6	2·0	2·4	1·8	1·2	0·6	0
		0 Dq	4	8	12	16	20	24	18	12	6	0
	Tetrahedral	0 Δ_0	0·27	0·54	0·81	1·08	0·90	0·72	0 54	0·36	0·18	0
		—	—	—	—	—	—	—	—	—	—	—
	Square planar	0 Δ_0	0·57	1·02	1·45	1·96	2·47	2·90	2 67	2·44	1·22	0
		0 Dq	5·14	10·28	14·56	19·70	24·84	29 12	26 84	24·56	12·28	0

Inverse spinels : $CuFe_2O_4$ or $Fe^{3+}(Cu^{2+}Fe^{3+})O_4$, $MgFe_2O_4$
or $Fe^{3+}[Mg^{2+}Fe^{3+}]O_4$, Fe_3O_4 or $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, $TiZn_2O_4$
or $Zn^{2+}[Ti^{4+}Zn^{2+}]O_4$, $SnCo_2O_4$ or $Co^{2+}[Sn^{4+}Co^{2+}]O_4$ etc.

The cations given in brackets occupy the octahedral holes while those given outside it are in the tetrahedral holes.

Now let us see how CFT helps in predicting the structure of spinels. For example with the help of CFT it can be shown why the oxide Mn_3O_4 or $Mn^{2+}Mn_2^{3+}O_4$ is a normal spinel while the oxide Fe_3O_4 or $Fe^{2+}Fe_2^{3+}O_4$ is an inverse spinel. CFSE values is octahedral and tetrahedral fields have been used for the interpretation. For this it is assumed that the oxide ions, O^{2-}, like water molecules, produce weak field. CFSE values (in terms of Δ_0) for $Mn^{3+}(d^4)$, Fe^{3+}, $Mn^{2+}(d^5)$ and $Fe^{2+}(d^6)$ ions in octahedral and tetrahedral weak ligand (*i.e.* high spin) field are given below :

	$Mn^{3+}(d^4)$	$Mn^{2+}(d^5)$	$Fe^{3+}(d^5)$	$Fe^{2+}(d^6)$
CFSE (*octahedral weak field*) :	0·60 Δ_0	0	0	0·40 Δ_0
CFSE (*tetrahedral weak field*) :	0·18 Δ_0	0	0	0·27 Δ_0

It is obvious that for $Mn^{3+}(d^4)$ and $Fe^{2+}(d^6)$ ions the CFSE values are greater for octahedral than for tetrahedral sites. Thus Mn^{3+} and Fe^{2+} ions will preferentially occupy the octahedral sites, maximising the CFSE values of the system Hence in Mn_3O_4 all the Mn^{3+} ions occupy octahedral sites and all Mn^{2+} ions are in the tetrahedral sites, *i e.* it is a normal spinel and its structure is, therefore, represented as $Mn^{2+}[Mn_2^{3+}]O_4$. In Fe_3O_4 all the Fe^{2+} ions and half of the Fe^{3+} ions are in the octahedral sites, while the remaining half of Fe^{3+} ions occupy tetrahedral sites. Thus it is an inveres spinel and is, therefore represented as : $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$.

(*ii*) **Stablisation of oxidation states.** CFSE values also explain why certain oxidation states are preferentially stabilised by coordinating with certain ligands. The following two examples illustrate this use :

(*a*) Although H_2O molecule which is a *weak ligand* should be expected to coordinate with Co^{2+} and Co^{3+} ions to form the high-spin octahedral complexes : $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$ respectively, experiments show that H_2O stablises Co^{2+} ion and not Co^{3+}, *i.e.* $[Co(H_2O)_6]^{2+}$ is more stable than $[Co(H_2O)_6]^{3+}$. This is because of the fact that $Co^{2+}(d^7)$ has a much higher value of CFSE in weak octahedral configuration (CFSE = 0·8 Δ_0) than $Co^{3+}(d^6)$ in the same configuration (CFSE = 0·4 Δ_0).

(*b*) If we consider the coordination of NH_3 molecules with Co^{2+} and Co^{3+} ions, it may be seen that NH_3 which is a *strong ligand* stablises Co^{3+} ion by forming $[Co(NH_3)_6]^{3+}$ rather than Co^{2+} ion. This is because of the fact that Co^{3+} ion (d^6 system) has much higher value of CFSE in strong octahedral configuration (CFSE = 2·4 Δ_0) than Co^{2+} ion (d^7 system) in the same configuration (CFSE = 1·8 Δ_0).

(*iii*) **Stereochemistry of complexes.** (*a*) CFSE values also predict why Cu^{2+} ion forms square planar complexes rather than tetrahedral or octahedral complexes in both the fields. This is because of the reason that Cu^{2+} ion (d^9 system) has a much higher CFSE value in a square planar configuration (CFSE $= 1{\cdot}22\ \Delta_0$) than in octahedral (CFSE $= 0{\cdot}6\ \Delta_0$) or tetrahedral configuration (CFSF $= 0{\cdot}18\ \Delta_0$).

(*b*) Most of the four coordinated complexes of Ni^{2+} ion (d^8 system) are square planar rather than tetrahedral $(NiX_4)^{2-}$ is an exception, $X = Cl^-, Br^-, I^-$). This is because CFSE values for d^8 ion are higher in square planar configuration than those of the same ion in tetrahedral configuration (*see* Table 12·15).

(*iv*) **Heats of hydration of divalent ions of first row transition elements.** The heat of hydration is the heat evolved in the hydration process :

$$M^{2+}(g) + 6\,H_2O \longrightarrow [M(H_2O)_6]^{2+}\,(aq) - \text{heat of hydration}$$

Minus sign indicates that heat of hydration is evolved in the hydration process.

We know that on passing from Ba^{2+} to Mg^{2+} (alkaline earth metals) in II A group of the periodic table there is a decrease in the ionic radii. This decrease in ionic radii values brings the ligands *viz.* H_2O molecules closer to the metal cation, M^{2+}, resulting in the increased electrostatic attraction between the cation and the ligands. Consequently the values of heats of hydration increase steadily from Ba^{2+} to Mg^{2+}.

Now we know that since the ionic radii of divalent ions of the first row transition elements (Ca^{2+} to Zn^{2+}) decrease, the experimental values of heats of hydration of these ions should also increase regularly from Ca^{2+} to Zn^{2+}. However this increase does not happen as is evident from the graph shown in Fig. 12·14 which shows that the experimental values, instead of increasing regularly, show maxima at V^{2+} (d^3 ion) and Ni^{2+} (d^8 ion) and minima at Ca^{2+} (d^0 ion), Mn^{2+} (d^5 ion) and Zn^{2+} (d^{10} ion). The unexpected maxima and minima can be explained on the basis of CFSE concept. The hexahydrated ions, $[M(H_2O)_6]^{2+}$ are high-spin octahedral complexes and for high-spin complexes CFSE is minimum (zero) for d^0 (Ca^{2+}), d^5 (Mn^{2+}) and d^{10} (Zn^{2+}) ions and maximum ($= 1{\cdot}2\ \Delta_0$) for d^3 (V^{2+}) and d^8 (Ni^{2+}) ions.

If these experimental values (shown by dots, ·) are corrected for each ion (the correction is done by substracting the calculated CFSE values given in Table 12·14 from the experimental values), we get a smooth curve on which these corrected values have been shown by crosses, ×. This curve indicates the expected regular increase. Experimental values are irregular and hence incorrect values while corrected values are regular and hence are the correct values. Note that the ions *viz.* $Ca^{2+}(d^0)$, $Mn^{2+}(d^5)$ and $Zn^{2+}(d^{10})$ which donot have CFSE (zero) have experimental values on the smooth curve.

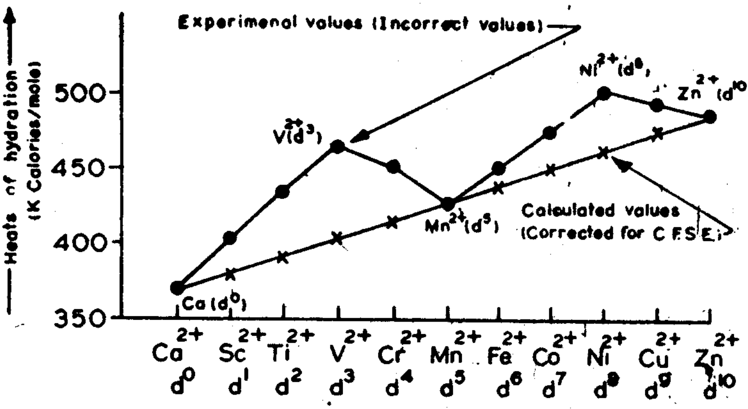


Fig. 12·14. Heats of hydration of divalent ions of first-row transition elements. Dots(·) are experimental values while crosses (×) show the corrected values.

Example. *The heat of hydration of* Cr^{2+} *ion is 460 kcal/mole. For* $[Cr(H_2O)_6]^{2+}$, $\Delta_0 = 13{,}900\ cm^{-1}$. *Calculate what heat of hydration would be, if there were no crystal field stablisation energy.*

Solution. We know that since Cr^{2+} ion is d^4 ion, the calculated CFSE for a high-spin octahedral complex of Cr^{2+} *viz.* $[Cr(H_2O)_6]^{2+}$ $= -0{\cdot}6\ \Delta_0 = -\ 0{\cdot}6 \times 13{,}900\ cm^{-1}$.

Now since $350\ cm^{-1} = 1$ kcal/mole,

$$\text{calculated CFSE} = \frac{-0{\cdot}6 \times 13{,}900}{350} = -24\ \text{kcal/mole}$$

$$\left.\begin{array}{l}\text{Thus, heat of hydration when}\\ \text{there is no crystal field}\\ \text{stabilisation energy}\end{array}\right\} = \text{Experimental value} - \text{calculated value}$$

$$= -460 - (-24)$$

$$= -436\ \text{kcal/mole.}$$

Limitations of CFT

(*i*) CFT considers only the metal ion *d*-orbitals and gives no consideration at all to other metal orbitals such as *s*-, p_x-, p_y- and p_z- orbitals and the ligand π-orbitals. Therefore, to explain all the properties of the complexes dependent on the π-ligand orbitals will be outside the scope of CFT. CFT does not consider the formation of π-bonding in complexes.

(*ii*) CFT is unable to account satisfactorily for the relative strengths of ligands, *e.g.*, it gives no explanation as to why H_2O appears in the spectro-chemical series as a stronger ligand than OH^-.

(*iii*) According to CFT, the bond between the metal and ligands are purely ionic. It gives no account of the partly covalent nature of the metal—ligand bonds. Thus the effects directly dependent on covalency cannot be explained by CFT.

Experimental Evidence for metal-ligand covalent bonding in complexes

The following evidences have been presented to show the metal-ligand covalent bonding in complexes.

(*i*) **Electron spin resonance (*esr*) spectra.** Most direct evidence is obtained from *esr* spectrum of complexes, *e.g.*, *esr* spectrum of $[Ir^{IV}Cl_6]^{2-}$ ion shows that it has a complex pattern of sub-bands which is called the *hyperfine structure.* The hyperfine structure has been explained by assuming that certain of the iridium orbitals and certain orbitals of the surrounding Cl^- ions overlap to such an extent that the single unpaired *d*-electron is not localised entirely on the metal ion but instead is about 5% localised on each Cl^- ion. Such study of other complexes also gives similar results.

(*ii*) **Nuclear magnetic resonance** (*nmr*). *nmr* studies of complexes like $KMnF_3$ and $KNiF_3$ show that the metal t_{2g} and e_g electrons pass a fraction of time around the fluorine nuclei.

(*iii*) **Nuclear quadrupole resonance** (*nqr*). The *nqr* spectrum of some of the square-planar complexes of Pt(II) and Pd(II) such as $[Pt^{II}X_4]^{2-}$ and $[Pd^{II}X_4]^{2-}$ suggest that there is considerable amount of covalency in the metal-ligand bonds (*i.e.* Pt—X or Pd—X bonds).

(*iv*) **The unusually large absorption band intensities** observed for tetrahedral complexes like $[Co^{II}Cl_4]^{2-}$ have been explained by saying that the metal-ligand bonds have appreciable covalent character.

LIGAND FIELD THEORY (LFT) OR MOLECULAR ORBITAL THEORY (MOT)

The crystal field theory takes no account of possible covalent bonding in complexes—and regards the bonding as purely electrostatic. But the physical measurements such as electron spin resonance, NMR and nuclear quadruple resonance suggest that there is some measure of covalent bonding also in complexes. It is because of this reason that a kind of modified form of CFT has been suggested in which some parameters are empirically adjusted to allow for covalence in complexes without explicitly introducing covalence into CFT. This modified form of CFT is often called **Ligand Field Theory,** LFT. However, LFT is sometimes also used as a general name for the whole gradation of theories from CFT to the molecular Orbital Theory, MOT. In our present discussion we shall use the term LFT in the latter sense. Cotton and Wilkinson have called LFT, Adjusted Crystal Field Theory, ACFT.

The covalent bonding complexes may be considered in terms of MOT. This theory starts with the premise that overlap of AO's of the central metal ion and those of the ligands will occur, to some degree, whenever the conditions of energy, overlap and symmetry permit. The first task in working out the MO treatment for a particular type of complex is to find out which AO's of the central ion and ligands can be combined. This can be done quite elegantly and systematically using some principles of group theory, but because this theory is outside the scope of this book, it will not be discussed here. Here we shall deal simply with the results. The MO's we shall be using here will be of the LCAO type and we shall consider the formation of MO's specifically in octahedral complexes only.

MOT as applied to octahedral complexes

According to MOT the metal-ligand σ-bonding in octahedral complexes results from the overlap of suitable atomic orbitals of the central metallic cation with ligand σ-orbitals.

The formation of six metal-ligand σ-bonds (or MO's) in an octahedral complex takes place through the following steps :

(*i*) The central metal cation of 3*d*-series elements contains in all nine valence-shell atomic orbitals which are : $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$. In this step we make a selection of only six suitable atomic orbitals which may overlap along the axis with group ligand σ-orbitals to form six metal-ligand σ-bonds (or MO's).

All the nine atomic orbitals have been grouped into four symmetry classes which are given below :

$4s \longrightarrow A_{1g}$ or a_{1g} ; $4p_x$, $4p_y$, $4p_z \longrightarrow T_{1u}$ or t_{1u}. $3d_{x^2-y^2}$,
$3d_{z^2} \longrightarrow E_g$ or e_g ; and $3d_{xy}$, $3d_{yz}$, $3d_{zx} \longrightarrow T_{2g}$ or t_{2g}.

Now, we know that since in an octahedral complex six σ-orbitals of the six ligands are approaching along the axes Fig. 12·15

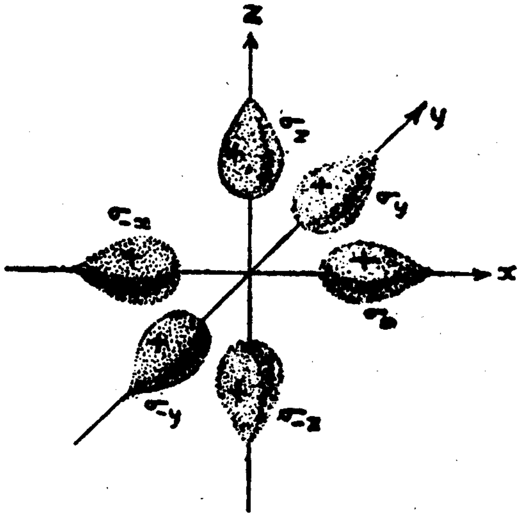


Fig. 12·15. Six ligand σ-orbitals in an octahedral complex.

in which ligand σ-orbitals along the $+x$, $-x$, $+y$, $-y$, $+z$ and $-z$ axes have been represented as σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z, and σ_{-z} respectively), these σ-orbitals, in order to form six metal-ligand σ-bonds or MO's, will overlap more effectively with only those metal ion valence AO's that are having their lobes along the axes (*i.e.*, along the metal-ligand direction). Quite evidently, such AO's are $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{z^2}$ and $3d_{x^2-y^2}$, since these orbitals have their lobes lying along the axes along which the six σ-orbitals of the six ligands are approaching towards the central metal cation to form six metal-ligand σ-bonds.

The remaining three AO's namely $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$ do not participate in σ-bonding process, since these have their lobes oriented in space between the axes. Thus these orbitals remain non-bonding and hence are called *non-bonding orbitals*. These can, however, overlap *sidewise* with filled or unfilled π-orbitals of the same six ligands (π-orbitals are those which are capable of forming metal-ligand π-bonds) to form metal-ligand π-bonds or π-MO's. Thus these orbitals are generally referred to as π_d, $\pi(d)$, d_π or $\pi_{xy} = \pi_{yz} = \pi_{zx}$ orbitals.

(*ii*) In this step the σ_x, σ_{-x}... etc. orbitals of the ligands combine together linearly to form such group ligand σ-orbitals that should be capable of overlapping with the central metal ion six AO's *viz* $4s$, $4p_x$. $4p_y$, $4p_z$, $3d_{z^2}$ and $3d_{x^2-y^2}$. The determination of such linear combination of ligand σ-orbitals is made by inspection method which is a straightforward and common sense method. It is shown below ,

(*a*) Since $4s$ orbital has the same sign in all directions, the linear combination of ligand σ-orbitals which can overlap with $4s$ orbital is : $\sigma_x+\sigma_{-x}+\sigma_y+\sigma_{-y}+\sigma_z+\sigma_{-z}$. This linear combination is represented by Σ_a which in its normalised form, is given by :

$$\Sigma_a=\frac{1}{\sqrt{6}}\,(\sigma_x+\sigma_{-x}+\sigma_y+\sigma_{-y}+\sigma_z+\sigma_{-z}) \qquad \ldots A_{1g} \text{ or } a_{1g}$$

A_{1g} or a_{1g} represents group symmetry class name of Σ_a.

(*b*) Since one lobe of $4p_x$ orbital has + sign and the other has — sign, the linear combination of ligand σ-orbitals that can overlap with $4p_x$ orbital is $\sigma_x-\sigma_{-x}$. It is represented by Σ_x which in its normalised form is given as :

$$\Sigma_x=\frac{1}{\sqrt{2}}\,(\sigma_x-\sigma_{-x}) \qquad \ldots E_g \text{ or } e_g$$

Similarly $\sigma_y-\sigma_{-y}$ and $\sigma_z-\sigma_{-z}$ are the linear combinations of ligand σ-orbitals that overlap with $4p_y$ and $4p_z$ atomic orbitals respectively. Thus :

$$\Sigma_y=\frac{1}{\sqrt{2}}\,(\sigma_y-\sigma_{-y}) \qquad \ldots E_g \text{ or } e_g$$

$$E_z=\frac{1}{\sqrt{2}}\,(\sigma_y-\sigma_{-z}) \qquad \ldots E_g \text{ or } e_g$$

(*c*) Since one opposite pair of lobes of $3d_{x^2-y^2}$ orbital has a + sign and the other has — sign, the linear combination of ligand σ-orbitals for this orbital is : $\sigma_x+\sigma_{-x}-\sigma_y-\sigma_{-y}$. Thus

$$\Sigma_{x^2-y^2}=\frac{1}{2}(\sigma_x+\sigma_{-x}-\sigma_{-y}-\sigma_{-y}) \qquad \ldots T_{1u} \text{ or } t_{1u}$$

(*d*) To find the ligand σ-orbital combination for $3d_{z^2}$ orbital poses some difficulty The analytical function for $3d_{z^2}$ orbital is proportional to $3z^2-r^2$. The proper σ-orbital combination is easily written down by substituting $x^2+y^2+z^2$ for r^2 in $3z^2-r^2$. Thus $3z^2-r^2=3z^2-(x^2+y^2+z^2)=2z^2-x^2-y^2$. Consequently the proper combination for $3d_{z^2}$ orbital is :

$$2(\sigma_z+\sigma_{-z})-(\sigma_x+\sigma_{-x})-(\sigma_y+\sigma_{-y})=2\sigma_z+2\sigma_{-z}-\sigma_x-\sigma_{-x}-\sigma_y-\sigma_{-y}$$

Thus

$$\Sigma_{z^2}=\frac{1}{2\sqrt{3}}\ (2\sigma_z+2\sigma_{-z}-\sigma_x-\sigma_{-x}-\sigma_y-\sigma_{-y})\ldots\ldots\ldots T_{1u} \text{ or } t_{1u}$$

The group symmetry names given above show that there is no ligand σ-orbitals with T_{2g} or t_{2g} symmetry name. Thus $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ atomic orbitals which are with T_{2g} or t_{2g} symmetry will not combine with any of the above group ligand σ-orbitals which are with $(a_{1g}+e_g+t_{1u})$ symmetry, *i.e.* these atomic orbitals will not participate in the formation of molecular orbitals and hence remain as non-bonding orbitals.

(*iii*) This is the final step in which the six atomic orbitals of the central metal cation *viz* $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{x^2-y^2}$ and $3d_{z^2}$ overlap with six group ligand σ-orbital *viz* Σ_s, Σ_x, Σ_y, Σ_z, $\Sigma_{x^2-y^2}$ and Σ_{z^2} respectively to form six sigma bonding (abbreviated as σ^b) and six sigma antibonding (abbreviated as σ^*) molecular orbitals. Here it should be noted that atomic orbitals and the group ligand σ-orbitals which are overlapping together to form the molecular orbitals are of the same symmetry. Thus :

(*a*) $4s$ and Σ_s which have the same symmetry (a_{1g} symmetry) overlap to form one $\sigma_s{}^b$ MO and one $\sigma_s{}^*$MO.

(*b*) $4p_x$ and Σ_x (both with e_g symmetry) overlap to form one $\sigma_x{}^b$-MO and $\sigma_x{}^*$-MO.

(*c*) $4p_y$ and Σ_y (both with e_g symmetry) overlap to form one $\sigma_y{}^b$-MO and one $\sigma_y{}^*$-MO.

(*d*) $4p_z$ and Σ_z (both are with e_g symmetry) overlap to generate one $\sigma_z{}^b$-MO and one $\sigma_z{}^*$-MO.

(*e*) $3d_{z^2}$ and Σ_{z^2} (both with t_{1u} symmetry) overlap to form one $\sigma_{z^2}{}^b$-MO and $\sigma_{z^2}{}^*$-MO.

(*f*) $3d_{x^2-y^2}$ and $\Sigma_{x^2-y^2}$ (both with t_u symmetry) overlap to give one $\sigma_{x^2-y^2}{}^b$-MO and one $\sigma_{x^2-y^2}{}^*$-MO.

Thus we see that the combination of six central metal atomic orbitals with six ligand σ-orbitals gives six σ^b and six σ^* molecular orbitals in an octahedral complex. It is thus obvious that on adding twelve molecular orbitals ($6\sigma^b$- and $6\sigma^*$-MO's) to the three non-bonding AO's *viz.* $3d_{xy}$, $3d_{yz}$ $3d_{zx}$, we get in all fifteen orbitals potentially available for electron filling.

σ^b-MO's are generated when the metal AO's and the group ligand σ-orbitals combine together with *maximum positive overlap* and σ-*MO's are formed when the orbitals overlap together with ***maximum negative overlap.***

Overlap of metal AO's : $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{x^2-y^2}$ and $3d_{z^2}$ with group ligand σ-orbitals : Σ_s, Σ_x. Σ_y, Σ_z, $\Sigma_{x^2-y^2}$ and Σ_{z^2} respectively, which are of the exact same symmetry, to produce σ^b-MO's is shown pictorially Fig. 12·16.

From Fig. 12·16, the following points may be noted :

(*i*) The wave functions of all the six ligand orbitals used for combination with 4*s*-orbital have the same sign (*i.e.* + sign) as the metal 4*s*-orbital. This is a case in which the orbitals combine together with maximum positive overlap and give the bonding MO's [Fig. 12·16 (*a*)]. The corresponding antibonding MO's would involve reversal of sign of the wave-fuction of the combining orbitals.

(*ii*) Each of the metal *p*-orbitals combines with a ligand combination orbital involving two ligands as shown for the $4p_z$ orbital [Fig. 12·16 (*b*)].

(*iii*) The d_{z^2} and $d_{x^2-y^2}$ orbitals of the central metal ion combine with the combination ligand orbitals of the same symmetry (e_g-symmetry with the signs as shown in Fig. 12·16 (*c*) and (*d*).

Energy order of orbitals and their filling with electrons.

The order of energy of different orbitals formed in an octahedral complex depends on the nature of the ligands *i.e.* whether the ligands are strong(er) or weak(er). Thus two cases arise :

(*i*) **When the ligands are strong(er).** Strong(er) ligands such as NH_3 molecules spilt the σ-bonding MO's namely σ_s^b, $\sigma_x^b = \sigma_y^b = \sigma_z^b$, $\sigma_{x^2-y^2}^b = \sigma_{z^2}^b$ more widely and the energy difference, Δ_0 between the t_{2g}-set of non-bonding AO's ($3d_{xy}$, $3d_{yz}$ and $3d_{zx}$) and e_g^*-set of MO's($\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ MO's) is greater than the electron pairing energy, P (*i.e* $\Delta_0 > P$). In this case, the order of energy of different orbitals is shown as follows :

stability decreasing ⟶
Energy Increasing ⟶

$\sigma_x^* = \sigma_y^* = \sigma_z^*$ (3)..................σ_p^* (t_{1u}^*) }
σ_s^* (1)....................................(a_{1g}^*) } six σ^* MO's
$\sigma_{x^2-y^2}^* = \sigma_{z^2}^*$(2)...$\sigma_d^*$ or $\sigma^*(d)$ (e_g^*) }

↕ Δ_0 or 10 D_q

$3d_{xy} = 3d_{yz} = 3d_{zx}$ (3)...π_d or $\pi(d)$or d_π or } Three non-bonding
$\pi_{xy} = \pi_{yz} = \pi_{zx}$ (t_{2g}) } AO's

$\sigma_{x^2-y^2}^b = \sigma_{z^2}^b$ (2)......σ_d^b (e_g). }
$\sigma_x^b = \sigma_y^b = \sigma_z^b$ (3).........σ_p^b (t_{1u}). } six σ^b MO's
σ_s^b (1) ... .(a_{1g}). }

Numbers given in brackets indicate the degeneracy of the MO's or AO's as the case may be, *e.g.* the MO's *viz.* σ_x^b, σ_y^b and σ_z^b are ***triply degenerate.***

Quite evidently the σ^b-MO's have the lowest energy, σ^*-MO's have the highest energy while the non-bonding orbitals *viz.* $3d_{xy}$, $3d_{yz}$

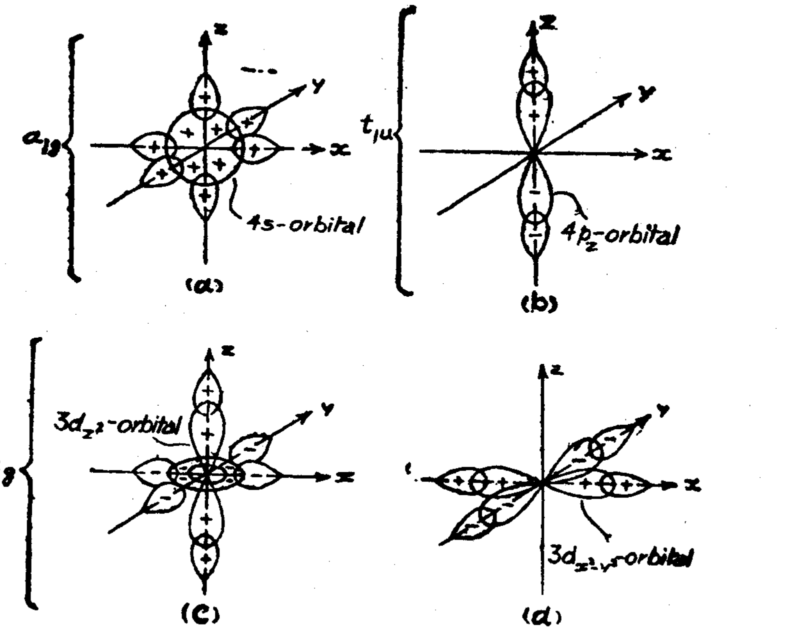


Fig. 12·16. Combination of 4s, $4p_z$ (similarly for $4p_x$ and $4p_y$), $3d_{z^2}$ and $3d_{x^2-y^2}$ AO's of the central metal atom with a group ligand σ-orbitals to form bonding σ-MO's in an octahedral complex.

(*a*) Overlap of metal 4s-orbital (a_{1g} symmetry orbital) with a group ligand σ-orbitals (a_{1g} symmetry).

$$\Sigma_s = \frac{1}{\sqrt{6}}\,(\sigma_x+\sigma_{-x}+\sigma_y+\sigma_{-y}+\sigma_z+\sigma_{-z})$$

(*b*) Overlap of metal $4p_z$-orbital (t_{1u} symmetry orbital) with a group ligand σ-orbital (t_{1u} symmetry).

$$\Sigma_z = \frac{1}{\sqrt{2}}\,(\sigma_z-\sigma_{-z})$$

(*c*) Overlap of metal $3d_{z^2}$-orbital (e_g symmetry orbital) with a group ligand σ-orbitals (e_g-symmetry).

$$\Sigma_{z^2} = \frac{1}{2\sqrt{3}}\,(2\sigma_z+2\sigma_{-z}-\sigma_x-\sigma_{-x}-\sigma_y-\sigma_{-y})$$

(*d*) Overlap of metal $3d_{x^2-y^2}$ orbital (e_g symmetry orbital) with a group ligand σ-orbitals (e_g symmetry).

$$\Sigma_{x^2-y^2} = \frac{1}{2}\,(\sigma_x+\sigma_{-x}-\sigma_y-\sigma_{-y})$$

and $3d_{xz}$ have an energy level intermediate between the bonding and antibonding MO's. Thus the non-bonding orbitals are more stable than the anti-bonding MO's but less stable than the bonding MO's. These orbitals remain unchanged in their energy.

Now let us see how the distribution of electrons in $[Co(NH_3)_6]^{3+}$ which contains strong(er) ligands *viz.* NH_3 molecules (*i.e.* it is a low-spin complex) takes place in various orbitals according to the above order. This complex has Co as Co^{3+} (d^6 system). Thus are in all 18 electrons in it : 12 electrons from six : NH$_3$ molecules and 6 from *d*-orbitals in Co^{3+} ion. The distribution of 18 electrons in various orbitals is shown in Fig. 12·17 which is commonly called the *MOT energy level diagram.*

Fig. 12·17 shows that the MOT configuration of [Co(NH$_3$)$_6$]$^{3+}$ can be represented by any of the following configurations :

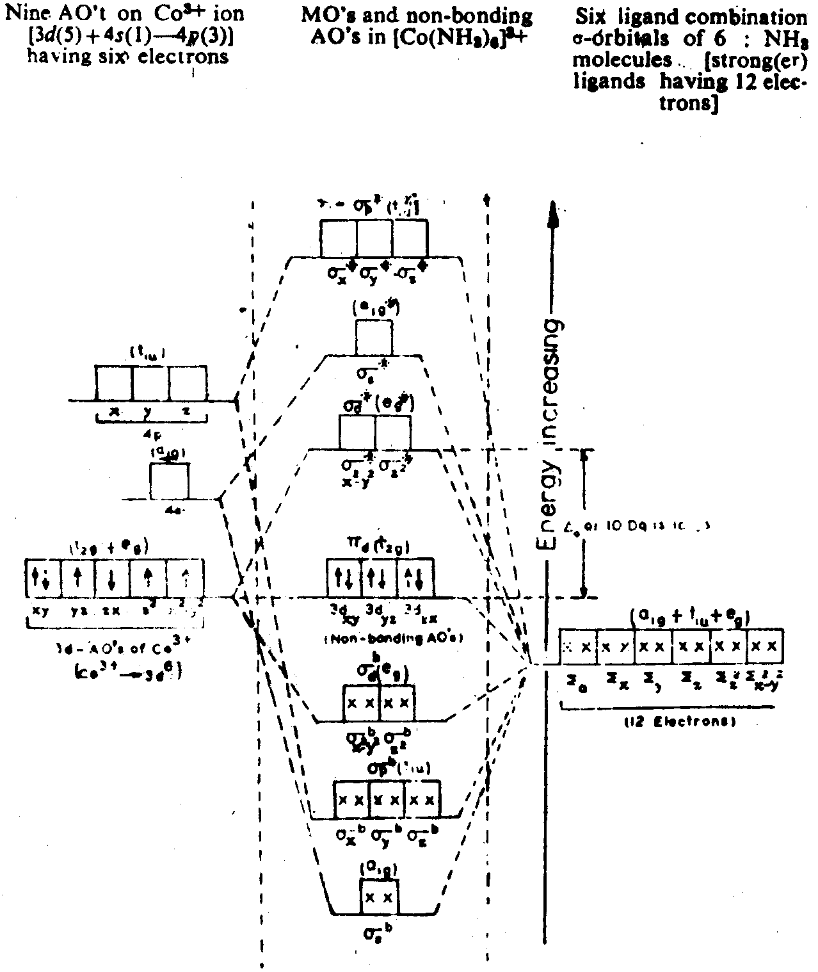


Fig. 12·17. Molecular Orbital Theory (MOT) energy level diagram (drawn not to scale) of [Co(NH$_3$)$_6$]$^{3+}$ which is a low-spin octahedral complex (π bonding not considered, only σ bonding considered). The electrons repretented by crosses are those of six : NH$_3$ molecules (ligands) and those represented by full arrows (↑ ↓) are 3*d* electrons of Co^{3+} ion (*d*^{6} ion)

(i) $(\sigma_s^b)^2, (\sigma_x^b)^2 = (\sigma_y^b)^2 = (\sigma_z^b)^2, (\sigma_{x^2-y^2}^b)^2 = (\sigma_{z^2}^b)^2, (3d_{xy})^2 = (3d_{yz})^2 = (3d_{zx})^2.$

(ii) $[6\sigma^b]^{12}, \quad (3d_{xy})^2 = (3d_{yz})^2 = (3d_{zx})^2.$

(iii) $(a_{1g})^2, (t_{1u})^6, (e_g)^4 \quad (t_{2g})^6.$

(iv) $(\sigma_s^b)^2, (\sigma_p^b)^6, (\sigma_d^b)^4, \quad (\pi_d)^6.$

The designation $[6\ \sigma^b]^{12}$ represents the six sigma-bonding MO's: σ_s^b, $\sigma_x^b = \sigma_y^b = \sigma_z^b$, $\sigma_{x^2-y^2}^b = \sigma_{z^2}^b$, all of which are completely filled. Hence the superscript 12.

In connection with MOT energy level diagram shown in Fig. 12·17 following points may be noted :

(a) Since the ligand orbitals are usually more electronegative than the metal AO's, we have drawn the right hand energy level below any of the left hand levels.

(b) The crystal field splitting energy (Δ_o or 10 Dq) in an octahedral complex, according to MOT, is the difference in energy between the t_{2g} (d_{xy}- d_{yz}- and d_{zx}-orbitals) and e_g^* ($\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ MO's) energy levels.

(c) In general it may be assumed that, if a MO is near in energy to the energy of the ligand orbital, it would have more of the character of the ligand. Thus six σ^b-MO's (*i.e.* σ_s^b, σ_x^b, σ_y^b, σ_z^b, $\sigma_{x^2-y^2}^b$ and $\sigma_{z^2}^b$ MO's) which are nearer the energy level of the ligands, are occupied mainly by the ligand electrons (two electrons in each ligand orbital have been shown by crosses, × ×) rather than the metal ion electrons (metal ion electrons are shown by full arrows ↓ ↑). In other words the electrons in the six σ^b-MO's are mainly localised on ligand orbitals, since σ-orbitals of the ligands are more stable than the metal orbitals. Conversely, electrons occupying any of the six σ^*-MO's are to be considered mainly metal ion electrons. Electrons in t_{2g} set of orbitals will be purely metal ion electrons when there are no ligand π-orbitals.

(ii) **When ligands are weak(er).** In case of weaker ligands such as F^- ion, the energy difference, Δ_o, between the t_{2g} set and e_g^* set is smaller than P (*i.e.* $\Delta_o < P$) and hence the lowest-energy anti-bonding MO's namely $\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ have approximately the same energy as the non-bonding AO's : $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ (t_{2g} set). Consequently, the order of energy becomes as shown below :

Energy increasing →

$$\left.\begin{array}{r}
\sigma_x^* = \sigma_y^* = \sigma_z^*\,(3)\ldots\ldots\ldots\sigma_p^*\,(t_{1u}^*)\\
\sigma_s^*\,(1)\ldots\ldots\ldots(a_{1g}^*)\\
3d_{xy} = 3d_{yz} = 3d_{zx} = \sigma_{x^2-y^2}^* = \sigma_{z^2}^*(5)\ldots\ldots d_\pi + \sigma_d^*\\
(t_{2g} + e_g^*)
\end{array}\right\}\text{six } \sigma^* \text{ MO's and three non-bonding AO's}$$

$$\left.\begin{array}{r}
\sigma_{x^2-y^2}^b = \sigma_{z^2}^b(2)\ldots\ldots\ldots\sigma_d^b(e_g)\\
\sigma_x^b = \sigma_y^b = \sigma_z^b(3)\ldots\ldots\ldots\sigma_p^b(t_{1u})\\
\sigma_s^b(1)\ldots\ldots(a_{1g})
\end{array}\right\}\text{six } \sigma^b \text{ MO's}$$

The distribution of 18 electrons in $[CoF_6]^{3-}$ which contains weak (er) ligands *viz.* F^- ions (*i.e.* it is a high-spin complex) takes place in various orbitals according to the above scheme as shown in MOT energy level diagram given in Fig. 12·18. This Fig. clearly shows that in case of high-spin complexes Hund's rule is obeyed.

The MO-configuration of $[CoF_6]^{3-}$ can thus be represented by any of the following configurations :

(*i*) $(\sigma_s^b)^2, (\sigma_x^b)^2=(\sigma_y^b)^2=(\sigma_z^b)^2, (\sigma_{x^2-y^2}^b)^2=(\sigma_{z^2}^b)^2, (3d_{xy})^2$
$=(3d_{yz})^1=(3d_{zx})^1=(\sigma_{x^2-y^2}^*)^1=(\sigma_{z^2}^*)^1$

(*ii*) $[6\sigma^b]^{12}, (3d_{xy})^2=(3d_{yz})^1=(3d_{zx})^1=(\sigma_{x^2-y^2}^*)^1=(\sigma_{z^2}^*)^1$

(*iii*) $(a_{1g})^2, (t_{1u})^6, (e_g)^4, (t_{2g})^4, (e_g^*)^2$

(*iv*) $(\sigma_s^b)^2, (\sigma_p^b)^6, (\sigma_d)^4, (\pi_d)^4, (\sigma_d^*)^2$

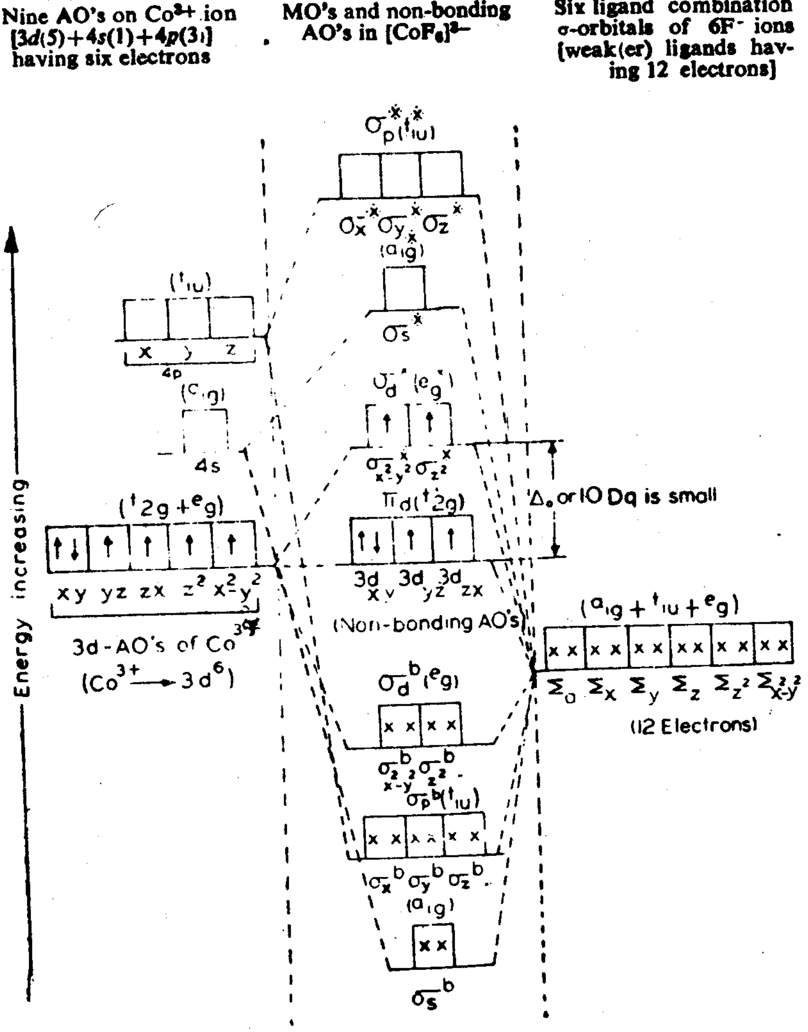


Fig. 12·18. MOT energy level diagram (drawn not to scale) of $[CoF_6]^{3-}$ which is a high-spin octahedral complex.

Comparison of Fig. 12·17 and Fig. 12·18 shows that the magnitude of Δ_o in case of high-spin complexes is smaller than that in low-spin complexes.

Table 12·16. *Distribution of electrons in different MO's and Non-bonding AO's (i.e., $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$) in strong(er) ligand fields of octahedral complexes. (i.e. LS-complexes).* $[6\sigma^b]^{12}$ *indicates* $(\sigma_s^b)^2.(\sigma_x^b)^2.(\sigma_y^b)^2.(\sigma_z^b)^2.(\sigma_{x^2-y^2}^b)^2.(\sigma_{z^2}^b)^2$.

d^x	No. of electrons in ligands	Total number of electrons in complex ion = $(x+12)$	Distribution of $(x+12)$ electrons in MO's and Non-bonding AO's	n	S
d^1	12	12+1=13	$[6\sigma^b]^{12}.(3d_{xy})^1$	1	0·5
d^2	12	12+2=14	$[6\sigma^b]^{12}.(3d_{xy})^1.(3d_{yz})^1$	2	1·0
d^3	12	12+3=15	$[6\sigma^b]^{12}.(3d_{xy})^1.(3d_{yz})^1.(3d_{zx})^1$	3	1·5
d^4	12	12+4=16	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^1.(3d_{zx})^1$	2	1·0
d^5	12	12+5=17	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^1$	1	0·5
d^6	12	12+6=18	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^2$	0	0·0
d^7	12	12+7=19	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^2.(\sigma_{x^2-y^2}^*)^1$	1	0·5
d^8	12	12+8=20	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^2.(\sigma_{x^2-y^2}^*)^1.(\sigma_{z^2}^*)^1$	2	1·0
d^9	12	12+9=21	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^2.(\sigma_{x^2-y^2}^*)^2.(\sigma_{z^2}^*)^1$	1	0·5
d^{10}	12	12+10=22	$[6\sigma^b]^{12}.(3d_{xy})^2.(3d_{yz})^2.(3d_{zx})^2.(\sigma_{x^2-y^2}^*)^2.(\sigma_{z^2}^*)^2$	0	0·0

Table 12·17. *Distribution of electrons in different MO's and non-bonding AO's in weak(er) ligand fields of octahedral complexes (i.e., HS-octahedral complexes).*

	No. of electrons in ligands	*Total number of electrons in complex ion=(x+12)*	*Distribution of (12+x) electrons in MO's and non-bonding AO's*	*n*	*S*
d^1	12	12+ 1=13	$[6\sigma^b]^{12} \cdot (3d_{xy})^1$	1	0·5
d^2	12	12+ 2=14	$[6\sigma^b]^{12} \cdot (3d_{xy})^1 \cdot (3d_{yz})^1$	2	1·0
d^3	12	12+ 3=15	$[6\sigma^b]^{12} \cdot (3d_{xy})^1 \cdot (3d_{yz})^1 \cdot (3d_{zx})^1$	3	1·5
d^4	12	12+ 4=16	$[6\sigma^b]^{12} \cdot (3d_{xy})^1 \cdot (3d_{yz})^1 \cdot (3d_{zx})^1 \cdot (\sigma_{x^2-y^2}^{*})^1$	4	2·0
d^5	12	12+ 5=17	$[6\sigma^b]^{12} \cdot (3d_{xy})^1 \cdot (3d_{yz})^1 \cdot (3d_{zx})^1 \cdot (\sigma_{x^2-y^2}^{*})^1 \cdot (\sigma_{z^2}^{*})^1$	5	2·5
d^6	12	12+ 6=18	$[6\sigma^b]^{12} \cdot (3d_{xy})^2 \cdot (3d_{yz})^1 \cdot (3d_{zx})^1 \cdot (\sigma_{x^2-y^2}^{*})^1 \cdot (\sigma_{z^2}^{*})^1$	4	2·0
d^7	12	12+ 7=19	$[6\sigma^b]^{12} \cdot (3d_{xy})^2 \cdot (3d_{yz})^2 \cdot (3d_{zx})^1 \cdot (\sigma_{x^2-y^2}^{*})^1 \cdot (\sigma_{z^2}^{*})^1$	3	1·5
d^8	12	12+ 8=20	$[6\sigma^b]^{12} \cdot (3d_{xy})^2 \cdot (3d_{yz})^2 \cdot (3d_{zx})^2 \cdot (\sigma_{x^2-y^2}^{*})^1 \cdot (\sigma_{z^2}^{*})^1$	2	1·0
d^9	12	12+ 9=21	$[6\sigma^b]^{12} \cdot (3d_{xy})^2 \cdot (3d_{yz})^2 \cdot (3d_{zx})^2 \cdot (\sigma_{x^2-y^2}^{*})^2 \cdot (\sigma_{z^2}^{*})^1$	1	0·5
d^{10}	12	12+10=22	$[6\sigma^b]^{12} \cdot (3d_{xy})^2 \cdot (3d_{yz})^2 \cdot (3d_{zx})^2 \cdot (\sigma_{x^2-y^2}^{*})^2 (\sigma_{z^2}^{*})^2$	0	0·0

Electronic configuration of octahedral complexes of d^1 to d^{10} ions having strong(er) (*i.e.* low-spin complexes) and weak(er) ligands (*i.e.* high-spin complexes) is shown Table 13·16 and 13·17 respectively. In both the tables the designation $[6\sigma^b]^{12}$ represents the six σ^b-MO's :

$$\sigma_s{}^b.\ \sigma_x{}^b = \sigma_y{}^b = \sigma_z{}^b,\ \sigma_{x^2-y^2}{}^b = \sigma_{z^2}{}^b$$

all of which are completely filled. Hence the superscript 12. It may be seen from these tables that MOT also predicts the same number of unpaired electrons, n (or the resultant spin, $S = \frac{1}{2} n$) in low-spin and high-spin octahedral complexes a CFT does.

π-BONDING IN OCTAHEDRAL COMPEXES

We have so far dealt with σ-bonding between the central metal cation and the ligands having σ-orbitals in octahedral complexes. Here we shall consider the formation of π-bond between the appropriate AO's of the central metal cation and π-orbitals of the ligands (usually called *ligand π-orbitals*).

The metal orbitals which take part in the formation of π-bonds are p_x, p_y, p_z, d_{xy}, d_{yz} and d_{zx} orbitals, since these can overlap with the ligand π-orbital in *sideway on* fashion to form the π-bond, while the ligand π-orbitals participating in π-bond formation may be any of the following three types :

(*a*) **Simple p-orbitals.** These may be simple *p*-orbitals (called *p*π orbitals) which are not directed along the line joining the ligand and the metal ion, *i.e.* *p*-orbitals taking part in π-bond formation are perpendicular to one another and also to the metal ligand. Thus there are two such *p*-orbitals on each of the six ligands in an octahedral complex as shown in Fig. 12·19 in which L_1......L_6 are the six ligands and π_{3x}, π_{4x}. π_{5x}, π_{6x} ; π_{1y}. π_{2y}, π_{5y}, π_{6y} and π_{1z}, π_{2z}, π_{3z}, π_{4z} are the *p*π-ligand orbitals along the *x*-, *y*- and *z*-axes respectively. In the first column of Table 12·18 are listed the ligands L_1......L_6 and in the second column are given their *p*π-orbitals The letter *x* in π_{3x}......π_{6x} indicates that these *p*π-orbitals are along the *x*-axis, the letter *y* in π_{1y}......π_{6y} indicates that these *p*π-orbitals lie along the y-axis. Similarly the letter *z* in π_{1z}......π_{4z} staonds t indicate

Table 12·18. *pπ-orbitals of ligands L_1......L_6*

Ligands	*pπ-orbitals on the ligands*	
L_1	π_{1z}, π_{1y}	Total 12 orbitals
L_2	π_{2z}, π_{2y}	
L_3	π_{3x}, π_{3z}	
L_4	π_{4x}, π_{4z}	
L_5	π_{5x}, π_{5y}	
L_6	π_{6y}, π_{6x}	

that these $p\pi$-orbitals are along the z-axis. The numbers 1, 2,...... 5, 6, used as coefficients of x, y and z in different $p\pi$-ligand orbitals indicate that these $p\pi$-ligand orbitals are of ligands namely L_1, L_2... ...L_5, L_6 respectively.

The arrow-heads of these $p\pi$-orbitals point in the direction of the + lobe of the orbitals.

Ligand $p\pi$-orbitals are always filled and are found in halide ions, O^{2-}, RO^-, RS^- etc.

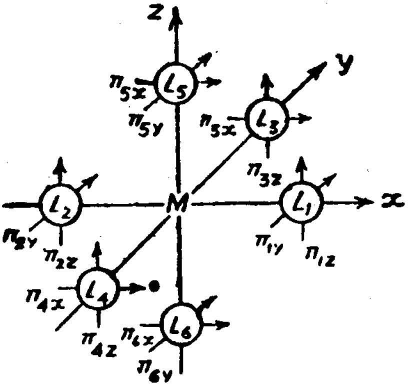


Fig. 12·19. Twelve ligand $p\pi$-orbitals in an octahedral complex.

Before combining with AO's of the central metal cation these ligand $p\pi$-orbitals combine together to form group ligand π-orbitals. It is quite easy to see that the group ligand π-orbitals (not in the normalised form) which can overlap with, for example, d_{zx} atomic orbital is :

$$(\pi_{1z}-\pi_{2z}+\pi_{5x}-\pi_{6x})$$

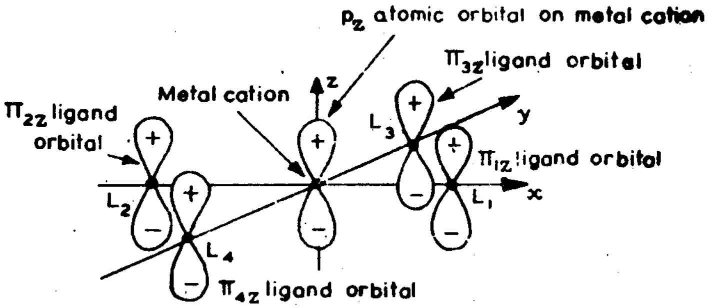
In the last column of Table 12·19 is given the appropriate

Table 12·19. *Proper metal-and-ligand π-orbitals combination (with symmetry class name) for octahedral complexes.*

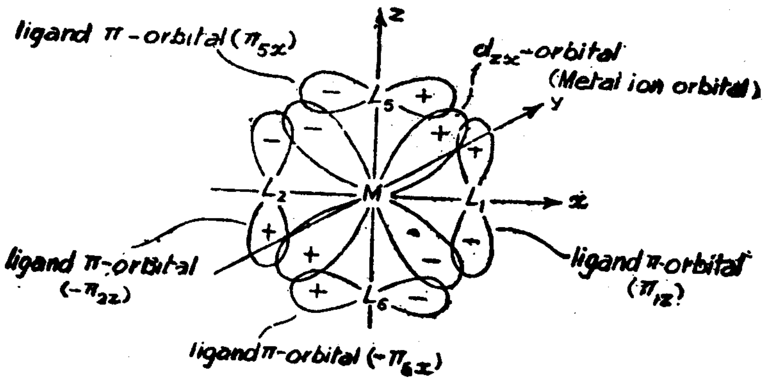
Group symmetry name	*Central ion orbitals*	*Appropriate combination of ligand pπ-orbitals*
t_{1u} or T_{1u}	$4p_x$	$\pi_x=\frac{1}{2}(\pi_{3x}+\pi_{4x}+\pi_{5x}+\pi_{6x})$
	$4p_y$	$\pi_y=\frac{1}{2}(\pi_{1y}+\pi_{2y}+\pi_{5y}+\pi_{6y})$
	$4p_z$	$\pi_z+\frac{1}{2}(\pi_{1z}+\pi_{2z}+\pi_{3z}+_{4z})$
t_{2g} or T_{2g}	$3d_{xy}$	$\pi_{xy}=\frac{1}{2}(\pi_{1y}-\pi_{2y}+\pi_{3x}-\pi_{4y})$
	$3d_{yz}$	$\pi_{yz}=\frac{1}{2}(\pi_{3z}-\pi_{4z}+\pi_{5y}-\pi_{6y})$
	$3d_{zx}$	$\pi_{zx}=\frac{1}{2}(\pi_{1z}-\pi_{2z}+\pi_{5x}-\pi_{6x})$

combination of $p\pi$-orbitals of the ligands that can overlap with p_x, p_y, p_z, d_{xy}, d_{yz} and d_{zx} atomic orbitals. These combinations are not given in their normalised form.

In Fig. 12·20 the overlap of p_z orbital of the central metal cation with group ligand $p\pi$-orbitals *viz.* $\frac{1}{2}(\pi_{1z}+\pi_{2z}+\pi_{3z}+\pi_{4z})$ and of d_{zx} orbital with group ligand $p\pi$-orbitals *viz.* $\frac{1}{2}(\pi_{1z}-\pi_{2z}+\pi_{5x}-\pi_{6x})$ is shown.



(*a*) Overlap of the metal p_z atomic orbital with group ligand $p\pi$-orbitals *viz.* $(\pi_{1z}+\pi_{2z}+\pi_{3z}+\pi_{4z})$.



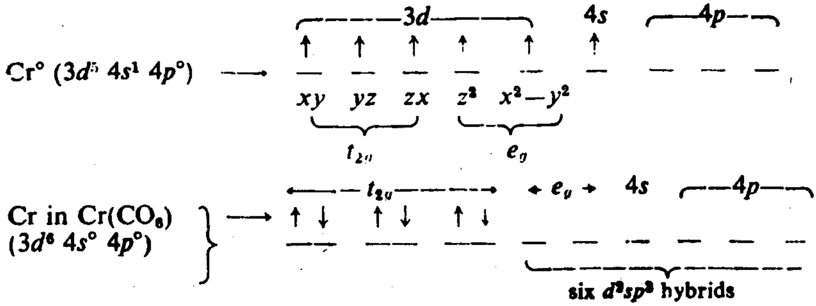
(*b*) Overlap of the metal d_{zx} atomie orbital with group ligand $p\pi$-orbitals *viz.* $(\pi_{1z}-\pi_{2z}+\pi_{5x}-\pi_{6x})$.

Fig. 12·20 overlap of (*a*) metal p_z orbital and (*b*) metal d_{zx} orbitals with group ligand $p\pi$-orbitals.

(b) **Simple dπ-orbitals** : These may be simple $d\pi$-orbitals (*i.e.* d_{xy}-, d_{yz}- and d_{zx}-orbitals). Such type of $d\pi$-orbitals are found in phosphines, arsines etc. These are always filled.

(c) π-MO's These may be π-MO's of poly-atomic ligands such as CO, CN^-, or pyridine.

Now let us consider how the combination of the π-MO's of poly-atomic ligands with the metal $d\pi$-orbitats occurs. In order to illustrate such type of combination let us consider the bonding in hexa carbonyl of chromium $Cr(CO)_6$ in which both σ- and π-bonds occur. In this compound Cr is in zero oxidation state ($Cr^\circ \rightarrow 3d^5 4s^1$). Since the coordination number of Cr in $Cr(CO)_6$ is six, Cr is d^2sp^3 hybridised as shown below :



We know that, according to MOT the electronic configuration of CO molecule is : (z-axis assumed to be the molecular axis).

$$\xrightarrow{\text{Energy Increasing}}$$
$$(sp)^2_o\ ,\ (\sigma_{sp}^b)^2,\ (\pi_x^b)^2 = (\pi_y^b)^2,\ (sp)^2_c\ ,\ (\pi_x^*)^0 = (\pi_y^*)^0,\ (\sigma_{sp}^*)^0$$

Now the *filled sp* hybrid on carbon atom overlaps with one (suitable) *vacant* d^2sp^3 hybrid orbital on Cr° to form Cr←CO σ-bond (*See* Fig. 12·21). Thus in the formation of σ-bond CO acts as a *Lewis base* (*i.e.* as a donor).

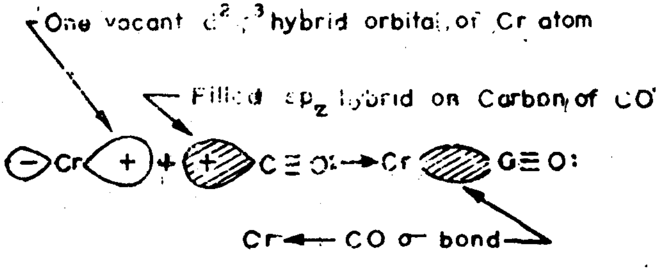


Fig. 12·21. Formation of Cr←CO σ-bond using an unshared electron pair on carbon atom.

One (suitable) of the *filled* d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} set) on Cr overlaps with either of the *empty* π* MO's of CO (π_x^* or π_y^* MO) to form Cr→CO π-bond (*see* Fig. 12·22). Thus we see that in the formation of Cr→CO π-bond, CO acts as a *Lewis acid* (*i.e.* as an acceptor). Cr→CO π-bond removes electron density from the metal and thus prevents the accumulation of too much negative charge on the metal. This bond is called **back-donation**, **back-bonding** or **back-coordination**. The infra-red spectroscopy has shown that back-coordination into the π*-MO's weakens the carbon to-oxygen bond.

The bond order in CO is three but in metal carbonyls it is less. The presence of both σ- and π-bonds in $Cr(CO)_6$ strengthens the metal-ligand bond and contributes to the usual stability of $Cr(CO)_6$.

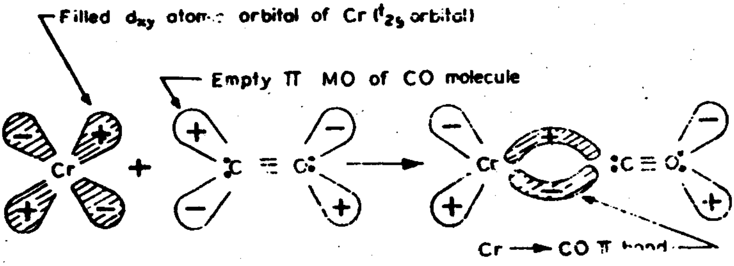


Fig. 12·22. Formation of Cr→CO π-bond in $Cr(CO)_6$.

Effects of π-Bonding on the Value of Δ_o

The formation of π-bonding in complexes affects the energy level of the metal t_{2g}-orbitals just as the formation of σ-bonding affects the energy of the e_g-orbitals of the central metal ion. These effects on the energy level of t_{2g} orbitals depend on two factors namely :

(*i*) *whether the ligand π-orbitals of t_{2g} symmetry are of higher or lower energy than the metal t_{2g}-orbitals and*

(*ii*) *whether the ligand π-orbitals are filled or empty.*

In π-bonding three t_{2g}-metal orbitals on combining with three ligand π-orbitals of t_{2g} symmetry give two sets of triply degenerate MO's namely t_{2g}^b-and t_{2g}^*-MO's. t_{2g}^*-MO's are of higher energy and t_{2g}^b-MO's are of lower energy. The splitting of three t_{2g}-metal orbitals on combining with three ligand π-orbitals of t_{2g} symmetry to produce three t_{2g}^b- and three t_{2g}^*-MO's can take place in the following two ways :

(*a*) **Empty (*i.e.* acceptor) ligand π-orbitals of higher energy than the metal t_{2g}-orbitals.** If the ligand π-orbitals are empty and of higher energy than the metal ion t_{2g}-orbitals, the splitting of t_{2g}-orbitals into t_{2g}^b- and t_{2g}^*-MO's on combining with the above said π-orbitals (of t_{2g}-symmetry) takes place as shown in Fig. 12·23.

In this case the net result of π-interaction is that the metal t_{2g}-orbitals are stabilised relative to the e_g^*-MO's *i.e.* the metal t_{2g} electrons will go into the t_{2g}^b-MO's which are of lower energy than t_{2g}^*-MO's and thus the value of Δ_o will be increased to Δ_o' ($\Delta_o < \Delta_o'$). In this case ligand exerts a stronger field. A ligand of this type is referred to as an acceptor ligand because of the presence of empty π-orbitals in it and the π-bonding established in such a case is sometimes referred to as metal-to-ligand (M ⟶ L) π-bon-

ding. Phosphines, arsines and CO are important examples of this type of ligands.

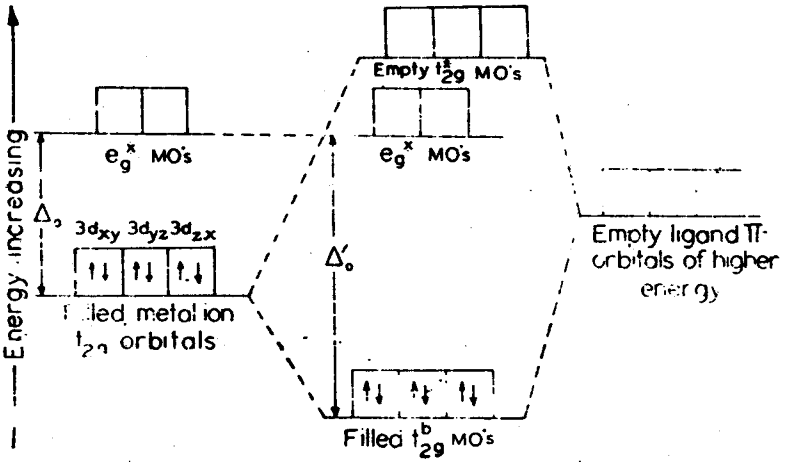


Fig. 12·23. MOT energy level diagram (drawn not to scale) showing the effects of π-bonding on the value of Δ_o, when the ligand π-orbitals are empty (*i.e.* acceptor) and of higher energy than the metal ion t_{2g} orbitals (filled). Note that $\Delta_o' > \Delta_o$.

(*b*) **Filled (*i.e.* donor) ligand π-orbitals of lower energy than the metal t_{2g}-orbitals.** If the ligand π-orbitals are filled and of lower energy than the metal t_{2g}-orbitals, the splitting of t_{2g} metal orbitals takes place as shown in Fig. 12·24.

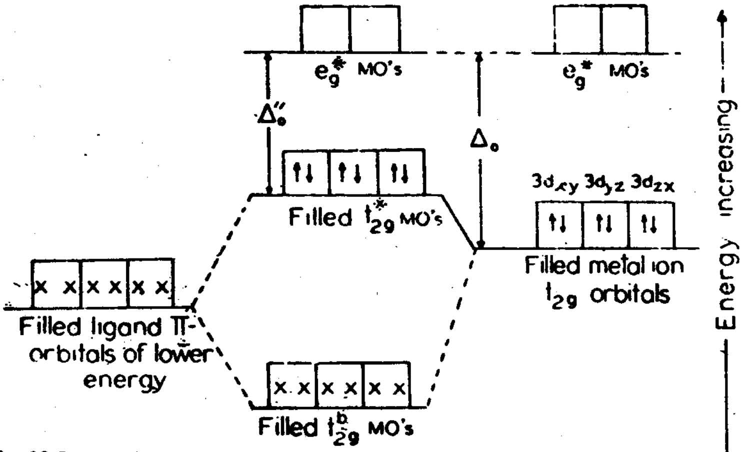


Fig. 12·24. MOT energy level diagram (drawn not to scale) showing the effects of π-bonding on the value of Δ_o when the ligand π-orbitals are filled (*i.e.* donor) and of lower energy than the metal ion t_{2g} orbitals (filled). Note that $\Delta_o'' < \Delta_o$

In this case the t_{2g} metal orbitals are destabilised relative to e_g^*-MO's. The electrons of the ligand π-orbitals enter the lower

t_{2g}^b-MO's and those of the t_{2g}-metal orbitals will go to higher t_{2g}^*-MO's. Since in this case, the π-interaction destabilises the t_{2g}-metal orbitals relative to e_g^* MO's, the value of Δ_0 is diminished to Δ_0'' as shown in Fig. 12·24 ($\Delta_0 > \Delta''$). The ligand in this case exerts a weaker field. A ligand of this type is generally called a donor ligand because of its filled π-orbitals. Halide ions are important examples of this type of ligands and the π-bonding of this type is generally referred to as ligand-to-metal (L ⟶ M) π-bonding. Such type of π-bonding occurs in complexes having metal ions in their normal oxidation states (especially lower oxidation states).

Relation between π-bonding ability of ligands and spectro-chemical series

The MOT also provides a correlation between the spectro-chemical series and the π-bonding abilities of the ligands. The ligands which can accept electrons from the metal ion orbitals into their π^*-orbitals (*i.e.*, the ligands having strong M → L π-bonding ability) are high in the spectrochemical series. Such ligands are called **π-acceptor ligands** and cause large splittings *i.e.*, have higher Δ_0 values, whereas the ligands which donate electrons to the metal orbitals (*i.e.*, the ligands having strong L → M π-bonding ability) are low in the series. Such ligands are called **π-donor ligands** and cause small splittings. The ligands having little or no π-bonding ability are intermediate in the series and have intermediate Δ_0 values. This trend is shown below :

$CO > CN^- \ NO^{2-} > o\text{-phen}$	$> NH_3 > OH_2$	$> OH^- > F^-$	$> SCN^- > Cl^- > Br^- > F^-$
Ligands having strong M → L π bonding ability. Such ligands are called π-acceptor ligands and cause large splittings *i.e*, have larger Δ_0 values.	**Ligands having no π-bonding ability.**	**Ligands having little L → M π-bonding ability.**	**Ligands having strong L → M π-bonding ability. Such ligands are called π-donor ligands and cause small splittings *i.e.*, have smaller Δ_0 values.**
⟵⟶	⟵⟶		⟵⟶
These ligands have larger Δ_0 values.	**These ligands have intermediate Δ_0 values.**		**These ligands have smaller Δ_0 value.**

⟶Value of Δ_0 decreasing⟶

Effect of the charge on the central metal ion on the magnitude of Δ_0

According to MOT of complexes Δ_0 is the difference in energy between σ_d^* [or $\sigma(d)^*$ or e_g^*] and π_d [or t_{2g} or $d\pi$ or $\pi_{xy} = \pi_{yz} = \pi_{zx}$] levels. In order to study the effect of the charge on the central metal on the magnitude of Δ_0, the following two types of complexes may be studied :

(*i*) **Complexes containing ligands that are not good π-acceptors.** In such complexes Δ_0 increases with the increase of positive charge on the metal ion, *e.g.*,

$$\Delta_o \text{ for } [V^{II}(H_2O)_6]^{2+} = 12{,}400 \text{ cm}^{-1}$$

and $$\Delta_o \text{ for } [V^{III}(H_2O)_6]^{3+} = 17{,}850 \text{ cm}^{-1}$$

The increase in the megnitude of Δ_o in these complexes is interpreted as a substantial increase in σ-bonding on increasing the positive charge on the metal ion. This results in an increase in the difference in energy between σ_d^* and π_d levels.

(*ii*) **Complexes containing ligands that are good π-acceptors.** In such complexes an increase in positive charge on the metal ion does not seem to be accompanied by a substantial increase in Δ_o; *e.g.*, both $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ have Δ_o values approximately equal to 34,000 cm^{-1}. In the transition, $[Fe^{II}(CN)_6]^{4-} \rightarrow [Fe^{III}(CN)_6]^{3}$ the π_d level is destabilished just as much as the σ_d^* level, probably the result of a decrease in M → L π-bonding when the positive charge on the central metal ion is increased.

Comparision of Different Theories

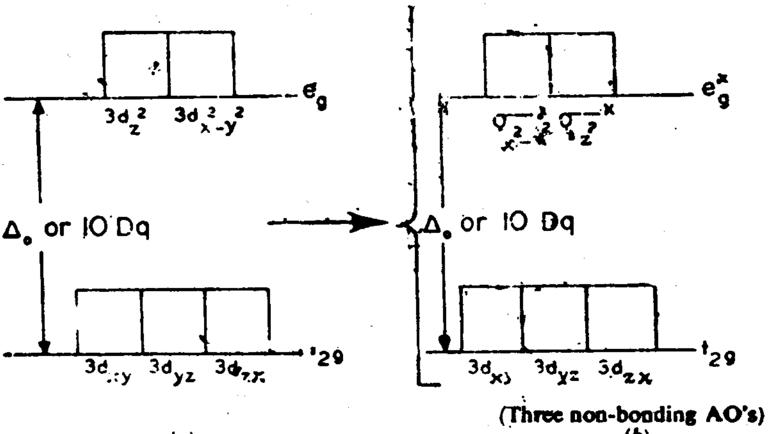
VBT Vs CFT

We have seen that according to VBT the atomic orbitals used in the formation of six d^2sp^3 hybrids in inner-orbital octahedral complexes of 3*d*-series elements are $3d_{x^2-y^2}$, $3d_{z^2}$ (e_g set) 4*s*, $4p_x$, $4p_y$ and $4p_z$. The remaining three 3*d*-atomic orbital *viz*, $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ (t_{2g} set) remain non-bonding and contain metallic electrons (non-bonding electrnos). In CFT as well the metallic electrons occupy t_{2g} set, since it is lower in energy than e_g set.

Inner-orbital octahedral complexes of VBT (d^2sp^3 hybridisation) are the same as spin-paired or low-spin octahedral complexes of CFT. Similarly outer-orbital octahedral complexes (sp^3d^2 hybridisation) of VBT are the ame as spin-free or high-spin octahedral complexes of CFT. In the formation of some inner-orbital octahedral complexes of VBT (*e.g.* complexes of d^7 ion) the promotion of an electron from *d*-orbital to *s*-orbital is required, while in the formation of spin-paired octahedral complexes of CFT no such promotion is required.

There are also certain points which make VBT different from CFT. According to VBT, the metal-ligand bonding in complexes is only covalent, since VBT assumes that ligand electrons are partially donated to metal orbitals. On the other hand CFT does not consider covalent bonding in complexes, but considers the bonding to be entirely electrostatic, an interaction between a positively charged metal ion and the partial negative charge invariably present on the ligands. In its pure state, CFT does not provide for ligand electrons to enter the metal orbitals.

CFT Vs MOT (*a*) **Similaries.** (*i*) From the MOT energy level diagram for an octahedral complex, it may be seen that t_{2g} (*i.e.* $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ AO's of the central metal ion and e_g^* (*i.e* $\sigma_{x^2-y^2}^* = \sigma_{z^2}^*$) energy levels are split apart (qualitatively) in the same manner in which the t_{2g} (*i.e.* $3d_{xy}$, $3d_{yz}$ and 3*d* orbitals; and e_g (*i.e.* $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals) are split apart in the crystal field splitting diagram. The set of triply degenerate non-bonding AO's namely $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ of MOT energy level diagram is merely the t_{2g} level of CFT ; and set of doubly degenerate antibonding MO's (*i.e.* $\sigma_{x^2-y^2}{}^* - \sigma_{z^2}$) of MOT energy level diagram is identical to the e_g-set of CFT (Fig. 12·25).



(*a*) (*b*)

Fig. 12·25. Relation between crystal field splitting diagram of an octahedral complex shown at (*a*) and a portion of MOT energy level diagram of the same complex shown at (*b*). Diagram drawn not to scale.

(*ii*) As regards the conceptions of HS- and LS- complexes, their different magnetic properties and the value of Δ_o, these are retained in the same manner in both the theories.

Differences. (*i*) *Mode of formation of bonding in complexes.* CFT considers that the metal-ligand interaction in complexes arises from the electrostatic attraction between the metal cation and ligands, while MOT says that metal-ligand interaction occurs through the MO's formed by the overlap of ligand and metal orbitals.

(*ii*) *Orbitals used in the bond formation.* CFT takes into account the metal ion *d*-orbitals only and ignores the behaviour of other metal orbitals such as *s*-, p_x-, p_y-, and p_z-orbitals and the σ- and/or π-type ligand orbitals. On the other hand MOT considers all the metal ion orbitals and also σ- and/or π-orbitals of the ligands.

(*iii*) *Cause of the splitting of d-orbitals.* Both the theories admit the splitting of the 3*d*-metal orbitals, when a complex compound is formed. According to CFT, the splitting is caused by the electrostatic fields exerted by the ligands on the central metal ion, while according to MOT it is caused by covalent bond formation.

(*iv*) *Cause of energy difference,* Δ_o. We have seen in the treatment of MOT that if the ligand π-orbitals are empty and of higher energy than the t_{2g}-metal orbitals, the energy difference, Δ_o, between t_{2g}- and e_g - orbitals, is increased. According to MOT the increased energy difference is caused by π-bonding and is responsible for causing pairing of the electrons (*i.e.* the formation of LS-complexes). On the other hand, CFT postulates the increased energy difference as due to the increased electrostatic field of the ligand.

According to CFT, the difference in energy between t_{2g}- and e_g-orbitals is simply because of the difference in the electrostatic field of the ligands on these orbitals, while according to Ligand Field Theory (MO-theory) the t_{2g}- and $e_g{}^*$-orbitals have different energies because one set (*viz.* t_{2g}-set) is non-bonding and the other set (*viz.* $e_g{}^*$-set) is anti-bonding.

(*v*) *σ- and π- bonding in complexes.* In addition to the σ-bonding in complexes, the LFT (MOT) postulates π-bonding as well in the complexes.

(*vi*) *Nature of bonding in complexes.* CFT, which considers the bonds as purely ionic gives no account of the partly covalent nature of the metal-ligand bonds. Thus the effects directly dependent on the covalency cannot be explained by CFT. However, LFT (MOT) takes the covalent character of the bond into account.

(*vii*) *Charge-transfer bands.* MOT energy level diagram shows that anti-bonding levels, $a_{1g}{}^*$ and $t_{1u}{}^*$ which lie above $e_g{}^*$-level also represent terminal levels for electronic transitions originating in t_{2g}-level and electrons residing in the bonding levels may be excited into higher levels giving so called charge transfer bands. Neither of these two informations given by MOT energy level diagram can be given by CFT energy level diagram.

VBT Vs MOT. We have seen that in VBT six atomic orbitals *viz.* $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$ are used to form six d^2sp^3 hybrids which accept six electron pairs from the six ligands to form an inner-orbital octahedral complex while in MOT the same six atomic orbitals overlap with six σ-ligand type orbitals to form six $\sigma^b(\sigma_s{}^b, \sigma_x{}^b=\sigma_y{}^b=\sigma_z{}^b, \sigma_{x^2-y^2}{}^b=\sigma_{z^2}{}^b)$ and six σ^* $(\sigma_s{}^*, \sigma_x{}^*=\sigma_y{}^*=\sigma_z{}^*, \sigma_{x^2-y^2}{}^*=\sigma_z{}^{2*})$ molecular/orbitals. In VBT $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ atomic orbitals do not participate in d^2sp^3 hybridisation process and hence contain metallic electrons. Similarly in MOT these atomic orbitals do not participate in the formation of molecular orbitals and hence remain as non-bonding atomic orbitals.

Since, unlike MOT, VBT does not include antibonding molecular orbitals namely $\sigma_{x^2-y}{}^{2*}=\sigma_z{}^{2*}$, $\sigma_s{}^*$, $\sigma_x{}^*=\sigma_y{}^*=\sigma_z{}^*$, it does not provide an explanation of the spectral bands of the metal complexes.

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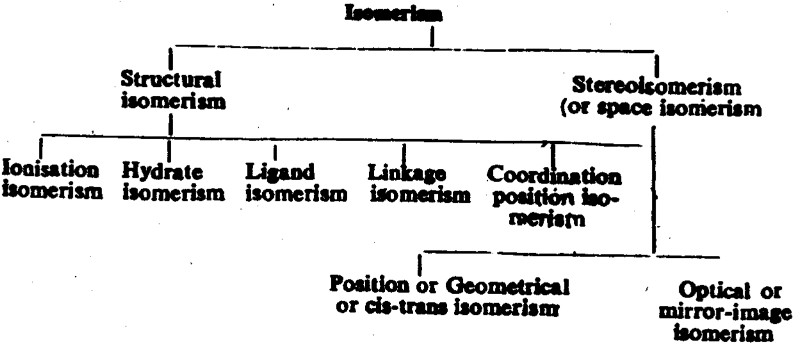
13

Isomerism Among Inorganic Complexes

The compounds which have the same chemical composition but have different structural arrangement of their atoms are called **isomers** and the phenomena that gives rise to isomers is called **isomerism**. Coordination compounds exhibit two main types of isomerism *viz*, ***structural isomerism*** and ***stereoisomerism***. Each of these is further subdivided as :



STRUCTURAL ISOMERISM

This isomerism arises due to the difference in structures of coordination compounds. This is of the following types :

(*i*) Ionisation Isomerism

Complexes which have the same emperical formula but give different ions in solution on ionisation are called **ionisation isomers**, *e.g.*, $[Co^{III}(NH_3)_5Br]SO_4$ (I) and $[Co^{III}(NH_3)_5SO_4]Br$ (II) are the two ionisation isomers. (I) gives white precipitate of $BaSO_4$ with $BaCl_2$ solution while (II) does not. Similarly (II) gives yellow precipitate of AgBr with $AgNO_3$ while (I) does not. Some other examples of ionisation isomers with their mode of ionisation in solution are given below :

Ionisation isomers	***Mode of ionisation***
(*i*) $[Co(NH_3)_4Cl_2]NO_2$	$[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + NO_2^-$
(*ii*) $[Co(NH_3)_4(Cl)(NO_2)]Cl$	$[Co(NH_3)_4(Cl)(NO_2)]Cl \rightleftharpoons [Co(NH_3)_4(Cl)(NO_2)]^+ + Cl^-$
(*i*) $Co(en)_2(NO_2)(Cl)]SCN$	$[Co(en)_2(NO_2)(Cl)]SCN \rightleftharpoons [Co(en)_2(NO_2)(Cl)]^+ + SCN^-$
(*ii*) $[Co(en)_2(NO_2)(SCN)]Cl$	$[Co(en)_2(NO_2)(SCN)]Cl \rightleftharpoons [Co(en_2)(NO)_2(SCN)]^+ + Cl^-$
(*iii*) $[Co(en)_2(SCN)(Cl)]NO_2$	$[Co(en)_2(SCN)(Cl)]NO_2 \rightleftharpoons [Co(en)_2(SCN)(Cl)]^+ + NO_2^-$

(*ii*) Hydrate Isomerism

There are three isomers of $CrCl_3.6H_2O$ which are

(*a*) $Cr(H_2O)_6]Cl_3$—violet, does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by Ag^+ ions.

(*b*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$—ligh grean, loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by Ag^+ ion

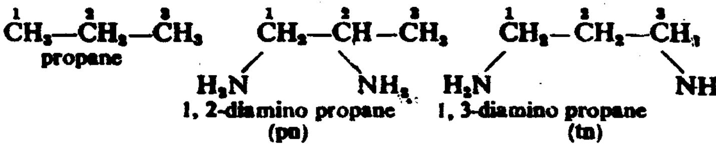
(*c*) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$—deep green, loses two water molecules over H_2SO_4 and only one Cl^- ion is precipitated by Ag^+ ions.

An example involving both ionisation and isomerism is provided by the complexes :

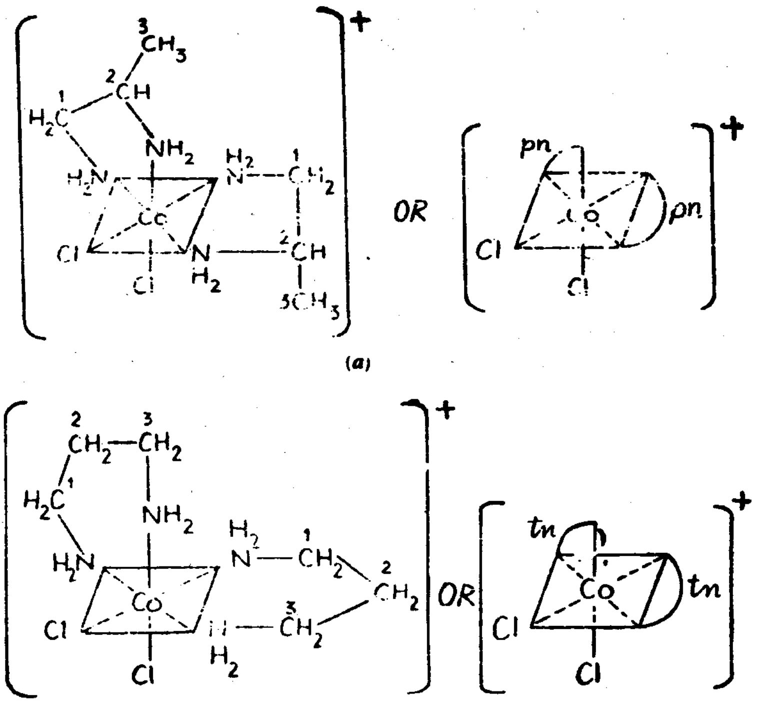
$$[Co^{III}(NH_3)_4(H_2O)Cl]Br_2 \text{ and } [Co^{III}(NH_3)_4Br_2]Cl.\ H_2O$$

(*iii*) Ligand Isomerism

Some ligands themselves are capable of existing as isomers, *e.g.*, diamino propane can exist both as 1, 2-diamino propane (pn) and 1, 3-diamino propane, also called trimethylene diamine (tn).



When these ligands (*i.e.*, pn and tn) are associated into complexes, the complexes are isomers of each other. One example of isomeric complexes having this ligand is : $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ ions. The structural formulas of these complex ions are shown below in Fig. 13·1.



(a)

(b)

Fig. 13·1. Structural formula (a) $[Co(pn)_2Cl_2]^+$ and (b) $[Co(tn)_2Cl]^+$ ions.

(iv) Linkage Isomerism

This type of isomerism is found in those complexes in which the ligands can coordinate with the central metal ion through either of the two atoms. The best known ligands of this type are NO_2^-, SCN^- and $S_2O_3^{2-}$ ions. In complexes containing NO_2^- ion as ligand, NO_2^- ion may attach with the central ion either through O-atom or through N-atom. Similarly in case of a complex having $S_2O_3^{2-}$ ion, the central ion may be coordinated with $S_2O_3^{2-}$ ion either through S-atom or O-atom. SCN^- ion may attach with the central ion either through N-or through S-atom.

The names of these ions (*i.e.*, ligands) when coordinated through different atoms and examples of complexes are given below :

Ions		Complexes
NO_2^- ion	Nitrito (ONO^-) ✓	$[Co^{III}(NH_3)_5-ONO]^{2+}$ ion
	Nitro (NO_2^-)	$[Co^{III}(NH_3)_5-NO_2]^{2+}$ ion
SCN ion	Thiocyanato $(SCN)^-$	$[Pd\ (diph)\ (SCN)_2]$
	Isothio cyanato (NCS^-)	$[Pd\ (diph)\ (NCS)_2]$
$S_2O_3^{2-}$ ion	Thiosulphato-S $(SSO_3)^{2-}$	$[Co(NH_3)_5SSO_3]^+$ ion
	Thiosulphato-O $(OSO_2S)^{2-}$	$[Co(NH_3)_5OSO_2S]^+$ ion

Members of each pair of complex ions given above are linkage isomers to each other.

(*v*) Coordination Isomerism

If both cation and anion of a complex compound are complex, there may be an exchange of ligands between the two coordination spheres, giving rise to isomers known as coordination isomers. This type of isomerism which is called coordination isomersim is illustrated by the following coordinated compounds :

(*a*) *Coordination compounds having similar central metal ions in both complex cation and complex anion* :

(*i*) $[Cr^{III}(NH_3)_6]^{3+}[Cr^{III}(SCN)_6]^{3-}$

and $[Cr^{III}(NH_3)_4(SCN)_2]^{+} Cr^{III}(NH_3)_2(SCN)_4]^{-}$

(*ii*) $[Pt^{II}(NH_3)_4]^{2+}[Pt^{IV}Cl_6]^{2-}$

and $[Pt^{IV}(NH_3)_4Cl_2]^{2+}[Pt^{II}Cl_4]^{2-}$

(*b*) *Coordination compounds having different central metal ions in complex cation and complex anion* :

(*i*) $[CO^{III}(NH_3)_6]^{3+}[Cr^{III}(CN)_6]^{3-}$

and $[Cr^{III}(NH_3)_6]^{3+}[Co^{III}(CN)_6]^{3-}$

(*ii*) $[Cu^{II}(NH_3)_4]^{2+}[Pt^{II}Cl_4]^{2-}$

and $[Pt^{II}(NH_3)_4]^{2+}[Cu^{II}Cl_4]^{2-}$

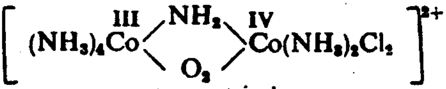
(*iii*) $[Co^{III}(en)_3]^{3+}[Cr^{III}(C_2O_4)_3]^{3-}$

and $[Co^{III}(en)_2(C_2O_4)]^{+}[Cr^{III}(en)(C_2O_4)_2]^{+}$

Here en stands for ethylene diamine, $H_2N—CH_2—CH_2—NH_2$.

(*vi*) Coordination Position Isomerism

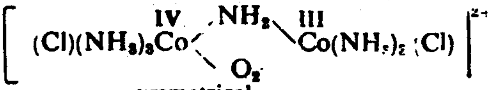
In some of the polynuclear complexes, to interchange the ligands between the metal nuclei which are present as part of the complex is possible. The type of interchange of ligands gives rise to coordination position isomerism, *e.g.*,



$$\left[(NH_3)_4\overset{III}{Co}\langle^{NH_2}_{O_2}\rangle\overset{IV}{Co}(NH_3)_2Cl_2\right]^{2+}$$

unsymmetrical

and



$$\left[(Cl)(NH_3)_3\overset{IV}{Co}\langle^{NH_2}_{O_2}\rangle\overset{III}{Co}(NH_3)_3(Cl)\right]^{2+}$$

symmetrical

are coordination position isomers.

STEREOISOMERISM OR SPACE ISOMERISM

When two compounds contain the same ligands coordinated to the same central ion, but the arrangement of ligands in space is different. the two compounds are said to be stereoisomers and the type of isomerism is called **stereoisomerism**. It is also called **space isomerism**. Stereoisomers are quite similar, *e.g.*, optical isomers (which are stereoisomers) differ only in their optical activity. On the other hand structural isomers differ from each other in various ways.

Stereoisomerism is of two types : (*i*) *Geometrical or cis-trans isomerism*, and (*ii*) *optical or mirror-image isomerism.*

GEOMETRICAL ISOMERISM IN 4— AND 6— COORDINATION COMPOUNDS

Geometrical isomers have identical empirical formula but differ in chemical and physical properties because of the different arrangement of ligands. They are usually easily separated by chemical or physical means. Some (not all) of the geometrical isomers may develop optical activity due to distinct mirror-image forms. Thus geometrical isomer which is capable of existing in non-superimposable mirror-image forms can be used tc isolate optical isomers.

In a *cis*-isomer two identical (*i.e.* similar) groups are adjacent to each other (Latin, *cis*   same) while in a *trans*-isomer the two identical groups are diametrically (*i.e.* diagonally) opposite to each other (Latin, *trans* ⟶ across): *i.e.*, a straight line connecting the two groups *trans* to each other passes through the central at which the metal ion is placed.

Geometrical isomerism cannot arise in a tetrahedral complex (C.N. = 4) because this geometry contains all the ligands in *cis* (*i.e.*, adjacent) position with respect to each other *i.e.* each ligand is equidistant from the other three ligands and all bond angles are the same (= 109.5°). This isomerism is, however, found in many square planar (C. N. = 4) and octahedral(C.N. = 6) complexes.

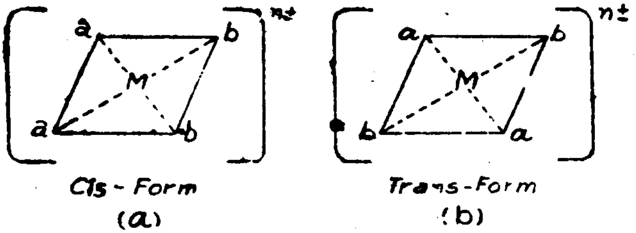
(A) Square planar complexes

$[Ma_4]^{n\pm}$, $[Ma_3b]^{n\mp}$, $[Mab_3]^{n\mp}$ type square planar complexes donot show geometrical isomerism, since every conceivable spatial arrangement of ligands round the metal ion is exactly equivalent. The following types of square planar complexes usually show *cis-trans* isomerism.

(*i*) **$[Ma_2b_2]^{n\pm}$ type complexes.** Here M = metal ion and *a* and *b* are monodentate ligands. Complexes of this type can exist in cis- and trans-isomers as shown below in Fig. 13·2.

Examples. Examples of this type of complexes are

$[Pt^{II}(NH_3)_2Cl_2]^0$ and $[Pd^{II}(NH_3)_2(NO_2)_2]^0$. Both these complexes have cis- and trans-isomers. The existence of cis- and trans-isomers in these complexes indicates that the four bonds are coplanar with the central metal ion.



a's and *b's* on adjacent points *i.e. a's* and *b's* both are cis to each other.

a's and *b's* diametrically opposite *i.e. a's* and *b's* both trans to each other.

Fig. 13·2. Cis-and trans-isomers of $[Ma_2b_2]^{n\pm}$ type complex (square planar complex).

Cis- and trans-forms for $[Pt^{II}(NH_3)_2Cl_2]^0$ are shown below in Fig. 13·3.

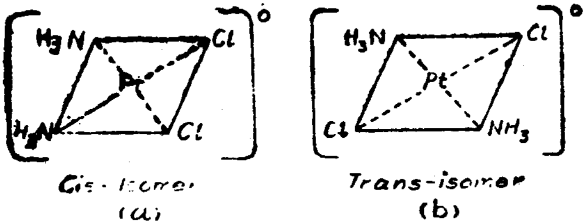


Fig. 13·3. Cis- and trans-isomers of $[Pt^{II}(NH_3)_2Cl_2]^0$ (square planar complex).

(*ii*) **$[Ma_2bc]^{n\mp}$ type complexes.** The complexes of this type also exist in cis- and trans- isomers, e.g. $[Pta_2bc]$ type complexes show *cis-trans* isomerism. Here *a* is a neutral ligand such as NH_3, *py*, H_2O and *b* and *c* are the anionic ligands like Cl^-, Br^-, NO_2^-, SCN^- etc. (*see* Fig. 13·4).

cis-isomer
(Two *a's* cis to each other)

trans-isomer
(Two *a's* *trans* to each other)

Fig. 13·4. *cis* and *trans* isomers of $[Pta_2bc]$ type complex.

(*iii*) **$[Mabcd]^{n\mp}$ type complexes.** Pt^{II} forms a number of complexes of this type. Complexes of this type exist in three isomeric forms as shown in Fig. 13·5.

Fixing any two groups in trans positions also fixes the other two positions. The fourth structure shown, in which *a* is trans to

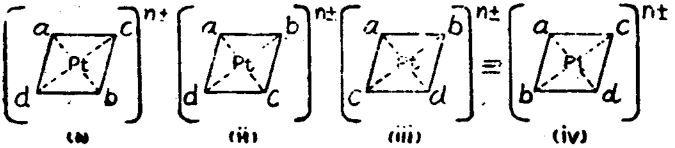


Fig. 13·5. Three isomeric forms of $[Pt^{II}abcd]^{n\pm}$ complex ion (square planar complex ion).

d, is identical to the third structure. Either of these structures can be obtained by rotation of the other through 180° about the axis through *a*-Pt-*d*. All possible isomers can easily be obtained by selecting one group, say *a*, and seeing how many different groups can be placed trans to *a*.

Examples. (*a*) Three isomers have been reported for

$$[Pt^{II}\ (NO_2)(py)(NH_3)(NH_2OH)]^+$$

ion corresponding to ammonia trans to each of the three groups where *py* stands for pyridine, C_6H_5N. This complex ion has a plane of symmetry, but since the four groups are different, it has no rotational symmetry axis.

(*b*) $[Pt^{II}\ (NH_3)(py)(Cl)(Br)]^0$ also exists in three isomeric forms as shown below in Fig. 13·6.

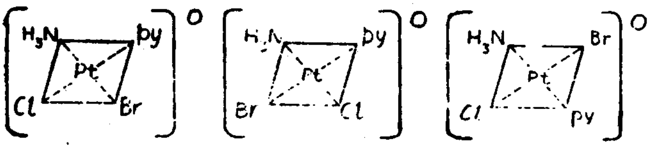
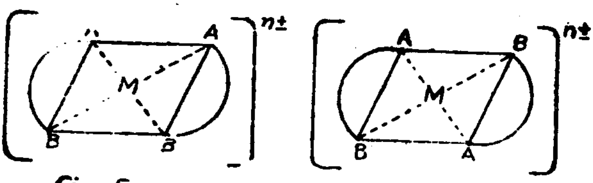


Fig. 13·6. **Three isomeric forms of $[Pt^{II}(NH_3)(py)(Cl)(Br)]^0$**

(*c*) $[Pt^{II}\ (C_2H_4)\ (NH_3)\ (Cl)\ (Br)]^0$ also gives three isomeric forms.

The existence of three isomeric forms in case of the complexes mentioned above indicates that these complexes have square planar geometry.

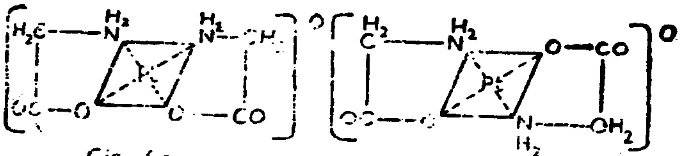
(*iv*) **Square planar complexes having unsymmetrical bidentate chelating ligands : $[M(AB)_2]^n$ type complexes.** Here M is the central metal ion and (AB) represents an unsymmetrical bidentate ligand. A and B are the two ends (*i.e.* co-ordinating atoms) of the bidentate chelating ligand, (AB). Such type of complexes also show cis- and trans-isomerism as shown Fig. 13·7.



Cis-Form (a) Trans-Form (b)

Fig. 13·7. Cis- and trans-isomers of $[M(AB)_2]^{n\pm}$ type square planar complex having two unsymmetrical bidentate chelating ligands.

Example. $[Pt^{II}(gly)_2]^0$ where gly is $NH_2-CH_2COO^-$ (glycine ion), is an important example of this type of complex. It exists in cis- and trans-isomers as shown below in Fig. 13·8.

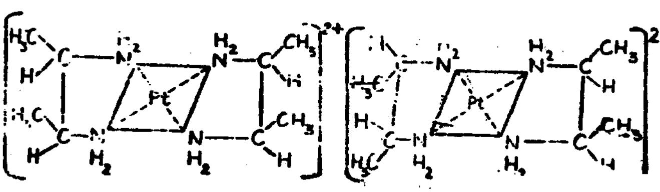


Cis-form Trans-form

Fig. 13·8. Cis- and trans-isomers of $[Pt^{II}(gly)_2]^0$ where gly is $NH_2-CH_2COO^-$ (glycine ion).

(v) **Square planar complexes having symmetrical bidentate chelating ligands : $[M(AA)_2]^{n\pm}$ type complexes.** Such type of complexes also have cis- and trans-isomers.

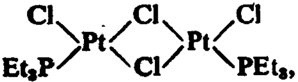
Example. $[Pt^{II}(NH_2.CH(CH_3).CH(CH_3).NH_2)_2]^{2+}$ is an important example of this type of complex. It has cis- and trans-isomers as shown in Fig. 13·9.



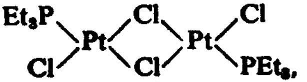
(a) (b)

Fig. 13·9. Cis- and trans-isomers of $[Pt^{II}(NH_2-CH(CH_3).CH(CH_3).NH_2)_2]^{2+}$ ion (a) Cis- form ; (b) trans-form.

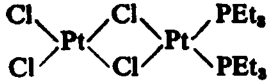
(vi) **Bridged binuclear planar complexes of $M_2a_2b_4$ type.** In bridged binuclear square planar complexes cis-trans isomers as well as the unsymmetrical isomers, are possible, although in the example $[Pt(PEt_3)Cl_2]_2$ cited below, and in all other cases, only the first two (*i.e.* cis- and trans-forms) have been found.



cis-form
(*i*)



trans-form
(*ii*)



unsymmetrical
form
(*iii*)

(B) Octahedral complexes

The arrangement of six ligands in a regular octahedral complex round the central metal ion, M can be represented as shown in Fig. 13·10.

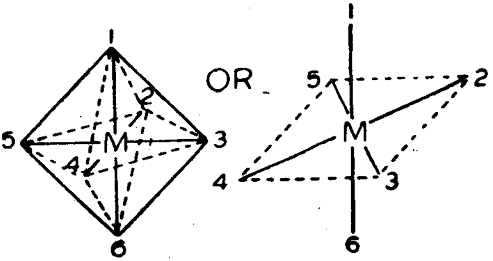


Fig. 13·10. Arrangement of six ligands in a regular octahedral complex round the metal ion, M.

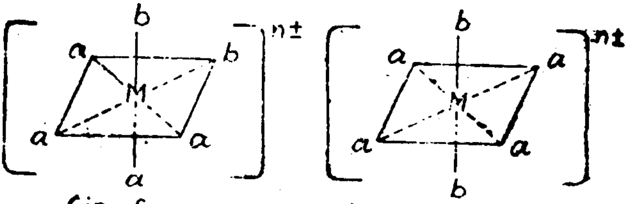
Here we shall discuss the cis-trans isomerism in different types of octahedral complexes containing monodentate ligands such as *a* and *b*, symmetrical bidentate chelating ligands, (AA) or unsymmetrical bidentate chelating ligands, (AB). In (AA) the two letters A and A indicate the two ends (*i.e.*, donor atoms—similar atoms) of the chelating ligand which get coordinated with the cental metal ion, M. (AA) ligand may be a neutral molecule (*e.g.* ethylene diammine, $H_2N—CH_2—CH_2—NH_2$, en) or a negative ion (*e.g.* $C_2O_4^{2-}$ ion). In (AB), A and B are two different coordinating atoms.

It may be seen that octahedral complexes of $[Ma_5b]^{n\pm}$ and $[Ma_6]^{n\pm}$ type will give only single isomer. Thus these complexes will show no isomerism.

The following types of octahedral complexes show cis-trans-isomerism.

(*a*) **Octahedral complexes containing only monodentate ligands.** Such complexes are those which have any of the following general formulae :

(*i*) **$[Ma_4b_2]^{n\pm}$ type complexes.** In case of this complex, two isomers are possible : cis-isomer in which two *b*'s have adjacent positions (*i.e.* they lie on any of the twelve edges of the octahedron) and trans-isomer in which two *b*'s are diagonally opposite to each other, *i.e.* the straight line connecting the two *b*'s *trans* to each other passes through the centre where the metal ion is placed. It may be seen from the octahedral shape shown in Fig. 13·10 that in *cis*-isomer two *b*'s can occupy any of the twelve positions *viz.* (1, 2), (1, 3) (1, 4), (1, 5), (6, 2), (6, 3), (6, 4), (6, 5), (2, 3), (3, 4), (4, 5) and (5, 2). These positions have been known by considering the twelve edges of the octahedron. In a *trans*-isomer two *b*'s occupy any of the position namely (1, 6), (2, 4) and (3, 5). These positions have been determined by considering the diagonals (2, 4) and (3, 5) of the square plane (2, 3, 4, 5) containing the central metal ion M and the line joining the vertices 1 and 6. Normally to avoid confusion it is assumed that in *cis*-isomer the two *b*'s occupy 1 and 2 positions while in *trans* isomer two *b*'s are at 1 and 6 positions as shown below in Fig. 13·11



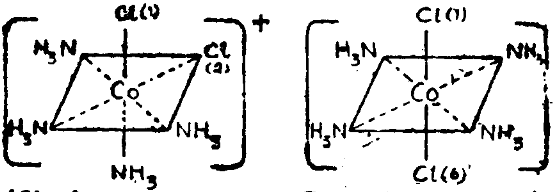
Cis - form
(a)

Trans - form
(b)

(1, 2) isomer (1, 6) isomer

Fig. 13·11. Cis- and trans-isomers of $[Ma_4b_2]^{n\pm}$ type octahedral complex. In cis-isomer two *b*'s have adjacent positions while in trans-isomer two *b*'s are diagonally opposite to each other. Numbers indicate positions of *b* groups,

Example. Dichlorotetraammine cobalt (III) ion, $[\text{Co}^{III}$ $\text{Cl}_2]^+$, is an important example of $[Ma_4b_2]^{n\pm}$ type complex ion. I cis-and trans-isomers as shown in Fig. 13·12.



(Cis-isomer or 1,2-isomer
(a)

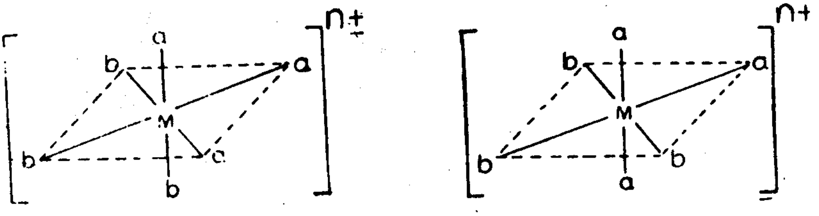
Trans-isomer or 1,6 isomer
(b)

Blue violet Bright green

Fig. 13·12. Cis- and trans-isomers of $[\text{Co}^{III}(\text{NH}_3)_4\text{Cl}_2]^+$ ion. In cis-isomer two Cl^- ions are in (any) two adjacent positions while in trans isomer these are in (any) two opposite positions.

In cis-isomer the two Cl^- ions are in (any) two adjacent positions. Cis-isomer is designated as 1, 2-isomer. In trans-isomer the two Cl^- ions are in (any) two opposite positions. Trans-isomer is designated as 1, 6-isomer. Cis-isomer has a beautiful blue-violet colour while trans-isomer has bright green colour.

(*ii*) **$[Ma_3b_3]^{n\pm}$ type complexes.** Complexes of this type also exist in cis-and trans-isomers. In *cis*-isomer three *a*'s occupy 1, 2 and 3 positions and in *trans*-isomer these are at 1, 2 and 6 positions as shown in Fig. 13·13.



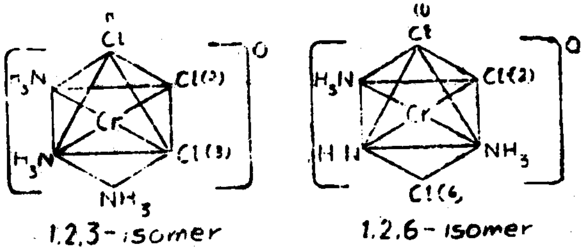
cis-isomer
(1, 2, 3) isomer

trans-isomer
(1, 2, 6) isomer

Fig. 13·13. Cis- and trans-forms of $[Ma_3b_3]^{n\pm}$ type octahedral complex ion. Numbers indicate the positions of *a*'s ligands.

Examples. (*a*) Trichloro tripyridine rhodium (III), $[Rh^{III}(py)_3Cl_3]^0$ is an example of this type of ion.

(*b*) Another example is $[Cr^{III}(NH_3)_3Cl_3]^0$ which exists in two isomeric forms. In one isomer, the three Cl^- ions are on one triangular face and the three NH_3 molecules are on the opposite triangular face of the regular octahedron. This isomer is called 1, 2, 3 or facial isomer. In the other isomer the Cl^- ions are around an edge of the octahedron and the NH_3 molecules are around the opposite edge. This isomer is called 1, 2, 6 or peripheral isomer. (Fig. 13·14).



1,2,3-isomer
(Facial isomer)

1,2,6-isomer
(Peripheral isomer)

Fig. 13·14. Two isomeric forms of $[Cr^{III}(NH_3)_3Cl_3]^0$.

(*iii*) **[Mabcdef] type complexes.** This type of octahedral complex can exist in 15 different geometrical isomers each of which would also have an optical isomer. The only compound of this type is $[Pt^{IV}(py)(NH_3)(NO_2)(Cl)(Br)(I)]$. It has been obtained in three different forms but no attempt has been made to isolate all the 15 isomers.

(*b*) **Octahedral complexes containing monodentate and symmetrical bidentate chelating ligands.** Now let us discuss the cis-trans-isomerism among octahedral complexes containing monodentate and symmetrical bidentate chelating ligands. These complexes may be those which have any of the following formulae :

(*i*) **$[M(AA)_2a_2]^{n\pm}$ type complexes.** Here (AA) is a symmetrical bidentate chelating ligand in which the two letters A and A indicate the two similar coordinating atoms. *a* is a monodentate ligand. Complexes having this general formula exist in cis- and trans-isomers as shown in Fig. 13·15.

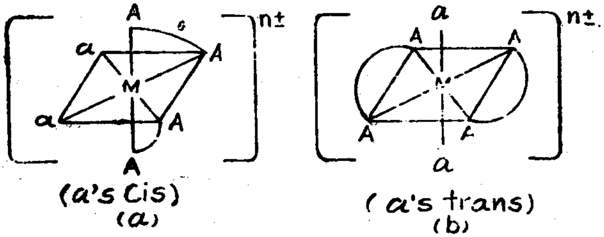


Fig. 13·15. Cis- and trans-isomers of $[M(AA)_2a_2]^{n\pm}$ type octahedral complex ion ;

(*a*) Cis-form in which a's are cis to each other.

(*b*) trans-form in which a's are trans to each other

Examples. The following complex ions are the examples of $[M(AA)_2a_2]^{n\pm}$ type ion :

$[Co^{III}(en)_2Cl_2]^+$, $[Co^{III}(en)_2(NO_2)_2]^+$, $[Ir^{IV}(C_2O_4)_2Cl_2]^{2-}$ $[Ir^{III}(C_2O_4)_2Cl_2]^{3-}$, $[Rh^{IV}(C_2O_4)_2Cl_2]^{2-}$, $[Cr^{III}(C_2O_4)_2(H_2O)_2]^-$

Cis- and trans-isomers of $[Co^{III}(en)_2Cl_2]^+$ ion can be represented as given in Fig. 13·16.

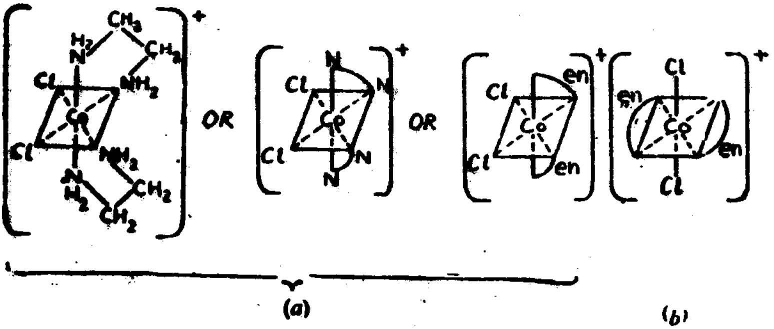


Fig. 13·16. Cis- and trans-isomers of $[Co^{III}(en)_2Cl_2]^+$ ion.
(*a*) Cis-isomer (*b*) trans-isomer.

(*ii*) **$[M(AA)_2ab]^{n\pm}$ type complexes.** These complexes exist in cis- and trans- isomers as shown below in Fig. 13·17.

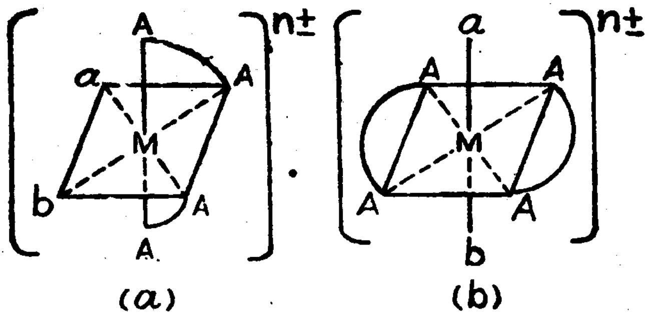


Fig. 13·17. Cis- and trans- isomers of $[M(AA)_2ab]^{n\pm}$ type octahedral complex ion.
(*a*) Cis- form (*b*) trans- form

Examples $[Co^{III}(en)_2(NH_3)(Cl)]^{2+}$ and $[Ru^{III}(py)(C_2O_4)_2(NO)]$. cis- and trans-isomers of $[Co^{III}(en)_2(NH_3)(Cl)]^{2+}$ ion are given below in Fig. 13·18.

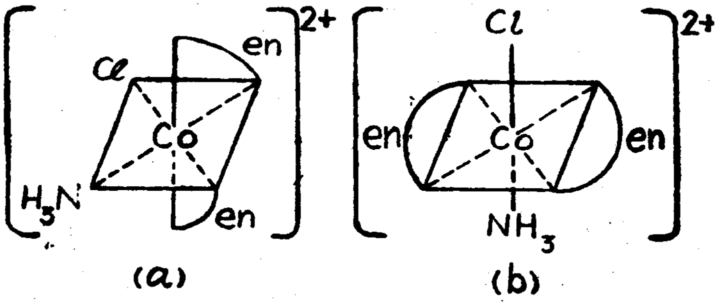
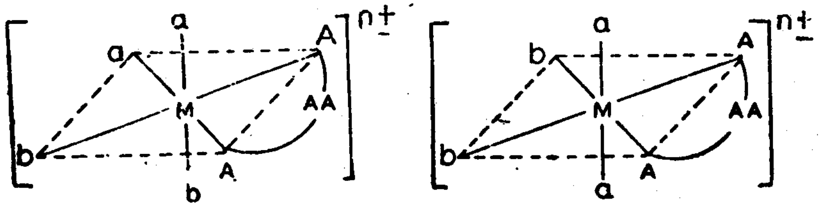


Fig. 13·18. Cis- and trans- isomers of $[Co^{III}(en)_2(NH_3)(Cl)]^{2+}$ ion.

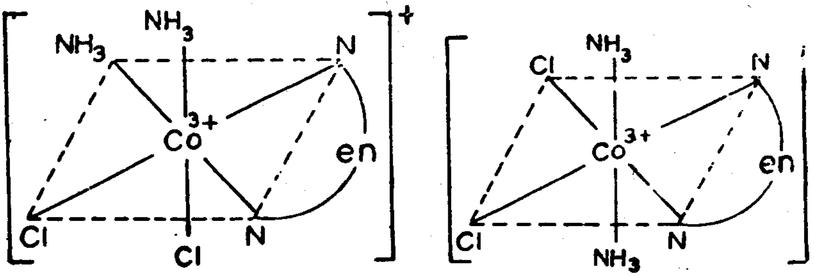
(*iii*) **$[M(AA)a_2b_2]^{n\pm}$ type complexes.** Complexes of this type also exist in *cis*- and *trans*-isomers as shown below in Fig. 13·19.



cis-isomer *trans*-isomer

Fig. 13·19. Cis- and trans-isomers of $[M(AA)a_2b_2]^{n\pm}$ type complexes.

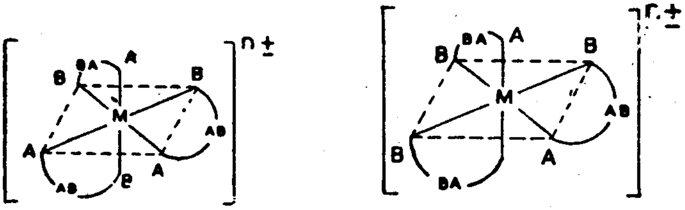
Examples. $[Co^{III}(en)(NH_3)_2(Cl)_2]^+$ is an important example whose *cis*- and *trans*-isomers are shown below in Fig. 13·20.



cis-isomer *trans*-isomer

Fig. 13·20. *cis*- and *trans*-isomers of $[Co^{III}(en)(NH_3)_2Cl_2]^+$

(*c*) **Octahedral complexes containing unsymmetrical bidentate chelating ligands.** $[M(AB)_3]^{n\pm}$ type complex is an important example of octahedral complexes containing unsymmetrical bidentate chelating ligands. Here (AB) is an unsymmetrical bidentate chelating ligand in which the letters A and B represent the two ends (*i.e.* coordinating atoms) of the ligand. Complex ion of $[M(AB)_3]^{n\pm}$ type exists as cis-and trans isomers as shown below in Fig. 13·21. Both cis- and trans-isomers have each a pair of optical isomers.

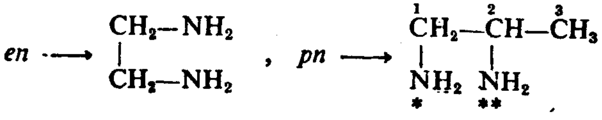


cis-isomer *trans*-isomer

Fig. 13·21. Cis-and trans-isomers of $[M(AB)_3]^{n\pm}$ complex ion.

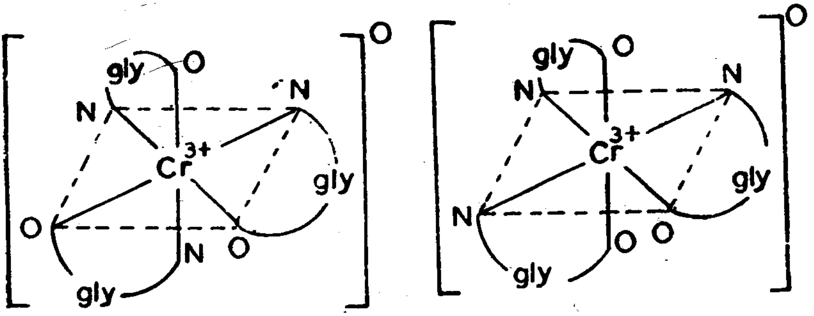
Example. *cis*-and *trans*-isomers of triglycinato chromium (III), $[Cr^{III}(gly)_3]^0$ has the structures as shown in Fig. 13·22. Each of these forms is optically active.

(*d*) **Octahedral complexes containing optically active bidentate ligands.** $[Co^{III}(en)(pn)(NO_2)_2]^+$ is an important examples of such type of octahedral complexes. Here *en* and *pn* are ethylene diamine and 1, 2-diamino propane and have the following formulae :



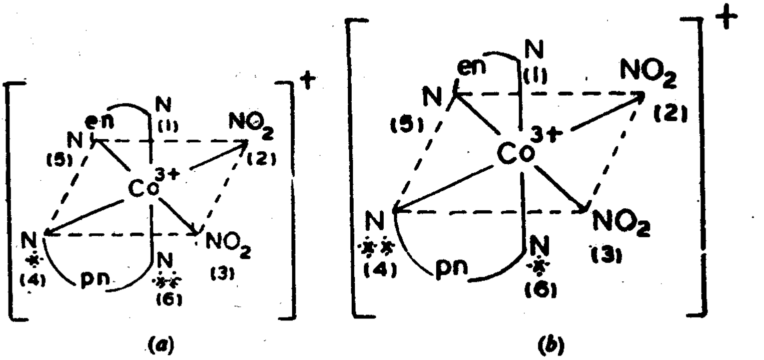
$$en \longrightarrow \begin{array}{l} CH_2{-}NH_2 \\ | \\ CH_2{-}NH_2 \end{array}, \quad pn \longrightarrow \begin{array}{lll} \overset{1}{C}H_2 & {-}\overset{2}{C}H & {-}\overset{3}{C}H_3 \\ | & \;| & \\ \underset{*}{NH_2} & \underset{**}{NH_2} & \end{array}$$

From their formulae it is evident that both the ligands are bidentate with two neutral donors *viz.* N-atoms and that *en* is symmetrical and hence optically inactive while *pn* is unsymmetrical and hence optically active. To differentiate the two donor atoms *viz.*



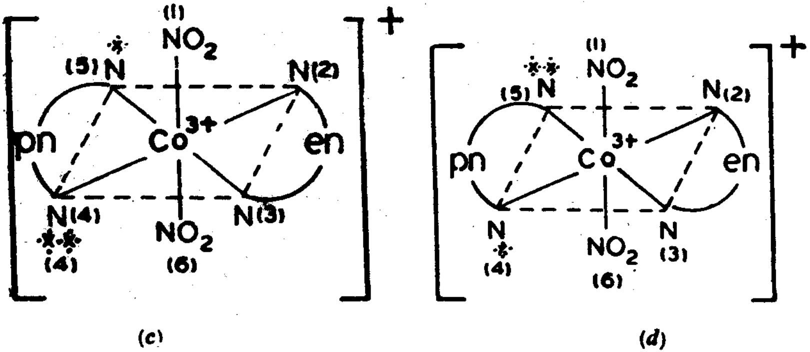
cis-form *trans*-form

Fig. 13·22. *Cis*- and trans-isomers of $[Co^{III}(gly)_3]^0$



(*a*) (*b*)

cis-isomers



(*c*) (*d*)

trans-isomers

Fig. 13·23. *cis*-and *trans*-isomers of $[Co^{III}(en)(pn)(NO_2)_2]^+$

N-atoms of *pn* they have been shown with one and two asterisks. $[Co^{III}(en)(pn)(NO_2)_2]^+$ ion exists in four geometrical forms : two are *cis* and two are *trans*. (*a*) *cis*-isomer has been obtained by placing $\overset{*}{N}H_2$ and $\overset{**}{N}H_2$ at 4 and 6 positions of the octahedron and in (*b*) *cis*-isomer their positions have been reversed. (*c*) and (*d*) which are *trans*-isomers have been obtained similarly. (*see* Fig. 13·23).

(*e*) **Polynuclear complexes.** The geometric isomers of a polynuclear hydroxy-bridged complex, $[Fe_2(OH)_4(H_2O)_6]^{2+}$, can be shown as follows (Fig. 13·24).

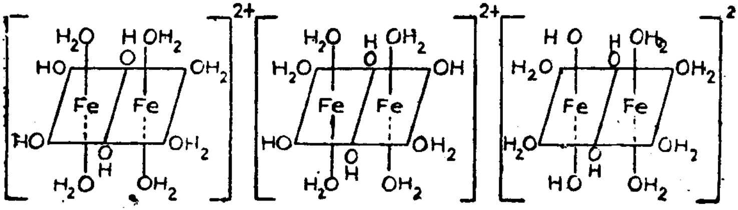


Fig. 13·24. Geometric isomers of $[Fe_2(OH)_4(H_2O)_6]^{2+}$ ion.

Such type of isomerism is called bridge-isomerism which interprets the linkage of two complexed species by ligands that are common to the coordination spheres of both, and which, consequently, must be mutually shared. In $[Fe_2(OH)_4(H_2O)_6]^{2+}$ ion the two OH^- groups act as bridges and connect the respective octahedral components of the overall structure.

TO DISTINGUISH BETWEEN CIS-AND TRANS-ISOMERS

The following methods may be used to distinguish between *cis*-and *trans*-isomers.

(1) Dipole Moments Measurements.

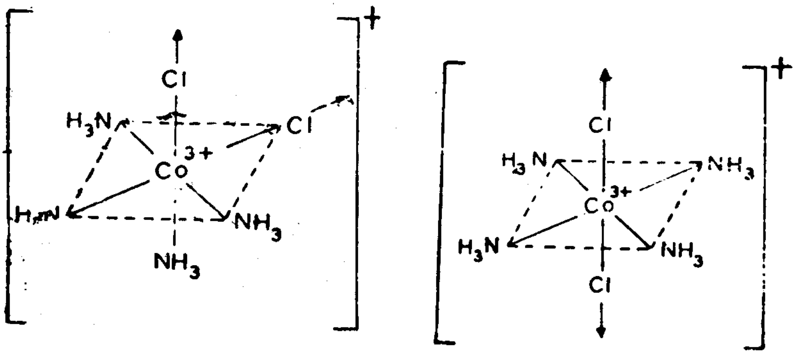
Jensen has shown that the Pt^{II} complexes of $[Pt^{II}A_2X_2]$ type, where A=substituted phosphine, arsine or stilbine such as $(C_2H_5)_3P$, $(C_3H_7)_3As$ or $(C_2H_5)_3Sb$ and X=a halogen, have their dipole moments (μ) either equal to zero or between 8 and 12 Debye units. In the compounds with $\mu=0$, the individual moments have cancelled one another and so these are *trans*-isomers. The compound with $\mu=8-12$ Debye units are *cis*-isomers.

(2) X-ray Crystal Analysis

X-ray crystal analysis and dipole moment measurements of several Pt^{II} complexes have confirmed the square-planarity of the bonds around the central metal atom. This square planar arrangement has also been established for 4-coordinated Pt^{II}, Ag^{II}, Cu^{II} and Au^{III}. Tetrahedral configurations have been assigned to Cu^{I} Ag^{I}, Au^{I}, B^{III}, Al^{III}, Zn^{II}, Cd^{II}, Hg^{II} and Co^{II} in their coordinated compounds. Some metals such as Ni^{II} appear to show either configuration for 4-coordination.

(3) Infrared Spectroscopic Technique.

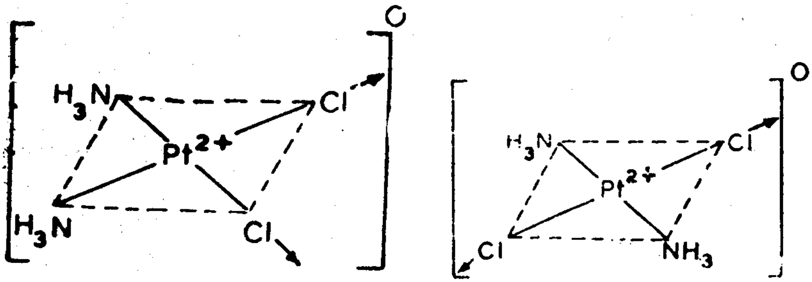
In a *trans* octahedral complex such as $[Co^{III}(NH_3)_4Cl_2]^+$ or in *trans* square planar complex like $[Pt^{II}(NH_3)_2Cl_2]^0$, the Cl-metal-Cl symmetrical stretching vibration produces no change in the dipole moment of the molecule [Fig. 13·25 (*b*) and (*d*)], and thus no band corresponding to this vibration is observed in the infrared spectrum. However, in the *cis*-form of each compound, the symmetrical stretching vibration [Fig. 13·25 (*a*) and (*c*)] as well the unsymmetrical stretching vibration produce appreciable changes in the dipole moment; hence the infrared spectrum of the *cis*-isomer will contain a large number of bands due the Cl-metal-Cl stretching.



(*a*)
cis-isomer

(*b*)
trans-isomer

cis-and *trans*-isomers of $[Co^{III}(NH_3)_4Cl_2]^+$ octahedral complex.



(c)
cis-isomer

(*d*)
trans-isomer

cis-and trans-isomers of $[Pt^{II}(NH_3)_2Cl_2]^0$ square planar complex

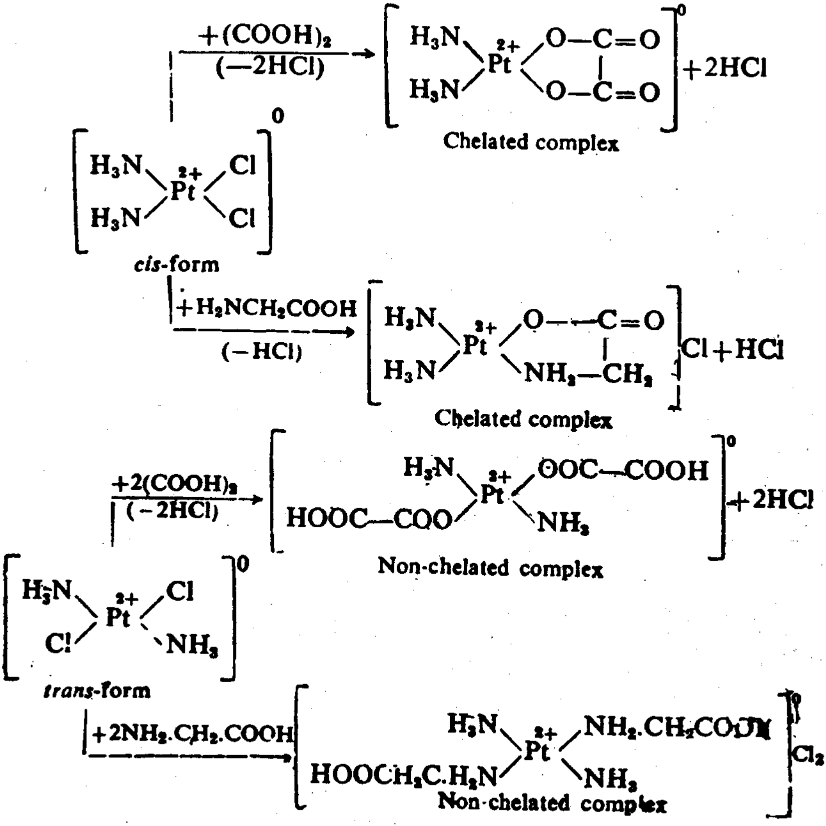
Fig. 13·25. Symmetrical Cl-metal-Cl stretching vibrations of *cis*- and *trans*-isomers of $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2Cl_2]^0$

(4) A *cis*-isomer has a high molar extinction coefficient (absorption) than the corresponding *trans*-isomer and sometimes the two isomers may differ significantly in their absorption spectra.

(5) The technique which consists of attempting to resolve the *cis*-isomer into the two possible optically active isomers is also commonly used to distinguish it from the *trans*-isomer.

(6) Grinberg's Method.

It is a chemical method and assumes that when a chelating ligand having two donor atoms separated by two to four other atoms reacts with *cis*-and *trans*-isomers separately, its two donor atoms coordinate to the central metal ion of the *cis*-form at two *cis*-positions and thus form five or six membered ring, while in the *trans*-form they coordinate to the central metal ion at *trans*-positions and thus the ligand acts as a manodentate ligand, *i.e.*, the ligand cannot form a ring complex with *trans* form. Typical chelating ligands used for the purpose are oxidic acid, (COOH), glycine ($H_2N\text{-}CH_2\text{-}COOH$) and ethylenediamine ($NH_2-CH_2-CH_2-NH_2$). The application of this method can by explained be considering the reaction of oxalic acid and glycine with *cis*-and *trans*-isomers of square planar complex of Pt (II), $[Pt^{2+}(NH_3)_2Cl_2]^0$. Quite obviously the *cis*-isomer gives a *chelated complex* while the *trans*-isomer yields a *non-chelated complex*.



(7) Kurnakov's Reaction

Kurnakov utilised the phenomena of *trans*-effect in distinguishing the pairs of *cis*- and *trans*-isomers of square planar complexes of [PtA_2X_2] type by treating them with thiourea.

For the details of this method *see uses of trans-effect.*

OPTICAL OR MIRROR-IMAGE ISOMERISM

Befor discussing the optical isomerism shown by various types of complexes we will define some important terms related to this isomerism.

When the solutions of certain complex compounds are placed in the path of a *plane-polarised light* (the waves of the plane-polarised light vibrate only in one direction ; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. *This property of a complex of rotating the plane of polarised light is called its optical activity and the complex possessing this property is said to be optically active.*

Optically active complexes are said to exist in the following forms :

(*a*) One which rotates the plane of polarised light towards right (*i.e.* in clockwise direction) is said to be **dextro-rotatory** or *d*-form. **d-form** is also represented by placing (+) sign before its name or formula.

(*b*) One which rotates the plane of polarised light towards left (*i.e.* in anti-clockwise direction) is called **laevo-rotatory** or *l*-form. *l*-form is also represented by putting (—) sign before its name or formula.

(+), dextro, and (—), laevo, refer to the sign of rotation of the optical isomer at the sodium D line wavelength.

The *d*- and *l*-forms have the following characteristics :

(*i*) Since *d*- and *l*-forms are capable of rotating the plane of polarised light, these are said to be **optically active forms** or **optical isomers** and this phenomena is called **optical activity** or **optical isomerism.** These two forms have exactly identical physical and chemical properties, although they differ in their action on polarised light.

(*ii*) *d*- and *l*-forms are mirror images to each other just as left hand is the mirror image of the right hand. Thus *d*- and *l*-forms can be superimposed on each other. Since these forms are related to each other as mirror-images, they are commonly called **enantiomorphs** (Latin : *enantio* = opposite, *morphs* = forms) *or* **enantiomers.** Thus optical isomerism is now often referred to as **enantiomerism.**

(*c*) One which is not capable of rotating the plane of polarised light is called **optically inactive.** Such an isomer is called **racemic-, dl- or (±)-form** A recemic substance is composed of 50% *d*- and

50% *l*-form. The solution of a recemic (*dl*-mixture) form in a solvent which contains equimolecular amounts of *d*- and *l*-forms is inactive, because the rotation (of the plane of polarised light) produced by one isomer, say *d*-isomer, is balanced or compensated by equal but opposite rotation produced by the other (*i.e.* *l*-isomer). Optical inactivity produced in *dl*-mixture is said to be due to **external compensation.**

Conditions for a molecule to show optical isomerism.

A molecule in which the grouping of the atoms in the molecule in asymmetric is called an **asymmetric or dissymmetric molecule.**

An asymmetric molecule has the following features :

(*i*) An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane which divides the molecule in such a way that the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always *inactive* while those *having no plane of symmetry are optically active and hence show optical isomerism.*

(*ii*) An asymmetric molecule cannot be superimposed on its mirror image.

Thus the most necessary and sufficient condition for a molecule to show optical isomerism (*i.e.* to exist in *d*- and *l*-forms) is that (*a*) *the molecule should be asymmetric, i.e. it should have no plane of symmetry,* and (*b*) *the molecule should not be superimposable on its mirror image.*

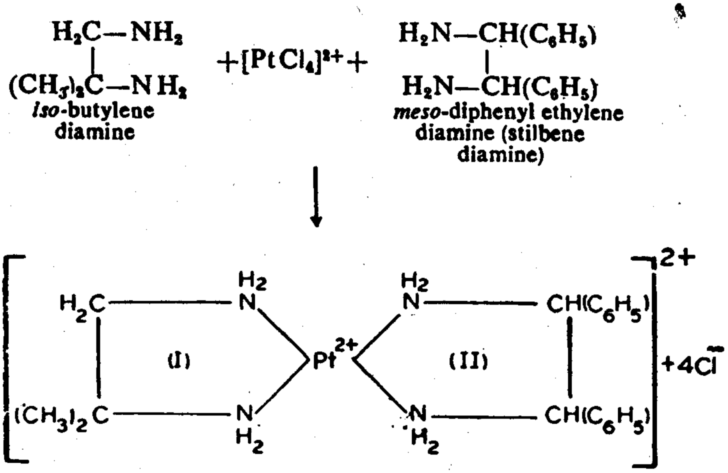
OPTICAL ISOMERISM IN 4-AND 6-COORDINATION COMPOUNDS

No mirror image isomerism is possible with tetrahedral and square planar complexes of the type : $[Ma_4]$, $[Ma_3b]$ and $[Ma\ b_3]$ because all the possible arrangements of the ligands round the central metal ion, M are exactly equivalent.

(*A*) Square planar Complexes

Optical isomerism rarely occurs in square planar complexes since they have all the four ligands and the central metal ion in the same plane and hence contain a plane or axis of symmetry. Thus these complexes are optically inactive, *i.e.* they cannot show optical isomerism even if all the four ligands are different.

Although, as mentioned above, square planar complexes seldom show optical isomerism, yet a four-coordinated complex of Pt (II) *viz.* *iso*-butylenediamine-*meso* stilbenediamine platinum (II) cation, $[Pt^{II}(NH_2.CH(C_6H_5).CH(C_6H_5).NH_2)(NH_2.CH_2.C(CH_3)_2.NH_2)]^{2+}$ which has square-planar shape has been resolved into two forms by Mills and Quibell is 1935. This complex was synthesised as follows :



iso butylene diamine *meso* stilbene diamine platinum (II) cation

Proof of square planar geometry. This complex cation consists of two rings : (I) and (II) as shown in its structure given above. If the donor atoms are supposed to be tetrahedrally arranged round the central Pt^{2+} ion, ring (II) would be in the plane of paper and ring (I) perpendicular to it. The plane of paper represents a plane of symmetry. Consequently the plane of symmetry of ring (II) will coincide with the plane of ring (I) [Fig. 13·26]. Thus this tetrahedral structure has a plane or axis of symmetry passing through the plane of ring (I) and at right angles to the plane of ring (II). *Consequently this complex will give no optical isomers*

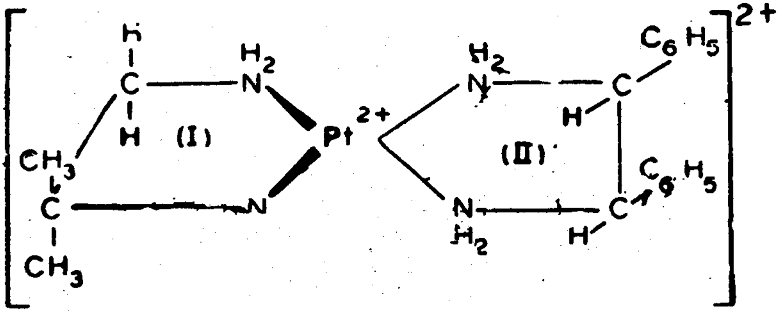


Fig. 13.26. Tetrahedral structure of $[Pt^{II}(NH_2.CH(C_6H_5).CH(C_6H_5).NH_2).(NH_2.CH_2.C(CH_3)NH_2]^{2+}$ ion. This structure has a plane or axis of symmetry and hence is symmetric and optically inactive i.e., it does not give any optical isomers.

On the other hand if the arrangement of the donor atoms is supposed to be square planar around Pt^{2+} ion [Fig. 13.27], C_6H_5

groups are below and H atoms are above the plane in ring (II) and hence *this structure has no plane or axis of symmetry, is assymmetric and consequently optically active.* Thus this complex would be expected to give optical isomers. Mills and Quibell have actually resolved this complex into optical isomers which proves that the cation is square planar in shape, *i.e.* the planes of the two rings are not perpendicular to each other, since the ion would then have a plane of symmetry. Thus the claim of the confused tetrahedral structure is ruled out.

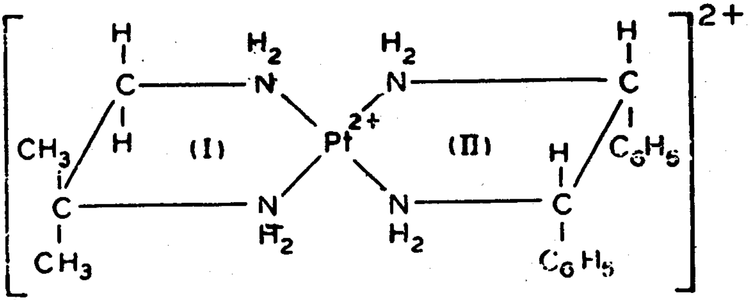


Fig. 13·27. Square planar structure of [Pt^{II} (NH$_2$. CH(C$_6$H$_5$). CH(C$_6$H$_5$). NH$_2$) (NH$_2$.CH$_2$.C(CH$_3$)$_2$.NH$_2$)]$^{2+}$ ion. This structure has no plane or axis of symmetry and hence is unsymmetric and optically active, *i.e.*, it gives optical isomers.

The symmetry which arises when a tetrahedral configuration is assigned to the complex cation is shown in Fig. 13·28. In this Fig. A, B, C and D are the corners of the tetrahedron. It is apparent that the plane of symmetry passes through the edge DC.

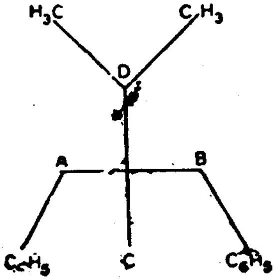


Fig. 13.28. Symmetry which arises when a tetrahedral structure is given to the cation, [Pt^{II} (NH$_2$.CH (C$_6$H (C$_2$H$_6$). NH$_2$) (NH$_2$.CH$_2$). C(CH$_3$)$_2$ (N$_3$H$_2$). This tetrahedral structure is ruled out, once Mills and Quibell were successful in resolving the ion.

(*B*) Tetrahedral Complexes.

(*i*) A tetrahedral complex of [Mabcd] type occurs in two optical isomers as shown in Fig. 13·29.

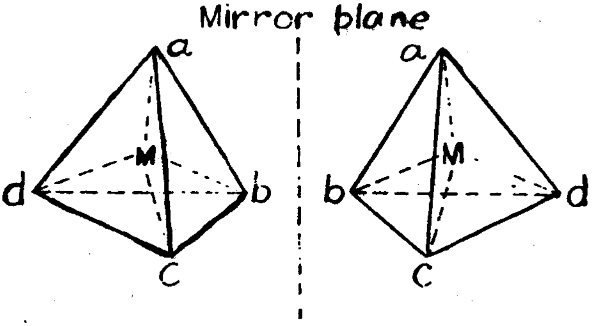


Fig. 13·29. Two optical isomers (mirror-image isomers) of a tetrahedral complex of [Mabcd] type.

Examples. (*i*) Mirror-image isomers of As^{3+} ion complex, $[As^{III}(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, with tetrahedral structure are shown below in Fig. 13·30.

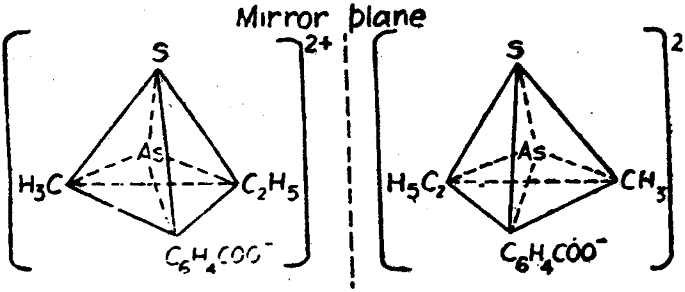
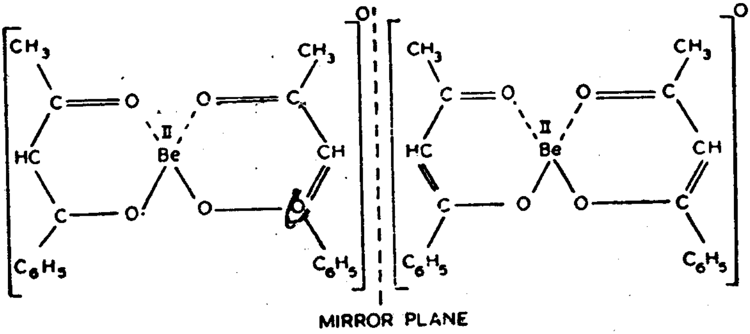


Fig. 13·30. Mirror-image isomers of $[As^{III}(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$ ion having tetrahedral structure.

Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (*i.e.*, unsymmetrical), *i.e.* it should have no plane of symmetry so that it can exist in two mirror-image forms.

(*ii*) Tetrahedral complexes of Be(II), B(III) and Zn(II) with unsymmetrical bidentate ligands have been made and resolved. An example is *bis*(benzoylacetonato) beryllium (II) complex.

$[(C_6H_5CO\ CHCOCH_3)_2Be]^0$ whose mirror-image isomers are shown in Fig. 13·31.



d-form *l*-form

Fig. 13·31. Mirror-image isomers of tetrahedral complex, $[(C_6H_5CO{\cdot}CHCOCH_3)_2Be^{II}]^0$

Here it may be noted from the Fig. that the complex has no centre or plane of symmetry and the two forms are not superimposable on each other. This explains the resolution of the complex into *d*- and *l*-forms.

(*C*) Octahedral Complexes.

Optical isomerism is very common in the following types of octahedral complexes :

(*a*) **Octahedral complexes containing only monodentate ligands.** The following types of octahedral complexes have optical isomers :

$[Ma_2b_2c_2]$, $[Ma_2b_2cd,]$, $[Ma_2bcde]$ and $[Mabcdef]$.

(*i*) **$Ma_2b_2c_2]$ type complex** : It has two optical isomers as shown below in Fig. 13·32.

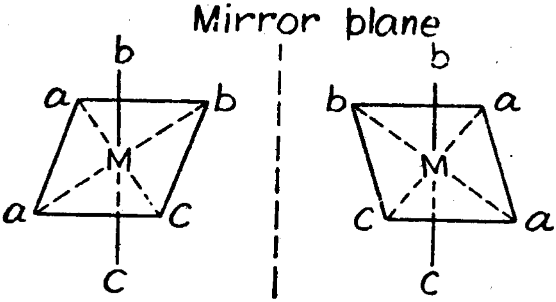
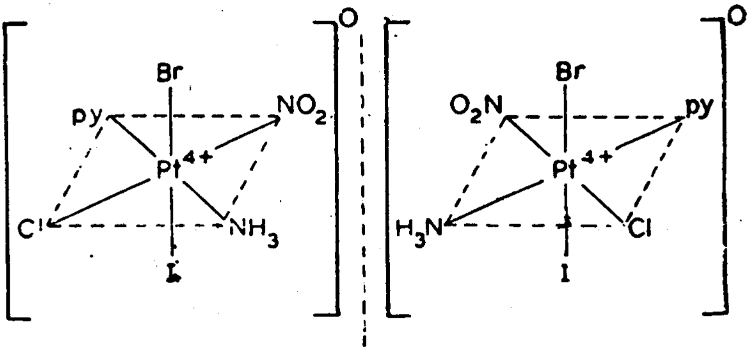


Fig. 13·32. Two optical isomers of an octahedral complex of $[Ma_2b_2c_2]$ type.

(*ii*) **[Mabcdef] type complex.** Complexes of this type having six different monodentate ligands have been prepared only for Pt(IV). Only a few isomers have been isolated, but there could be 15 geometrical isomers, each of which could exist in *d*- and *l*-form to give a total of 30 isomers.

Thus for one form of $[Pt^{IV}(py)(NH_3)(NO_2)(Cl)(Br)(I)]^0$ the optical isomers are those shown in Fig. 13·33.

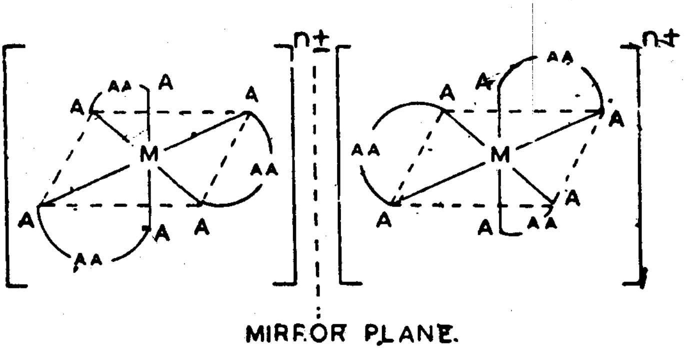


d-isomer *l*-isomer

Fig. 13·33. Optical (*d*- and *l*-) forms of $[Pt^{IV}(py)(NH_3)(NO_2)(Cl)(Br)(I)]^0$

(*b*) **Octahedral complexes containing only symmetrical bidentate chelating ligands.** Such complexes may be of the following types :

(*i*) **$[M(AA)_3]^{n\pm}$ type complexes :** Here (AA) is a symmetrical bidentate chelating ligand which may be a neutral molecule or a negative ion. The optical isomers of this type of complexes are shown below in Fg. 13·34.

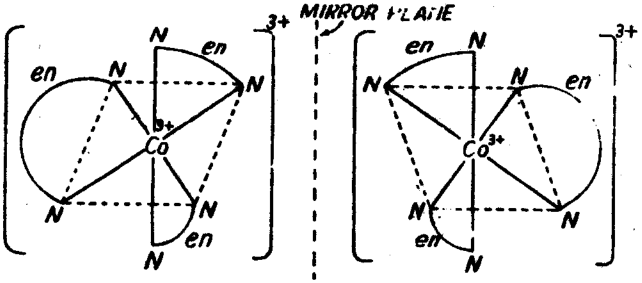


d-isomer *l*-isomer

Fig. 13·34. Mirror-image isomers of $[M(AA)_3]^{n\pm}$ type octahedral complex ion.

Examples: $[Co^{III}(en)_3]^{3+}$, $[Co^{III}(pn)_3]^{3+}$, $[Pt^{IV}(en)_3]^{4+}$, $[Pt^{IV}(pn)_3]^{4+}$, $[Co^{II}(pn)_3]^{2+}$, $[Fe^{II}(diph)_3]^{2+}$, $[Fe^{III}(diph)_3]^{3+}$, $[Rh^{IV}(en)_3]^{4+}$, $[Ir^{IV}(pn)_3]^{4+}$, $[Zn^{II}(en)_3]^{2+}$, $[M^{III}(C_2O_4)_3]^{3-}$ where M^{III} = Al^{3+}, Co^{3+}, Fe^{3+}, Rh^{3+}, Cr^{3+} and Ir^{3+}

The two optical isomers of $[Co^{III}(en)_3]^{3+}$ ion are shown in Fig. 13·35.



d-form *l*-form

Fig. 13·35. Optical isomers of $[Co^{III}(en)_3]^{3+}$ ion. These cannot be superimposed on each other.

The fact that the complexes of $[M(AA)_3]^{n\pm}$ type can be resolved into optical isomers confirms that these complexes have octahedral shape. Neither hexagonal nor trigonal prismatic geometry of 6-coordinate complex can give rise to optical activity.

(*ii*) **$[M(AA)_2(BB)]^{n\pm}$ type complexes.** Here (AA) and (BB) are two different symmetrical bidentate chelating ligands. Note that (AA) is a neutral ligand while (BB) is an anionic ligand. The two enantiomers (or enantiomorphs) of $[M(AA)_2(BB)]^{n\mp}$ type complexes are shown below in Fig. 13·36.

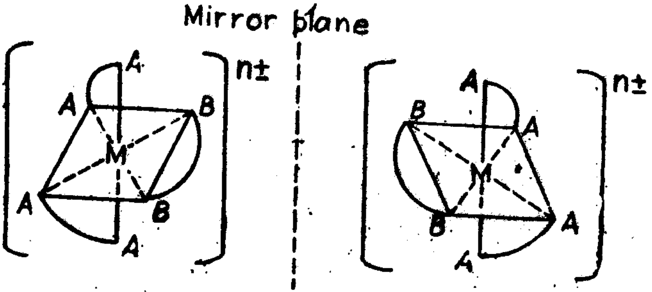


Fig. 13·36. The two enantiomers (or enantiomorphs) of $[M(AA)_2(BB)]^n$ type complex ion.

Examples. The ions namely $[Co^{III}(en)_2(CO_3)]^+$ and $[Co^{III}(en)_2(C_2O_4)]^+$ belong to this class of complexes

(*c*) **Octahedral complexes containing monodentate and symmetrical bidentate chelating ligands.** Such complexes may be of the following types :

(*i*) **$[M(AA)_2a_2]^{n\mp}$ type complexes.** Here (AA) is a chelating ligand and *a* is a unidentate (*i.e.* mono-dentate) ligand.

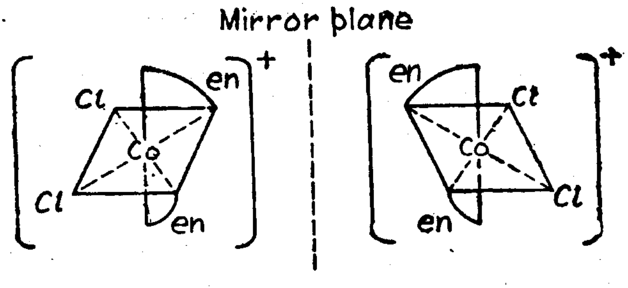
Examples. The ions namely $[\mathrm{Co^{III}(en)_2Cl_2}]^+$, $[\mathrm{Co^{III}(en)_2(NO_3)_2}]^+$, $[\mathrm{Ir^{IV}(C_2O_4)_2Cl}]^{2-}$, $[\mathrm{Rh^{IV}(C_2O_4)_2Cl_2}]^{2-}$, $[\mathrm{Cr^{III}(C_2O_4)_2(H_2O)_2}]^-$, $[\mathrm{Ir^{III}(C_2O_4)_2Cl_2}]^{3-}$ etc. belong to this type of complexes.

Optical isomerism in $[\mathrm{Co^{III}(en)_2Cl_2}]^+$ ion. Now let us discuss the optical isomerism in $[\mathrm{Co(en)_2Cl_2}]^+$ ion in detail. We have already seen that this ion has two geometrical isomers namely cis- and trans-isomers.

The cis-isomer of $[\mathrm{Co(en)_2Cl_2}]^+$ ion shown in Fig. 13·37(*a*) can be resolved into two optically active isomers, since it has no plane of symmetry. Its trans-isomer shown at (*b*) cannot be resolved into two forms, since no mirror-image of this ion is possible *i.e.* it has a plane of symmetry. Thus trans-isomer is an optically inactive form (meso-form). Consequently $[\mathrm{Co(en)_2Cl_2}]^+$ ion has the following three optical isomers :

(*a*) Two optically active isomers corresponding to cis-configuration (*i.e. d-* and *l*-forms). One form is the mirror image of the other.

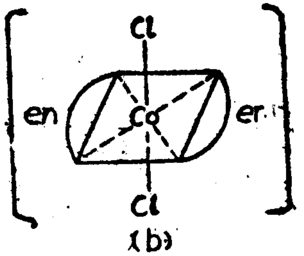
(*b*) One optically inactive form corresponding to trans-form (meso-form).



(*a*)

d-cis-form *l-cis*-form

Unsymmetrical and hence optically active forms

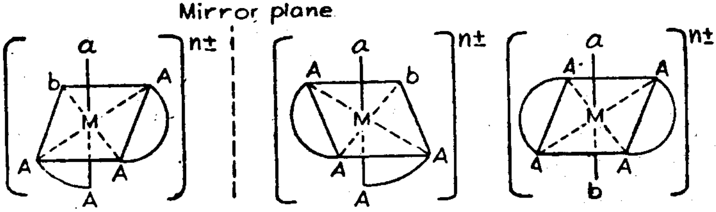


(*b*)

***trans-meso*-form (symmetrical and hence optically inactive)**

Fig. 13·37. Optical isomers of $[\mathrm{Co(en)_2Cl_2}]^+$ ion.

(*ii*) **$[M(AA)_2ab]^{n\pm}$ type complexes.** These complexes exist in three forms : two are optically active (*d*- and *l*-forms) and the third one is inactive (meso-form) as shown below in Fig. 13·38.



d-*cis*-isomer *l*-*cis*-isomer — unsymmetrical and hence optically active forms

trans-meso isomer — symmetrical and hence optically inactive form.

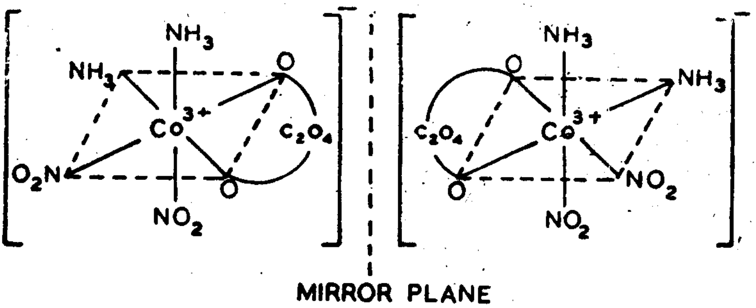
Fig. 13·38. Optical isomers of $[M(AA)_2ab]^{n\pm}$ type complex.

Examples. Important examples of this type of complexes are :

$[Co^{III}(en)_2(NH_3)(Cl)]^{2+}$ and $[Ru^{III}(py)(C_2O_4)_2(NO)]^-$

(*iii*) **$[M(AA)a_2b_2]^{n\pm}$ type complexes.** These also exist in three forms : two are optically active and the third is inactive or symmetrical.

Examples. $[Co^{III}(en)(NH_3)_2Cl_2]^+$, $[Co^{III}(C_2O_4)(NH_3)_2(NO_2)_2]^-$ etc. Three forms of $[Co^{III}(C_2O_4)(NH_3)_2(NO_2)_2]^-$ are shown in Figs. 13·39 and 13·40.



d-*cis*-form *l*-*cis*-form

Fig. 13·39. *d* and *l* forms of *cis*-isomer of $[Co^{III}(C_2O_4)(NH_3)_2(NO_2)_2]^-$. These are unsymmtrical forms and hence are optically active.

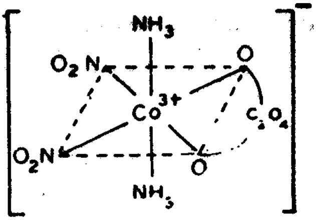
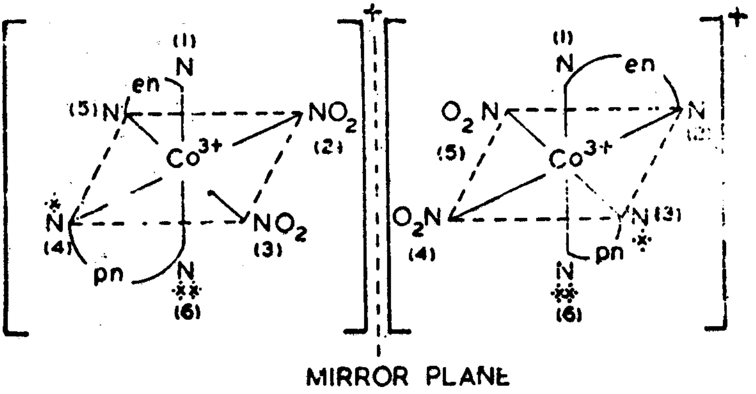
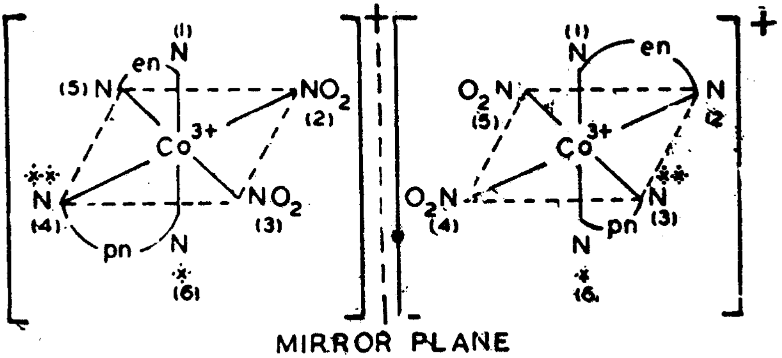


Fig. 13·40. *trans*-isomer of $[Co^{III}(C_2O_4)(NH_3)_2(NO_2)_2]^-$. It is a symmetrical form and hence is optically inactive.

(*d*) **Octahedral complexes containing optically active ligands.** $[Co^{III}(en)(pn)(NO_2)_2]^+$ ion is an important example of such type of octahedral complexes. We have already seen that this complex exists in two *cis* and two *trans* isomers (*see* Fig. 13·23). Each of the two cis-forms namely (*a*) and (*b*) shown below gives its corresponding optical isomer (*e*) and (*f*) respectively as shown below in Fig. 13·41.



(*a*) *cis*-form (*e*)



(*b*) *cis*-form (*f*)

Fig. 13·41. Cis-forms namely (*a*) and (*b*) of $[Co^{III}(en)(pn)(NO_2)_2]^+$ ion give two optical isomers. (*e*) and (*f*) respectively.

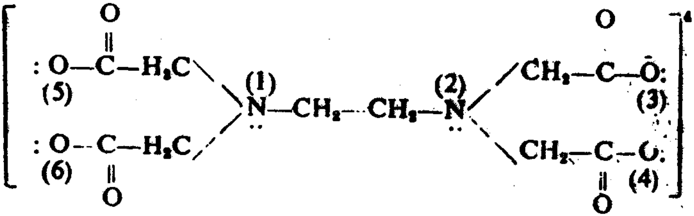
Trans-isomers (*c*) and (*d*) shown in Fig. 13·23 are symmetrical and hence are optically inactive *i.e.* they do not give any optical isomers.

If we consider the complex of $M(AA)_3$ type where AA is a symmetric bidentate optically active (*i.e.* asymmetric) ligand, it would be expected to give the following eight isomers :

D-[M(*d*-AA)$_3$]	L-[M(*l*-AA)$_3$]
D-[M(*d*-AA)$_2$(*l*-AA)]	L-[M(*l*-AA)$_2$(*d*-AA)]
D-[M(*d*-AA)(*d*-AA)$_2$]	L-[M(*l*-AA)(*d*-AA)$_2$]
D-[M(*l*-AA)$_3$]	L-[M(*d*-AA)$_3$]

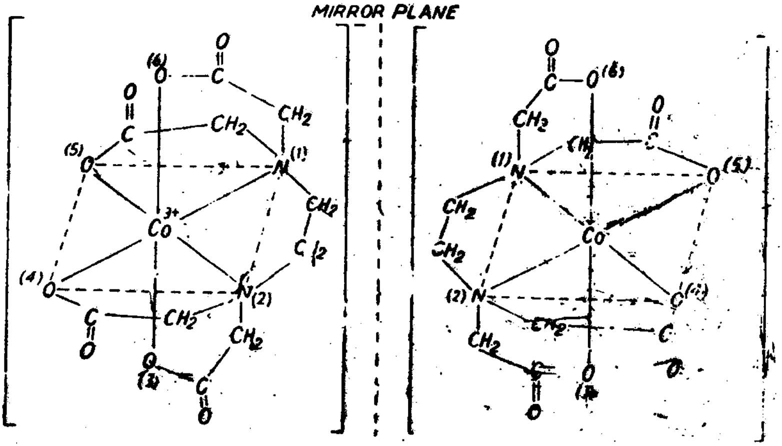
In these isomers D and L refer to the optical rotation of the complex and *d* and *l* refer to the optical rotation of the asymmetric ligand. However, generally only two isomers are obtained, *e.g.* only two isomers of $[Co(chxn)_3]^{3+}$ where *chxn* is *trans* 1, 2-cyclohexane diamine have been obtained and these are : D-$[Co(l\text{-}chxn)_3]^{3+}$ and L-$[Co((d\text{-}chxn)_3]^{3+}$.

(*e*) **Octahedral complexes containing polydentate ligands.** Complexes containing hexadentate ligand like *ethylene diamine tetra-acetate ion viz.*



(abbreviated as $EDTA^{4-}$) which is a polydentate ligand also shows optical isomerism, *e.g.* the complex anion, $[Co^{III}(EDTA)]^-$ exists in two optical isomers : *d*- and *l*-forms (Fig. 13·42).

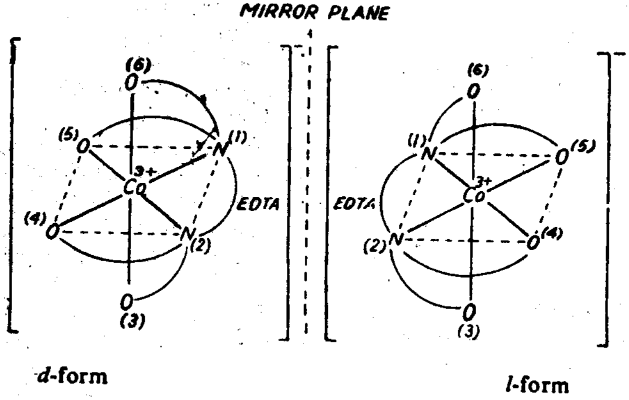
$EDTA^{4}$ has four donor oxygen atoms (numbered as 3, 4, 5 and 6) and two donor nitrogen atoms (numbered as 1 and 2). Thus it has six coordinating sites and four negative charges. In $[Co(EDTA)]^-$ ion, Co^{3+} is attached with four oxygens of CH_2COO^- component and with two nitrogen atoms.



d-form *l*-form

Fig. 13·42. Optical isomers of $[Co^{III}(EDTA)]^-$ ion

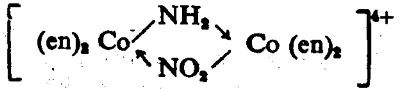
Two optical forms shown in Fig. 13·42 can also be shown in a simpler way as given in Fig. 13·43.



d-form *l*-form

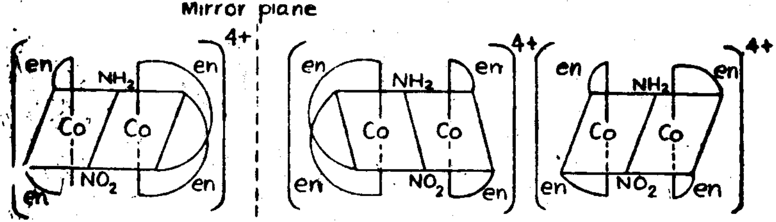
Fig. 13·43. *d*- and *l*-forms of $[\text{Co}^{\text{III}}(\text{EDTA})]^-$ ion shown in simpler way.

(*f*) **Polynuclear Complexes.** Optical activity is not limited to mononuclear complexes only. Optical isomerism is also found in polynuclear ions. Werner in 1913 isolated the polynuclear ion,



$$\left[(\text{en})_2\,\text{Co}\begin{matrix}\nearrow\text{NH}_2\searrow\\ \nwarrow\text{NO}_2\swarrow\end{matrix}\text{Co}\,(\text{en})_2\right]^{4+}$$

into three forms : (*i*) *d*- form (*ii*) *l*-form and (*iii*) meso-form which is optically inactive and is an internally compensated form. *d*- and *l*-forms are mirror images to each other and are optically active. It has been observed that both *d*- and *l*-forms revert to the meso form when their solutions are heated. Optical isomers of this ion are shown in Fig. 13·44.



d-form l-form Meso-form

Fig. 13·44. Optical isomers of $[(\text{Co}(\text{en})_2)_2(\text{NH}_2)(\text{NO}_2)]^{4+}$ ion. *d*- and *l*-forms are optically active while meso-form is optically inactive.

RESOLUTION OF RECEMIC MIXTURES

The separation of a recemic mixture into its d-and l-forms is termed as resolution. Since the *d*- and *l* forms of which recemic mixture is composed have identical physical and chemical properties, they cannot be separated by ordinary methods like fractional crystallisation, fractional distillation etc.

The most widely used method consists of the *formation of diastereoisomers or diastereomers. The stereoisomers which are optically active isomers but are not mirror images to each other are called diasteroisomers or diastereomers.* Thus *these are not enantimorphs* and hence have different solubility in water and can be separated by fractional crystallisation.

If the enantiomers of a *dl* mixture are acids, they should be treated with an *optically active base* and if they are bases, they are treated with an *optically active acid.* The reaction of each pair (*i.e.*, acid or base) of enantiomers with an optically active acid or base gives two diastereomers which are salts. Since these diastereomers have different solubilities and other physical properties, they can be separated from each other by means of their different solubilities in a given solvent. The seperated salts are then treated with an optically inactive material when the optically active *d*- and *l*-forms are regenerated and the resolving agent is removed.

How this method is used can be explained by considering the resolution of *cis*-$[Co(en)_3]Cl_3$. When a solution of recemic mixture containing *d-cis*- $[Co(en)_3]Cl_3$ and *l-cis*- $[Co(en)_3]Cl_3$ is treated with an optically active *d*-tartaric acid, two of the Cl^- ions in *d-cis*-$[Co(en)_3]Cl_3$ and *l-cis*- $[Co(en)_3]Cl_3$ are replaced by *d*-tartrate ion [abbreviated as $(d\text{-tart})^{2-}$] and we get two diastereomers *viz*, *d-cis*-$[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-}$ and *l-cis*-$[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-}$ which are salts and are not mirror-images because the $(d\text{-tart})^{2-}$ ion has the same configuration in each salt.

$$\begin{array}{l}
d\text{-}cis\text{-}[Co(en)_3]Cl_3 + (d\text{-tart})^{2-} \longrightarrow d\text{-}cis\text{-}[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-} + 2Cl^- \\
\underbrace{l\text{-}cis\text{-}[Co(en)_3]Cl_3}_{\substack{\text{Recemic mixture} \\ \text{(opticallly inactive)}}} + \underbrace{(d\text{-tart})^{2-}}_{\substack{\text{Resolving agent} \\ \text{(optically active)}}} \longrightarrow \underbrace{d\text{-}cis\text{-}[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-} + 2Cl^-}_{\substack{\text{Pair of diastereoisomeric salts} \\ \text{which have different solubili-} \\ \text{ties (optically active)}}}
\end{array}$$

On crystallisation the *d-cis*- $[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-}$ separates in the form of large crystals. The *l-cis*-$[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-}$ complex is much soluble and the solution becomes a thick gelatineous mass before fine needles begin to crystallise. The diastereomers can be converted to the active *d*- and *l*- chloride complexes by the treatment with concentrated HCl which is an optically inactive material.

$$\begin{array}{l}
d\text{-}cis\text{-}[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-} + 2HCl \longrightarrow d\text{-}cis\text{-}[Co(en)_3]Cl_3 + d\text{-tartaric} \\
\underbrace{l\text{-}cis\text{-}[Co(en)_3]Cl^{2+}(d\text{-tart})^{2-}}_{\substack{\text{Pair of diastereoisomeric} \\ \text{salts}}} + \underset{\left(\substack{\text{optically} \\ \text{inactive}}\right)}{2HCl} \longrightarrow \underset{\left(\substack{\text{optically active} \\ d\text{- and } l\text{- form}}\right)}{l\text{-}cis\text{-}[Co(en)_3]Cl_3} \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + \underset{\text{(Resolving agent)}}{d\text{- tartaric acid}}
\end{array}$$

A number of resolving agents have been used, *e.g.* *d*-antimonyl tartrate ion, SbO*d*-tart⁻ and *d*- α- bromocomphor -π- sulphonate anion have been used as resolving agents for cationic complexes. Anionic complexes like $[M(C_2O_4)_3]^{3-}$ are usually resolved by using an optically active cations such as those obtained from the bases like strychnine and brucine.

Neutral complexes are resolved by other methods because they cannot form diastereomers in the usual way. Dwyer achieved partial resolution of $[Co(acac)_3]^0$ by extraction into an organic solvent from an aqueous solution containing *d*- $[Co(en)_3]I_3$. The solubilities of *d*- and *l*-$[Co(acac)_3]^0$ are not the same in water containing an optically active ion.

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14

Stability of Complexes in Aqueous Solution

Definition of Stability

The term "stability" can be used in a number of different ways. The statement that a complex is 'stable' is rather loose, since several interpretations can be placed upon it. When the term "stability" is used without qualification, it means that the complex exists and under suitable conditions it may be stored for a long time. This term cannot be generalised for complexes, since a complex may be quite stable to one reagent and may decompose readily in presence of another reagent. This term may also refer to the action of heat or light on a compound.

In studying the formation of complexes in solution, two kinds of stability of complexes come in question. These are :

(*i*) **Thermodynamic Stability**. - This is a measure of the extent to which the complex will form or will be transformed into another species (under certain conditions), *when the system has reached equilibrium*. When we are concerned with this type of stability, we deal with metal-ligand bond energies, stability constants, etc.

(*ii*) **Kinetic Stability**. This refers to the speed with which transformations leading to the attainment of equilibrium will occur. When we are interested in kinetic stability, and this is primarily for complex ions in solutions, we deal with rates and mechanisms of chemical reactions such as substitution, isomerisation, racemisation and electron or group transfer reactions, as well as with the thermodynamic variables involved in the formation of intermediate species or activated complexes. In the kinetic sense it is more proper to call the complexes inert or labile complexes rather than stable or unstable complexes. The complexes in which the ligands are rapidl replaced by others are called **labile or non-inert complexes** while those in which substitution occurs slowly are termed **inert complexes.**

Stepwise formation of complexes, stepwise formation constants and overall formation constants

According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n (M = central metal cation, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L. n varies from one ligand to another for the same metal ion) may be supposed to take place by the following n consecutive steps and equilibrium constants:

$$M+L \xrightleftharpoons{K_1} ML, \quad K_1 = \frac{]ML]}{[M]\,[L]}$$

$$ML+L \xrightleftharpoons{K_2} ML_2, \; K_2 = \frac{[ML_2]}{[ML]\,[L]}$$

$$\vdots \qquad \vdots \qquad \qquad \vdots \qquad \vdots$$

$$ML_{n-1}+L \xrightleftharpoons{K_n} ML_n, K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$

The equilibrium constants K_1, K_2, ... K_n are called **stepwise formation constants or stepwise stability constants.**

The formation of the complex ML_n may also be expressed by the following steps and equilibrium constants :

$$M+L \xrightleftharpoons{\beta_1} ML, \; \beta_1 = \frac{[ML]}{[M]\,[L]}$$

$$M+2L \xrightleftharpoons{\beta_2} ML_2, \; \beta_2 = \frac{[ML_2]}{[M]\,[L]^2}$$

$$\vdots \qquad \vdots$$

$$M+nL \xrightleftharpoons{\beta_n} ML_n, \; \beta_n = \frac{[ML_n]}{[M]\,[L]^n}$$

The equilibrium constants β_1, β_2 ...... β_n are called **overall (or cumulative) formation constants** or **overall (or cumulative) stability constants.** β_n is termed as nth **overall (or cumulative) formation constant** or **overall (or cumulative) stability constant.**

With a few exceptions the values of successive stability constants decrease regularly from K_1 to K_n. *i.e.*, $K_1 > K_2 > K_3 ... > K_{n-1} > K_n$. This is illustrated by the data for the Cd^{II} —NH_3 system where the ligands are neutral molecules and by Cd^{II} —CN^- system where the ligands are charged.

$$\begin{array}{lcll}
Cd^{2+} + NH_3 & \longrightarrow & [Cd(NH_3)]^{2+} & K_1 = 10^{2.65} \\
[Cd(NH_3)]^{2+} + NH_3 & \longrightarrow & [Cd(NH_3)_2]^{2+} & K_2 = 10^{2.10} \\
[Cd(NH_3)_2]^{2+} + NH_3 & \longrightarrow & [Cd(NH_3)_3]^{2+} & K_3 = 10^{1.44} \\
[Cd(NH_3)_3]^{2+} + NH_3 & \longrightarrow & [Cd(NH_3)_4]^{2+} & \underline{K_4 = 10^{0.93}} \\
 & & & \beta_4 = 10^{7.12} \\
Cd^{2+} + CN^- & \longrightarrow & [Cd(CN)]^+ & K_1 = 10^{5.48} \\
[Cd(CN)]^+ + CN^- & \longrightarrow & [Cd(CN)_2] & K_2 = 10^{5.12} \\
[Cd(CN)_2] + CN^- & \longrightarrow & [Cd(CN)_3]^- & K_3 = 10^{4.63} \\
[Cd(CN)_3]^- + CN^- & \longrightarrow & [Cd(CN)_4]^{2-} & \underline{K_4 = 10^{3.65}} \\
 & & & \beta_4 = 10^{18.8}
\end{array}$$

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The steady decrease in the values of $K_1, K_2, \ldots K_n$ with increasing number of ligands is due to the fact that as more and more ligands move into the coordination zone, less and less aqua-molecules are available to fresh ligands for replacement. With progressive intake of ligands the metal ion becomes less electron greedy. In case of the complexes of the charged ligands the more important factors responsible for the steady decrease are statistical, steric hindrance and coulombic factors.

The higher the value of stability constant for a complex ion, the greater will be it's stability. Alternatively $1/K$ values sometimes called **instability constant**, give a measure of the extent to which the equilibrium representing the formation of a complex lies to the right. *A high value of $1/\beta_n$ (or $1/\beta$) means a complex ion.*

Stepwise and cummulative stability constants are also expressed as $\log_{10} K_1 \ldots \log_{10} K_n$ and $\log_{10} \beta_n$ respectively.

In all the above equilibria we have not specified the charge of metal ion and degree of solvation. The former omission is of no importance, since the equilibria may be expressed as above whatever the charges. Omission of water molecules is a matter of convention, since it is usually convenient and harmless. This omission should not be allowed whenever necessary. Square brackets indicate the concentrations of the enclosed species.

Relationship between β_n and $K_1, K_2 \ldots\ldots K_n$.

K's and β's are related to one another. Consider, for example, the expression for β_3 *viz.*

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

On multiplying both numerator and denominator by [ML] [ML₂] and on rearranging, we get

$$\begin{aligned}
\beta_3 &= \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \\
&= \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \\
&= K_1 \, . \, K_2 \, . \, K_3
\end{aligned}$$

Thus :

$$\beta_n = \frac{[ML]}{[M]\,[L]} \cdot \frac{[ML_2]}{[ML]\,[L]} \cdot \cdots\cdots\cdots \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$

$$= K_1.K_2 \ldots\ldots\ldots K_n \qquad \ldots(i)$$

or

$$\beta_n = \sum_{n=1}^{n=n} , K_n$$

From relation (*i*) it is evident that the overall stability constant, β_n (or simply β), is equal to the product of the successive (*i.e.* stepwise) stability constants $K_1, K_2, \ldots\ldots K_{n-1}, K_n$. This in other words means that the value of stability constant for a given complex is actually made up of a number of step-wise stability constants as is evident from Table 14·1 in which the value of overall stability constant as β_n and $\log_{10}\beta_n$ for $[Ni^{II}(NH_3)_6]^{2+}$ ion and those of stepwise stability constants as $K_1, K_2, \ldots, K_5, K_6$ and $\log_{10} K_1, \log_{10} K_2 \ldots\ldots, \log_{10} K_6$ corresponding to the six equilibria given in the first column through which $[Ni^{II}(NH_3)_6]^{2+}$ ion can be regarded as being formed, are given. This table shows that

$$\beta_n = K_1 \times K_2 \times \ldots \times K_5 \times K_6$$

and

$$\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \ldots + \log_{10} K_6$$

In Table 14·1 we also see that $\log K_6$ is negative (= −0·10). This negative value shows that the pentamine complex, $[Ni(H_2O)(NH_3)_5]^{2+}$ is thermodynamically favoured with respect to the hexamine complex, $[Ni(NH_3)_6]^{2+}$ [see equilibrium No. (vi)].

Kinetic Vs. thermodynamic stability

Since the terms : labile and inert show the speed or rates at which the substitution of one ligand by other occurs, these terms represent the kinetic stability of complexes. These terms should, therefore, not be confused with or used for thermodynamic stability terms *viz. unstable and stable* respectively Although thermodynamically stable complexes may be labile or inert, and unstable complexes which are usually labile may also be inert, there is no correlation between thermodynamic and kinetic stability terms, *e.g.* $[Hg(CN)_4]^{2-}$ which is thermodynamically very stable (formation constant $= 10^{42}$) is labile, since in solution it exchanges CN^- ligands with labelled cyanide ions, $^{14}CN^-$ at a very fast rate.

$$[Hg(CN)_4]^{2-} + 4\,{}^{14}CN^- \rightleftharpoons [Hg({}^{14}CN)_4]^{2-} + 4CN$$

Thus the stability of this complex does not ensure its inertness.

Table 14·1. *Stability constant value (i.e., $\log_{10}$ K value) of $[Ni^{II}(NH_3)_6]^{2+}$ ion*

Six equilibria	*Values of $K_1, K_2, \ldots K_6$ and β_n*	*Values of $\log_{10} K_1, \log_{10} K_2, \ldots \log_{10} K_6$ and $\log_{10} \beta_n$*
(*i*) $[Ni(H_2O)_6]^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Ni(H_2O)_5(NH_3)]^{2+} + H_2O$	$K_1 = 5 \times 10^2$	$\log_{10} K_1 = 2{\cdot}70$
(*ii*) $[Ni(H_2O)_5NH_3]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Ni(H_2O)_4(NH_3)_2]^{2+} + H_2O$	$K_2 = 1{\cdot}3 \times 10^2$	$\log_{10} K_2 = 2{\cdot}11$
(*iii*) $[Ni(H_2O)_4(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Ni(H_2O)_3(NH_3)_3]^{2+} + H_2O$	$K_3 = 40$	$\log_{10} K_3 = 1{\cdot}60$
(*iv*) $Ni(H_2O)_3(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Ni(H_2O)_2(NH_3)_4]^{2+} + H_2O$	$K_4 = 12$	$\log_{10} K_4 = 1{\cdot}08$
(*v*) $[Ni(H_2O)_2(NH_3)_4]^{2+} + NH_3 \overset{K_5}{\rightleftharpoons} [Ni(H_2O)(NH_3)_5]^{2+} + H_2O$	$K_5 = 4$	$\log_{10} K_5 = 0{\cdot}60$
(*vi*) $[Ni(H_2O)(NH_3)_5]^{2+} + NH_3 \overset{K_6}{\rightleftharpoons} [Ni(NH_3)_6]^{2+} + H_2O$	$K_6 = 0{\cdot}8$	$\log_{10} K_6 = -0{\cdot}10$
On adding (*i*) to (*vi*)	$\beta_n = K_1.K_2 \ldots K_5.K_6$	$\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \ldots + \log_{10} K_6$
$[Ni(H_2O)_6]^{2+} + 6NH_3 \overset{\beta_n}{\rightleftharpoons} [Ni(NH_3)_6]^{2+} + 6H_2O$	$= 9{\cdot}98 \times 10^7$	$= 7{\cdot}99$

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On the other hand the complex, $[Co(NH_3)_6]^{3+}$ which is thermodynamically unstable can remain unchanged in acid solution for weeks. Thus this complex is unstable but inert in acid solution.

It may be concluded from this description that the *inert complexes are not necessarily thermodynamically stable and that labile complexes are not necessarily thermodynamically unstable.*

The stability of a complex depends on the reaction energy while the lability of a compound depends on the activation energy. Larger the activation energy, lower will be the lability of the compound, *i.e. the compound with larger activation energy will react slowly.*

Labile and Inert Octahedral Complexes according to VBT

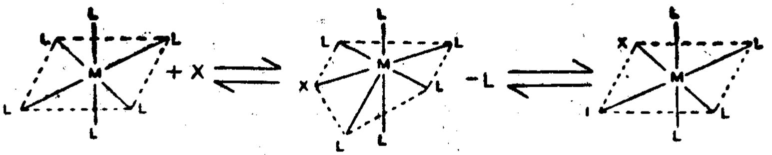
We have seen that according to VBT octahedral complexes are of two types (*i*) *outer orbital complexes* which involve sp^3d^2 hybridisation, and (*ii*) *inner-orbital complexes* which result from d^2sp^3 hybridisation. Note that the two *d*-orbitals involved in sp^3d^2 and d^2sp^3 hybridisation are $d_{x^2-y^2}$ and d_{z^2} orbitals (e_g set).

With the help of VBT it is possible to predict which octahedral complex is labile and which is inert as shown below :

(*i*) **Outer-orbital octahedral complexes.** Outer-orbital octahedral complexes (sp^3d^2 hybridisation) are generally *labile, e.g.* the octahedral complexes of Mn^{2+} $(3d^5)$, $Fe^{2+}(3d^6)$, $Fe^{3+}(3d^5)$, $Co^{2+}(3d^7)$, $Ni^{2+}(3d^8)$, $Cu^{2+}(3d^9)$ and $Cr^{2+}(3d^4)$ exchange ligands rapidly and hence are labile. In terms of valence-bond theory this observation can be correlated with the weakness of the bonds of sp^3d^2 type as compared with d^2sp^3 bonds.

(*ii*) **Inner-orbital octahedral complexes.** Since the six d^2sp^3 hybrid orbitals are filled with the six electron pairs donated by the six ligands, d^n electrons of the central metal will occupy d_{xy}, d_{yz} and d_{zx} orbitals. This distribution for labile and inert inner-orbital octahedral complexes is shown in Table 14·2 from which the following points are obvious.

(*a*) In the labile inner orbital octahedral complexes there is at least one *d*-orbital of t_{2g} set empty so that this empty *d*-orbital may be used to accept the electron pair from the incoming ligand in forming the transition state (unstable intermediate) with coordination number of seven. The formation of transition state can be shown as :



Labile inner-orbital octahedral complex, ML_6 (C.N. = 6) with one empty *d*-orbital of t_{2g} set

Incoming ligand with electron pair

Seven coordinated unstable intermediate (transition state), ML_6X (C.N. = 7)

Octahedral complex, ML_5X (C.N. = 6)

Due to the extremely fast reactions of these complexes it has not been possible to determine whether the intermediate exists in these reactions.

(*b*) In the inert inner-orbital octahedral complexes every *d*-orbital of t_{2g} set (*i.e.* d_{xy}, d_{yz} and d_{zx}) contains at least-one electron.

Labile and Inert Octahedral Complexes According to CFT

Whether an octahedral complex reacts by an S_N1 dissociation or S_N2 association mechanism the symmetry is lowered and a decrease in CFSE usually occurs in going from octahedral to 5-coordinated square pyramidal activated intermediate or from octahedral to 7-coordinated pentagonal bipyramidal transition state. The change in CFSE in going from octahedral to square pyramidal (S_N1 mechanism) and in going from octahedral to pentagonal bipyramidal (S_N2 mechanism) structure is called *activatidn energy* and is denoted by E_a. The values of E_a have been calculated by Basolo and Pearson and are given in Tables 14·3 and 14·4. The values of CFSE mentioned are in the units of Dq and have been given for both the fields *viz* strong field (spin paired or low spin complex) and weak field (spin free or high spin complex) and for both the mechanisms. In these tables negative values of E_a denote a loss of CFSE when octahedral complex is changed into an activated complex which may be square pyramidal or pentagonal bipyramidal. In cases where the CFSE of the activated complex is greater than that of octahedral complex, E_a has been given *zero* value. Thus in case of these complexes it has been assumed that there is no loss in CFSE when they are changed into activated complexes.

The octahedral complexes formed by the ions for which there is *large loss in* CFSE are *least labile*, *i.e. such complexes are inert*. On the other hand octahedral complexes given by ions for which there is *little* or *no loss* in CFSE are *labile*, *i.e.* such complexes react rapidly. Following examples make these facts evident :

(*i*) Both high spin and low spin octahedral complexes of d^0, d^1 and d^2 ions will react rapidly, *i.e. these are labile complexes*, since these is no loss in CFSE for these ions by either mechanism.

(*ii*) We have seen that according to VBT inner-orbital octahedral complexes of d^3, d^4, d^5 and d^6 ions are inert (see Table 14·2). These inner-orbital complexes are called low-spin or spin-paired complexes by. CFT. CFT also predicts that low-spin complexes of these ions are also inert whether the mechanism is assumed to be S_N1 or S_N2, since there is a loss in CFSE values (as indicated by the negative values).

The ion with maximum loss of CFSE will form the most inert (*i.e.* least labile) complex. Thus the order of inertness of low-spin complexes formed by d^3, d^4, d^5 and d^6 ions is :

Order of inertness :	d^6 >	d^3 >	d^4 >	d^5
Loss in CFSE for S_N1 mechanism :	−4·00	−2·00	−1·43	−0·86
Loss in CFSE for S_N2 mechanism :	−8·52	−4·26	−2·98	−1·7

Table 14·2. *Distribuion of d^n-electrons in various t_{2g} orbitals for labile and inert inner-orbital octahedral complexes according to VBT.*

Type of the complex	d^n configuration	*Distribution of d^n electrons (shown by arrows) in t_{2g} orbitals Electrons shown by crosses in e_g orbitals have been donated by six ligands to enter d^2sp^3 hybrids and are in opposite spins*									*Examples of central metal ions*
		d					s	p			
		t_{2g}			e_g						
		xy	yz	zx	x^2-y^2	z^2		p_x	p_y	p_z	
Inner-orbital laible octahedral complexes	d^0				××	××	××	××	××	××	Sc(+3), Y(+3), rare earth (+3), Te(+4), Zr (+4), Hf (+4) Ce (+4), Th (+4) Nb (+5), Ta (+5), Mo (+6), W (+6)
	d^1	↑			××	××	××	××	××	××	Ti (+3), V (+4), Mo (+5), W (+5). Re (+6)
	d^2	↑	↑		××	××	××	××	××	××	Ti (+2), V (+3), Nb (+3); Ta (+3), W (+4), Re (+5). Ru (+6)
Inner-orbital inert octahedral complexes.	d^3	↑	↑	↑	××	××	××	××	××	××	V (+2), Cr (+3), Mo (+3), W (+3), Mn (+4), Re (+4)
	d^4	↑↓	↑	↑	××	××	××	××	××	××	$[Cr(CN)_6]^{4-}$, $Mn(CN)_6]^{3-}$ Re (+3), Ru (+4), Os (+4)
	d^5	↑↓	↑↓	↑	××	××	××	××	××	××	$[Mn(CN)_6]^{4-}$, Re (+2), $[Fe(CN)_6]^{3-}$, Ru (+3), Os (+3), Ir (+4)
	d^6	↑↓	↑↓	↑↓	××	××	××	××	××	××	$[Fe(CN)_6]^{4-}$, Ru (+2), Os (+2). Co (+3) (except $Co\,F_6^{3-}$), Rh (+3), Ir (+3)

Consequently the order of liablity or the reactivity (*i.e.*, rate of reaction) will be reverse of that shown above, *i.e*

Order of lability : $d^6 < d^3 < d^4 < d^5$

Experiments have also supported the above order.

(*iii*) High-spin octahedral complexes of d^3 ion will react slowly, *i.e. these are inert complexes*, because for this ion there is substantial loss in CFSE whether the substitution mechanism is assumed S_N1 or S_N2.

(*iv*) High-spin octahedral complexes of d^5 ion react rapidly, *i.e., these are labile complexes,* since there is no loss in CFSF.

(*v*) Both high-spin and low-spin octahedral complexes of d^8 ion (*e.g.*, Ni^{2+}) are *inert*, since for any mechanism there is significant loss of CFSE. Note that, according to VBT, d^8 ion ($3d_{xy}^2$, $3d_{yz}^2$, $3d_{zx}^2$, $3d_{x^2-y^2}^1$, $3d_{z^2}^1$) will form outer-orbital complexes which will be *labile.* Thus we see that in case of d^8 ion VBT and CFT give different predictions.

(*vi*) Both high-spin and low-spin octahedral complexes of d^{10} ion are *labile*. The reasons are the same as for other labile complexes.

Table 14·3. *Loss in CFSE, E_a (in the units of Dq) in the formation of a square pyramidal intermediate in octahedral substitution reactions on the basis af S_N1 dissociation mechanism.*

S_N1 dissociation mechanism

Octahedral (*oct.*) (C.N=6) ⟶ Square pyramidal (*squ. py.*) (C.N.=5)

d^n ion	*Strong ligand fields (spin-paired or low-spin complexes)*			*Weak ligand fields (spin-free or high-spin complexes)*		
	Oct. (*C.N.=6*)	*squ. py.* (*C.N.=5*)	E_a	*Oct.* (*C.N.=6*)	*Squ. py.* (*C.N.=5*)	E_a
d^0	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq	0Dq
d^1	4	4·57	0	4	4·57	0
d^2	8	9·14	0	8	9·14	0
d^3	12	10·00	−2·00	12	10·00	−2
d^4	16	14·57	−1·43	6	9·14	0
d^5	20	19·14	−0·86	0	0·00	0
d^6	24	20·00	−4·00	4	4·57	0
d^7	18	19·14	0	8	0·14	0
d^8	12	10·00	−2·00	12	10·00	−2
d^9	6	9·14	0	6	9·14	0
d^{10}	0	0·00	0	0	0·00	0

Table 14·4. *Loss in CFSE, E_a (in the units of Dq) in the formation of a pentagonal bipyramidal intermediate in octahedral substitution reactions on the basis of S_N2 association mechanism.*

S_N2 association mechanism

Octahedral (*oct.*) ⟶ Pentagonal bipyramidal (pent. *bipy.*)
(C.N.=6) (C.N.=7)

d^n ion	*Strong ligand fields (spin-paired or low-spin complexes)*			*Weak ligand fields (spin-free or high-spin complexes)*		
	Oct. (C.N.=6)	*pent. bipy. (C.N.=7)*	E_a	*Oct. (C.N.=6)*	*pent. bipy. (C.N.=7)*	E_a
d^0	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq
d^1	4	5·28	0	4	5·28	0
d^2	8	10·56	0	8	10·56	0
d^3	12	17·74	−4·26	12	7·74	−4·26
d^4	16	13·02	−2·98	6	4·93	−2·07
d^5	20	18·30	−1·70	0	0·00	0
d^6	24	15·48	−8·52	4	5·28	0
d^7	18	12·66	−5·34	8	10·56	0
d^8	12	7·74	−4·26	12	7·74	−4·26
d^9	6	4·93	−1·07	6	4·93	−1·07
d^{10}	0	0·00	0	0	0·00	0

Other Factors Affecting the Lability of a Complex

In the preeding pages we have seen that how the electronic configuration of the central metal ion forming the complex affects the lability of the complex. In addition to this the following factors also influence the lability.

(*i*) **Charge of the central ion.** Highly charged ions form complexes that react slowly, *i.e. with the increase of the charge of the central metal ion for the isoelectronic complexes there is a decrease in lability ,e.g.*

(*a*) The lability of the complexes, $[AlF_6]^{3-}$, $[SiF_6]^{2-}$, $[PF_6]^-$ and $[SF_6]^0$ is in the order :

Lability order	:	$[AlF_6]^{3-} > [SiF_6]^{2-} > [PF_6]^- > [SF_6]^0$
Cationic charge	:	$+3 < +4 < +5 < +6$

(*b*) The rate of water exchange represented by

$$[M(H_2O)_6]^{n+} + 6H_2O^* \rightleftharpoons [M(H_2O^*)_6]^{n+} + 6H_2O$$

decreases with the increase of cationic charge in the series : $[Na(H_2O)_n]^+$, $[Mg(H_2O)_n]^{2+}$, $[Al(H_2O)_6]^{3+}$ in the order :

Rate of water exchange , $[Na(H_2O)_n]^+ > [Mg(H_2O)_n]^{2+} > [Al(H_2O)_6]^{3+}$
Cationic charge : $+1 < +2 < +3$

(*ii*) **Radii of the central ion.** Complexes having central atoms with small ionic radii react more slowly than those having larger central ions, *i.e.*, *the lability increases with the increase of ionic radius, e.g.*,

Order of lability : $[Mg(H_2O)_6]^{2+} < [Ca(H_2O)_6]^{2+} < [Sr(H_2O)_6]^{2+}$
Cationic Size (A°) : $0{\cdot}65 < 0{\cdot}99 < 1{\cdot}13$

(*iii*) **Charge-to-radius ratio values.** For a series of octahedral complexes containing the same ligands, the complexes having the central metal ions with the largest charge-to-radius ratio will react slowest. The validity of this rule is evident from Fig. 14·1 which contains half-lives for the exchange of water by some hydrated metal ions.

$$[M(H_2O)_x]^{n+} + xH_2O \longrightarrow [M(H_2O)_x]^{n+} + xH_2O$$

From this figure the following points may be noted :

(*a*) Of the first-row transition elements, $[Ni(H_2O)_6]^{2+}$ (a d^8 system) has the largest value of half life, *i.e.* it reacts slowest. The same conclusion has been drawn from CFT. The hydrated M^{2+} ions, $[M(H_2O)_x]^{2+}$ of the first-row transition elements are all high-spin complexes.

(*b*) $[Cu(H_2O)_6]^{2+}$ reacts most rapidly. This may be due to the fact that the two water molecules above and below the square

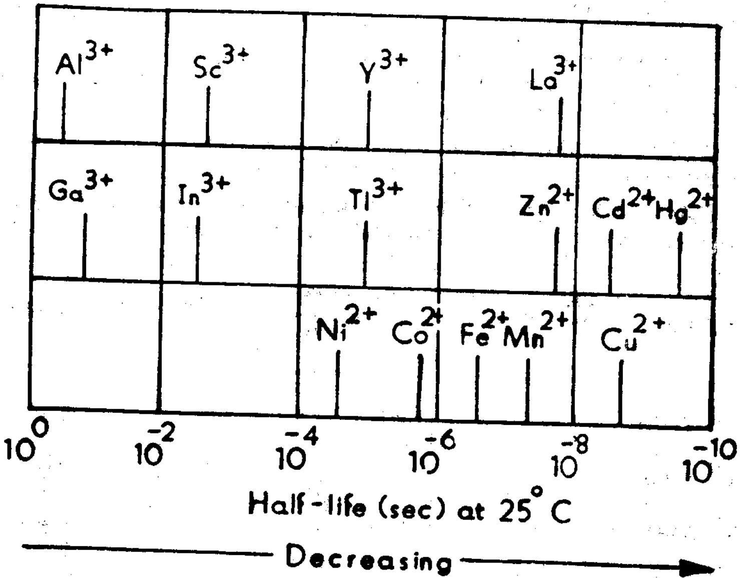


Fig. 14·1. Half-lives (in sec) at 25°C for the exchange of water by some hydrated metal ions.

plane of the tetragonally distorted octahedral shape of $[Cu(H_2O)_6]^{2+}$ are exchanged. The remaining four water molecules lying in the square plane react slowly.

For square planar complexes charge-to-radius ratio does not work.

(*iv*) **Geometry of the complex.** In general 4-coordinated complexes (both tetrahedral and square planar) react more rapidly than analogous 6-coordinated complexes, *e.g.* the very stable $[Ni(CN)_4]^{2+}$ undergoes rapid exchange with $^{14}CN^-$

$$[Ni(CN)_4]^{2+} + 4^{14}CN^- \rightleftharpoons [Ni(^{14}CN)_4]^{2-} + 4CN^-,$$

while 6-coordinated complexes like $[Mn(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ which have almost about the same stability as $[Ni(CN)_4]^{2+}$ undergo slow exchange. The greater rapidity of reactions of 4-coordinated complexes may be due to the fact that there is enough room round the central ion for the entry of a fifth group into the coordination sphere to form on activated complex. The presence of this additional group helps in the release of one of the original four ligands already present in the 4-coordinated complexes.

Factors Affecting the Stability of Complexes

A number of factors affect the stability of complexes. Some of these factors depend on the nature of the central ion, while others depend on the nature of the ligand.

(*a*) Properties of the Central Metal Ion

Nature

With reference to the properties of the central metal ion the following factors may be mentioned :

(*i*) **Charge and size.** In general the metal ion with larger charge and smaller size form more stable complexes. A smaller but more highly charged cation permits a more closer approach of the ligands and larger electrostatic attraction resulting from large charge on the cation gives a more stable complex. These points are illustrated in the following examples :

(*a*) The stability of the hydroxide complexes of the alkaline earth metals in which the central metal cation contains the same

Table 14·5. *Effect of the central metal ions with equal charges but with different ionic size on the stability of complexes.*

Complex ion	*Charges on the central metal ion*	*Size of the central metal ian, (A°)*	*Value of β*	*Stability*
$[Be^{II}(OH)]^+$	+2	0·31 increasing ↓	10^7 increasing ↑	Stability of complex ions increasing ↑
$[Mg^{II}(OH)]^+$	+2	0·65	120	
$[Ca^{II}(OH)]^+$	+2	0·99	30	
$[Ba^{II}(OH)]^+$	+2	1·35	4	

charge increases with the decrease of the size of the central metal ion as shown by their stability constant values (*see Table* 14·5).

(*b*) The stability of the complexes having the central metal cations with almost equal size but with different charges increases with the increase of the charge on the central metal ion. This is shown in Table 14·6.

Table 14·6. *Stability for Fe^{3+}, Fe^{2+}-, Co^{3+}- and Co^{2+}- complexes.*

Complex ion	*Changes on the central metal ion*	*Size of the central metal ion (A°)*	*Value of $\log_{10}\beta$ (stability constant)*	*Stability of the complex ion*
$[Fe^{III}(CN)_6]^{3-}$	+3	almost same	31·0	increases
$[Fe^{II}(CN)_6]^{4-}$	+2		8·3	
Co^{3+}-complex	+3	almost same	higher	increases
Co^{2+}-complex	+2		low	

Combination of the factors *viz*. charge and size of the central metal cation shows that it is charge/radius ratio for the central ion (called *ionic potential* or *polarising power* of the cation) which is important. A large value of charge/radius ratio for a central ion means that the central ion will be forming more stable complexes. The correlation between charge-to-radius ratio and stability of OH^- complexes of some metal ions is shown in Table 14·7. It may be noted from this table that charge on the metal ion is somethat more important than its ionic radius.

Table 14·7. *Effect of the change-to-radius ratio on the stability of some OH^- complexes.*

$$M^{n+} + OH^- \rightleftharpoons [MOH]^{(n-1)+}$$

Central metal cation (M^{n+})	*Ionic Radius (A°)*	*Charge-to-radius ratio*	*Stability constant of the complex*
Li^+	0·60	1·7	2
Ca^{2+}	0·99	2·0	3×10^1
Ni^{2+}	0·69	2·9	3×10^3
Y^{3+}	0·93	3·2	1×10^7
Th^{4+}	1·02	4·0	1×10^{10}
Al^{3+}	0·50	6·0	1×10^9
Be^{2+}	0·31	6·5	1×10^7

The stability of the complexes of non-transition metals of the same group has been found in the following order provided that the ligand is not changed from one ion to the next.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$

$Al^{3+} > Sc^{3+} > Y^{3+} > La^{3+}$

There are also some exceptions to the above order, *e.g.* EDTA complex of Mg^{2+} is less stable than that of Ca^{2+}.

For the metal ions of approximately constant ionic radius, the stability constants are in the order :

Th^{4+} (=0·95 A°) > Y^{3+} (=0·93) > Ca^{2+} (=0·99) > Na^+ (=0·95)
and La^{3+} (=1·15 A°) > Sr^{2+} (=1·13) > K^+ (=1·33)

(*ii*) **Crystal Field Effects and natural order (or Irving-William order) of stability.** Stabilities of high spin complexes of the ions between Mn^{2+} and Zn^{2+} with a given ligand frequently vary in the order :

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This order which is called **natural order** (sometimes called the **Irving-William order) of stability** is consistant with charge-to-radius ratio concept, since the radii of these ions are in the order :

Mn^{2+} (=0·91 A°) > Fe^{2+} (=0·83) > Co^{2+} (=0·82) > Ni^{2+} (=0·78) > Cu^{2+} (=0·69) < Zn^{2+} (=0·74).

The high spin complexes of these ions are primarily octahedral with the exception of those of Cu^{2+} which forms tetragonally distorted octahedral complexes.

The relative stability of high spin octahedral $[M^{II}L_6]^{2+}$ complexes of the first-row transition elements as predicted by crystal field theory is shown in Fig. 14·2.

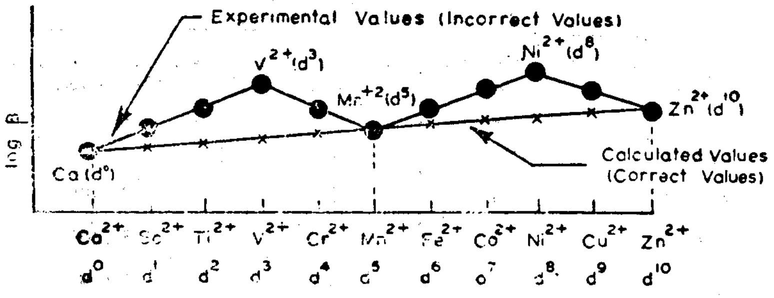


Fig. 14·2. The logrithms of stability constants for a series of $[M^{II}L_6]^{2+}$ complexes as predicted by crystal field theory.

$$M^{2+} + 6L \rightleftharpoons [ML_6]^{2+}, \ \beta = \frac{[ML_6^{2+}]}{[M^{2+}][L]^6}$$

It is obvious from this figure that the octahedral complexes of V^{2+} (d^3 ion) and Ni^{2+} (d^8 ion) ions are the most stable with respect to their neighbours. This is because of the fact that the high spin (weak ligand) octahedral complexes of these ions have the greatest crystal field stablisation energy values (CFSE's values) as given below :

$$d^1=0\cdot4\ \Delta_0,\ d^2=0\cdot8.\Delta_0,\ d^3\ (V^{2+})=1\cdot2\ \Delta_0,\ d^4=0\cdot6\ \Delta_0,\ d^5=0\cdot0.$$

$$d^6=0\cdot4\ \Delta_0,\ d^7=0\cdot8\ \Delta_0,\ d^8\ (Ni^{2+})=1\cdot2\ \Delta_0,\ d^9=0\cdot6\ \Delta_0,\ d^{10}=0\cdot0$$

The order of stability as predicted by crystal field theory and shown in Fig. 14·2 is the same as natural order of stability for complexes of these metals except for Cu^{2+}. The discrepency for Cu^{2+} is not completely, understood but is certainly related to the fact that Cu^{2+} complex assumes a distorted octahedral structure in order to assume maximum CFSE.

If the experimental values shown by dots are corrected for CFSE for each ion (the correction is done by substracting the calculated CFSE values given as above from the experimental values), we get a smooth curve which has *corrected values* (shown by crosses), since it indicates the expected regular increase in values. The ions *viz.* Ca^{2+} (d^0), Mn^{2+} (d^5) and Zn^{2+} (d^{10}) which do not have CFSE have experimental values on the smooth curve.

(*iii*) **Class** *a* **and Class** *b* **metals.** Chatt and Ahrland have classified the metals into three categories : *a*, *b* and *borderline*, on the basis of their electron acceptor properties. This classification is shown below (normal valence states are assumed).

Class a metals : H, the alkali and alkaline earth metals, the elements Sc ⟶ Cr, Al ⟶ Cl, Zn ⟶ Br, In, Sn, Sb and I, the lanthamides and actinides.

Class b metals : Rh, Pd, Ag, Ir, Pt, Au, Hg.

Border line metals : The elements Mn ⟶ Cu, Tl ⟶ Po, Mo, Te, Ru, W, Re, Os, Cd.

Class *a* metals form *more stable* complexes with ligands having the coordinatng atoms from the second period elements (*e.g.* N, O, F) than those of an analogous ligand in which the donor atom is from third or later period (*e.g.* P, S, Cl). Class *b* metals have the relative stabilities reversed. If the ligand contains the heavier donor atoms, class *a* and *b* metals are characterised by the stability order :

$$\left.\begin{array}{l} F^- > Cl^- > Br^- > I \\ O >> S > Se > Te \\ N >> P > As > Sb > Bi \end{array}\right\}\text{Class } a \text{ metals}$$

and

$$\left.\begin{array}{l} F^- < Cl^- < Br^- < I^- \\ O << S \simeq Se \simeq Te \\ N << P < As < Sb < Bi \end{array}\right\}\text{Class } b \text{ metals}$$

Class *b* metals are characterised by the presence of a number of *d*-electrons beyond an inert-gas core. These *d*-electrons are used to form π-bond with ligand atoms. It is believed that the stability of the complexes of class *b* metals results from covalent contribution to metal-ligand bonds and from the transfer of electron density from the metal to the ligand *via* π-bonding. The most stable complexes of class *b* metals are formed with ligands like PMe_3, S^{2} and I^- which have vacant *d*-orbitals or like CO CN^- which have vacant molecular orbitals of low energy.

For *borderline metals* the stability constants do not display either class *a* or class *b* behaviour uniquely.

(*iv*) **Electronegativity of the central ion.** The bonding between a central ion and a ligand is, to some extent, due to the donation of electrons by the ligand to the central ion. Thus, it might be concluded that a central ion with higher electronegativity (*i.e.* a central ion with a strong electro-attracting tendency) would give the most stable complexes.

(*b*) **Properties of the Ligand.**

With reference to the role of the ligands in determining the stability of the metal complexes, the following factors are important :

(*i*) **Size and charge of ligand.** For charged ligands, the higher the charge carried by them and the smaller their size, the more stable are the complexes formed ; *e.g.*, the F^- ions, which are smaller, form stable complexes than the Cl^- ions which are larger ions. This fact is evident from the stability constant values of $[Fe^{III}F]^{2+}$ and $[Fe^{III}Cl]^{2+}$ ions which are 10^6 and 20 respectively. Thus for class *a* metals the order of stability of the halide complexes is $F^- > Cl^- > Br^- > I^-$, but this order is reversed for class *b* metals (Pt^{II}, Cu^{I}, Ag^{I}, Hg^{II} etc).

For monodentate neutral ligands, the higher the dipole moment and smaller the size, the more stable are the complexes formed.

(*ii*) **Basic character of ligands.** The more basic is the ligand, more easily it can [illegible] electron pairs to the central ion and hence more easily it can form complexes of greater stability. The ligands that bind H^+ firmly form stable complexes with metal ions. Thus F^- should form stable complexes than Cl^-, Br^- or I^-, and NH_3 should be better ligand than H_2O which in turn should be better than HF. This behaviour is observed for alkali, alkaline earth and other electropositive metals like first-row transition elements, lanthanides and actinides.

(*iii*) **Chelate effect.** Complexes containing chelate rings are usually more stable than similar complexes containing no rings. *i.e.* multidentate ligands (chelating ligands) in general form more stable complexes than the monodentate ligands. This is termed as **chelate effect.** This effect is obvious from the values of stability constants of Ni^{2+}—NH_3 and Ni^{2+}—*en* systems :

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq), \quad \log \beta = 7{\cdot}99$$

$$Ni^{2+}(aq) + 3en\,(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq), \quad \log \beta = 18{\cdot}1$$

Note that NH_3 is a monodentate ligand while ethylene diamine, $NH_2—CH_2—CH_2—NH_2$ (*en*) is a bidentate ligand. Obviously the complex $[Ni(en)_3]^{2+}$ is much more stable than $[Ni(NH_3)_6]^{2+}$, since the former complex contains cheate rings while the latter one has no chelate ring. The chelate effect is also evident from the fact that the stability of NH_3, ethylene diamine, $NH_2—CH_2—CH_2—NH_2$ (*en*) and triethylenetetra amine, $NH_2—(CH_2)_2—NH—(CH_2)_2—NH—(CH_2)_2—NH_2$ (*trien*) complexes of Cu^{2+} ion is in the order :

$$\log\beta = \begin{array}{ccccc} [Cu(NH_3)_4]^{2+} & < & [Cu(en)_2]^{2+} & < & [Cu(trien)]^{2+} \\ 12{\cdot}7 & < & 19{\cdot}7, & < & 20{\cdot}5, \end{array}$$

In order to understand this effect we should note the following well-known thormodynamic relationship :

$$-RT\ ln\ \beta = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\ (\Delta H^\circ \text{ is negative})$$

Here ΔG° = Standard free energy change, R = Gas constant, T = Absolute temperature, ΔH° = Enthalpy (or heat) change and ΔS° = Entropy change.

Enthalpy change between chelated and non-chelated complex is small due to similar metal-donor atom linkages as is evident from the thermodynamic data given for the following two reactions leading to the formation of non-chelated and chelated complex respectively.

$$(i)\ Cd^{2+} + \underset{\substack{\text{Monodentate}\\ \text{ligand}}}{4CH_3NH_2} \rightleftharpoons \underset{\substack{\text{Non-chelated}\\ \text{complex}}}{[Cd(NH_2CH_3)_4]^{2+}} \text{ with } \log\beta = 6{\cdot}52,$$

$$\Delta H^\circ = -57{\cdot}3,\ \Delta S^\circ = -67{\cdot}3,\ -T\Delta S^\circ = 20{\cdot}1 \text{ and } \Delta G^\circ = -37{\cdot}2$$

$$(ii)\ Cd^{2+} + \underset{\substack{\text{Bidentate}\\ \text{ligand}}}{2\,en} \rightleftharpoons \underset{\substack{\text{Chelated}\\ \text{complex}}}{[(Cd(en)_2]^{2+}} \text{ with } \log\beta = 10{\cdot}6,$$

$$\Delta H^\circ = -56{\cdot}3,\ \Delta S^\circ = +14{\cdot}1,\ -T\Delta S^\circ = -4{\cdot}2 \text{ and } \Delta G^\circ = -60{\cdot}7.$$

All the thermodynamic data are given in KJ/mole.

It follows from the above relation that β increases as ΔG° becomes more negative. The value of ΔG° becomes more negative when that of ΔS° becomes more positive (see above), *i.e.* more positive value of ΔS° will lead to a more negative value of ΔG° and *hence a more stable complex is formed*. In the language of thermodynamics the equilibrium constant of a reaction is the measure of the *heat released* in the reaction and the *entropy change* during the reaction. The greater the amount of heat released in a reaction, the more stable are the reaction products. The entropy of a system is a measure of the amount of disorder. *The greater the amount of disorder produced in the products during the reaction relative to the reactants, the greater the increase in entropy during the reaction and hence the greater the stability of the products.*

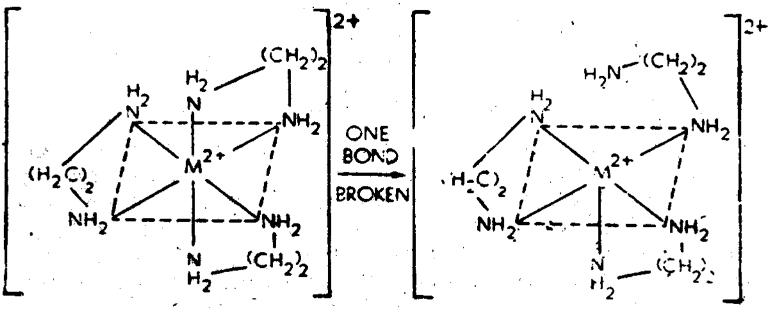
The fact that the stability of the complex increases with the increase of entropy can be illustrated by the following example : when ethylene diamine molecule, $NH_2—CH_2—CH_2—NH_2$ (*en*) is allowed to react with hydrated complex ion, $[M(H_2O)_6]^{2+}$, it replaces two H_2O molecules from it, since it is a bidentate ligand.

$$[M(H_2O)_6]^{2+} + en \longrightarrow [M(H_2O)_4(en)]^{2+} + 2H_2O$$

This process increases the number of particles in the system and hence its disorder and entropy. Thus the complex, $[M(H_2O)_4(en)]^{2+}$ is more stable than $[M(H_2O)_6]^{2+}$.

Following sidgwick the explanation of the chelate effect may be presented more pictorially. If one of the two metal-ligand bonds of a bidentate chelate system is broken, the remaining bond still remains attached with the metal ion so that the broken bond can be re-established. On the other hand if the metal-ligand bond of a monodentate complex (non-chelated complex) is broken, the ligand will leave away from the vicinity of the metal ion. Thus a chelated complex dissociates less than a non-chelated complex and hence will register a higher stability constant. This explanation is illustrated by the following example :

The removal of an NH_3 molecule from the non-chelated complex, $[M(NH_3)_6]^{2+}$ in aqueous solution results in breaking of the bond and the displaced ligand molecule *viz.* NH_3 molecule moves away from the vicinity of the metal ion, M^{2+}. But when one bond of the chelated complex, $[M(NH_2—CH_2—CH_2—NH_2)_3]^{2+}$ is broken, the metal ion, M^{2+} still remains attached to the ligand, $NH_2—CH_2—CH_2—NH_2$ by the second bond and hence displaced $—NH_2$ is not allowed to move away from the metal ion.



Thus there is greater possibility of the reformation of the broken bond in the chelated complex than in the non-chelated complex. This explains the greater inherent stability of a chelated complex as compared to a non-chelated complex.

(*iv*) **Chelate ring size.** The larger the number of the chelate rings in a complex, the greater is its stability. This is illustrated in Table 14·8.

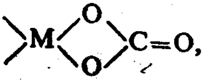
Table 14·8. *Overall stability constant values (i.e. $\log_{10} \beta$ values) for some ammonia and polyamine complexes illustrating the effect of chelate ring size on the stability of the complexes.*

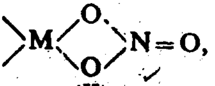
The abbreviations used in this Table have the following meaning :
en = ethylene diamine, $NH_2CH_2CH_2NH_2$
trien = triethylene tetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$
tren = triamino triethylamine, $(NH_2CH_2CH_2)_3N$
dien = diethylene triamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$
penten = tetrakis (aminoethyl) ethylene diamine,
$(NH_2CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2$
M = Metal.

Metal complexes	*No. of chelate rings*	*Values of stability constants ($\log_{10} \beta$ values)*						
		Mn^{2+}	*Fe^{2+}*	*Co^{2+}*	*Ni^{2+}*	*Cu^{2+}*	*Zn^{2+}*	*Cd^{2+}*
$M(NH_3)_4$	0	—	23·7	5·31	7·79	12·59	9·06	6·92
$M(en)_2$	2	4·9	7·7	10·9	14·5	20·2	11·2	10·3
M(trien)	3	4·9	7·8	11·0	14·1	20·5	12·1	10·0
M (tren)	3	5·8	8·8	12·8	14·0	18·8	14·6	12·3
$M(dien)_2$	4	7·0	10·4	14·1	18·9	21·3	14·4	13·8
M (penten)	5	9·4	11·2	15·8	19·3	22·4	16·2	16·2

Table 14·8 clearly shows that the greater the number of chelate rings in the complex, the greater is the stability of the complex.

The stability of the complexes also depends on the number of the atoms present in the ring. The chelates containing 3-membered ring including the metal are very unstable and hence are unknown. 4-membered chelate rings are rare and occur in carbonate (I), nitrate (II) and sulphate (III) chelates.


(I)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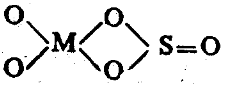
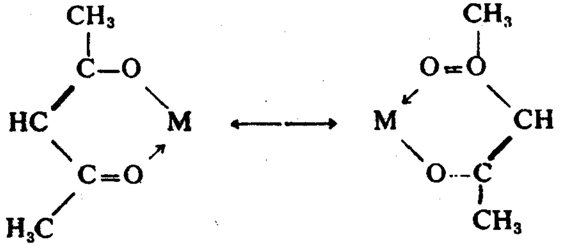

(III)

The most common and the most stable chelates are 5- and 6-membered chelates. 5-membered chelates are frequently more stable than the 6-membered chelates when the atoms in the ring are joined by single bonds only. On the other hand 6 membered chelates are more stable than 5-membered chelates of heterocyclic ligands or of ligands involving conjugation in the chelate ring. For example, acetylacetone complexes of the metal ions which contain 6-membered conjugate chelate rings are more stable than the corresponding ethylene diamine complexes which contain only 5-membered chelate rings. In acetylacetone complexes the π-electron density gets spread up over the whole ring which increases the stability of this 6-membered ring system. The possibility of the resonance in its chelate ion is an additional factor contributing to the stability of acetylacetone complexes.

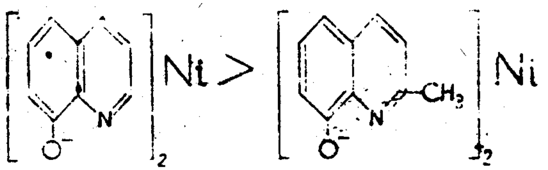


(*v*) **Steric effects.** When a bulky group is either attached to or present near the donor atom of a ligand, mutual repulsion among the ligands occurs and consequently the metal-ligand bond is weakened. Thus large bulky ligands form less stable complexes than do the analogous smaller ligands. This effect is commonly referred to as **steric hindrance (steric effect or steric strain).** This effect can be illustrated by the following examples :

(*a*) ethylene diamine, $NH_2—(CH_2)_2—NH_2$ complexes are more stable than those of tetramethyl ethylene diamine, $(CH_3)_2N—(CH_2)_2—N(CH_3)_2$ which is the tetramethyl substituted derivative of $NH_2—(CH_2)_2—NH_2$. Thus :

$$[M(NH_2—CH_2—CH_2—NH_2)_2]^{2+} > [M(N(CH_3)_2—CH_2—CH_2—N(CH_3)_2)_2]^{2+}$$

(*b*) Complex of Ni^{2+} with 8-hydroxy quinoline is more stable than that of 2-methyl-8-hydroxy quinoline. Thus :



(log β=21·8)   (log β = 17·8)

The strain effect is sometimes due to the geometry of ligand coupled with the stereo-chemistry of the metal complex. For example triethylene tetraamine, $NH_2—(CH_2)_2—NH(CH_2)_2—NH—(CH_2)_2—NH_2$ (*trien*) can coordinate its all the four nitrogens at the corners of a square but triethyltriamine, $(NH_2—CH_2—CH_2)_3N$ (*tren*) can not do so. Thus straight-chain in *trien* forms more stable complexes with Cu^{2+} ion than does the branched-chain in *tren* because *tren* is unable to assume the preferred square planar geometry.

Other Factors

The amount of metal-ligand covalent character also influences the stability of the complexes of relatively electronegative metals like those in copper and zinc families and Sn and Pb. For example the order of stability of the complexes, $[AgX_2]^-$ and $[AgX_3]^-$ is as :

$$AgI_2^- > AgBr_2^- > AgCl_2^- > AgF_2^-$$
$$AgI_3^- > AgBr_3^- > AgCl_3^- > AgF_3^-$$

This order is attributed to the increase in covalent character in Ag—X bond from Ag—F to Ag—I.

EXPERIMENTAL DETERMINATION OF STABILITY CONSTANT AND COMPOSITION OF A COMPLEX

1. Spectrophotometric Method

Most of the complexes absorb light differently than the metal ions from which they are formed. The relationship between the absorbance or optical density (A) at a particular wavelength and concentration is expressed by Beer's law which is given as :

$$A = \epsilon . l . c .$$

where ϵ = mole extinction coefficient

l = length of the absorption cell

c = concentration of the complex (in moles/litre)

If we measure the absorbance (A) with a spectrophotometer, know the extinction coefficient (ϵ) at that wave length and the cell length (l), the concentration (c) can be calculated from the Beer's law equation given above.

How the spectrum of a metal ion, M^{2+}, changes on coordination with ligand, L, has been shown in Fig. 14·3 which contains representative spectra of a metal ion, M^{2+} (shown by broken lines) and its complex ion, ML^{2+} (shown by unbroken lines). It will be seen that the absorption by the complex takes place over the entire region

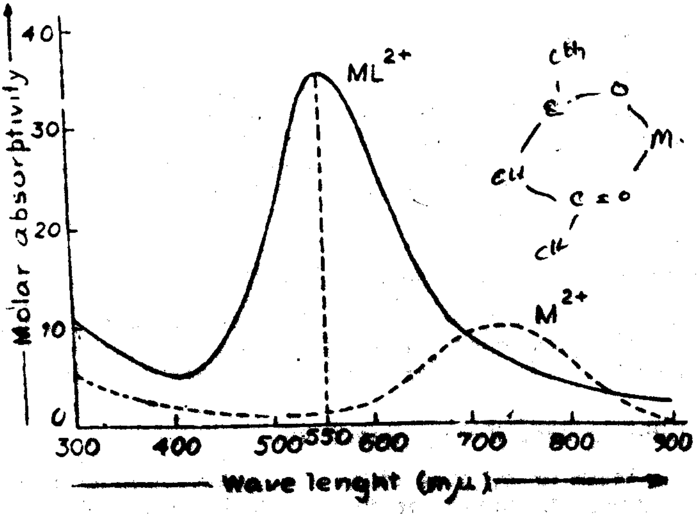


Fig. 14·3. Spectrum of a metal ion, M^{2+} and its complex, ML^{2+}

of the metal ion absorption, while at 550 $m\mu$ only the complex absorbs.

Clearly, the value of K_F (formation constant) for the reaction :

$$M^{2+} + L \overset{K_F}{\rightleftharpoons} ML^{2+}, \text{ will be given by}$$

$$K_F = \frac{[ML^{2+}]}{[M^{2+}][L]} \qquad ...(14\cdot1)$$

In order to obtain the value of formation constant, K_F, solutions containing known amounts of total M^{2+} and total L are equiliberated. The absorption of these solutions at 550 $m\mu$ is measured and the value of K_F is evaluated as follows :

We know that :

$$C_M = [M^{2+}] + [ML^{2+}] \qquad ...(14\cdot2)$$

$$C_L = [L] + [ML^{2+}] \qquad ...(14\cdot3)$$

and $$A = \epsilon_{(ML^{2+})} \; l \,.\, [ML^{2+}] \text{ (From Beer's Law)}$$

or $$[ML^{2+}] = \frac{A}{\epsilon_{(ML^{2+})} \,.\, l} \qquad ...(14\cdot4)$$

where C_M = total concentration of the metal ion

C_L = total concentration of the ligand.

Put the value of $[ML^{2+}]$ obtained from equation (14·4) in equation (14·2) and (14·3) to get the values of $[M^{2+}]$ and [L]. Thus :

$$[M^{2+}] = C_M - \frac{A}{\epsilon_{(ML^{2+})} \,.\, l} \qquad ...(14\cdot5)$$

$$[L] = C_L - \frac{A}{\epsilon_{(ML^{2+})} \,.\, l} \qquad ...(14\cdot6)$$

Thus, if we put the values of $[ML^{2+}]$, $[M^{2+}]$ and [L] as obtained from equations (14·4), (14·5) and (14·6) respectively in equation (14·1), we shall get the value of K_F. For the evaluation of the value of K_F, the values of A, $\epsilon_{(ML^{2+})}$, l, C_M and C_L must be known. The constancy of K_F is checked by repeating the measurements at different C_M and C_L values.

2. Method of Continuous Variation (Job's Method)

This method is a variation of the spectrophotometric method and is used to determine the composition of a complex. This is mainly used for solutions where only one complex is formed.

Different steps of the procedure are :

(*i*) **Make 10 solutions of the complex** containing metal ion and ligand in such proportions that the total volume of each solution is 10 ml. as shown below :

Solutions No. (10 solutions) :	1	2	3	4	5	6	7	8	9	10
Volume of the metal ion (ml) :	0	1	2	3	4	5	6	7	8	9
Volume of the ligand (ml) :	10	9	8	7	6	5	4	3	2	1

Thus we see that the sum of the concentration of the ligand, C_L and that of the metal ion, C_M is constant. Only their ratios, $C_L : C_M$ are changed. Thus :

$$C_L + C_M = C \qquad \ldots(i)$$

where C is a constant.

(*ii*) Determine the optical densities of the solutions as prepared in step (*i*) with the help of a spectrophotometer at such a wave length of light that the complex absorbs strongly and the metal ion and the ligand donot.

(*iii*) Draw a graph between the mole fraction of the ligand, *m. f.* $\left(m.f. = \frac{C_L}{C} \right)$ and optical density (or absorbance). The graph obtained is of the type as shown in Fig. 14·4.

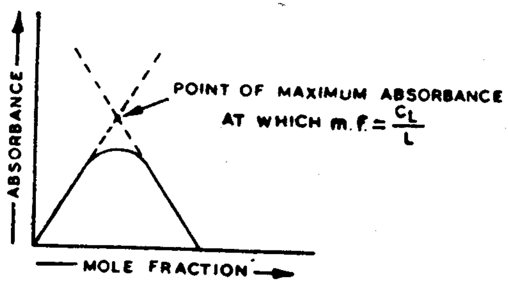


Fig. 14·4. Job's method of continuous variation for the determination of the composition of a complex.

When the legs of the curve are extrapolated, they cross each other at a point at which the absorbance is maximum.

If the formula of the complex is ML_n, then

$$n = \frac{C_L}{C_M} \qquad \ldots(ii)$$

Equation (*i*) can also be written as :

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C} = 1 \qquad \ldots(iii)$$

With the help of equation *viz.*,

$$m.f. = \frac{C_L}{C} \qquad \ldots(iv)$$

equation (*iii*) reduces to :

$$m.f. + \frac{C_M}{C} = 1$$

or

$$\frac{C_M}{C} = 1 - m.f. \qquad \ldots(v)$$

Dividing equation (*iv*) by equation (*v*), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{m.f.}{1-m.f.}$$

or

$$\frac{C_L}{C_M} = \frac{m.f.}{1-m.f.}$$

or

$$n = \frac{m.f.}{1-m.f.} \quad \text{[See equ. (}ii\text{)]} \qquad \ldots(vi)$$

From the value of *n* as given by equation (*vi*) we can determine the composition of the complex, ML_n.

Limitations. (*i*) This method can be used when only one complex is formed under the experimental conditions.

(*ii*) This method is used when there is no change in the total volume of the solutions containing metal ions and ligand.

3. Potentiometric Method (Bjerrum Method)

When the ligand is a weak base or acid, competition between hydrogen ions and metal ions for the ligand can be used for the determination of the formation constant.

Let us consider the equilibiria in which an acid and metal ions are added to a basic ligand in solution. Thus the following equations hold good :

$$\underset{\text{Basic ligand}}{L} + \underset{\text{Acid}}{H^+} \overset{K_a}{\rightleftharpoons} HL^+, \quad K_a = \frac{[HL^+]}{[L]\,[H^+]}$$

$$\underset{\text{Basic ligand}}{L} + \underset{\text{Metal ion}}{M^+} \overset{K_F}{\rightleftharpoons} ML^+, \quad K_F = \frac{[ML^+]}{[L]\,[M]^+}$$

Here K_a and K_F are the acid association constant of the ligand and formation constant respectively.

Now if C_H, C_M and C_L are the total amounts in moles/lit of acid (H^+). metal (M^+) and basic ligand (L), we have

$$C_H = [H^+] + [HL^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

$$C_M = [M^+] + [ML^+]$$

Solving the last three equations given above and using the acid association constant of the ligand, K_a, we get :

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a[H^+]}$$

$$[M^+] = C_M - [ML^+]$$

$$[L] = \frac{C_H - [H^+]}{K_a[H^+]}$$

Thus, on putting the values of $[ML^+]$, $[M^+]$ and $[L]$ from the above equations in

$$K_F = \frac{[ML^+]}{[M^+][L]},$$

the value of K_F can be evaluated. For the determination of $[ML^+]$, $[M^+]$ and $[L]$, the values of C_H, C_L, C_M, K_a and $[H^+]$ must be known. The last quantity, $[H^+]$, is generally determined potentiometrically using a pH meter.

In order to get precise results, the ligand must be a medium weak acid or base and the formation constant, K_F, should be within a factor of 10^5 of the value of the acid association constant of the ligand, K_a.

References :

1. F. J. C. Rossotti and H. Rossotti. *The Determination of Stability Constants*, McGraw-Hill, New York, 1961.
2. J. Bjerrum, G. Schwarzenbach and L. G. Sillen (eds.) *Stability Constants of Metal-Ion Complexes*, Part I, *Organic Ligands*, Part II, *Inorganic Ligands*, Chemical Society of London, 1957, 1958.

15

Ligand Substitution Reactions In Octahedral Complexes

Before starting the study on kinetics and mechanism of ligand substitution reactions in coordination compounds the following terms should be defined.

Transition State or Activated complex

Let us consider the energy changes occuring during the course of the reaction,

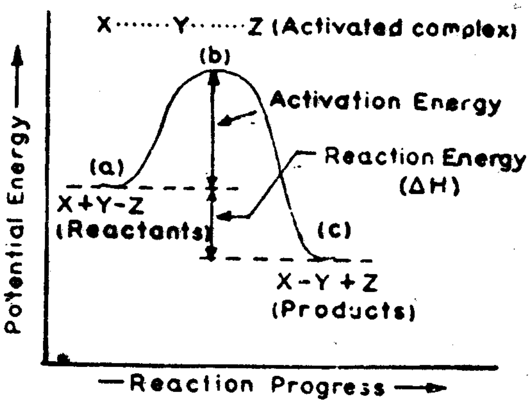
$$\underbrace{X+Y-Z}_{\text{Reactants}} \longrightarrow \underbrace{X-Y+Z}_{\text{Products}}$$

In the beginning both X and Y—Z possess certain amount of potential energy represented by the point (*a*) on the curve shown in Fig. 15·1. The approach of X to the molecule Y—Z causes an increase in the potential energy until a critical energy state (which is a temporary state) represented by the point (*b*) is reached. By this Y—Z bond is weakened (partially broken) and ultimately the products, X—Y and Z are formed as shown at point (*c*) in Fig. 15·1. In this process the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy. Fig. 15·1 (*a*) illustrates that for an exothermic reaction the reactants originally possess more potential energy than the products and excess energy (= $\triangle$H) is liberated as heat. Fig. 15·1 (*b*) shows that for an endothermic reaction the reactants have less potential energy than the products and, therofore, the reactants absorb heat equal to $\triangle$H from the surroundings during their change into products. Obviously $\triangle$H is the energy difference between the reactants and the products. It is called **reaction energy**.

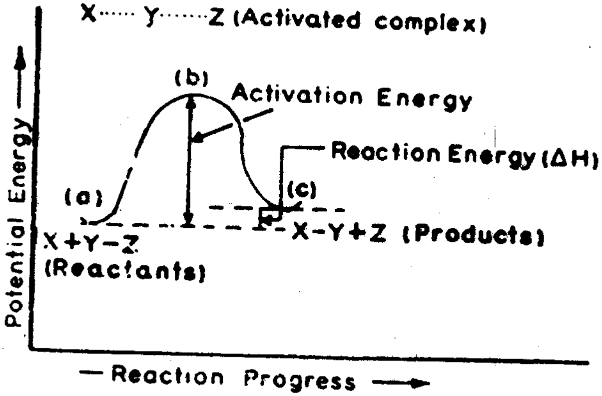
The reaction,

$$X+Y-Z \longrightarrow X-Y+Z,$$

can be visualised to take place by the following steps : The molecule X approaches Y—Z from a direction remote from Z (proper allignment). While X draws nearer to Y, Z starts being repelled from Y until a stage is reached in which X and Z are rather loosely attached to Y and approximately equidistant from it. In this stage the species X...Y...Z is formed. This species is called the transition state or **activated complex** which has the following characteristics : (*i*) In this



(*a*) Energy changes in an exothermic reaction :
X+Y—Z ⟶ X—Y+Z+ΔH



(*b*) Energy changes in an endothermic reaction :
X+Y—Z+ΔH ⟶ X—Y+Z

Fig. 15·1. Energy changes in exothermic and endothermic reactions.

X to Y and Y to Z distances are slightly greater than the normal bond lengths (*ii*) It is not a true molecule, the bonds being partial. Thus it is of a transitory nature and refers to an imaginary molecule and hence cannot be isolated. (*iii*) It has the maximum energy and hence is the most unstable and has very-very short life time.

The activated complex which is the most unstable changes to give the products X—Y and Z. Thus the various steps responsible for the reaction are :

$$\underbrace{X+Y-Z}_{\text{Reactants}} \longrightarrow \underset{\substack{\text{Activated complex}\\ \text{(transition state-}\\ \text{unstable)}}}{X...Y...Z} \longrightarrow \underbrace{X-Y+Z}_{\text{Products}}$$

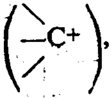
The difference in energy between the reactants and the activated complex is called **activation energy.**

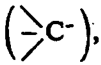
Substrate

A substrate may be defined as the reactant in which some bonds are broken and some new ones are formed as a result of the attack of a reagent.

Attacking reagents

We have mentioned above that a reaction proceeds when a reagent attacks on a substrate. These reagents are called **attacking reagents** and are of two types : (*i*) *Electrophilic reagents* (*ii*) *Nucleophilic reagents.*

(*i*) **Electrophilic reagents.** These are also called **electrophiles.** As signified by the name electrophilic (*electro* = electron, *philic* = loving) these are *electron loving* (*electron-seeking*) or *electron pair acceptor,* since these are deficient by two electrons. Thus these are *Lewis acids.* These may be positively charged ions like carbonium ion , bromonium ion (Br^+), nitronium ion (NO_2^+), nitrosonium ion (NO^+), diozonium ion ($C_6H_5N_2^+$), bisulphonium ion (SO_2OH^+), proton (H^+), hydronium (H_3O^+) or neutral molecules such as BF_3, $AlCl_3$, SO_3, $FeCl_3$ etc.

(*ii*) **Nucleophilic reagents.** These are also called **nucleophiles.** As implied by the name nucleophilic (*nucleo*=nucleus, *philic*=loving) these reagents are *nucleus-loving* (*nucleus-seeker*). Since the nucleus is electrically positive, the nucleophiles are electrically negative ions like carbanion , chloride ion (Cl^-), hydroxide ion (OH^-), cyanide ion (CN^-), bisulphide ion (SH^-), hydride ion (H) or electron-rich neutral molecules such as NH_3, H_2O. Since these have unshared pair of electrons, these are *Lewis bases* (*i.e. electron pair donor*).

In coordination chemistry the central metal ion is an electrophile, since it accepts an electron pair while the ligands are nucleophiles because these donate electron pairs. Thus :

$$\underset{\substack{\textbf{Electrophile}\\ \textbf{(Lewis acid)}}}{M^{n+}} \quad \underset{\substack{\textbf{Nucleophile}\\ \textbf{(Lewis base)}}}{+L} \quad \longrightarrow \underset{\textbf{Complex}}{[ML]^{n+}}$$

Types of Substitution Reactions

Following are the important types of substitution reactions met with in coordination chemistry.

(*i*) **Nucleophilic or Ligand Substitution (S_N) Reactions.** In these reactions a nucleophile (*i.e.* a ligand, L) in a coordination complex, say ML_n is replaced by another nucleophile, L′.

$$\underset{(C.N.=n)}{ML_n+L'} \longrightarrow \underset{(C.N.=n)}{ML_{n-1}L'+L}$$

(*ii*) **Electrophilic or Metal Substitution (S_E) Reactions.** In these reactions an electrophile (*i.e.* central metal atom) in a coordination complex is replaced by another electrophile, M′.

$$ML_n+M' \longrightarrow M'L_n+M$$

Although S_E reactions such as that between Hg^{2+} and $[Co^{II}(NH_3)_5Cl]^+$ are known, they are much less common than S_N reactions and hence will not be considered here.

Mechanism of Nucleophilic (Ligand) Substitution Reactions (S_N Reactions) in Octahedral Complexes

Two different paths of nucleophilic substitution reactions have been suggested :

(1) S_N1 or Dissociation Mechanism

S_N1 indicates *substitution(S) nucleophilic(N) unimolecular* or *first order* (1) reaction. The reaction is nucleophilic because the incoming ligand seeks a positive centre (like the nucleus of an atom), the metal ion. For a general ligand substitution reaction in an octahedral complex this mechanism can be shown as :

$$\underset{\substack{\text{Octahedral}\\ \text{complex}\\ (C.N.=6)}}{MX_5Y+Z} \longrightarrow \underset{(C.N.=6)}{MX_5Z+Y}$$

The above reaction actually procceds through a two-step mechanism.

(*a*) In this step which is a *slow* and *rate-determining step*, Y is lost and a five-coordinated intermediate (*activated complex*) is formed. This is a *metal ligand bond breaking step* and the reaction occuring in this step is *unimolecular* because this step which is the rate-determining step involves only one reactant species, MX_5Y to form the activated complex, MX_5 which is an electron-deficient intermediate. This has either *square pyramidal* or *trigonal bipyramidal shape*, since its coordination number is *five*.

$$\underset{(C.N.=6)}{MX_5Y} \xrightarrow[\substack{\text{Unimolecular and}\\ \text{rate-determing}\\ \text{step}}]{\text{Slow }(-Y)} \underset{\substack{\text{5-coordinated}\\ \text{intermediate}\\ (C.N.=5)}}{MX_5+Y}$$

In this step MX_5Y is dissociated to give MX_5. Hence the name dissociation mechanism.

(*b*) In this step the short-lived penta-coordinated intermediate of very limited stability is attracted *rapidly* by the nucleophilic reagent, Z to give the complex, MX_5Z.

$$\underset{\substack{\text{5-coordinated}\\ \text{intermediate}}}{MX_5} \xrightarrow[+Z]{\text{Fast}} \underset{(\text{C.N.} = 6)}{MX_5Z}$$

This is *fast* and *bimolecular* reaction. As normally the *activation energy* for the first step will be *high* and that for the second step will be *low*. The rate of overall reaction will depend on the concentration of MX_5Y and not on that of Z. Thus the rate of reaction is first order with respect to MX_5Y and zero order with respect to Z. Hence

Rate of reaction = $K[MX_5Y]$

The formation of MX_5Z can be shown by combining the two steps as :

$$\underset{(\text{C.N.}=6)}{MX_5} \xrightarrow[\substack{\text{Unimolecular and}\\ \text{rate-determining}\\ \text{step}}]{\text{Slow } (-Y)} \underset{\substack{\text{5-coordinated}\\ \text{intermediate}\\ (\text{C.N.} = 5)}}{MX_5} \xrightarrow{\text{Fast } (-Z)} \underset{(\text{C.N.} = 6)}{MX_5Z}$$

These two steps are diagrammatically shown in Fig. 15.7.

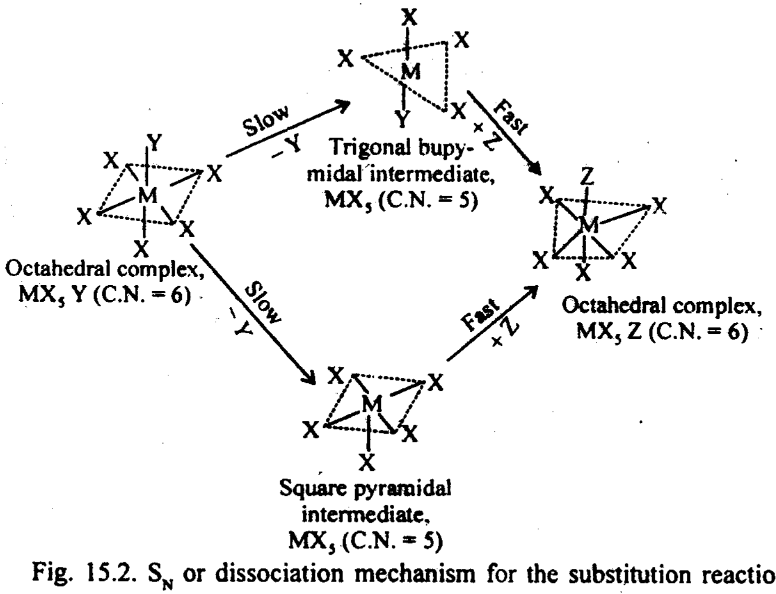


Fig. 15.2. S_N or dissociation mechanism for the substitution reaction

$$MX_5Y + Z \longrightarrow MX_5Z + Y$$

(2) S_N2 or Association or Displacement Mechanism

S_N2 stands to indicate *substitution* (S), *nucleophilic* (N), *bimolecular or second order* (2) reaction This also proceeds, through the two steps:

(*a*) This is a *slow* step and involves the attachment of the incoming nucleophile, Z to MX_5 Y to form a seven-coordinated unstable intermediate (perhaps transition state) which is probably *pentagonal bipyramidal* in shape. Obviously it is a *metal-ligand bond-making* step.

$$\underset{(\text{C.N.} = 6)}{MX_5Y} \xrightarrow[\substack{\text{Bimolecular and} \\ \text{rate determining} \\ \text{step}}]{\text{Slow } (+Z)} \underset{\substack{\text{Unstable seven-} \\ \text{coordinated} \\ \text{intermediate} \\ (\text{C.N.} = 7)}}{MX_5YZ}$$

This reaction is *rate-determining* and *bimolecular* because two reactants *viz* MX_5Y and Z are involved in this step. Thus the rate of this rate determining reaction is of second order : first order with respect to the complex, MX_5Y and first order with respect to the entering ligand, Z, *i.e*,

$$\text{Rate of reaction} = K[MX_5Y][Z]$$

In this step Z associates with MX_5Y to form MX_5YZ. Hence the name association mechanism.

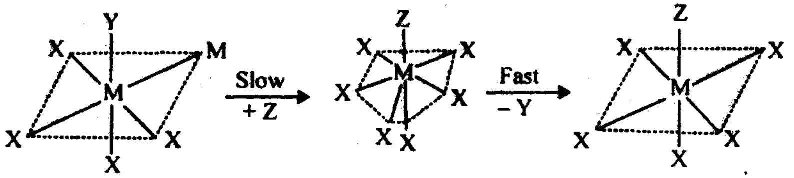
(*b*) Either at the same time as Z adds to MX_5 Y or shortly thereafter, Y leaves MX_5YZ *rapidly* to give MX_5Z. This is a fast step.

$$\underset{\substack{\text{Seven coordinate} \\ \text{unstable intermediats} \\ (\text{C.N.} = 7)}}{MX_5YZ} \xrightarrow[-Y]{\text{Fast}} \underset{(\text{C.N.} = 6)}{MX_5Z}$$

Both the steps can be represented as :

$$\underset{(\text{C.N.} = 6)}{MX_5Y} \xrightarrow[\substack{\text{Bimolecular and} \\ \text{rate determining} \\ \text{step}}]{\text{Slow } (+Z)} \underset{\substack{\text{Seven-coordi-} \\ \text{nated unstable} \\ \text{intermediate} \\ (\text{C.N.} = 7)}}{MX_5YZ} \xrightarrow[-Y]{\text{Fast}} \underset{(\text{C.N.} = 6)}{MX_5Z}$$

Both these steps are shown diagramatically in Fig. 15.3.



Octahedral complex MX_5 Y(C.N. = 6)

Seven co-ordinated unstable intermediate, MX_5 YZ (C.N. = 7)

Octahedral complex, MX_5 Z (C.N. = 6)

Fig. 15.3 : S_N2 or association mechanism for the substitution reaction

$$MX_5Y + Z \longrightarrow MX_5\,Z + Y$$

S_N1 Vs S_N2 Mechanisms

S_N1 and S_N2 mechanism can be differentiated from each other by noting the following points :

(*i*) In S_N1 process the rate-determing slow step is a metal-ligand bond breaking step, since the coordination number of the complex, MX_5Y (=6) is decreased to 5 which is the coordination number of the intermediate, MX_5. On the other hand in S_N2 process the rate-determining step involes a metal-ligand bond making step, since C.N.=6 is increased to 7.

(*ii*) The rate of S_N1 mechanism is first order with respect to MX_5Y, *i.e*, the rate-determining step in this mechanism is unimolecular. On the other hand the rate-determining step for S_N2 mechanism is bimolecular, *i.e.* its rate of reaction is second order : first order with respect to MX_5Y and first order with respect to Z. Thus :

for S_N1 mechanism rate$=K[MX_5Y]$

and for S_N2 mechanism rate$=K[MX_5Y]\,[Z]$

Labile and Inert Complexes

On the basis of the difference in rates of replacement of one ligand by the other, Taube has classified the complexes into two classes :

(*i*) *The complexes in which the ligands are rapidly replaced by others are called* **labile or non-inert complexes.**

(*ii*) *The complexes in which substitution takes place slowly are called* **inert complexes.**

In order to make this distinction somewhat quantitative Taube suggested that the complexes in which the substitution of ligands takes place in less than one minute are called labile complexes. The reaction conditions are specified as a temperature of 25°C and 0·1 M solutions.

Hydrolysis Reactions

These are the substitution reactions in which a ligand is replaced by a water molecule or by OH^- groups. The reactions in which an aquo complex is formed as a result of the replacement of a ligand by H_2O molecules are called **acid hydrolysis** or **aquation reactions** while those in which a hydroxo complex is formed by the replacement of a ligand by OH^- group are called **base hydrolysis reactions.** Acid hydrolysis reactions occur in neutral and acid solutions (pH < 3) while base hydrolysis reactions occur in acid solution (pH > 10). For intermediate pH ranges the reaction is referred to just as hydrolysis reactions. Examples of these reactions are given below :

$$\left.\begin{array}{l}[\mathrm{Co^{III}(NH_3)_5Cl}]^{2+}+\mathrm{H_2O}\longrightarrow[\mathrm{Co^{III}(NH_3)_5(H_2O)}]^{3+}+\mathrm{Cl^-}\\ [\mathrm{Co^{III}}\,(en)_2\mathrm{ACl}]^{+}+\mathrm{H_2O}\longrightarrow[\mathrm{Co^{III}}(en)_2\mathrm{A(H_2O)}]^{2+}+\mathrm{Cl^-}\\ \quad(\mathrm{A=OH^-,\ Cl^-,\ NCS^-,\ NO_2^-})\end{array}\right\}\text{Acid hydrolysis reactions}$$

$$[\mathrm{Co(NH_3)_5Cl}]^{2+}+\mathrm{OH^-}\longrightarrow[\mathrm{Co(NH_3)_5(OH)}]^{2+}+\mathrm{Cl^-}\text{.........Base hydrolysis reaction}$$

Aquation or Acid Hydrolysis Reactions of Six-coordinated Co(III) Ammine Complexes

Ammine complexes of Co(III) have been most widely studied. Since work on these complexes has been done exclusively in water, the reactions of the complexes with solvent water had to be considered first. In general it has been observed that NH_3 or ammines like ethylene diamine or its derivatives coordinated to Co(III) are replaced very slowly by H_2O molecules and hence in acid hydrolysis only the replacement of ligands other than amines is usually considered.

The rates of hydrolysis of the reactions of the type

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

(X=any anion)

have been studied and found to be first order in the complex. Since in aqueous solution the concentration of water is always constant (about equal to 55·5 M), the effect of changes in water concentration on the rate of the reaction cannot be determined. Rate laws given below are experimentally indistinguishable in aqueous solution, since

$$K = K'\,[H_2O] = K'\,[55{\cdot}5],$$

$$\begin{aligned}\text{Rate} &= K\,[Co(NH_3)_5X^{2+}]\\ &= K'\,[Co(NH_3)_5X^{2+}]\,[H_2O]\\ &= K'\,[Co(NH_3)_5X^{2+}]\,[55{\cdot}5]\end{aligned}$$

Thus the rate law does not tell us whether H_2O is involved in the rate-determining step.

The rate-law given above does not indicate whether these reactions proceed by an S_N2 displacement of X^- by H_2O or by an S_N1 dissociation followed by the addition of H_2O. However, a study as to how the following factors affect the rate constant of these reactions can give us an information about the nature of mechanism by which these reactions proceed.

(*i*) **Effect of charge on the complex.** The values of rates of acid hydrolysis of some Co(III) complexes at pH=1 are given in Table 15·1. This Table clearly shows that the *divalent monochloro complexes* react about 100 times slower than the *monovalent dichloro-complexes*. Since a decrease in rate is observed as the charge of the complex increases, a dissociation S_N1 process seems to be operative and hence the acid hydrolysis (*i.e.* replacement of one Cl^- ion by H_2O) of the monovalent complexes like $[Co(NH_3)_4Cl_2]^+$ occurs in two steps.

$$\underset{\text{6-coordinate complex}}{[Co(NH_3)_4Cl_2]^+} \xrightarrow[(-Cl^-)]{\text{Slow}} \underset{\text{5-coordinate intermediate}}{[Co(NH_3)_4Cl]^{2+}} + Cl^- \qquad \ldots(i)$$

$$[Co(NH_3)_4Cl]^{2+} \xrightarrow[(+H_2O)]{\text{Fast}} [Co(NH_3)_4Cl(H_2O)]^{2+}$$

Table 15·1. *Rates of acid hydrolysis of some Co(III) complexes at pH = 1 corresponding to the replacement of only one Cl⁻ ion by H_2O molecule.*

The symbols used represent the following molecules :

en ≡ ethylene diamine, $NH_2—CH_2—CH_2—NH_2$
trien ≡ triethylene tetramine,
$H_2N—(CH_2)_2—NH—(CH_2)_2—NH—(CH_2)_2—NH_2$
dien ≡ diethylene triamine, $H_2N—(CH_2)_2—NH—(CH_2)_2—NH_2$
tetraen ≡ tetraethylene pentamine,
$NH_2—(CH_2)_2—NH(CH_2)_2—NH(CH_2)_2—NH(CH_2)_2—NH_2$

Monovalent complex ions	*K* × 10^4 (*min*$^{-1}$)	*Divalent complex ions*	*No. of chelate links*	*K* × 10^4 (*min*$^{-1}$)
cis-$[Co(NH_3)_4Cl_2]^+$	Very fast	$[Co(NH_3)_5Cl]^{2+}$	0	4·0
cis-$[Co(en)_2Cl_2]^+$	150	*cis*-$[Co(en)_2(NH_3)Cl]^{2+}$	2	0·85
cis-$[Co(trien)Cl_2]^+$	90	*cis*-$[Co(tren)(NH_3)Cl]^{2+}$	3	0·40
trans-$[Co(NH_3)_4Cl_2]^+$	1100	$[Co(en)(dien)Cl]^{2+}$	3	0·31
trans-$[Co(en)(NH_3)_2Cl_2]^+$	130	$[Co(tetraen)Cl]^{2+}$	4	0·15
trans-$[Co(en)_2Cl_2]^+$	19			

The acid hydrolysis of divalent complexes like $[Co(NH_3)_4(H_2O)Cl]^{2+}$ also takes place in two steps :

$$\underset{\text{6-coordinate complex}}{[Co(NH_3)_4(H_2O)Cl]^{2+}} \xrightarrow[(-Cl^-)]{\text{Slow}} \underset{\substack{\text{5-coordinate}\\ \text{intermediate}}}{[Co(NH_3)_4(H_2O)]^{3+}} + Cl^- \qquad \ldots(ii)$$

$$[Co(NH_3)_4(H_2O)]^{3+} \xrightarrow[(+H_2O)]{\text{Fast}} [Co(NH_3)_4(H_2O)_2]^{3+}$$

Since the energy of charging a sphere varies as q^2, the change in electrostatic energy on going from 6- to 5-coordinated complex is $1^2—2^2 = 3$ [for equation (*i*)] and $2^2—3^2 = 5$ [for equation (*ii*)]. Thus acid hydrolysis of $[Co(NH_3)_4Cl_2]^+$ would be expected to proceed more rapidly than that of $[Co(NH_3)_4(H_2O)Cl]^{2+}$, *i.e.* the acid hydrolysis represented by equation (*i*) would proceed more rapidly than that represented by equation (*ii*). This in other words means that the separation of a negative charge in the form of Cl⁻ ion from a complex ion with higher charge is more difficult.

(*ii*) **Effect of chelation.** When NH_3 molecules in $[Co(NH_3)_5Cl]^{2+}$ complex ion are replaced partially or completely by polyamines like en, trien, dien, tetraen etc., the rate of aquation of the complex (replacement of Cl⁻ ion by H_2O molecule) is decreased as is evident from Table 15·1. The rates of aquation of the divalent complex ions given in this Table show that as the number of —CH_2—CH_2— or —$(CH_2)_2$— chelate links increases, the rate values decrease. The effect of chelation should be to shorten the Co—N bond distance and to transfer more charge to the cobalt in chelated complex compared to those continuing monodentate ligands. Thus this effect should enhance the rate of aquation. Actually, as is evident from Table 15·1, the rates are decreased. Obviously some other factor is responsible for the decrease. A more reliable explanation is that the chelated complex in both the ground state and in the transition state is solvated. Again it is known that the replacement of NH_3 molecules by polyamines increases the size of the complex, *i.e.* the chelated complex has larger size. The larger the size of the ion, less its solvation energy will be and hence less easily it will be formed. Thus the stability of the transition state in which the Cl^- ion is only partially lost and in which the solvation is less efficient will be reduced. The rate of aquation is slowed down by chelation because of reduced stability of the transition state due to less efficient solvation. This solvation theory, if true, does not distinguish between S_N1 and S_N2 mechanisms. All that may be concluded is that ionic bond-breaking in the transition state is important.

(*iii*) **Effect of substitution on ethylenediamine.** When H atoms on carbon atom or on nitrogen atom of *en* groups of *trans*-$[Co(\textit{en})_2Cl_2]^+$ are replaced by the alkyl groups like CH_3, C_2H_5 etc., the ligand becomes more bulky (*i.e.* crowded or strained). Now if the strained complex having bulky ligand reacts by S_N1 dissociative mechanism, the crowding on the complex with coordination number six is reduced as it is converted into 5-coordinated intermediate, since the removal of one Cl^- ion from the complex reduces the congestion round the metal. Thus the intermediate is less strained than the complex and hence S_N1 process is an easier process (*steric assistance*), *i.e.* S_N1 process which consists of the loss of Cl^- ion should occur more rapidly.

On the other hand if the strained complex reacts by S_N2 displacement process, the crowding on the complex is increased as it is converted into a transition state of coordination number seven. Thus the transition state is more strained than the original complex and hence S_N2 process is difficult to operate, *i.e.* the S_N2 process is retarded by the steric crowding (*steric hindrence*). Experiments have shown that the complexes containing substituted diamines react more rapidly than those having *en*. In Table 15·2 the rates of hydrolysis of *trans*-$[Co(AA)_2Cl_2]^+$ at 25°C and pH = 1 corresponding to the replacement of only one Cl^- ion by H_2O molecule are given. Here AA is the diamine.

From these values it is obvious that with only one exception *viz* $[Co(\textit{i-bn})_2Cl_2)]^+$ the effect of the increase in the number or size of the alkyl groups substituted in place of hydrogen atoms of CH_2 or NH_2 groups leads to an increase in rate of hydrolysis for the loss of one Cl^- ion. The increase in rates observed when more bulky ligands are used is a good evidence in favour of S_N1 mechanism.

Table 15·2. *Rates of hydrolysis of trans-*$[Co(AA)_2Cl_2]^+$ *at 25°C and pH = 1 in aqueous solution*

$$[Co(AA)_2Cl_2]+H_2O \longrightarrow [Co(AA)_2Cl(H_2O)]^{2+}+Cl^-$$

	Diamines AA with their names, formulae and symbols	$K\times 10^3$ (min^{-1})	
1.	Ethylene diamine (*en*) $NH_2—CH_2—CH_2—NH_2$	1·9	Increasing ↓
2.	Propylene diamine (*pn*) $NH_2—CH_2—CH(CH_3)—NH_2$	3·7	
3.	*dl* Butylene diamine (*dl-bn*) *dl*-$NH_2—CH(CH_3)—CH(CH_3)—NH_2$	8·8	
4.	*meso*-Butylene diamine (*m-bn*) *meso*—$NH_2—CH(CH_3)—CH(CH_3)—NH_2$	250	
5.	Isobutylene diamine (*i-bn*) $NH_2—CH_2—C(CH_3)_2—NH_2$	130	
6.	Tetramethyl ethylene diamine (*tetrameen*) $NH_2—C(CH_3)_2—C(CH_3)_2—NH_2$	Instantaneous	
7.	N-methyl ethylene diamine (*meen*) $NH_2—CH_2—CH_2—NH(CH_3)$	1·0	Increasing ↓
8.	N-ethyl ethylene diamine (*eten*) $NH_2—CH_2—CH_2—NH(C_2H_5)$	3·6	
9.	N-propyl ethylene diammine (*n-pren*) $NH_2—CH_2—CH_2—NH(n\text{-}C_3H_7)$	7·1	

(*iv*) **Effect of leaving group.** The rate of aquation of $[Co(NH_3)_5X]^{2+}$ corresponding to the replacement of X^- with H_2O molecule depends on the nature of X because the bond-breaking step is important in rate-determing step. It has been observed experimentally that the reactivity of X groups decreases in the order :

$$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^- .$$

This order corresponds to the order of the decreasing thermodynamic stability of the complexes formed with these groups. The results of various investigations are in favour of S_N1 mechanism. Bond-breaking is important in the activated complex.

Base Hydrolysis Reactions of Six-coordinated Co(III) Ammine Complexes.

Most of the kinetic work has been done on six-coordinated Co(III) ammine complexes. For ammine complexes of Co(III) containing N—H bonds it has been seen that the rate of base hydrolysis is often as much 10^6 times faster than the corresponding rate of acid hydrolysis. Here we shall discuss the mechanism of the base hydrolysis reaction of $[Co(NH_3)_5Cl]^{2+}$ only. The base hydrolysis reaction represented by

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

can proceed by any of the following two mechanisms :

(1) S_N2 Displacement Mechanism

According to this mechanism the reaction proceeds as .

$$\underset{(C.N.=6)}{[Co(NH_3)_5Cl]^{2+}} \xrightarrow[\text{Rate-determining step}]{\text{Slow }(+OH^-)} \underset{(C.N.=7)}{[Co(NH_3)_5(OH)Cl]^{+}} \xrightarrow{\text{Fast}(-Cl^-)} \underset{(C.N.=6)}{[Co(NH_3)_5(OH)]^{2+}} + Cl^-$$

The slow step which is a rate-determing step is a second-order reaction: first order with respect to the complex and first order with respect to the base. Thus :

$$\begin{aligned}\text{Rate of reaction} &= K[\text{complex}][\text{base}]\\ &= K[Co(NH_3)_5Cl^{2+}][OH^-]\end{aligned}$$

(2) S_N1 Dissociation Mechanism

This has been suggested by Garrick (1937). Before this mechanism could be applied, the complex which acts as a Bronsted acid is converted into its conjugate base (abbreviated as CB), $[Co(NH_3)_4(NH_2)Cl]^+$ which is obtained by removing a proton (H^+) from the amino group (NH_3) present in the complex. CB is an amido complex, since it contains an amido group : $\ddot{N}H_2^-$. OH^- which is a base is converted into its conjugated acid, H_2O.

Conjugate acid-base pair

$$(a)\ \underset{\substack{\text{Acid}_1\\ \text{(Ammino complex)}}}{[Co(NH_3)_5Cl]^{2+}} + \underset{\text{Base}_2}{OH^-} \overset{\text{Fast}}{\rightleftharpoons} \underset{\substack{\text{Base}_1\\ \text{(Amido complex, CB)}}}{[Co(NH_3)_4(NH_2)Cl]^{+}} + \underset{\text{Acid}_2}{H_2O}$$

Conjugate acid-base pair

Obviously, if K=equilibrium constant for acid-base equilibrium (*a*), then

$$K = \frac{[CB]\,[H_2O]}{[Co(NH_3)_5Cl^{2+}][OH^-]}$$

or

$$[CB] = \frac{K[Co(NH_3)_5Cl^{2+}][OH^-]}{[H_2O]} \qquad \ldots(i)$$

CB obtained as above is more labile than the original complex, $[Co(NH_3)_5Cl]^{2+}$ and hence undergoes S_N1 dissociation mechanism by a slow step to lose Cl^- ion and gives a *5-coordinated intermediate.*

$$(b)\ \underset{\text{(CB with C.N}=6)}{[Co(NH_3)_4(NH_2)Cl]^+} \xrightarrow[\substack{(S_N1\text{ dissociation,}\\ \text{rate-determining}\\ \text{and unimolecular}\\ \text{step}}]{\text{Slow }(-Cl^-)} \underset{\substack{\text{5-coordinated}\\ \text{intermediate}\\ (\text{C.N.}=5)}}{[Co(NH_3)_4(NH_2)]^{2+}} + Cl^-$$

This is the rate-determining and unimolecular step. Thus :

$$\text{Rate} = k_1[CB]$$

$$= \frac{k_1K\,[Co(NH_3)_5\ Cl^{2+}]\,[OH^-]}{[H_2O]}$$

[from equ. (*i*)]

$$= K_B\ [\text{complex}]\ [\text{Base}] \qquad \ldots(ii)$$

where K_B=rate constant used for the dissociation of the conjugate base as in (*b*) step and is equal to $k_1K/[H_2O]$

The intermediate formed as above reacts with the abundent solvent molecules (*i.e.* H_2O molecules) to give the *hydroxo complex,* $[Co(NH_3)_5(OH)]^{2+}$. This is a relatively fast step.

$$(c)\ \underset{\substack{\text{5-coordinated}\\ \text{intermediate}}}{[Co(NH_3)_4(NH_2)]^{2+}} \xrightarrow[]{\substack{\text{Fast}\\ (+H_2O)}} \underset{\text{Hydroxo complex}}{[Co(NH_3)_5(OH)]^{2+}}$$

Although base hydrolysis involves an S_N1 mechanism, yet it is consistent with second-order : first order with respect to the complex and first order with respect to the base [see equ. (*ii*)].

Since the S_N1 dissociation step (*b*) which is the rate-determing step uses the conjugate base of the initial complex, the symbol S_N1 CB (*substitution, nucleophile, conjugate-base*) has been used by Garrick in place of S_N1 symbol.

Evidences in favour of S_N1 CB mechanism.

The proposed rapid acid-base equilibirium (*a*) given above requires that the reacting complex sholud have at least one protonic hydrogen atom (H^+) on a non-leaving ligand so that H^+ may transfer to OH^- to form its conjugate acid, H_2O and conjugate base, $[Co(NH_3)_4(NH_2)Cl]^+$ of $[Co(NH_3)_5Cl]^{2+}$ which acts as an acid. Thus a complex having no proton (or no N–H hydrogen) should react with OH^- much more slowly and the rate of reaction would be independent of the concentration of OH^-, $[OH^-]$. In fact it has been observed that the complexes like [Co(CN)$_5$Br] and *trans*-[Co(*py*)$_4$Cl$_2$]$^+$ which, donot have N—H hydrogen undergo hydrolysis much more slowly in basic solution at a rate which is independent of [OH$^-$] over a wide range. Thus in the absence of an acidic proton on the ligands an S$_N$1CB mechanism is not possible. The failure of such complexes to undergo rapid base hydrolysis supports the S$_N$1CB mechanism and the fact that the acid-base properties of the complexes are more important to the rate reaction than the nucleophilic properties of OH .

It may be noted that both the mechanisms *viz* S$_N$2 displacement and S$_N$1 CB give the same rate laws (second-order kinetics) and the same hydroxo products in aqueous solution, because water is a good coordinating agent and because proton shift is very fast. However in a non-hydroxylic solvent (*i.e.* non protonic solvent) different products are predicted to be formed for both the mechanisms under the condition that an excess of some nucleophile reagent other than OH$^-$ ion or H$_2$O (*e.g.* N$_3^-$, NO$_2$, SCN$^-$) is present, *e.g.* the results obtained for the reaction of the type :

$$[\mathrm{Co}(en)_2\mathrm{NO_2Cl}]^+ + \mathrm{Y}^- \xrightarrow[(\mathrm{Y}^- = \mathrm{N_3^-},\ \mathrm{NO_2^-}\ \text{or}\ \mathrm{SCN^-})]{(\mathrm{CH_3})_2\mathrm{SO}} [\mathrm{Co}(en)_2\mathrm{NO_2Y}]^+ + \mathrm{Cl}^-$$

occuring in dimethyl sulphoxide, (CH$_3$)$_2$SO (which is a non hydroxylic solvent) are readily explained by S$_N$1CB mechanism but cannot be explained with S$_N$2 mechanism. The fact that these results can be explained by S$_N$1CB mechanism is a great evidence in favour of S$_N$1CB mechanism. Above reaction in (CH$_3$)$_2$SO is *slow* (half-life in hours) but when trace amount of OH$^-$ or piperidine (which act as catalysts) are added, the reaction is catalysed and thus becomes fast (half-life reduced to minutes), although the same product *viz.* [Co(*en*)$_2$NO$_2$Y]+ is formed in both the cases. Furthermore [Co(*en*)$_2$NO$_2$Cl]$^+$ reacts equally rapidly with equivalent amount of OH$^-$ in the absence of Y$^-$ to form [Co(*en*)$_2$(NO$_2$)(OH)]$^+$. It has been shown that [Co(*en*)$_2$(NO$_2$)(OH)]$^+$ reacts with Y$^-$ very slowly and hence a rapid S$_N$2 mechanism with this as an intermediate followed by rapid reaction with Y$^-$ is ruled out. Instead an active 5-coordinated intermediate (S$_N$1mechanism), [Co(*en*) (*en*-H)NO$_2$]$^+$ is formed in a rate-determining step by the loss of Cl$^-$ ion from the conjugate base, [Co(*en*)(*en*-H)(NO$_2$)Cl] of the original complex, [Co(*en*)$_2$(NO$_2$)Cl]$^+$. This intermediate then in a rapid step picks up Y$^-$. This mechanism is further supported by the observations that the rate of formation of [Co(*en*)$_2$(NO$_2$)Y]+ depends only on the concentration of the base, OH$^-$, not on the nature or concentration of Y$^-$. OH$^-$ and piperidine are used as catalysts while N$_3^-$, NO$_2^-$, SCN$^-$ ions are used as nucleophiles, Y$^-$. For a given catalyst solution the rate of reaction is independent of the concentration of Y$^-$, *i.e.* rate of reaction is the same for N$_3^-$, NO$_2^-$ and SCN$^-$, though different products are formed in each case.

It is clear that these observations can be explained by the S$_N$1CB mechanism but not by the S$_N$2 mechanism which can produce only hydroxo complex. Various steps to get [Co(*en*)$_2$(NO$_2$)Y]$^+$ from [Co(*en*)$_2$(NO$_2$)Cl]$^+$ based on S$_N$1CB mechanism are :

$$(a)\quad \underset{\text{Acid}_1}{[Co(en)_2(NO_2)Cl]^+} + \underset{\text{Base}_2}{B} \xrightleftharpoons{\text{Fast}} \underset{\substack{\text{Base}_1\\ \text{(CB)}}}{[Co(en)(en-H)(NO_2)Cl]} + \underset{\text{Acid}_2}{BH^+}$$

$$(b)\quad \underset{\text{(CB)}}{[Co)en)(en-H)(NO_2)Cl]} \xrightarrow[\substack{\text{Rate-deter-}\\ \text{mining step}}]{\text{Slow }(-Cl^-)} \underset{\substack{\text{5-coordinated}\\ \text{intermediate}}}{[Co(en)(en-H)NO_2]^+} + Cl^-$$

$$(c)\quad \underset{\text{Intermediate}}{[Co(en)(en-H)NO_2]^+} + Y^- \xrightarrow{\text{Fast}} [Co(en)(en-H)(NO_2)Y]$$

$$(d)\quad [Co(en)(en-H)(NO_2)Y] + BH^+ \xrightarrow{\text{Fast}} [Co(en)_2(NO_2)Y]^+ + B.$$

Further interesting evidence in favour of S_N1CB mechanism comes from the study of the reaction of $[Co(NH_3)_5Cl]^{2+}$ and OH^- in aqueous solution at 25°C in presence of H_2O_2. When H_2O_2 is added to the reaction mixture of $[Co(NH_3)_5Cl]^{2+}$ and OH^-, the following changes take place.

Since HO_2^- ion in H_2O_2 is a weaker base but a better nucleophile towards metal ions than OH^-, the reaction of H_2O_2 with OH^- reduces the concentration of OH^- and increases that of H_2O. Thus the reaction between OH^- and H_2O_2 occurs as :

$$OH^- + H_2O_2 \longrightarrow H_2O + HO_2^- \qquad \ldots(i)$$

The tendency of O_2H^- ion to act as a better nucleophile than OH^- should, therefore, increase the rate of base hydrolysis reaction by it compared to OH^-, if it attacks the metal by S_N2 mechanism to form the *peroxo product* as shown below :

$$[Co(NH_3)_5Cl]^{2+} \xrightarrow{\text{Slow }(+HO_2^-)} [Co(NH_3)_5Cl(HO_2)]^+ \xrightarrow{\text{Fast }(-Cl^-)} \underset{\text{Peroxo product}}{[Co(NH_3)_5(HO_2)]^{2+}} + Cl^-$$

On the other hand if the reaction occurs by an S_N1CB mechanism (*i.e.* if the function of OH^- is to form the conjugate base by removing a proton), the addition of H_2O_2 to the reaction mixture should reduce the rate of base hydrolysis reaction compared to OH because of the reduction in the concentration of OH^- ions as is evident from the equilibrium represented by equation (*i*) given above. The rate of an S_N1CB reaction is directly proportional to the concentration of OH^-, $[OH^-]$. Experimentally it has been seen that when 0·018 M H_2O_2 is added to a reaction mixture consisting of 0·0029 M $[Co(NH_3)_5Cl]^{2+}$ and 0·0029 M OH^- in aqueous solution at 25°C, there is a decrease in the value of rate constant by a factor of 3·6, *i.e.* if K_A = rate constant in the absence of H_2O_2 and K_P = rate constant in the presence of H_2O_2 then $K_A/K_P = 3{\cdot}6$. This experimental data supports S_N1CB mechanism.

Anation Reactions

These are the reactions in which an aquo ligand (*i.e.* H_2O molecule) from an aquo complex is replaced from the coordination shell by some anion.

$$\underset{\text{Aquo complex}}{[Co(NH_3)_5(H_2O)]^{3+}} + X^- \longrightarrow [Co(NH_3)_5X]^{2+} + H_2O$$

Thus we find that *an anation reaction is the reverse of acid hydrolysis reaction* (*i.e. aquation*).

Kinetic studies of these reactions in aqueous solutions show that these are bimolecular reactions with a rate which depends on the concentration of the complex and X . However, this information alone is not sufficient to prove that these reactions are bimolecular. The same second-order kinetics would be observed for a unimolecular process such as :

$$\underset{\text{Aquo complex}}{[Co(NH_3)_5(H_2O)]^{+3}} \underset{\substack{\text{Fast}\\(+H_2O)}}{\overset{\substack{\text{Slow}\\(-H_2O)}}{\rightleftharpoons}} \underset{\substack{\text{5-coordinated}\\\text{intermediate}}}{[Co(NH_3)_5]^{3+}} \xrightarrow[+X^-]{\text{Fast}} [Co(NH_3)_5X]^{2+} + H_2O$$

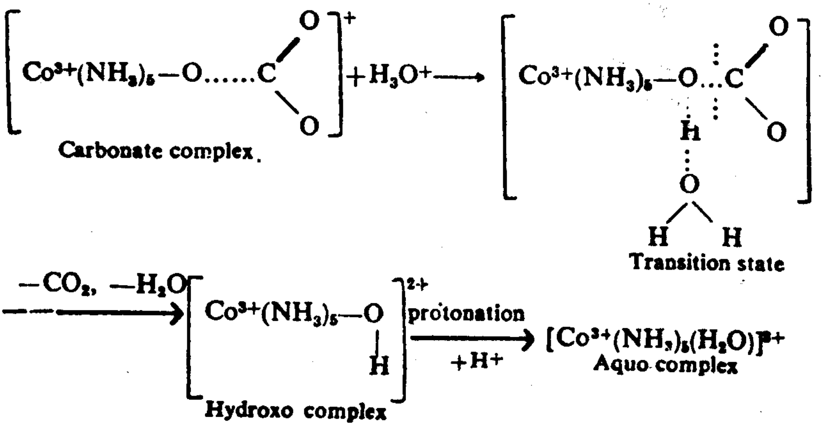
Substitution Reactions Without Breaking Metal-Ligand Bond

There are reactions in which ligand exchange takes place without breaking the metal-ligand bond. One well-known reaction is the preparation of an aquo complex, $[Co^{3+}(NH_3)_5(H_2O)]^{3+}$ from its corresponding carbonato complex, $[Co^{3+}(NH_3)_5CO_3]^+$ with the production of CO_2. When this reaction is carried out in presence of $(H_3O^{18})^+$, none of O^{18} is found in the resulting aquo complex and CO_2. Hence CO_2 is produced by the cleavage of C—O bond which keeps Co—O bond intact during the aquation reaction

$$\underset{\substack{\text{Carbonate}\\\text{complex}}}{\left[(NH_3)_5Co^{3+}-O\vdots-CO_2\right]^+} + 3(H_3O^{18})^+ \longrightarrow \underset{\text{Aquo complex}}{[Co^{3+}(NH_3)_5(H_2O)]^{3+}} + 2H_2O^{18} + CO_2$$

Mechanism

The most likely path for this reaction is believed to involve proton attack on the oxygen atom bonded to Co followed by the expulsion of CO_2 and H_2O and then protonation of the hydroxo complex.



Thus this is a decarboxylation reaction rather than an acid hydrolysis reaction.

Another interesting reaction which takes place without the cleavage of metal-ligand bond is the formation of a nitrito complex, $[Co^{3+}(NH_3)_5ONO]^{2+}$ from its corresponding aquo complex, $[Co^{3+}(NH_3)_5(H_2O)]^{3+}$.

$$\underset{\text{Aquo complex}}{[Co^{3+}(NH_3)_5(H_2O)]^{3+}} + NO_2^- \longrightarrow \underset{\text{Nitrito complex}}{[Co^{3+}(NH_3)_5ONO]^{2+}} + H_2O$$

The reaction is quite rapid which in itself suggests that Co—O bond is not broken. Confirmatery evidence for this view is provided by studies using O^{18}, *e.g.*

$$\underset{\text{Aquo complex}}{[(NH_3)_5Co^{3+}-O^{18}H_2]^{3+}} + NO_2^- \longrightarrow \underset{\text{Nitrito complex}}{[(NH_3)_5Co^{3+}-O^{18}NO]^{2+}} + H_2O$$

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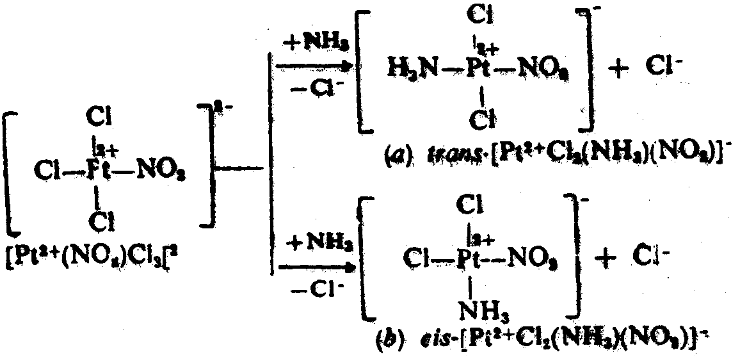
16

Ligand Substitution Reactions in Square-planar Complexes

Much of the discussion in this chapter deals with the kinetics and mechanism of substitution reactions of Pt(II) square-planar complexes. It will be seen that these complexes generally proceed by *bimolecular displacement* (S_N2) *mechanism* while octahedral comlexes run by dissociative process as we have already seen.

The Trans-Effect

Consider the substitution reactions in Pt(II) square-planar complex, $[Pt(NO_2)Cl_3]^{2-}$ with NH_3 to yield $[Pt(NO_2)Cl_2(NH_3)]^-$. Theoretically there are two possible reaction products : (*a*) and (*b*) shown below :



$[Pt^{2+}(NO_2)Cl_3]^{2-}$

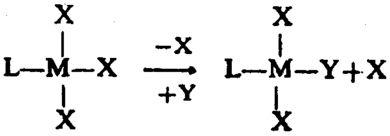
(*a*) *trans*-$[Pt^{2+}Cl_2(NH_3)(NO_2)]^-$

(*b*) *cis*-$[Pt^{2+}Cl_2(NH_3)(NO_2)]^-$

Experiments have, however, shown that it is only (*a*) (*i.e.* *trans*-isomer) which is formed. (*a*) is formed by the replacement of Cl^- lying *trans* to NO_2^- in $[Pt(NO_2)Cl_3]^{2-}$ by NH_3. The formation of (*a*) is explained by saying that Cl^- ion lying *trans* to NO_2^- in

$[Pt(NO_2)Cl_3]^{2-}$ is far more easily replaced by NH_3 than either of the two Cl^- ions lying *cis* to NO_2^- ion. The phenomena of such type of replacement is called **trans effect.** Groups like NO_2^- which direct the entering ligand to occupy the position *trans* to them are called *trans directing groups* and the property of these groups due to which the groups lying *trans* to them are replaced far more readily by the entering ligand is called *trans- directing character* (or *trans-directing influence* or *simply trans-effect*).

Chatt *et al* have proposed that *the trans-effect of a group coordinated to a metal ion is the tendency of that group to direct an incoming group to occupy the position trans to that group. Trans-*effect is also defined as the *effect of a coordinated group on the rate of the replacement of a group lying trans to it in a metal, complex, e.g.* in the *trans* form of square-planar complex, MLX_3 (L and X are *trans* to each other), if the ligand X which is *trans* to L is rapidly replaced by another group, say Y, to give MLX_2Y, L is said to have large *trans* effect or *trans* directing character. Thus L has greater *trans* effect than X (L > X).



$$\text{L—}\underset{\text{X}}{\overset{\text{X}}{\text{M}}}\text{—X} \xrightarrow[+Y]{-X} \text{L—}\underset{\text{X}}{\overset{\text{X}}{\text{M}}}\text{—Y} + \text{X}$$

trans-MLX_3 MLX_2Y

(L and X *trans* to each other)

By measuring rates a series of ligands can be put into an order of decreasing *trans*-effect. Such an order would not necessarily be invariant but might depend on the metal complex and also on the incoming group, Y. The approximate order of decreasing *trans*-effect of some common ligands is :

High end——————trans effect decreasing——————→Low end

CN^-, CO, C_2H_4, NO > PR_3, H^- > CH^-, $SC(NH_2)_2$ > $C_6H_5^-$, NO_2^-, I^-, SCN^- (S-bonded) > Br^-, Cl^- > *py*, NH_3, OH^-, H_2O.

The series given above is called **trans-effect series.**

The ligands lying at the high end of the series have vacat π or π* orbitals which can accept electrons from metal orbital to form metal-ligand π-bond (*dπ—dπ* or *dπ—pπ* bond). These ligands are, therefore, called π-bonding ligands. The *trans*-directing ability of these π-bonding ligands increases with the increase of their ability to form metal-ligand π-bonds.

The *trans*-effect of the ligands which are not able to form metal-ligand π-bonds increases with the increase of their polarisability *e.g.*

——— polarisability increases ———→

$Cl^- < Br^- < I^-$

——— *trans*-effect increases ———→

Most of the work on *trans*-effect has been done on square planar Pt(II) complexes.

Uses of Trans-Effect

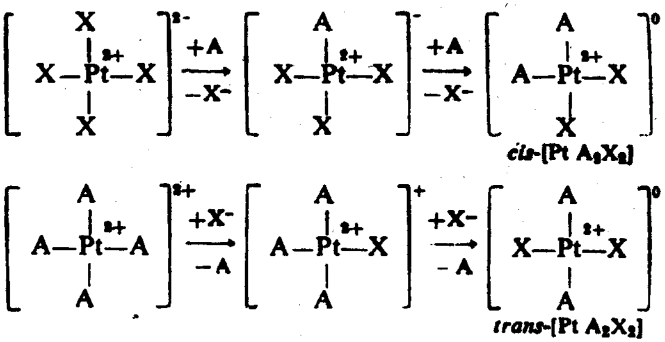
The following are important uses.

(1) Synthesis of Pt(II) Complexes

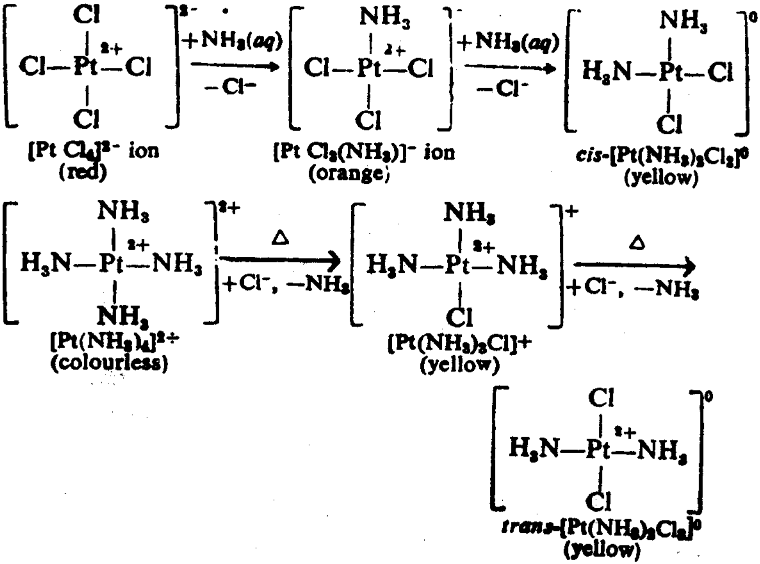
The preparation of the following Pt (II) complexes illustrate the synthesis uses of *trans*-effect.

(A) **Synthesis of cis- and trans-$[PtA_2X_2]^0$.** Here A = amine, NH_3, PR_3 and X = halide ion, NO_2^-, SCN^-. The synthesis of these isomers is based on the following facts :

(*a*) If the *trans*-effect of X^- is greater than that of A ($X^- > A$), the *cis*-isomer is obtained from $[PtX_4]^{2-}$ while the *trans*-isomer is isolated from $[PtA_4]^{2+}$ as shown below :



For the synthesis of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ where $Cl^- > NH_3$, the following scheme is applied.



Cis-isomer is obtained by treating $[Pt^{II}Cl_4]^{2+}$ ion with NH_3. The reaction giving the cis-isomer proceeds through the following two steps :

(*i*) In this step any of the four Cl^- ions is replaced by NH_3 molecule to give $[Pt^{II}(NH_3)Cl_3]^-$ ion.

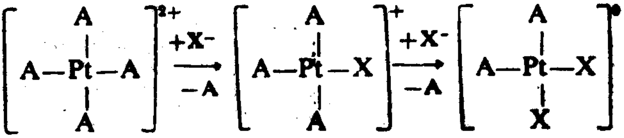
(*ii*) In this step since Cl^- ion has a greater *trans*-directing influence than NH_3, $(Cl^- > NH_3)$, Cl^- ion lying *trans* to another Cl^- in $[PtCl_3(NH_3)]^-$ is readily replaced by NH_3 than is the Cl^- ion lying *trans* to NH_3.

The *trans*-isomer is obtained by heating $[Pt^{II}(NH_3)_4]^{2+}$ ion with Cl^- ion (*i.e.* with HCl). Here also the reaction proceeds through two steps :

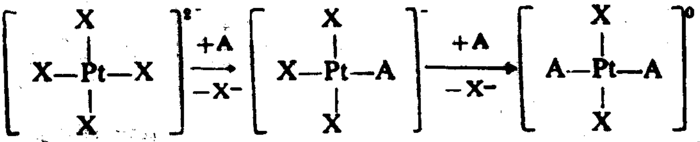
(*i*) In this step any of the four NH_3 molecules is replaced by Cl^- ion to give $[Pt(NH_3)_3Cl]^+$ ion.

(*ii*) In this step since Cl^- ion has the superior *trans*-directing influence $(Cl^- > NH_3)$, the remaining NH_3 molecule to be most readily displaced is the one *trans* to Cl^- ion to give the *trans*-isomer. This can be said in other words that the superior *trans*-directing influence of Cl^- ion causes the second Cl^- ion to occupy a position trans to the first one, producing *trans*-$[Pt^{II}(NH_3)_2Cl_2]^0$.

(*b*) If the *trans*-effect of $A > X^-$, then *cis*-isomer is obtained from $[PtA_4]^{2+}$ while the *trans*-isomer is isolated from $[PtX_4]^{2-}$ as shown below :

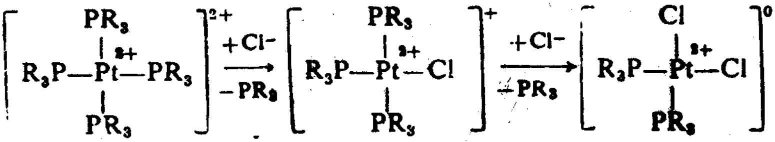


cis-$[PtA_2X_2]^0$

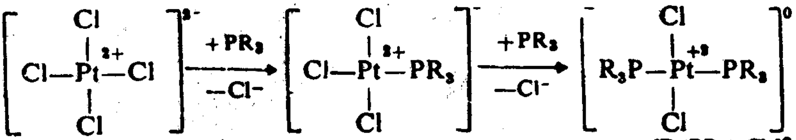


trans-$[Pt\,A_2X_2]^0$

Synthesis of *cis*- and *trans*-$[PtCl_2(PR_3)_2]^0$ where $PR_3 > Cl^-$ is done according to the following scheme



cis-$[Pt(PR_3)_2Cl_2]^0$

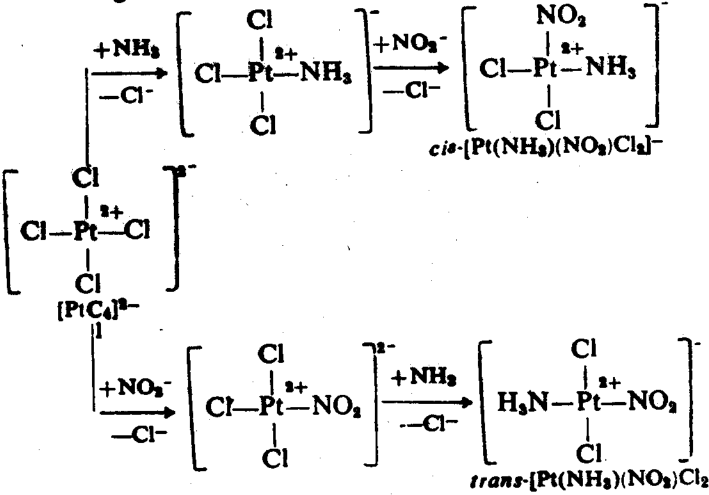


trans-$[Pt(PR_3)_2Cl_2]^0$

In the first reaction PR_3 molecule lying *trans* to another PR_3 molecule is more easily replaced by Cl^- ion than is PR_3 molecule lying *trans* to Cl^- ion and thus *cis*-isomer is obtained. The formation of *cis*-isomer shows that PR_3 has greater *trans* effect than Cl^- ion. On the basis of similar reasoning the formation of *trans*-isomer can also be explained.

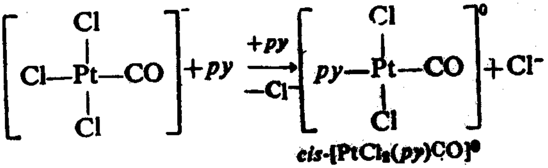
(B) **Cis- and trans-$[PtCl_2(NO_2)(NH_3)]^0$.** The preparation of the two isomers is based on the fact that the *trans* directing ability of Cl^-, NH_3 and NO_2^- groups is in the order : $NH_3 < Cl^- < NO_2^-$.

The *cis*-isomer is made by the action of NH_3 on $PtCl_4^{2-}$ and of NO_2^- on the product. The *trans*-isomer is obtained by reversing the order of reagent addition.



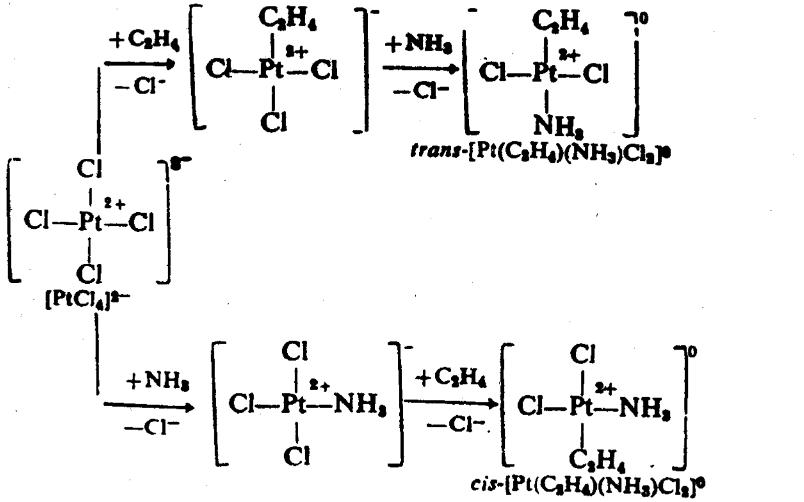
Quite evidently *cis*-isomer is obtained because $Cl^- > NH_3$ while in *trans*-isomer $NO_2^- > Cl^-$.

(C) **Cis-$[PtCl_2(py)(CO)]^0$.** It is prepared as follows :



In this reaction the Cl^- ion lying *trans* to CO group is more easily replaced by *py* than either of the two Cl^- ions lying *trans* to each other and the resulting product is the *cis*-isomer. The replacement of Cl^- ion *trans* to CO group is due to greater *trans* directing ability of CO than Cl ($CO > Cl^-$).

(D) **Cis- and trans-$[Pt(C_2H_4)(NH_3)Cl_2]^0$.** Since ethylene (C_2H_4) is more *trans*-directing than Cl^- ($C_2H_4 > Cl^-$) which in turn is more so than NH_3 ($Cl^- > NH_3$), different isomers may be prepared by $[PtCl_4]^{2-}$ by changing the order of substitution as follows :

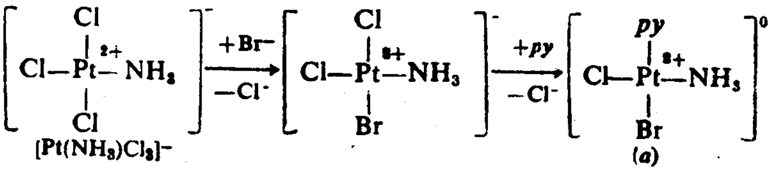


$[PtCl_4]^{2-}$

trans-$[Pt(C_2H_4)(NH_3)Cl_2]^0$

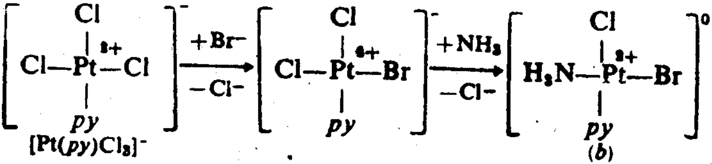
cis-$[Pt(C_2H_4)(NH_3)Cl_2]^0$

(E) **Isomers of $[Pt(py)(NH_3)BrCl]^0$.** This complex exists in three isomeric forms : (*a*), (*b*) and (*c*) which are prepared as follows. Their preparation is based on the fact that the *trans*-directing ability of NH_3, *py*, Cl^- and Br^- is in the order : $NH_3 < py < Cl^- < Br^-$ and Pt—N bond strength is greater than that of Pt—Cl bond.



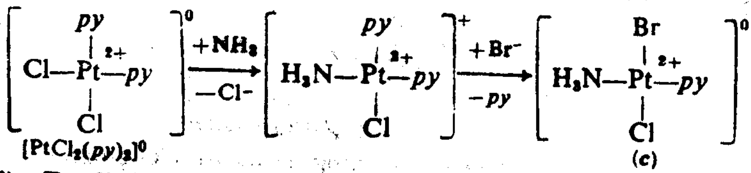
$[Pt(NH_3)Cl_3]^-$

(*a*)



$[Pt(py)Cl_3]^-$

(*b*)

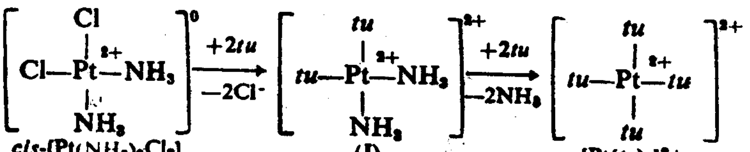


$[PtCl_2(py)_2]^0$

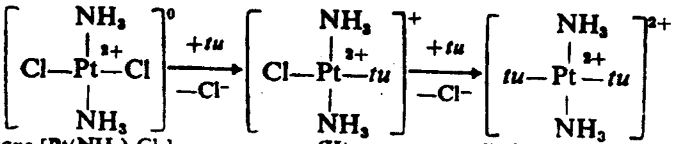
(*c*)

(2) **To distinguish between cis- and trans-isomers of $[PtA_2X_2]^0$ type complexes** :

In addition to its utility in the synthesis of the desired Pt(II) complexes, the *trans*-effect has also been used by Russian chemists to distinguish between the *cis*- and *trans*- isomers of $[PtA_2X_2]^0$ type complexes (A = NH_3 or amine, X = a negative group), *e.g.* *cis*-$[Pt(NH_3)_2Cl_2]$ reacts with thiourea, $NH_2.CS.NH_2$ (abbreviated as *tu*) to give $[Pt(tu)_4]^{2+}$ whereas under the same conditions the *trans*-$[Pt(NH_3)_2Cl_2]^0$ gives $[Pt(tu)_2(NH_3)_2]^{2+}$.



cis-$[Pt(NH_3)_2Cl_2]$ (I) $[Pt(tu)_4]^{2+}$



trans-$[Pt(NH_3)_2Cl_2]$ (II) $[Pt(NH_3)_2(tu)_2]^{2+}$

Compound (I) in the first reaction reacts further with *tu* to give the completely substituted product, $[Pt(tu)_4]^{2+}$ because of the larger *trans* effect of *tu* than NH_3. In (II) the *trans* effect of NH_3 being smaller than that of *tu*, NH_3 molecules are not sufficiently reactive to be replaced by *tu*. Thus Cl^- ion *trans* to *tu* in (II) is replaced by further *tu* molecule to form $[Pt(NH_3)_2(tu)_2]^{2+}$. The use of thiourea reaction, to assign structures is known as **Kurnakov's test**. Similar results have been reported for reactions of thiosulphate ion ($S_2O_3^{2-}$) instead of thiourea, *e.g. cis-* and *tran*-$[Pt(NH_3)_2Cl_2]^0$ reacts with the excess of $S_2O_3^{2-}$ ion to form $[Pt^{II}(S_2O_3)_4]^{6-}$ and $[Pt^{II}(NH_3)_2(S_2O_3)_2]^{2-}$ respectively.

Theories of Trans-Effect

Several theories have been proposed for the explanation of the trans-effect. Only two theories representing different approaches will be discussed here :

(1) Electrostatic Polarisation Theory

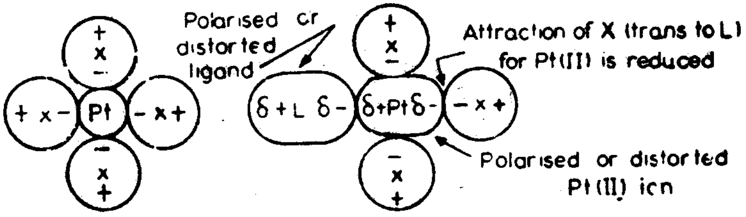
This is the earliest theory proposed by *Grinberg* (1927) to account for the *trans*-effect and is a thermodynamic approach.

In order to understand this theory, we shall consider the following two types of square planar complexes of Pt(II).

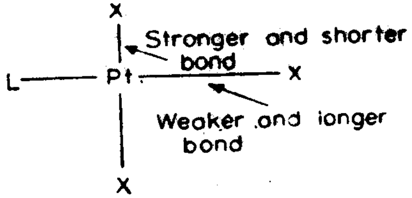
(*i*) **PtX_4 type complex.** According to this theory the primary positive charge on Pt(II) induces a dipole in all the four X's ligands. These dipoles induced by the cental metal ion cancel each other and the resultant dipole is zero [Fig. 16·1(*a*)]. Thus *none of the four ligands shows trans effect.*

(*ii*) **$PtLX_3$ type complex.** In case of this type of complex as well, the primary positive charge on Pt(II) induces a dipole in all the four ligands. The two X's ligands which are similar and *trans* to each other balance each other, while the other two ligands *viz.* L and X (also *trans* to each other) donot, since L is large and has greater polarizability than X. The net result is that the dipole induced by the positive charge of Pt(II) on the ligand L induces a corresponding dipole in Pt(II), *i.e.* Pt(II) and the ligand L both become polarised or distorted [*see* Fig. 16·1(*b*)]. This polarisation takes place in such a way that the positive charge at the point of Pt(II) directly opposite (*i.e. trans*) to L is reduced. Hence the attraction of X for Pt(II) is also reduced and the bond *trans* to L is *weakened and conse-*

quently lengthed, i e. Pt—X bond *trans* to L is weaker and longer than Pt—X bonds *cis* to L [*see* Fig. 16·1(*c*)]. The weakening of Pt—X bond *trans* to L fascilitates the replacement of X *trans* to L by the entering ligand. Thus the ligand L which has the greatest polarisability also has greatest *trans* effect. As the *trans* effect of L increases the bond length of Pt—X also increases [Fig. 16·1(*c*)].



(*a*) PtX_4 complex **(*b*) PtX_3L complex**



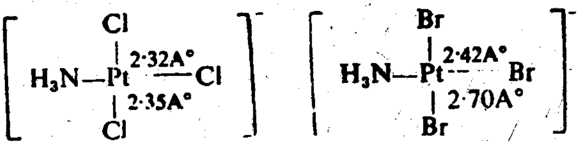
(*c*) PtX_3L complex with bonds of unequal length

(L shows greater *trans* effect than X)

Fig. 16·1. Electrostatic polarisation theory (due to Grinberg, 1927) to explain the trans-effect in square planar complexes. This diagram represents the polarisation of metal ion induced by highly polarisable ligand, L in MX_3L as compared to MX_4 (signs show only polarisation effect ; the central atom normally carries positive charge and the ligands are electrondonating).

This theory predicts that the *trans*-effect will be important only if the central metal is itself polarisable.

Experimental evidence in favour of polarisation theory. We have seen that if L is highly polarisable in PtX_3L complex, Pt—X bond *trans* to L is longer than the Pt—X bond *cis* to L, *i.e.* as the *trans* effect of L increases, the length of Pt—X bond also increases. This fact becomes evident when we find that Pt—X bond *trans* to X^- in the complexes of $[Pt(NH_3)X_3]^-$ type (were X = Cl, Br^-) is longer than the Pt—X bond *cis* to it (*see* Fig. 16·2). *Thus the ligand oppo-*



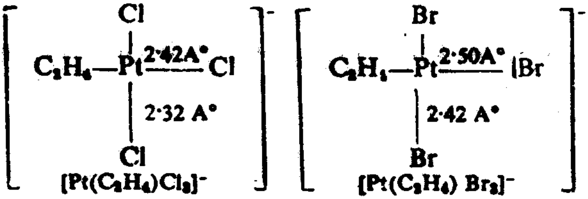
$[Pt(NH_3)Cl_3]^-$ $[Pt(NH_3)Br_3]^-$

Trans-effect order : $Cl^- > NH_3$ $Br^- > NH_3$

Fig. 16·2. Trans-order of X^- and NH_3 in $[Pt(NH_3)X_3]^-$ type complexes.

site to the longer bond will show greater trans effect, i.e, the trans effect order is $X^- > NH_3$.

Similary in case of complexes of $[Pt(C_2H_4)X_3]^-$ type (where $X=Cl^-$ Br^-) the Pt—X bond *trans* to C_2H_4 is longer than that *cis* to it (see Fig, 16·3). Thus the ligand opposite to the longer bond has greater *trans* effect, *i.e.* $C_2H_4 > X^-$.



Trans-effect-order : $C_2H_4 > Cl^-$ $C_2H_4 > Br^-$

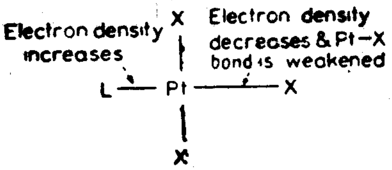
Fig. 16·3. Trans-order of X^- and C_2H_4 in $[Pt(C_2H_4)X_3]^-$ type complex.

(2) π-Bonding Theory

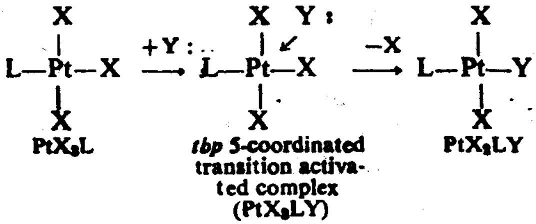
Electrostatic polarisation theory can well explain the *trans*-effect of the ligands lying at the low end of the series like H_2O, OH^-, NH_3 etc. However, this theory cannot explain the high *trans*-effect of the π-bonding ligands like PR_3, NO, CO, C_2H_4, CN^- which lie at the high end of the series. π-bonding theory which is due to Chatt (1955) and Orgel (1956) accounts well for the high *trans* effect of such ligands.

According to this theory the vacant π or π* orbitals of the π-bonding ligands accept a pair of electrons from the filled *d*-orbitals of the metal (d_{xz} or d_{yz} orbital) to form metal-ligand π-bond ($d\pi-d\pi$ or $d\pi-p\pi$ bond).

In case of Pt(II) square-planar complex, PtX_3L (L is the π-bonding ligand) the d_{yz} orbital of Pt(II) with a pair of electrons overlaps with the empty p_z orbital of the π-bonding ligand, L to form the $d\pi-p\pi$ bond between Pt(II) and L. The formation of the π-bond in the complex increases the electron density in the direction of L and diminishes it in the direction of the ligand, X *trans* to L. Thus Pt—X bond *trans* to L is weakened (*see* in the margin).



The weakening of Pt—X bond *trans* to L fascilitates the approach of the entering ligand, say Y : with its lone pair in the direction of diminished electron density to form the five-coordinated transition state complex, $PtLX_3Y$ which, on losing X, yields $PtLX_2Y$. In the formation of $PtLX_2Y$ the ligand X *trans* to L is replaced by the incoming group, Y. The transition state complex has distorted *trigonal-bipyramidal* (*tbp*) structure in which two X's groups which are *cis* to L both in the initial and final states form the apexes.



The formation of $d\pi-p\pi$ bond between Pt(II) and the π-bonding ligand, L in the 5-coordinated transition activated complex is shown below in Fig. 16·4.

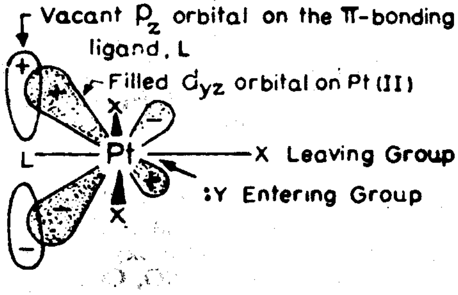


Fig. 16·4. Formation of $d\pi-d\pi$ bond in *tbp* 5-coordinated activated complex formed during the substitution reaction in Pt(II) square-planar complex, $PtLX_3$:

$$PtLX_3+Y \longrightarrow PtLX_2Y+X.$$

Smaller *d*-orbital lobes adjacent to the group X which is to be replaced by Y, may be noted in the figure.

A schematic representation of double bond in $Pt{=}PR_3$ is shown in Fig. 16·5. σ-bond is formed by the donation of a pair of electrons from phosphorus to platinum and the π-bond by the overlap of a filled *d*-orbital of platinum and a vacant *d*-orbital of phosphorus atom. If the ligand PR_3 and X are in the *xy* plane, the *d*-orbital shown is either d_{xz} or d_{yz}.

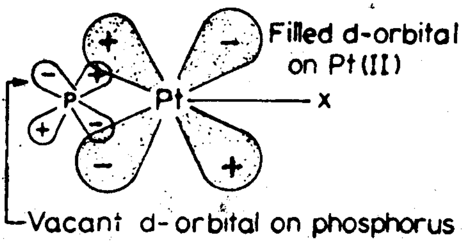


Fig. 16·5. Schematic representation of R_3P-Pt double bond.

Chatt *et al* emphasises that the removal of charge from Pt(II) by π-bonding of L enhances the addition of the entering group, Y and favours a more rapid reaction. According to Orgel the formation of π-bond between Pt(II) and π-bonding ligand L enhances the stability of the 5-coordinated transition state complex, thus lowering the activation energy for its formation and speeding up the reaction.

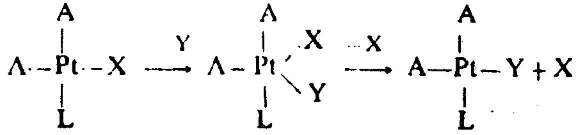
That the formation of π-bond weakens the metal-ligand bond *trans* to a π-bonding ligand is evident from the fact that in the square-planar complex anion, $[(C_2H_4)PtCl_3]$, the Pt—Cl bond *trans* to C_2H_4 is slightly larger than those *cis* to C_2H_4. Pt-*trans*-Cl stretching frequency is lower than the average of the two Pt-*cis*-Cl frequencies. Lower the frequency, the weaker (*i.e.* logner) the bond.

Mechanism of Substitution Reactions

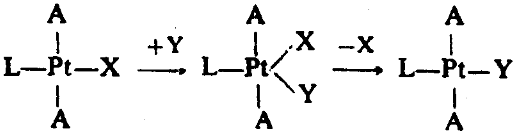
Substitution reactions in Pt(II) square-planar complexes proceed by *bimolecular displacement* (S_N2) *mechanism* involving either the solvent or the entering ligand as the nucleophilic agent.

Experimental evidence in favour of S_N2 mechanism has been presented. Because of steric and electronic reasons the coordination number of the metal is increased to include the entering ligand. The metal is exposed for attack above and below the plane. Furthermore Pt(II) which is a d^8 system has a vacant p_z-orbital of relatively low energy which accepts the pair of electrons donated by the entering ligand.

Substitution reactions of *cis*- and *trans*- PtA_2LX with Y to yield PtA_2LY have been explained on the basis of nucleophilic attack of Y through *trigonal bipyramidal* (*tbp*) structure. The process is entirely stereospecific : *cis*-PtA_2LX yields *cis* product and *trans* gives *trans*.



cis-PtA_2LX (L and X *cis* to each other) *tbp* *cis*-product (PtA_2LY)



tras-PtA_2LX (L and X *trans* to each other) *tbp* *trans*-product (PtA_2LY)

Martin and his students have shown that the rates of hydrolysis reaction of the four complexes *viz.* $[PtCl_4]^{2}$, $[Pt(NH_3)Cl_3]$, $[Pt(NH_3)_2Cl_2]^0$ and $[Pt(NH_3)_3Cl]^+$ vary only by a factor of two (quite a small effect), although the charge on the reactant Pt(II) complex changes from −2 to +1. This variation in rate is remarkably small. The breaking of a Pt—Cl bond should become much more difficult in this series of four complexes as the charge on the complex becomes more positive. However, the formation of a new bond (*i.e.* the attraction of Pt for a nucleophile) should increase in the same order. Since there is small effect of change of charge on the complex on the rate of reaction, both Pt—Cl bond breaking and Pt...OH_2 bond making are of comparable importance. This is a strong evidence in favour of S_N2 mechanism.

For the substitution reaction of square planar complex, $[PtA_3X]^{n+}$ with Y^- to yield $[PtA_3Y]^{n+}$ in water involves a complication, since the solvent water also behaves as a potential ligand.

$$[PtA_3X]^{n+}+Y^- \xrightarrow{H_2O} [PtA_3Y]^{n+}+X^-$$

For this reaction a two-term rate law is given by the expression :

$$\text{Rate} = k_1[PtA_3X^{n+}]+k_2[PtA_3X^{n+}][Y^-] \quad ...(i)$$

Here k_1 = first-order rate constant for solvent-controlled reaction,

and k_2 = second-order rate constant for reaction with Y^-.

A convenient analysis of rate constants can be made by running the reactions with a large excess of nucleophile, Y^-. Under this condition the observed rate-constant, k_{obs}, is pseudo first-order and is related to k_1 and k_2 as :

$$k_{obs} = k_1 + k_2[Y] \quad ....(ii)$$

This equation shows that for the same complex with different reagents linear plots of k_{obs} against nucleophile concentration, [Y]

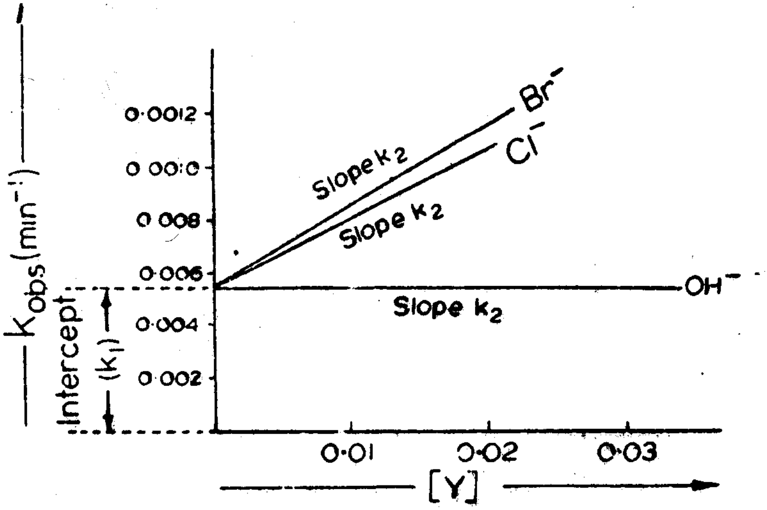


Fig. 16·6. Plot of observed rate-constant, k_{obs} for the reaction : $[Pt^{2+}(dien)Cl]^{+}+Y^- \longrightarrow [Pt^{2+}(dien)Y]^{+}+Cl^-$ ($Y=OH^-, Cl^-, Br^-$) against concentration of the nucleophile, [Y]. *dien* = $NH_2(CH_2)_2NH(CH_2)_2NH_2$.

should be obtained having the same intercepts, k_1 and different slopes, k_2 (*see* Fig. 16·6).

The rate-law represented by equation (*ii*) indicates that the reaction of $[PtA_3X]^{n+}$ with Y^- to yield $[PtA_3Y]^{n+}$ is occurring by two-path mechanism only one of which involves Y^- in the rate-determining step. These two paths are shown in Fig. 16·7. The upper path is the solvent path (also called Y^- *independent path*) and the lower path is the direct path (*reagent path*). In the solvant path the solvent, H_2O replaces X^- in a slow and is subsequently replaced by Y^- in a rapid step. Experience shows that Y^- independent path is not an S_N1 process, but is a direct (S_N2) displacement of leaving group by nucleophile in brobably the second-order path while the solvent path gives pseudo first-order kinetics.

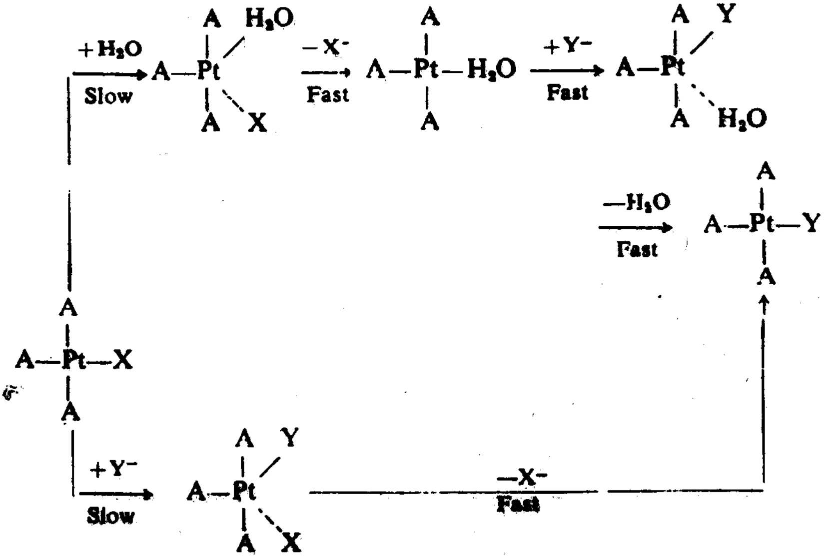


Fig. 16·7. Two-path mechanism proposed for the substitution reaction: $[PtA_3X]+Y \longrightarrow [PtA_3Y]+X$

For the sake of convenience charges have been omitted.

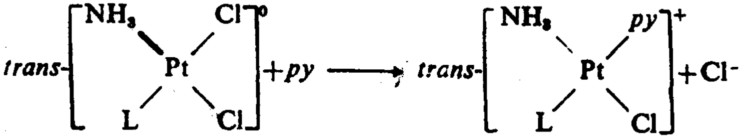
The rate-constant, k_1 is due to the solvent path, while k_2 is due to the direct displacement of the leaving group by nucleophile. Thus it becomes convenient to designate the solvent path k_1 as k_S and the direct displacement path k_2 as k_Y so that equation (*ii*) becomes

$$k_{obs} = k_S + k_Y[Y^-] \qquad ...(iii)$$

Factors affecting the rates of substitution reactions in square planar complexes

Most of the kinetic data available deal with the effects of various factors on the rates of substitution reactions in Pt(II) square planar complexes. Some factors are :

(*i*) **Trans-effect.** In order to see the effect of ligands L *trans* to the leaving group, Cl^- in some analogous Pt(II) square-planar complexes, relative rates of the following reaction have been studied

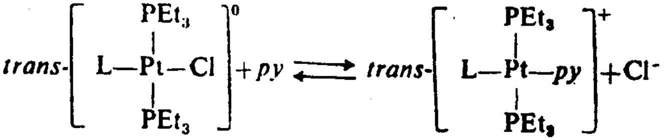


($L=C_2H_4, NO_2^-, Br^-, Cl^-$)

In this reaction it has been found that when L is replaced by C_2H_4, NO_2^-, Br^- or Cl^- in the comblex, $[Pt(NH_3)Cl_2L]^0$, the relative rates of reaction decrease with the decrease of relative *trans*-effect of these groups while the activation energies, E_a increase in this order.

Relative *trans*-effect	:	C_2H_4 >	NO_2^- >	Br^- >	Cl^-
Relative rates	:	> 100 >	90	> 3	> 1
E_a (kcal/mole)	:	—	11	< 17	< 19

In order to see the *trans*-effect of some unusual ligands the relative rates of the following reaction have been evaluated



$$trans\text{-}\left[\begin{array}{c} PEt_3 \\ | \\ L\text{—}Pt\text{—}Cl \\ | \\ PEt_3 \end{array}\right]^0 + py \rightleftharpoons trans\text{-}\left[\begin{array}{c} PEt_3 \\ | \\ L\text{—}Pt\text{—}py \\ | \\ PEt_3 \end{array}\right]^+ + Cl^-$$

in ethanol solution at 25°C. In this reaction only the ligand L which is *trans* to the leaving group *viz.* Cl^- group is changed by other groups like H^-, CH_3^-, $C_6H_5^-$ etc. Cl^- is replaced by *py* to yield *trans*-$[Pt(PEt)_2pyL]^+$. The rate data given below are in terms of k_1 and k_2 defined by the equation :

$$k_{obs}=k_1+k_2\,[Y]$$

These reactions donot go to completion. The approach to equilibrium is given by a pseudo-first-order process with a rate-constant given by the above equation. In this case k_1 and k_2 are composite quantities for forward and reverse reactions and both contribute to the over all observed rates.

***Trans*-directing ability of group L *trans* to Cl⁻ which is leaving group** : H^- > methyl > phenyl ~ *p*-chlorophenyl ~ *p*-methoxy phenyl > biphenyl > Cl^-

k_1 (min⁻¹) : $1{\cdot}1 > 1\times10^{-2} > 2\times10^{-3} \sim 2\times10^{-3} \sim 1{\cdot}7\times10^{-3} > 1\times10^{-3} > 6\times10^{-6}$

k_2 (min⁻¹) : $2{\cdot}5\times10^{2} > 4 > 9{\cdot}5\times10^{-1} \sim 9\times10^{-1} \sim 7{\cdot}9\times10^{-1} > 5{\cdot}8\times10^{-1} > 2{\cdot}4\times10^{-3}$

These results show that the effect on the rates of reaction of different L groups *trans* to Cl^- which is being replaced by *py* decreases in the following order :

H^- > methyl > phenyl ~ *p*-chlorophenyl ~...... This is also the order of *trans*-effect of these groups.

(*ii*) **Effect of leaving group.** The reaction :

$[Pt^{2+}(dien)X]^{+} + py \longrightarrow [Pt(dien)(py)]^{2+} + X^{-}$

$[X = NO_3^-, H_2O, Cl^-$ etc).

has been studied and the rates of reaction have been obtained. The rates of reaction show that if the leaving group, X^- is replaced by NO_3^-, H_2O, Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_2^- and CN^-, the rates decrease in the order :

$$NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$

Note that in the square-planar complex, $[Pt(dien)X]^+$ three coordination positions are always occupied by the inert *dien* ligand while the fourth one is occupied by X^- which may be NO_3^-, H_2O, Cl^- etc.

(*iii*) **Solvent effect.** Since there is considerable evidence of the fact that in the solvent path the solvent replaces X^- directly, it is to be expected that with the increase in the coordinating ability of the solvent, the contribution made by this path to the overall rate of reaction would also increase. This is in accordance with the experimental results of the solvent on the rate of $^{36}Cl^-$ exchange with *trans* $[Pt(py)_2Cl_2]$. Some of the results are given in Table 16·1. Under the experimental condition *viz*., moderately low concentration of Cl^-, the solvents were divided into two categories :

(*a*) Those where the rate of exchange does not depend on $[Cl^-]$. These are good coordinating solvents like H_2O, ROH and provide almost entirely a solvent path for exchange ($k_S >> k_{Cl}[Cl^-]$ or $k_1 >> k_2$).

(*b*) Those where the rate of exchange depends on the concentration of Cl^-. These are poor coordinating solvents like CCl_4, C_6H_6 and contribute little to the overall rate of reaction. The exchange occurs by Cl^- acting a nucleophile ($k_S < k_{Cl}[Cl^-]$ or $k_1 < k_2$).

For good solvents it may by noted that the values of k_{obs} increases in the order : ROH < H_2O < CH_3NO_2 < $(CN_3)_2SO$ (Table 16·1). This series shows that the rate of exchange is faster in $(CH_3)_2SO$ than in water.

Table 16·1 *Effect of solvent on the rate of* $^{36}Cl^-$ *exchange with trans* $[Pt(py)_2Cl_2]$ *at 25°C.*

Solvents in which rate of exchange is independent of $[Cl^-]$	k_{obs} (*min*$^{-1}$)	*Solvents in which rate is dependent on* $[Cl^-]$	k_{obs} (*min*$^{-1}$)
H_2O	$2{\cdot}1\times10^{-3}$	CCl_4	1×10^{-4}
C_2H_5OH	$8{\cdot}5\times10^{-4}$	C_6H_6	2×10^{-4}
m-C_3H_7OH	$2{\cdot}5\times10^{-4}$	*m*-cresol	2×10^{-4}
$(CH_3)_2SO$	$2{\cdot}3\times10^{-2}$	*tert*-C_4H_9OH	1×10^{-3}
CH_3NO	$1{\cdot}9\times10^{-3}$		

(*iv*) **Effect of charge on the complex.** This has already been discussed under *Mechanism of substitution reactions.*

Cis-trans isomerisation in planar complexes

Cis-trans isomerisations in Pt (II) complexes are not common, yet they do occur. Unfortunately neither kinetic nor exchange studies have been made to obtain information in the mechanism of isomerisations. However some observations suggest that the isomerisation proceeds by an inter molecular process. The strongest evidence in support of this process is that a trace of some catalyst is required for these isomerisations.

Since substitution reactions of Pt(II) complexes are generally stereospecific (*i.e.*, they proceed with retention of configuration), *cis-trans* isomerisation is explained in terms of two-steps mechanism which is shown below in Fig. 16·8 for the isomerisation of *cis*-[Pt(PR$_3$)$_2$Cl$_2$]^0 in solution containing excess of PR$_3$ to the corresponding *tras*-isomer. In the first step the Cl$^-$ group is replaced by the catalyst PR$_3$ to from [Pt(PR$_3$)$_3$Cl]$^+$. In the second step the reverse happens and *trans*-[Pt(PR$_3$)$_2$Cl$_2$]^0 is formed along with the catalyst. Steps have been shown as (*i*) and (*ii*).

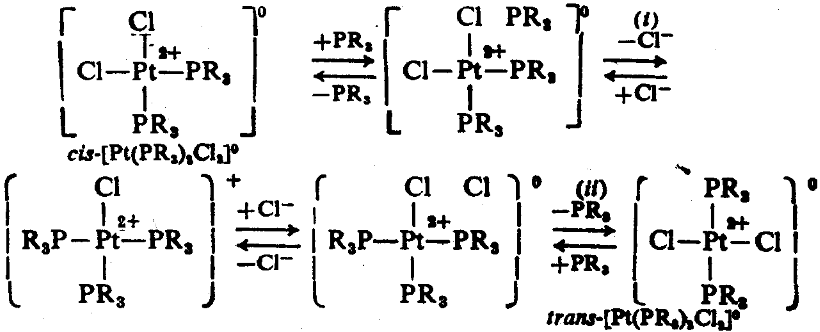


Fig. 16·8. Two-steps mechanism for isomerisation of *cis*-[Pt(PR$_3$)$_2$Cl$_2$]^0 to the corresponding *trans*- form.

References

See the references of chapter 15.

17

Electron-transfer (or Oxidation-Reduction) Reactions in Coordination Compounds

These are the reactions in which the transfer of an electron from one atom to the other occurs, and hence the oxidation state of some atoms change. These reactions may be divided into the following two classes :

(*i*) Those in which the electron transfer results in *no net chemical change*. These are called *electron-exchange processes* and are examplified by $[Fe(CN)_6]^{3-}-[Fe(CN)_6]^{4-}$, $[Co(en)_3]^{3+}-[Co(en)_3]^{2+}$, $[Fe(dipy)_3]^{3+}-[Fe(dipy)_3]^{2+}$, $[Co(NH_3)_6]^{3+}-[Co(NH_3)_6]^{2+}$ etc. These can be followed only indirectly, for example, by isotopic labelling or by *nmr*. .

(*ii*) Those in which there is net chemical change. These are examplified by $[Cr(NH_3)_5X]^{2+}-[Cr(H_2O_6)]^{2+}$, $[Cr(H_2O)_5Cl]^{2+}-[Cr(H_2O)_6]^{2+}$ etc, where $X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NCS^-$ etc. and can be followed by many standard chemical and physical methods.

Mechanism of One Electron-Transfer Reactions

Most of such reactions are believed to occur by the following two mechanisms : (*i*) *Bridge or inner-sphere mechanism*, and (*ii*) *Electron-transfer or outer-sphere mechanism*.

(1) Atom (or Group)-Transfer of Inner-Sphere Mechanism.

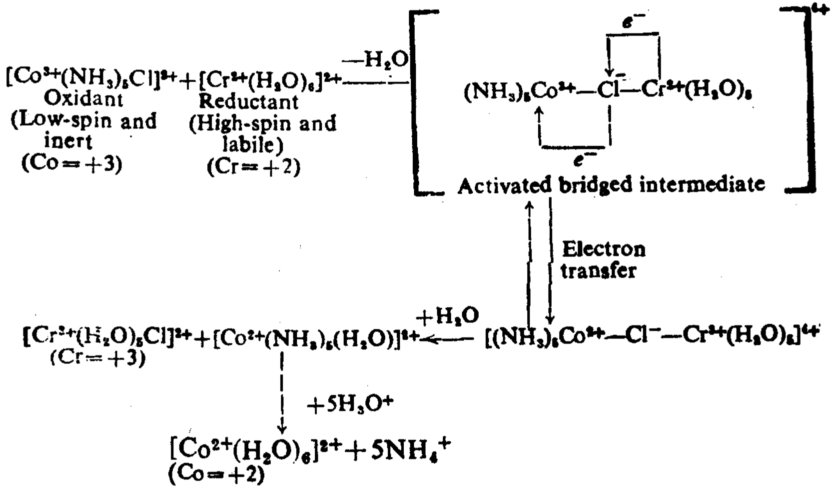
These are electron-transfer reactions in which concomitant electron transfer and ligand transfer occur. In such reactions an intimate contact between oxidant and reductant is required. This requirement is fulfilled when a *bridged activated complex* is formed as a result of an intimate attachment between the oxidant and reductant, and this activated complex has at least one ligand which is common to the coordinate sphere of both the reacting complexes and this forms a bridge between them. Hence the name inner-sphere mechanism. For obvious reasons this mechanism is also called **ligand-bridged, atom (or group) transfer or bridged activated complex mechanism.** It is the bridging group through which the electron can pass.

Taube and his coworkers have shown (1959) that oxidation of aqueous Cr(II), $[Cr(H_2O)_6]^{2+}$ by pentammine cobalt (III) chloride, $[Co(NH_3)_5Cl]^{2+}$ in acidic medium represented by the equation :

$$[Co^{3+}(NH_3)_5Cl]^{2+} + [Cr^{2+}(H_2O)_6]^{2+} + 5H_3O^+ \rightarrow [Co^{2+}(H_2O)_6]^{2+} + [Cr^{3+}(H_2O)_5Cl] + 5NH_4^+$$

Oxidant	Reductant	Reduced product	Oxidised product
$Co^{3+} \rightarrow 3d^6$	$Cr^{2+} \rightarrow 3d^4$	$Co^{2+} \rightarrow 3d^7$	$Cr^{3+} \rightarrow 3d^3$
Low-spin and inert	High-spin and labile	High-spin and labile	Low-spin and inert

can be explained by the mechanism as follows :

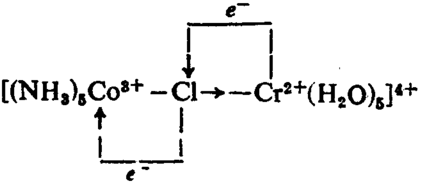


It is obvious from this mechanism that the above reaction proceeds through the following steps :

(*i*) The labile nature of $[Cr(H_2O)_6]^{2+}$ allows this complex to lose a molecule of water readily to form an activated bridged intermediate which contains Co^{3+} and Cr^{2+} ions linked together through Cl^- ion which acts as a bridge between the two co-ordinate spheres. The bridging Cl^- ion is brought into the activated intermediate by the inert reactant *viz* $[Co(NH_3)_5Cl]^{2+}$. That $[Co(NH_3)_5Cl]^{2+}$ is the only source of Cl^- is proved by the following observation. If $[Co(NH_3)_5Cl]^{2+}$ containing radioactive $^{36}Cl^-$ is dissolved in a solution containing Cr^{2+} (*i.e.* in $[Cr(H_2O)_6]^{2+}$) and unlabelled Cl^-, it is found that, after the reduction which is very fast, the product $[Cr(H_2O)_5Cl]^{2+}$ contains only labelled $^{36}Cl^-$. This proves that Cl^- ion is supplied by $[Co(NH_3)_5Cl]^{2+}$. The Cl^- bridge provides a good path between the two metals for electron transfer in a manner as copper wire connecting two electrodes provides a path for passing electric current.

(*ii*) In the activated intermediate an electron is transferred from Cr^{2+} to Co^{3+} through the bridging Cl^- ion to convert Cr^{2+} to Cr^{3+} and Co^{3+} to Co^{2+}.

(*iii*) The Cr^{3+} ion formed attracts Cl^- ion more strongly than does Co^{2+} and, therefore, Cl^- ion becomes a part of the complex of Cr^{3+}. Thus we find that the electron is transferred from Cr^{2+} to Co^{3+} through the bridging Cl^-, but Cl^- ion goes from Co^{3+} to Cr^{3+} (I) and these two acts are mutually interdependent, *i.e.* neither is possible without the other.



$$[(NH_3)_5Co^{3+}-Cl\rightarrow-Cr^{2+}(H_2O)_5]^{4+}$$

Activated bridged intermediate (I)

Thus we find that after electron transfer the initial labile partner *viz* $[Cr(H_2O)_6]^{2+}$ becomes inert to substitution and the inert partner *viz* $[Co(NH_3)_5Cl]^{2+}$ becomes labile.

A direct transfer from $[Cr(H_2O)_6]^{2+}$ to $[Co(NH_3)_5Cl]^{2+}$ followed by the transfer of $^{36}Cl^-$ seems unlikely, since in this case unlabelled Cl^- from the solution would be readily incorporated into the Cr^{3+} complex as the $^{36}Cl^-$ is attached to cobalt.

The reaction is first-order with respect to the oxidant and the reductant.

$$\begin{aligned} \nu &= k[\text{oxidant}]\,[\text{reductant}] \\ &= k[Co(NH_3)_5Cl^{2+}]\,[Cr(H_2O)_6{}^{2+}] \end{aligned}$$

Similar mechanism has been suggested for the following general reaction :

$$[Co^{3+}(NH_3)_5X]^{2+}+[Cr(H_2O)_6]^{2+}+3H_3O^+\longrightarrow[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5X]^{2+}+5NH_4{}^+$$

Here $X=F^-$, Cl^-, Br^-, I^-, $SO_4{}^{2-}$, NCS^-, $N_3{}^-$, $PO_4{}^{4-}$, $P_2O_7{}^{4-}$ CH_3COO^-, etc. With these ligands which form bridges the rates of these reactions increase in the order : $SO_4{}^{2-} < Cl^- < Br^-$. The ions that form bridges most readily and provide the best path for electron transfer produce fastest reactions.

There are some redox reactions in which multiple bridges are formed, *e.g.*, in the following reaction three oxygen atoms of EDTA serve as bridges

$$\underset{(Co=+3)}{[Co^{3+}(EDTA)]^-}+\underset{(Cr=+2)}{Cr^{2+}}\longrightarrow\underset{(Co=+2)}{Co^{2+}}+\underset{(Cr=+3)}{[Cr^{3+}(H_2O)_3\,(EDTA)]^-}$$

In reactions with two bridging groups, two ligands but only one electron are transferred. Conversely, in various Pt^{II}/Pt^{IV} exchanges two electrons but only one ligand is transferred. There is even a reaction in which electron-transfer by an inner-sphere mechanism is not accompanied by ligand transfer, *e.g.*,

$$\underset{(\mathrm{Co}=+2)}{[\mathrm{Co}^{2+}(\mathrm{EDTA})]^{2-}} + \underset{(\mathrm{Fe}=+3)}{[\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-}} \longrightarrow \underset{(\mathrm{Co}=+3)}{[\mathrm{Co}^{3+}(\mathrm{EDTA})]^{-}} + \underset{(\mathrm{Fe}=+2)}{[\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-}}$$

(2) Direct Electron-Transfer or Outer-Sphere Mechanism

Here we shall discuss the electron-transfer reactions in which only the formal valence states of the metal ions involved change. These reactions occur by *direct electron transfer* and the electron effectively hops from one species to the other and the ligands act as electron-conduction media. Recent work on electron spin resonance of paramagnetic complexes has shown that unpaired electrons spend part of their time on ligands. Consequently electron transfer can occur by a mechanism which involves movement of an electron from the outside of a ligand in one coordination sphere over the outside of a second sphere. This mechanism seems particularly appropriate with large conjugated ligands like phenanthroline and bipyridine.

In this mechanism direct transfer of an electron occurs. For this process to occur there is a critical requirement which is given by *Frank-Condon principle* which states that there can be no appreciable change of atomic arrangement during the time of an electronic transition, *i.e.* very light electrons move much more rapidly than much heavier atoms. In order to understand its effect let us consider the transfer of an electron from $[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_4]^{4-}$ to $[\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_6]^{3-}$. The rate of this redox reaction (which is actually no reaction at all) can be studied by labelling either of the complexes with a radioactive isotope of Fe or with ^{14}C.

$$[{}^*\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-} \xrightarrow{\;e\;} [\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-}$$

$$[{}^*\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-} + [\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-} \longrightarrow [{}^*\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-} + [\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-}$$

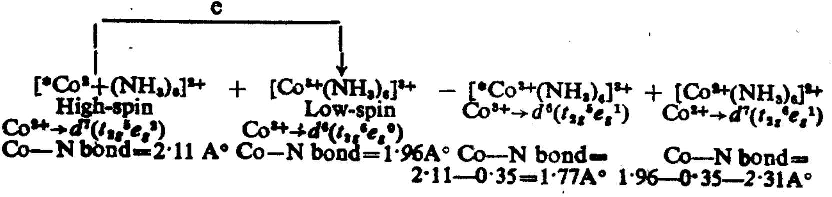
$[{}^*\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-}$	$[\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-}$	$[{}^*\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-}$	$[\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-}$
Ferrocyanide ion	Ferricyanide ion	Fe—C bonds longer	Fe—C bonds shorter
Low-spin and inert	Low-spin and inert		
$\mathrm{Fe}^{2+} \rightarrow d^6$ $(t_{2g}^6\, e_g^0)$	$\mathrm{Fe}^{3+} \rightarrow d^5$ $(t_{2g}^5\, e_g^0)$		
Fe—C bonds longer	Fe—C bonds shorter		

The above reaction is *fast* with second-order constant ~ 10^5 at 25°C and there is no heat change in the reaction, since we obtain the same products after the electron transfer. Both the anions are *inert*. $[\mathrm{Fe(CN)}_6]^{4-}$ is a low-spin d^6 $(t_{2g}^6 e_g^0)$ system and $[\mathrm{Fe(CN)}_6]^{3-}$ is a low-spin d^5 $(t_{2g}^5 e_g^0)$ system. Thus the loss or exchange of CN^- or any substitution reaction is very fast. The possibility of electron transfer through a bridged activated complex is eliminated, since formation of the activated complex amounts to a substitution reaction. During this reaction none of the elements *viz*. Fe, C or N moves. The Fe—O bond in $[\mathrm{Fe(CN)}_6]^{3-}$ is slightly shorter than that in $[\mathrm{Fe(CN)}_6]^{4-}$. Thus, if an electron is to be transferred between the anions in their ground-state equilibrium configurations by the Franck-Condon principle, the product $[Fe(CN)_6]^{3-}$ would be expanded (*i.e.* Fe—C bonds must become longer) and the $[Fe(CN)_6]^{4-}$ would be compressed (*i.e.* Fe—C bonds must become shorter). For this to be so, the energy must be added to the system, *i.e.* the products would be of higher energy than the reactants. This, however, contradicts the fact that there is no heat change associated with this electron transfer reaction. It follows that an electron-transfer reaction can only occur when the vibrations within the two anions have made them of identical geometries and electronic configurations. Then the products and the reactants in the electron-transfer process would be equivalent and no energy would be produced as a result of the electron transfer. Since both the anions are similar, a relatively small addition of energy (the activation energy) would make the anions alike. Thus electron-transfer reaction can occur rapidly.

When both the reactants are inert as in the present case, the close approach of the metal atoms is impossible and hence the electron-transfer takes place by a **tunnelling** or **outer-sphere mechanism**. In this mechanism each complex retains its full coordination shell in the activated complex so that there is no ligand common to each central metal atom and an electron is believed to pass through both the coordination shells. This mechanism is sure to be correct when both the reactants exchange their ligands more slowly *i.e.* are inert than they undergo electron transfer and differ only in their charges. Although for an isotopic change the equilibrium constant is nearly unity and $\Delta G°$ is nearly zero, activation energy is required (*i*) to overcome the electrostatic repulsion between ions of like charges) *electrostatic energy*) (*ii*) to distort the coordination shells of both species, and (*iii*) to modify the solvent structure around both species. Thus activation energy is made up of the above three contributions.

Outer-sphere electron-transfer reactions are more rapid for complexes containing ligands such as *o*-phenanthroline and CN^- ion than for corresponding complexes with ligands like H_2O or NH_3.

Now consider an electron-transfer between $[Co^{III}(NH_3)_6]^{3+}$ and $[Co^{II}(NH_3)_6]^{2+}$, both the complexes being octahedral. This reaction is *slow*.



These complexes do not differ greatly in size and hence one might expect that the electron-transfer reaction is fast. The two complexes, however, do differ in electronic configurations and Co—N bond lengths : $(Co(NH_3)_6]^{2+}$ is a high-spin $d^7(t_{2g}^5e_g^2)$ system while $[Co(NH_3)_6]^{3+}$ is a low-spin $d^7(t_{2g}^6e_g^0)$ system, Co—N bond lengths in

$[Co(NH_3)_6]^{2+}$ and $(Co(NH_3)_6]^{3+}$ are 2·11A° and 1·96A° respectively. After electron-transfer these configurations presumably become $t_{2g}{}^5e_g{}^1$ and $t_{2g}{}^6e_g{}^1$ respectively. Neither of these is the ground state cofiguration of the ion, *i.e.* after electron-transfer reaction both the complexes will be electronically excited. This excess of energy will rapidly be lost either by radiation or more probably it will be converted into thermal energy. Because this electronic energy contributes to the activation energy of the process, the rate of electron-transfer reaction between $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ is much slower than that between $[Fe(CN_6)]^{3-}$ and $[Fe(CN)_6]^{4-}$.

Outer-sphere exchange reactions between complexes having different central metal ions with different oxidation states (*e.g.* $[Os^{II}(dipy)_3]^{2+}-[Mo^{V}(CN)_8]^{3-}$ reaction] are usually faster than outer sphere exchange reaction between the complexes of the same metals with different oxidation states. For such reactions when excited states of the products are converted into ground states the decrease in energy can appear as the free energy of the reaction (ΔG^{0} must be negative or the reaction would not take place). This means that for such reactions the structure of the transition state is more like that of the reactants and consequently the activation energy is decreased and the rate is increased.

There are now a number of electron-transfer reactions such as those of $[Co^{III}(NH_3)_4X)]^{2+}$ with $[Co^{II}(CN)_5]^{2-}$, where $X=F^-$, CN^-, NO_3^- and NO_2^-, and that of Cr^{2+} with $[IrCl_6]^{2-}$ in which the electron trasfer takes place by both inner-and outer-sphere mechanisms.

Factors affecting the rates of direct electron-transfer reactions

The factors affecting the rates of direct electron-transfer reactions have been summarised by Halpern as follows :

(*i*) **Electrostatic repulsion between ions of like charges.** This contributes to the activation energy. Because of electrostatic repulsion the energy of activation also increases. The increase in activation energy tends to decrease the rate of exchange of electrons.

(*ii*) **Identity and concentration of the cations present in solution.** In several cases the rate constants for the electron-transfer reactions have been found to depend on the identity and concentration of the cations present in the solution. Generally an increase in the concentration of the cations increases the rate, but certain cations are particularly effective. The general effect can be attributed to the formation of ion pairs which then decrease the electrostatic contribution to the activation energy.

(*iii*) **Conductivity of the ligands.** The greater the conductivity of the ligands, the more readily should electron-transfer proceed between the two complexes. Electron transfer between a variety of similar cyanide complexes has been found to be rapid. The same is true for the highly conducting complexes *viz.* $[M(phen)_3]^{n+}$ and $[M(bipy)_3]^{n+}$ relative to $[M(en)_3]^{n+}$ and $[M(NH_3)_6]^{n+}$.

(*iv*) **Reorganisation energy.** The bond lengths in MnO_4^- and MnO_4^{2-} differ and the activated complex for exchange between these must involve a "stretched" MnO bond in MnO_4^-. Slow reactions are expected when the oxidant and the reductant have greatly different bond lengths, geometries or solvation shells. For octahedral complexes bond lengths are changed more drastically when e_g electrons are involved in the transfer as compared to t_{2g} electrons in the *d*-orbitals.

(*v*) **Free energy change in the reaction.** The greater the negative free energy change for the overall reaction, the faster the reaction will proceed.

Two Electron-Transfer Reactions

The electron-transfer reactions we have discussed so far involve the transfer of a single electron from one species to the other. Reactions in which two electrons are transferred are also known, *e.g.*, the reactions :

$$^*Tl^+ + Tl^{3+} \longrightarrow {}^*Tl^{3+} + Tl^+ \qquad \ldots(i)$$

$$^*Pt^{2+} + Pt^{4+} \longrightarrow {}^*Pt^{4+} + Pt^{2+}$$

have been studied in detail. In aqueous perchlorate solution the rate-law for reaction (*i*) is

$$v = k_1 [Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH^{2+}]$$

In presence of other anions like NO_3^-, Cl^-, CN^-, SO_4^{2-}, Br^- etc. more complicated rate-laws are found indicating that two-electron transfers occur through various Tl^{3+} complexes

Complementary and Non-complementary Electron-Transfer Reactions,

Electron-transfer reactions (shown below) in which oxidant gains the same number of electrons as the reductant loses are called complementary electron-transfer reactions :

$$\begin{array}{cccccccc} Sn^{2+} & + & Tl^{3+} & \longrightarrow & Sn^{4+} & + & Tl^+ \\ Sn^{2+} & + & Hg^{2+} & \longrightarrow & Sn^{4+} & + & Hg^0 \\ \text{Reductant} & & \text{Oxidant} & & \text{Oxidant} & & \text{Reductant} \end{array}$$

When the number of electrons gained and lost are different, the electron-transfer reactions are called non-complementary reactions and generally these reactions proceed by more complicated mechanisms, *e.g.* in the reaction,

$$\underset{\text{Oxidant}}{Tl^{3+}(aq)} + \underset{\text{Reductant}}{2Fe^{2+}(aq)} \longrightarrow \underset{\text{Reductant}}{Tl^+(aq)} + \underset{\text{Oxidant}}{2Fe^{3+}(aq)}$$

$Tl^{3+}(aq) \longrightarrow Tl^+(aq)$ is a two electron transfer reaction while $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$ is one-electron transfer reaction.

Mechanism

The experimental data show that a reactive intermediate, $Tl^{2+}(aq)$ is produced in the slow step which is then followed by a fast step.

$$Tl^{3+}(aq) + Fe^{2+}(aq) \xrightarrow[\text{Slow}]{k_1} \underset{\substack{\text{Reactive}\\ \text{intermediate}}}{Tl^{2+}(aq)} + Fe^{3+}(aq) \qquad \ldots(i)$$

$$\underset{\text{Intermediate}}{Tl^{2+}(aq)} + Fe^{2+}(aq) \underset{\text{Fast}}{\xrightarrow{k_2}} Tl^{+}(aq)+Fe^{3+}(aq)$$

When $Fe^{3+}(aq)$ builds up in the course of reaction or when it is added initially, the reverse of reaction (*i*) *viz.*

$$Tl^{2+}(aq)+Fe^{3+}(aq) \xrightarrow{k_3} Tl^{3+}(aq)+Fe^{2+}(aq)$$

competes for the $Tl^{2+}(aq)$ formed.

The complete rate expression for this mechanism is given as :

$$\text{Rate}=\frac{k_1k_2[Tl^{3+}]\,[Fe^{2+}]^2}{k_2[Fe^{2+}]+k_3[Fe^{3+}]}$$

The non-complementary electron-transfer reactions :

$$2Co^{3+}(aq)+Tl^{+}(aq) \longrightarrow 2Co^{2+}(aq)+Tl^{3+}(aq)$$

$$\underset{\text{Oxidant}}{2V^{4+}(aq)}+\underset{\text{Reductant}}{Tl^{+}(aq)} \longrightarrow \underset{\text{Reductant}}{2V^{3+}(aq)}+\underset{\text{Oxidant}}{Tl^{3+}(aq)}$$

have also been explained on the basis of this mechanism.

References

See the References of Chapter 16.

18

Electron-deficient Compounds : Boranes

What are Electron-deficient Compounds ?

Electron-deficient compounds are those in which the total number of atomic orbitals available on all the atoms of the compound is more than the total number of valence shell electrons. In other words the molecules which do not contain enough electrons to form two-electron covalent bonds between all the atoms are called electron-deficient molecules. For example, since in diborane molecule (B_2H_6) the total number of atomic orbitals on both B-and six H-atoms is 14 (two 2*s* orbitals on two B-atoms, six 2*p* orbitals on two B-atoms and six 1*s* orbitals on six H-atoms) and that of valence-shell electrons is only 12 (4 electrons in two 2*s* orbitals on two B-atoms, two electrons in six 2*p* orbitals on two B-atoms and six electrons in six 1*s* orbitals on six H-atoms [$B=2s^2.\ 2p_x^1\ 2p_y^0\ 2p_z^0$, $H=1s^1$], it is an electron-deficient molecule.

Examples of Electron-deficient Compounds

The elements like Be, Mg, B, Al, Ga, In and Tl give many electron-deficient compounds. Examples are : beryllium hydride, $(BeH_2)_n$; beryllium dimethyl, $[Be(CH_3)_2]_n$; beryllium chloride, $(BeCl_2)_n$; magnesium diethyl, $Mg(C_2H_5)_2$; boron hydrides like B_2H_6, B_4H_{10}, B_5H_9, $B_{10}H_{14}$ etc ; derivatives of diborane like methyl diborane, $(CH_3)_2BH\ .\ BH(CH_3)_2$; aminodiborane, $H_2B[NH_2\ .\ H]BH$; monomethyl amino diborane, $H_2B\ [NH(CH_3)\ .\ H]\ BH_2$; dimethyl aminodiborane, $H_2B[N(CH_3).H]BH_2$; disilylylamine diborane, $H_2B[N(SiH_3)_2\ .\ H]BH_2$ etc ; aluminium trimethyl, $Al_2(CH_3)_6$; aluminium halides, Al_2X_6 ($X=Cl$, Br, I) ; digallane, Ga_2H_6 ; gallium trimethyl, $Ga(CH_3)_3$; tetramethyl digallane, $Ga_2H_2(CH_3)_4$; gallium halides, Ga_2X_6($X=Cl$, Br, I), indium trimethyl, $In\ (CH_3)_3$; indium halides, In_2X_6 ($X=Cl$, Br I) ; diethyl thallium ethoxide, $[C_2H_5)_2Tl(OC_2H_5)]_2$

HYDRIDES OF BORON : BORANES

Although boron does not combine directly with hydrogen, yet a number of hydrides of boron are known. These hydrides are covalent compounds and are also called *boranes* by analogy with alkanes. These are electron-deficient compounds.

The boranes are named as *di-*, *tri-*, *tetra-*, *penta-*, *hexa-boranes* and so on according to the number of boron atoms followed by the numeral which indicates the number of hydrogen atoms. For example, B_5H_9 is called penta borane-9 Here penta indicates the number of boron atoms and 9 indicates the number of H-atoms.

The boranes have been grouped into two classes namely (*i*) B_nH_{n+4} ($n=2$, 5, 6, 8, 10 and 18). The boranes of this class are quite stable and have high m.pts. Examples of boranes of this class are diborane, B_2H_6 ; penta borane-9, B_5H_9 ; hexaborane-10, B_6H_{10} ; octaborane-12, B_8H_{12} ; pentaborane-11, B_5H_{11} etc., (*ii*) B_nH_{n+6} ($n=4$, 5, 6, 9 and 10). The boranes of this class are unstable and have low m.pts. Examples of boranes of this class are tetraborane, B_4H_{10} ; pentaborane-11, B_5H_{11} ; hexaborane-12, B_6H_{12} ; enneaborane -15, B_9H_{15} ; decaborane-16, $B_{10}H_{16}$ etc.

General Methods of Preparation of Boranes

1. **Stock's method.** Stock obtained all the boranes, excepting B_9H_{15}, by the action of dil. aqueous acids like HCl or H_3PO_4 on magnesium boride (Mg_3B_2). This method gave a mixture of several boranes, magnesium salt of the acid and H_2. The chief component of the volatile mixture obtained by the action of HCl on Mg_3B_2 was B_4H_{10} and very little B_2H_6.

$$2Mg_3B_2+12HCl \longrightarrow 6MgCl_2+B_4H_{10}+H_2$$

Stock separated the different components of the volatile mixture of boranes by fractional distillation under reduced pressure.

2. **Wurtz's method.** This method has been used to prepare B_4H_{10} which is obtained by the action of C_2H_5I on sodium amalgam (Na/Hg).

$$2C_2H_5I+2Na/Hg \longrightarrow B_4H_{10}+2NaI.$$

3. **From B_2H_6** (*i*) Higher boranes like B_5H_{11}, B_4H_{10}, $B_{10}H_{14}$, B_5H_9, B_5H_{11} can be obtained by heating B_2H_6 at different temperatures as shown below :

$$5B_2H_6 \xrightarrow{115^\circ C\ (\text{U-tube})} 2B_5H_{11}+4H_2$$

$$2B_2H_6 \xrightleftharpoons{-78 \text{ to } 100^\circ C} B_4H_{10}+H_2$$

$$5B_2H_6 \xrightarrow{100^\circ C\ (\text{sealed bulb})} B_{10}H_{14}+8H_2$$

$$5B_2H_6 \xrightarrow{200-250^\circ C} 2B_5H_9+6H_2$$

$$5B_2H_6 \xrightarrow{250^\circ C,\ 120\text{ mm (tube)}} B_5H_9+B_5H_{11}+5H_2$$

(*ii*) B_5H_9 is formed in good yield when a mixture of B_2H_6 and H_2 is circulated through a glass tube at 200—250°C.

(*iii*) Decomposition of B_2H_6 in silent electric discharge in presence of an inert gas gives a mixtnre consisting of $B_4H_{10}=40\%$, $B_5H_9=20\%$, $B_5H_{11}=30\%$ and a small quantity of B_9H_{15}

4. **By the conversion of one borane into the other.** Higher boranes can also be obtained by the conversion of one borane into the other as shown by the following examples :

$$B_4H_{10} \xrightarrow{95^\circ C} B_{10}H_{14} \xrightarrow{200^\circ C} B_5H_9 \xrightarrow[\text{discharge}]{\text{silent electric}} B_{10}H_{16}$$

$$B_4H_{10} \xrightarrow{60^\circ C} B_5H_{11} \xrightarrow{25^\circ C} B_{10}H_{14} \;;\; B_4H_{10} \xrightarrow{200^\circ C} B_5H_9$$

General Properties of Boranes

1. **Physical state.** Boranes are volatile gases, liquids or solids.

2. **Melting and boiling points.** The melting and boiling points of some boranes (in °C) are : $B_4H_{10}=-120^\circ$, 18° ; $B_5H_9=-46{\cdot}6^\circ$, 48°; $B_5H_{11}=-62{\cdot}3^\circ$, 108°; $B_6H_{12}=-82{\cdot}3^\circ$, $80-90^\circ$; $B_{10}H_{14}=-92{\cdot}7^\circ$, 213°.

3. **Decomposition.** When heated, these are decomposed into different boranes. The nature of boranes obtained depends on the temperature at which the decomposition takes place as shown in method (4) of the preparation of boranes.

4. **Hydrolysis.** These are hydrolysed by water and aqueous alkalies, but the rate of their hydrolysis varies from one borane to another. Hydrogen is evolved. Examples are :

$$B_4H_{10}+12H_2O \rightarrow 4H_3BO_3+11H_2$$
$$B_4H_{10}+4KOH+4H_2O \rightarrow 4KBO_2+11H_2$$
$$B_6H_{12}+18H_2O \rightarrow 6H_3BO_3+15H_2$$
$$B_6H_{12}+6KOH+6H_2O \rightarrow 6KBO_2+15H_2$$

5. **Action of O_2 or air.** All the boranes are easily oxidised by O_2 and give dark coloured products of determined composition. A mixture of the gaseous boranes with air is highly explosive in the presence of a trace of moisture.

6. **Formation of addition compounds.** Since all the boranes are electron-deficient compounds, these form addition compounds (or adducts) with a variety of donor molecules.

7. **Action of NH_3.** All the boranes react with NH_3 to give various products, depending on the experimental conditions.

8. **Properties of tetraborane-10 (B_4H_{10}).** (i) It is a colourless gas and poisonous gas with a disgusting odour. This can be readily condensed to a colourless liquid with m.pt.$=-120^\circ$C and b.pt. $=18^\circ$C. It is non-inflammable in dry air at room temperature.

A mixture of the gas with air is highly explosive in presence of a trace of moisture.

(*ii*) It is soluble in dry benzene but slightly so in cold water.

(*iii*) *Decomposition.* It is stable in the absence of air and moisture. It decomposes at ordinary temperature, giving H_2 and lower boranes.

(*iv*) *Action of HCl.* With HCl, H_2 is liberated

$$B_4H_{10}+HCl \rightarrow B_4H_9Cl+H_2$$

(*v*) *Reaction with CO.* B_4H_{10} reacts with CO at 120°C in a hot-cold flow reactor and gives the carbonyl adduct, B_4H_8CO :

$$B_4H_{10}+CO \rightarrow B_4H_8CO+H_2$$

(*vi*) *Hydrolysis.* It is slowly hydrolysed by H_2O and aqueous alkalies, evolving H_2 as shown above.

(*vii*) *Action of NaH and NaBH₄.* When B_4H_{10} reacts with NaH or $NaBH_4$, $Na^+[B_3H_8]^-$ which is an ionic compound is formed.

$$2B_4H_{10}+2NaH \rightarrow 2Na^+[B_3H_8]^-+B_2H_6$$
$$B_4H_{10}+2NaBH_4 \rightarrow 2Na^+[B_3H_8]^-+H_2$$

9. **Properties of pentaborane-9 (B_5H_9).** Some of the reactions shown by B_5H_9 are :

$$B_5H_9+C_2H_4 \xrightarrow{AlCl_3} B_5H_8C_2H_5$$
$$B_5H_9+2LiH \xrightarrow{\text{Diethyl ether}} Li_2B_5H_{11}$$
$$B_5H_9+2Na(Hg) \xrightarrow{\text{Ether}} Na_2B_5H_9 \xrightarrow{\text{Vacuum}} B_5H_9$$
$$B_5H_9+2Li \xrightarrow{\text{Liq. }NH_3} Li_2B_5H_9$$

10. **Properties of pentaborane-11 (B_5H_{11}).** (*i*) In presence of weak Lewis bases like ethers, amines etc B_5H_{11} gives B_6H_{10} and B_2H_6

$$2B_5H_{11} \xrightarrow[\text{a Lewis base}]{\text{In presence of}} B_6H_{10}+2B_2H_6$$

(*ii*) B_5H_{11} reacts with CO in a hot-cold flow reactor and gives the carbonyl adduct, B_4H_8CO.

$$B_5H_{11}+2CO \longrightarrow B_4H_8CO+BH_3CO$$

(*iii*) When heated with H_2 at 100°C, it gives B_4H_{10}.

11. **Properties of decaborane—14 ($B_{10}H_{14}$).** Some reactions shown by this hydride are :

$$B_{10}H_{14}+NaH \xrightarrow{(C_2H_5)_2O} NaB_{10}H_{13}.(C_2H_5)_2O+H_2$$

$$B_{10}H_{14} \xrightarrow[\text{liq. } NH_3]{2Na^+ \text{ in}} (Na^+)_2[B_{10}H_{14}]^{2-}$$

$$B_{10}H_{14} + 2L\ (L = CH_3CN,\ R_3N,\ R_3P) \xrightarrow{\Delta} B_{10}H_{12}L_2 + H_2$$

$$B_{10}H_{14} + CH_3MgI \longrightarrow B_{10}H_{13}MgI + CH_4$$

DIBORANE, B_2H_6

Preparation of Diborane. B_2H_6 is prepared : (*i*) *By the action of ionic hydrides (e.g. NaH, CaH_2), H_2, and Li $[AlH]_4$ on BCl_3*

$$6NaH + 2BCl_3 \longrightarrow 6NaCl + B_2H_6$$

$$3CaH_2 + 2BCl_3 \longrightarrow 3CaCl_2 + B_2H_6$$

$$4BCl_3 + 3Li[AlH_4] \longrightarrow 3LiCl + 2B_2H_6 + 3AlCl_3$$

$$2BCl_3(\textit{vapours}) + 6H_2 \longrightarrow 6HCl + B_2H_6$$

(*ii*) *By the action of boron trifuoride ether complex, $(C_2H_5)_2O.BF_3$ on metallic hydrides like LiH, Li$[BH_4]$, Na$[BH_4]$ etc.*

(*a*) $6LiH + 8(C_2H_5)_2O.BF_3 \longrightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$

(*b*) $3Li[BH_4] + (C_2H_5)_2O.BF_3 \longrightarrow 2B_2H_6 + 3LiF + (C_2H_5)_2O$

$3Na[BH_4] + (C_2H_5)_2O\,.\,BF_3 \longrightarrow 2B_2H_6 + 3NaBF_4 + (C_2H_5)_2O$

Reaction (*a*) is used for the manufacture of B_2H_6 in U.S.A.

(*iii*) *By reducing BF_3 with LiH, Li$[BH_4]$ or Na$[BH_4]$.*

(*a*) $8BF_3 + 6LiH \longrightarrow 6LiBF_4 + B_2H_6$

(*b*) $BF_3 + 3Li[BH_4] \xrightarrow{\text{Ether}} 3LiF + 2B_2H_6$

(*c*) $BF_3 + 3Na[BH_4] \longrightarrow 3NaF + 2B_2H_6$

B_2H_6 is generally produced *in situ* in reactions (*b*) and (*c*).

(*iv*) *By treating an alkali metal borohydride with HCl.*

$$2Li[BH_4] + 2HCl \longrightarrow B_2H_6 + + 2LiCl + 2H_2\uparrow$$

$$2Na[BH_4] + 2HCl \longrightarrow B_2H_6 + 2NaCl + 2H_2\uparrow$$

Properties of Diborane. **1.** It is an inflammable colourless gas with a sticky sweet odour and is extremely toxic. It is an extremely reactive gas and hence should be handled in a special apparatus so that it comes in contact only with glass and mercury.

2. *Decomposition.* (*a*) *By heat.* It is stable at low temperature only in the absence of moisture. A higher temperatures B_2H_6 gets decomposed into a number of higher boranes. For example :

$$5B_2H_6 \xrightarrow{115^\circ C\ (\text{U-tube})} 2B_5H_{11} + 4H_2$$

$$2B_2H_6 \xrightarrow{-78 \text{ to } 100^\circ C} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow{100^\circ C,\ (\text{sealed bulb})} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow[\text{(tube)}]{250°C,\ 120\ mm} B_5H_9 + B_5H_{11} + 5H_2$$

$$5B_2H_6 \xrightarrow{200-250°C} 2B_5H_9 + 6H_2$$

At red heat B_2H_6 gets decomposed into boron and H_2.

$$B_2H_6 \xrightarrow{\text{Red heat}} 2B + 3H_2$$

(*b*) *By water : Hydrolysis.* It is readily decomposed by water into boric acid and H_2.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(*c*) *By aqueous alkalies : Hydrolysis.* When B_2H_6 is passed into a *concentrated* aqueous solution of KOH at 0°C, reaction occurs and the solution obtained on evaporation in vacuo deposite potassium hypoborate, $K_2(BH_2OH.BH_2OH)$ or $K_2(B_2H_6O_2)$.

$$B_2H_6 + 2KOH \xrightarrow{0°C} K_2(B_2H_6O_2) + H_2 \quad \text{... (i)}$$

If KOH solution is *diluted*, then potassium hypoborate, $K_2(B_2H_6O_2)$ is converted into potassium metaborate, KBO_2.

$$K_2(B_2H_6O_2) + 2H_2O \longrightarrow 2KBO_2 + 5H_2 \quad \text{...(ii)}$$

Thus the hydrolysis of B_2H_6 by a dilute solution of KOH can be shown by the following equation which is obtained by combining equation (*i*) and (*ii*)

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

The evolution of H_2 by the action of aqueous alkalies makes B_2H_6 as a useful reducing agent.

2. *Action of ethyl lithium (LiC_2H_5) and alkali metal hydrides.* LiC_2H_5 and alkali metal hydrides suspended in ether react with B_2H_2 and produce alkali metal borohydrides, MBH_4.

$$2B_2H_6 + 2LiC_2H_5 \longrightarrow 3LiBH_4 + B(C_2H_5)_3$$

$$B_2H_6 + 2LiH \longrightarrow 2LiBH_4$$

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

4. *Reaction with trimethyl aluminium, $Al(CH_3)_3$.* Aluminium borohydride, $Al(BH_4)_3$ is produced

$$Al(CH_3)_3 + 2B_2H_6 \rightarrow B(CH_3)_3 + Al(BH_4)_3$$

5. *Action of O_2 : Ignition or combustion.* Pure B_2H_6 undergoes no change when mixed with dry air or O_2 at room temperature, but it may ignite (*i.e.* burn), if impure. In this reaction a large amount of energy is produced.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O + 480\ \text{Kcal}$$

The production of large amount of heat in the above reaction makes B_2H_6 a useful rocket fuel.

6. *Action of halogens.* It reacts with halogens (not iodine) under different conditions to give different products.

$$B_2H_6+6Cl_2 \xrightarrow{25^\circ C} 2BCl_3+6HCl \quad (\textit{vigorous reaction})$$

$$B_2H_6+Br_2 \xrightarrow{100^\circ C} B_2H_5Br+HBr \quad (\textit{slow reaction})$$

7. *Action of halogen acids.* B_2H_6 reacts readily with HCl acid in presence of $AlCl_3$ as catayst to form chlorodiborane (B_2H_5Cl). With HBr it reacts at 90°C in presence of $AlBr_3$ to give B_2H_5Br while with HI at 50°C in the absence of a catalyst to give B_2H_5I.

$$B_2H_6+HX(X=Cl, Br, I) \rightarrow B_2H_5X+H_2$$

8. *Action of sodium or potassium amalgam.* When B_2H_6 is treated with sodium or potassium amalgam (*reducing agents*) in cold, crystalline product of the composition, $B_2H_6.2Na$ or $B_2H_6.2K$ is formed.

$$2Na\ (\textit{in the form of amalgam})+B_2H_6 \rightarrow B_2H_6.2Na$$

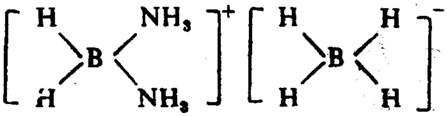
$$2K\ (\textit{in the form of amalgam})+B_2H_6 \rightarrow B_2H_6.2K$$

9. *Reaction with NH_3.* Diborane reacts with NH_3 giving various products depending on the experimental conditions. For example :

(*a*) When B_2H_6 reacts with *excess of NH_3 at low temperature* (−120°C), it forms an addition compound called *diammoniate of diborane*, $B_2H_6.2NH_3$ which forms a conducting solution in liquid ammonia.

$$B_2H_6+2NH_3\ (\textit{Excess}) \xrightarrow{\text{Low temp } (-120^\circ C)} B_2H_6.2NH_3$$

$B_2H_6.2NH_3$ is a white non-volatile solid and is soluble in water. It is an ionic compound and hence is represented as $[BH_2(NH_3)_2]^+ . [BH_4]^-$ or as follows :



The formation of $B_2H_6.2NH_3$ represents the only case of non-symmetrical cleavage of B_2H_6 by consecutive substitution.

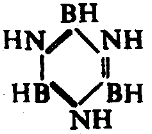
(*b*) With *excess of NH_3* and at *high temperature*, boron nitride, $(BN)_x$ is formed.

$$xB_2H_6+2xNH_3\ (\textit{Excess}) \xrightarrow{\text{High temp}} 2(BN)_x+6xH_2$$

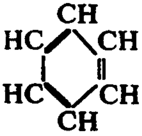
(*c*) When B_2H_6 and NH_3 are treated at high temperature in 1 : 2 ratio, *borazole*, $B_3N_3H_6$ (also called *borazine*) is formed.

$$3B_2H_6+6NH_3 \xrightarrow{\text{High temp.}} 2B_3N_3H_6+12H_2$$

Borazole has a flat hexagonal ring structure containing—BH= and —NH=groups alternately. Thus it has an analogous electronic structure to that of C_6H_6 and is, therefore, called *inorganic benzene*.



Borazole
($B_3N_3H_6$)

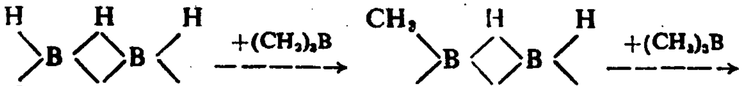


Benzene
(C_6H_6)

10. *Formation of adducts.* Because of its electron-deficient nature, B_2H_6 reacts with a number of molecules having lone pairs of electrons [*e.g.*, $(CH_3)_2O$, $(CH_3)_2S$, CO, PF_3, $N(CH_3)_3$ etc.] (Lewis bases) to form adducts or addition compounds. Thus in these reactions B_2H_6 acts as an acceptor (Lewis acid) and the molecules like $(CH_3)_2O$, $(CH_3)_2S$ etc. act as donors (Lewis bases).

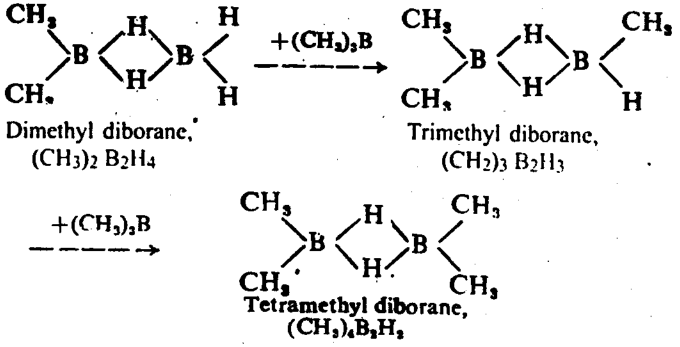
Acceptor (*Lewis acid*)		*Donor* (*Lewis bases*)		*Adduct or addition compound*
$\frac{1}{2}B_2H_6$	+	$(CH_3)_2O$ Ether	→	$(CH_3)_2O \rightarrow BH_3$ Ether borane
$\frac{1}{2}B_2H_6$	+	$(CH_3)_2S$ Thioether	→	$(CH_3)_2S \rightarrow BH_3$ Thioether borane
$\frac{1}{2}B_2H_6$	+	CO	$\xrightarrow[\text{20 atm.}]{200°C}$	$CO \rightarrow BH_3$ Carbonyl borane

11. *Methylation of B_2H_6 with trimethyl borane, $B(CH_3)_3$.* B_2H_6 reacts at ordinary temperature with $B(CH_3)_3$ to produce a series of methyl derivatives of B_2H_6 which are called methyl diboranes. No more than four H atoms in B_2H_6 molecule can be replaced by CH_3 groups or any alkyl groups as shown below :



Diborane, B_2H_6

Monomethyl diborane, $(CH_3)B_2H_5$



Dimethyl diborane, $(CH_3)_2 B_2H_4$

Trimethyl diborane, $(CH_2)_3 B_2H_3$

Tetramethyl diborane, $(CH_3)_4B_2H_2$

The above reactions clearly indicate that none of the bridge H-atoms in B_2H_6 is replaced by CH_3 group *i.e.* in the reaction between B_2H_6 and $B(CH_3)_3$, both three-centre B-H-B bonds remain undisturbed.

12. *Reactions with PH_3 and its derivatives.* (*a*) At ordinary temperature B_2H_6 reacts with PH_3 to give a non-volatile white solid with the composition $(PH_2BH_2)_x$.

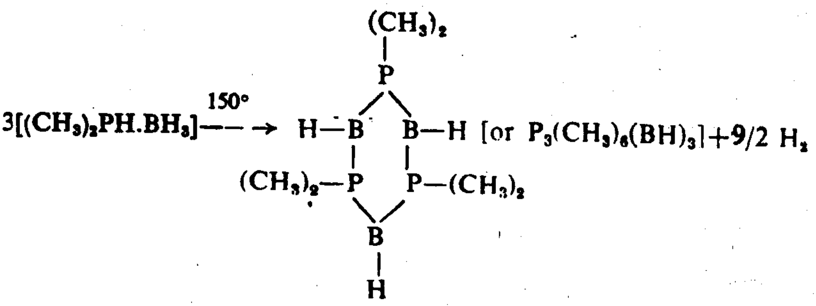
$$\frac{x}{2}B_2H_6+xPH_3 \xrightarrow{-xH_2} (PH_2BH_2)_x+xH_2$$

(*b*) At −110°C B_2H_6 reacts with PH_3 to yield an unstable product with the composition $PH_3.BH_3$.

$$\tfrac{1}{2}B_2H_6+PH_3 \xrightarrow{-110^\circ C} PH_3.BH_3$$

(*c*) When $(CH_3)_2PH$ reacts with B_2H_6, we get $(CH_3)_2 PH.BH_3$ which, on being heated at 150°C gives $P_3(CH_3)_6(BH)_3$ which is a cyclic compound, since it has ring structure like C_6H_6.

$$\tfrac{1}{2} B_2H_6+(CH_3)_2 PH \rightarrow (CH_3)_2PH.BH_3$$



$$3[(CH_3)_2PH.BH_3] \xrightarrow{150^\circ} \text{[or } P_3(CH_3)_6(BH)_3]+9/2\ H_2$$

13. *Reaction with alkali metals (M) in liq.NH_3.* The reaction is believed to occur as follows :

$$B_2H_6+M+NH_3 \rightarrow M[BH_4]+BH_2.NH_2+\tfrac{1}{2}H_2$$

Uses of Diborane. Among the boranes, diborane is the only frequently used borane, although other boranes may also find certain uses. Diborane is used : (*i*) as rocket fuel for supersonic bombers, (*ii*) for the preparation of high energy fuels and propellents. (*iii*) for the preparation of higher boranes, organic boron compounds and metal boron hydrides like $LiBH_4$, $NaBH_4$ etc. (*iv*) as a reducing agent in organic reactions. (*v*) as a catalyst in polymerisation reactions (*vi*) for welding torches.

Structure and Bonding in Diborane. Electron diffraction and infra-red spectroscopic studies of this molecule have shown that B_2H_6 has *hydrogen-bridge structure* shown in Fig. 18·1.

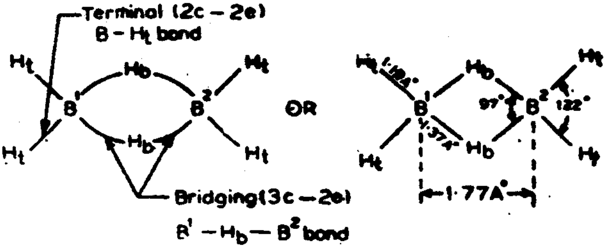


Fig. 18·1. Hydrogen-bridge structure of diborane molecule, B_2H_6

This structure contains two irregular BH_4 tetrahedrons which have one edge in common Thus *two boron atoms* (represented as B^1 and B^2) and *four terminal hydrogen atoms* (represented as H_t) lie in the plane of the paper (*i.e.* two boron atoms and four H_t atoms are co-planar) while the remaining two *bridge hydrogen atoms* (represented as H_b) are located centrally above and below this plane and thus prevent the rotation between the two boron atoms. Specific heat measurements also show that rotation is hindered. Thus we see that the plane containing the two boron atoms and four terminal hydrogen atoms is perpendicular to that containing the two bridging hydrogen atoms. The following points may be noted from the hydrogen-bridge structure :

(*i*) B^1-H_t bond length $= B^2-H_t$ bond length $= 1{\cdot}19A°$. This bond length is almost equal to that expected for a single bond given by the sum of the single-bond normal covalent radii of boron and hydrogen. *i.e.* $r_B + r_H = 0{\cdot}85 + 0{\cdot}30 = 1{\cdot}15A° \simeq 1{\cdot}19A°$.

(*ii*) B^1-H_b bond length $= B^2-H_b$ bond length $= 1{\cdot}37A°$ which is greater than $r_B + r_H$ $(= 1{\cdot}15A°)$.

(*iii*) $B^1—B^2$ bond length $= 1{\cdot}77A°$.

(*iv*) $H_tB^1H_t$ bond angle $= H_tB^2H_t$ bond angle $= 122°$ while $H_bB^1H_b$ bond angle $= H_bB^2H_b$ bond angle $= 97°$.

(*v*) B_2H_6 molecule has two types of bonds discussed below :

(*a*) *Four terminal* (*2c – 2e*) *$B-H_t$ bonds.* Each of these bonds is formed by the sharing of two electrons between two atoms (or nuclei) namely B and terminal H-atom (*i.e.* H_t atom). This bond is called *terminal two-centre-two-electron* $B-H_t$ *bond* and is denoted as ($2c-2e$) $B-H_t$ bond. It is a normal σ-covalent bond. Thus we see that ($2c-2e$) $B-H_t$ bond holds two atoms together.

(*b*) *Two bridging* ($3c-2e$) $B^1-H_b-B^2$ *bonds.* Each of these bonds is formed by the sharing of two electrons between three atoms (or nuclei) namely B^1, B^2 and bridging H (H_b) atoms This bond is called *bridging three-centre-two-electron* $B^1-H_b-B^2$ *bond* and is denoted as ($3c-2e$) $B-H_b-B$ bond. This bond makes a bridge between two *B*-atoms and is also called *bannana bond.* The briding ($3c-2e$) $B^1-H_b-B^2$ bond holds three atoms (B^1, B^2 and H_b) together. This bond is also called *open* ($3c-2e$) $B^1-H_b-B^2$ bond.

How are two bridging (3c—2e) $B^1-H_b-B^2$ bonds and four terminal (2c—2e) $B-H_t$ bonds formed ? Both boron atoms in B_2H_6 are sp^3 hybridised as shown below :

$2s^2.\ 2p_x^1\ 2p_y^0\ 2p_z^0$ (*Boron atom in its ground state*) ———→

$2s^1.\ 2p_x^1\ 2p_y^1\ 2p_z^0$ (*Boron atom in its excited state*) $\xrightarrow{sp^3\ hybridisation}$
$(sp^3)^1\ (sp^3)^1\ (sp^3)^1\ (sp^3)^0$ [*Four sp^3 hybrid orbitals, one being empty and the remaining three are singly-filled*]

sp^3 hybridisation scheme shown above makes it evident that each B-atom has four sp^3 hybrid orbitals, one being empty and the remaining three are singly-filled. Now, one singly-filled sp^3 hybrid orbital on B^1—atom, one empty sp^3 hybrid orbital on B^2—atom and singly-filled $1s$-orbital on one H_b atom overlap together and form one bridging ($3c-2e$) $B^1-H_b-B^2$ bond. Similarly one empty sp^3 hybrid orbital on B^1—atom, one singly-filled sp^3 hybrid orbital on B^2—atom and one singly-filled $1s$ orbital on the other H_b atom overlap together and form other bridging ($3c-2e$) $B^1-H_b-B^2$ bond. Obviously this bond results from sp^3 (B^1)—$1s$ (H_b)—sp^3 (B^2) ovarlap. Thus, in all, two bridging ($3c-2e$) $B^1-H_b-B^2$ bonds are obtained in B_2H_6 molecule. Each of these bonds makes a bridge between the two boron atoms namely B^1 and B^2 and holds three atoms (B^1, B^2 and H_b) together (Fig. 18·2). Sometimes this bond is represented as B—H—B or B......H......B.

It may be seen that, after two bridging ($3c-2e$) $B^1-H_b-B^2$ bonds have been formed, two of the four sp^3 hybrid orbitals on each B—atom are consumed in the formation of these bonds and the remaining two sp^3 hybrid orbitals (both being singly-filled) on each B—atom are still left unused. Each of these two unused sp^3 hybrid orbitals is singly-filled. Each of these two singly-filled sp^3 hybrid orbitals of each boron atom overlaps with singly-filled $1s$ orbital of H_t atom to form terminal ($2c-2e$). $B-H_b$ bond (Fig. 18·2). This bond is a normal σ-bond and results from $sp^3(B)-1s(H_t)$ overlap. This bond holds two atoms (B and H_t) together. Thus we see that B_2H_6 has four terminal ($2c-2e$) $B-H_t$ bonds.

The formation of two bridging (3*c*—2*e*) $B^1—H_b—B^2$ and four terminal (2*c*—2*e*) $B—H_t$ bonds in B_2H_6 molecule has been shown in Fig. 18·2.

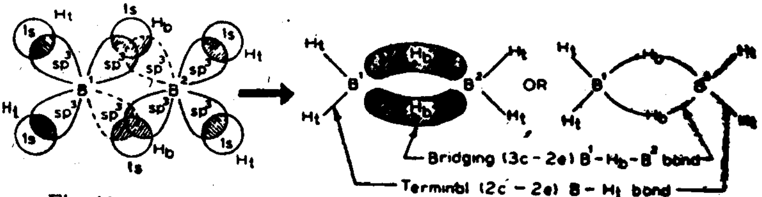
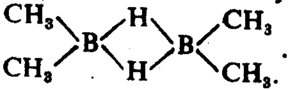


Fig. 18·2. Formation of two bridging (3*c*—2*e*) $B^1—H_b—B^2$ and four terminal (2*c*—2*e*) $B—H_t$ bonds in B_2H_6 molecule. Empty sp^3 hybrid orbitals have been shown by dotted lines.

Facts supporting the bridging structure. (*i*) Nuclear magnetic resonance study and Raman spectra have shown that in B_2H_6 molecule four terminal hydrogen atoms are of one type while the remaining two bridging hydrogen atoms are of different type.

(*iii*) That the four terminal hydrogen atoms are different from the remaining two bridging hydrogen atoms has also been confirmed by the fact that when B_2H_6 is methylated by $B(CH_3)_3$, only terminal H atoms can be replaced at the most by CH_3 groups to give the tetramethyl diborane, $(CH_3)_4B_2H_2$ whose structure is



$$\begin{matrix} CH_3 & & H & & CH_3 \\ & B & & B & \\ CH_3 & & H & & CH_3 \end{matrix}$$

. Thus the bridging H-atoms remain undisturbed in the reaction between B_2H_6 and $B(CH_3)_3$.

(*iii*) Specific heat measurements have shown that the two ends of B_2H_6 molecule cannot be rotated against each other. This hindered rotation clearly shows that the two bridging hydrogen atoms lie in a plane which is at right angle to that in which the two boron atoms and the four terminal hydrogen atoms lie.

Types of Bonds Found in Higher Boranes

Higher boranes may contain some or all of the following types of bonds :

(*i*) *Terminal* (2*c*--2*e*) *B—H bond.* This is a normal covalent bond and is represented as B—H. The formation of this bond has already been explained in the discussion of B_2H_6 molecule.

(*ii*) *Direct* (2*c*—2*e*) *B—B bond.* It links two B-atoms and is represented as B—B.

(*iii*) *Open or bridging* (3*c*—2*e*) *B—H—B bond.* It links two B-atoms and one H-atom together and is represented as B—H—B or B...H...B. The formation of this bond has already been explained in the discussion of B_2H_6 molecule.

(*iv*) *Closed (3c—2e) B--B—B bond.* It links three B-atoms. Its formation has been shown in Fig. 18·3.

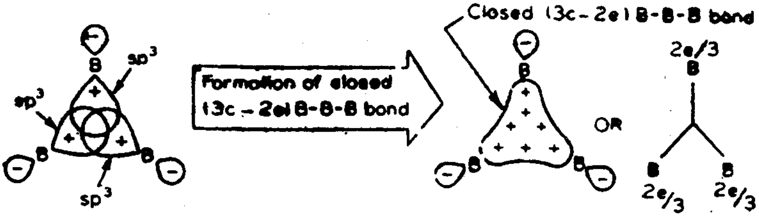


Fig. 18·3. Formation of closed (*3c--2e*) B—B—B bond.

It may be seen from Fig. 18·3 that the closed (3*c*—2*e*) B—B—B bond results by the overlap of three hybrid orbitals on B-atoms which are situated at the three corners of an equilateral triangle. Thus to this bond each boron atom contributes 2*e*/3 electrons.

(*v*) *Open or bridging (3c—2e) B—B—B bond.* This bond links three B-atoms and is also called *boron bridge bond.* Its formation has been shown in Fig. 18·4.

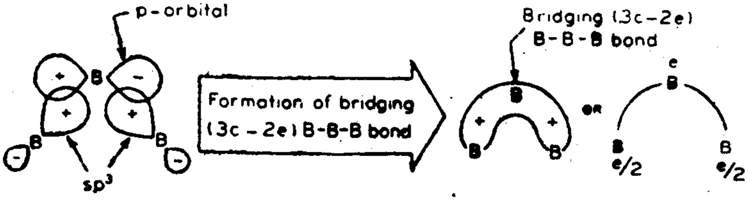


Fig. 18·4. Formation of a bridging (3*c*—2*e*) B—B—B bond.

It may be seen from Fig. 18·4 that the bridging (3*c*—2*e*) B—B—B bond is formed by the overlap of two hybrid orbitals on two B-atoms and one *p* orbital on the third B-atom. Thus we find that the difference between these bonds lies in the choice of orbitals overlapping together for their formation. Since theoretical studies have not shown the presence of bridging (3*c*—2*e*) B—B—B bonds in boranes, all the structures of boranes shown in this book have closed (3*c*—2*e*) B—B—B bonds.

Structure and Bonding in Higher Boranes

Now let us discuss the bonding in some higher boranes such as B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$.

1. **Tetraborane, B_4H_{10}.** In this molecule four B-atoms may be regarded as a portion of a slightly distorted octahedron. The structure of this molecule has been shown in Fig. 18·5 which indicates that this molecule contains : (*i*) Four bridging (3*c*−2*e*) B−H−B bonds *viz* B^1-H-B^3, B^2-H-B^3, B^1-H-B^4 and B^2-H-B^4 (*ii*) one direct (2*c*—2*e*) B—B bond (B^1-B^2 bond) (*iii*) six terminal (2*c*—2*e*) B−H bonds namely B^3-H, B^3-H, B^2-H, B^2-H, B^4-H and B^4-H bonds.

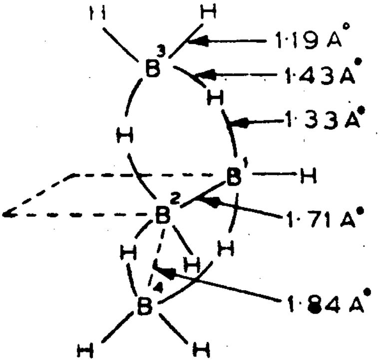


Fig. 18·5. Structure of tetraborane, B_4H_{10}.

2. **Pentaborane-9, B_5H_9.** In this molecule five B-atoms occupy the five corners of a square pyramid. Each boron atom is linked with one H-atom by a terminal (2*c*−2*e*) B−H bond. Four B-atoms located in the base of the square pyramid (*i.e.* basal B-atoms namely B^1, B^2, B^3 and B^4 atoms) are bonded to each other by four bridging (3*c*−2*e*) B−H−B bonds while the B-atom (namely B^5 atom) located at the apex (apical B-atom) of the pyramid is bonded to the basal two B-atoms (namely B^1 and B^4 atoms) by two (2*c*—2*e*) B−B bonds. This molecule also contains one closed (3*c*−2*e*) B−B−B bond. Thus the structure of this molecule can be shown as depicted in Fig. 18·6. This figure indicates that B_5H_9 molecule contains five terminal B−H bonds (*viz* B^1-H, B^4-H, B^2-H, B^3-H and B^5-H bonds), four bridging B−H−B bonds (namely B^1-H-B^2, B^2-H-B^3, B^3-H-B^4, and B^4-H-B^1 bonds), two B−B bonds (B^1-B^5 and B^5-B^4 bonds) and one closed (3*c*—2*e*) $B^5-B^3-B^2$ bond. Thus this molecule contains all the types of bonds found in higher boranes.

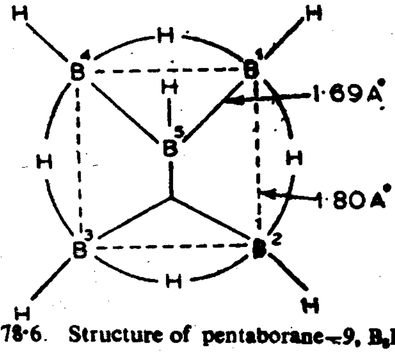


Fig. 78·6. Structure of pentaborane-9, B_5H_9.

3. **Pentaborane-11, B_5H_{11}.** This molecule has an unsymmetrical square pyramidal structure. Like five B-atoms of B_5H_9 molecule, the five B-atoms of B_5H_{11} molecule also occupy the five corners of a square pyramid. B^2 and B^3 basal boron atoms and B^5 apical boron atom each are linked with two H-atoms by two terminal B—H bonds while the remaining B^1 and B^4 basal boron atoms each are linked with one H-atom by one terminal B—H bond. This molecule also contains three brigding (3*c*—2*e*) B—H—B bonds and two closed (3*c*—2*e*) B—B—B bonds. Thus this molecule contains eight terminal B—H bonds (*viz* B^1—H, B^2—H, B^2—H, B^3—H, B^3—H, B^4—H, B^5—H and B^5—H bonds), three bridging (3*c*—2*e*) B—H—B bonds (namely B^1—H—B^4, B^4—H—B^3 and B^2—H—B^1 bonds) and two closed (3*c*—2*e*) B—B—B bonds (B^1—B^4—B^5 and B^2—B^3—B^5 bonds). (See Fig. 18·7)

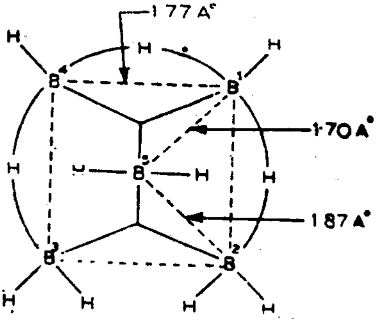


Fig. 18·7. Structure of pentaborane—11, B_5H_{11}

4. **Hexaborane-10, B_6H_{10}.** In this molecule the six boron atoms lie at the corners of a pentagonal bipyramid. Each boron atom is linked with one H-atom by terminal B—H bond. Thus this molecule has six terminal B—H bonds namely B^1—H, B^2—H, B^3—H B^4—H, B^5—H and B^6—H bonds. This molecule also contains four bridging (3*c*—2*e*) B—H—B bonds (*viz* B^1—H—B^2, B^2—H—B^3, B^3—H—B^4 and B^4—H—B^5 bonds), two B—B bonds (B^1—B^5 and B^3—B^6 bonds) and two closed (3*c*—2*e*) B—B—B bonds (B^4—B^5—B^6 and B^1—B^2—B^6 bonds). All these bonds have been shown in Fig. 18·8.

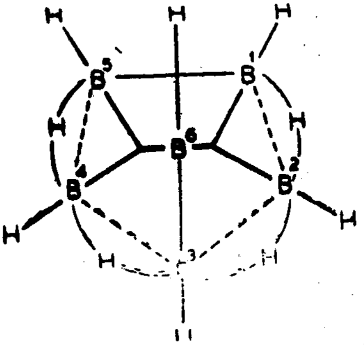


Fig. 18·8. Structure of hexaborone—10, B_6H_{10}

5. Decaborane—14, $B_{10}H_{14}$. The structure of this molecule has been determined by X-ray analysis. The boron atoms are arranged in two pentagonal pyramids with an edge common to both the pentagonal pyramids. This molecule has four bridging ($3c$—$2e$) B—H—B bonds namely B^5—H—B^6, B^6—H—B^7, B^8—H—B^9 and B^9—H—B^{10} in the open face. Each of B-atoms is linked with one H-atom by terminal B—H bonds. Thus the molecule has ten terminal B—H bonds *viz* B^1—H, B^2—H, B^3—H, B^4—H, B^5—H, B^6—H, B^7—H, B^8—H, B^9—H and B^{10}—H bonds. In addition to these bonds, the molecule also has four B—B bonds (B^2—B^5, B^2—B^7, B^4—B^8, B^4—B^{10}) and four closed ($3c$—$2e$) B—B—B bonds (B^1—B^2—B^3 B^1—B^3—B^4, B^1—B^5—B^{10} and B^3—B^7—B^8 bonds). (See Fig. 18·9)

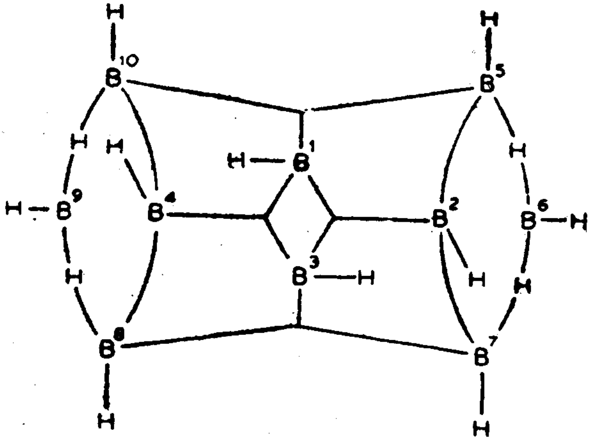


Fig..18·9. Structure of decaborane—14, $B_{10}H_{14}$

19

Metallic Carbonyls and Metallic Nitrosyls

METALLIC CARBONYLS

The electronic configuration of CO molecule shows that it has a lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair to a transition metal atom (M), forming OC → M coordinate bond. The compounds formed by the combination of CO molecules with transition metals are known as metallic carbonyls. Since the electrons forming OC → M bond are supplied solely by CO molecules, metal atom in carbonyls is said to be in zero oxidation state. In metal carbonyls CO molecules act as neutral ligands. Depending on the number of metal atoms in a given carbonyl, carbonyls have been classified into the followiug two types :

1. *Mononuclear* (or *monomeric*) *carbonyls which contain only one metallic atom per molecule* and are of the type $M(CO)_y$. Examples are : $V(CO)_6$, $Cr(CO)_6$ etc.

2. *Polynuclear carbonyls which contatn two or more metallic atoms per molecule* and are of the type $M_x(CO)_y$. However some authors call the carbonyls containing two metal atoms as *bridged carbonyls* and those containing more than two metal atoms as *polynuclear carbonyls*. Polynuclear carbonyls may be *homonuclear* [*e.g.* $Fe_3(CO)_{12}$] or *heteronuclear* [*e.g.* $MnCo(CO)_9$, $MnRe(CO)_{10}$].

General methods of preparation (*i*) *By direct synthesis.* The carbonyls like $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$ can be prepared by the direct combination of CO with finely-divided metals at suitable temperature and pressure. For example :

$$Fe+5CO\xrightarrow{\text{200°C, 100 atm. pressure}}Fe(CO)_5$$

$$Ni+4CO\xrightarrow{\text{Room temp., one atm. pressure}}Ni(CO)_4$$

$$2Co+8CO\xrightarrow{\text{200°C, 100 atm. pressure}}Co_2(CO)_8$$

(*ii*) *By carbonylating the metallic salts with CO in presence of a reducing agent.* When salts like RuI_3, $CrCl_3$, VCl_3, CoS, $CoCO_3$, CoI_2 etc, are treated with CO (carbonylation) in presence of a suitable reducing agent like Mg, Ag, Cu, Na, H_2, $LiAlH_4$ etc, metallic carbonyls are obtained. For example :

$$CrCl_3+CO+LiAlH_4 \xrightarrow{\text{115°C, 70 atm. pressure}} Cr(CO)_6+LiCl+AlCl_3$$

$$2RuI_3+10CO+6Ag \xrightarrow{\text{175°C, 250 atom pressure}} 2Ru(CO)_5+6AgI$$

$$\underset{\text{(in diethyl ether)}}{2MnI_2+10CO+2Mg} \xrightarrow{\text{25°C, 210 atm. pressure}} Mn_2(CO)_{10}+2MgI_2$$

$$2CoS+8CO+4Cu \xrightarrow{\text{200°C, 200 atm. pressure}} Co_2(CO)_8+2Cu_2S$$

$$2FeS+10CO+2Cu \xrightarrow{\text{200°C, 200 atom. pressure}} 2Fe(CO)_5+Cu_2S$$

$$2CoI_2+8CO+4Cu \xrightarrow{\text{200°C, 200 atm. pressure}} Co_2(CO)_8+4CuI$$

$$FeI_2+5CO+2Cu \xrightarrow{\text{200°C, 200 atm. pressure}} Fe(CO)_5+Cu_2I_2$$

$$2CoCO_3+8CO+2H_2 \xrightarrow{\text{120-200°C, 250—300 atm. pressure}} Co_2(CO)_8 + 2CO_2+2H_2O$$

$$\underset{\text{(in pyridine)}}{2Cr(acac)_3+12CO+3Mg} \xrightarrow{\text{160°C, 300 atm. pressure}} 3Mg(acac)_2 + 2Cr(CO)_6$$

$$MoCl_5+6CO+5Na \xrightarrow{\text{(in diglyme)}} Mo(CO)_6+5NaCl$$

Sometimes CO acts both as a carbonylating and reducing agent. For example in the preparation of $Os(CO)_5$ and $Re_2(CO)_{10}$ from OsO_4 and Re_2O_7 respectively, CO acts both as a carbonylating and reducing agent.

$$OsO_4+5CO \xrightarrow{\text{250°C, 350 atm. pressure}} Os(CO)_5+2O_2$$

$$2Re_2O_7+10CO \longrightarrow Re_2(CO)_{10}+7O_2$$

$V(CO)_6$ is prepared by the method represented by the following equation :

$$\underset{\text{(in diglyme)}}{VCl_3+6CO+Na} \xrightarrow[\text{Acidification by } H_3PO_4]{\text{100°C, 150 atm. pressure}} V(CO)_6+3NaCl$$

Here *diglyme* indicates diethylene glycol dimethyl ether.

(*iii*) *Preparation of $Mo(CO)_6$ and $W(CO)_6$ from $Fe(CO)_5$.* Since CO groups present in $Fe(CO)_5$ are labile, they can be replaced by Cl^- ions by treating $Fe(CO)_5$ with $MoCl_6$ or WCl_6 and thus $Mo(CO)_6$ and $W(CO)_6$ can be obtained. Thus :

$$MoCl_6+3Fe(CO)_5 \xrightarrow{100°C,\ ether} Mo(CO)_6+3FeCl_2+9CO$$

$$WCl_6+3Fe(CO)_5 \xrightarrow{100°C,\ ether} W(CO)_6+3FeCl_2+9CO$$

(*iv*) *Preparation af $Fe_2(CO)_9$ and $Os_2(CO)_9$ from $Fe(CO)_5$ and $Os(CO)_5$.* When cooled solution of $Fe(CO)_5$ and $Os(CO)_5$ in glacial CH_3COOH is irradiated wath ultra-violet light, $Fe_2(CO)_9$ and $Os_2(CO)_9$ are obtained respectively.

$$2Fe(CO)_5 \xrightarrow{ultra\text{-}violet\ light} Fe_2(CO)_9+CO$$

$$2Os(CO)_5 \xrightarrow{ultra\text{-}violet\ light} Os_2(CO)_9+CO$$

General properties (*a*) **Physical.** With the exception of $Ni(CO)_4$, $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$ which are liquids at ordinary temperatures, all other carbonyls are crystalline solids. They melt or decompose at low temperatures. All are typical covalent compounds and for this reason they are soluble in non-polar solvents. With the exception of $Fe_2(CO)_9$, all are more or less soluble in organic solvents. Excepting $V(CO)_6$, all the carbonyls are *diamagnetic*. $V(CO)_6$ is *paramagnetic* and its paramagnetic property corresponds to the presence of one unpaired electron. The metals in carbonyls are in zero oxidation state.

(*b*) **Chemical** (*i*) *Substitution reactions.* Some or all CO groups present in carbonyls can be replaced by monodentate ligiands like alkyl or aryl isocyanide (CNR), PR_3, PCl_3, *py*, CH_3OH etc. For example :

$$Ni(CO)_4+4CNR \rightarrow Ni(CNR)_4+4CO$$

$$Ni(CO)_4+4PCl_3 \rightarrow Ni(PCl_3)_4+4CO$$

$$Fe(CO)_5+2CNR \rightarrow Fe(CO)_3(CNR)_2+2CO$$

$$Mn_2(CO)_{10}+PR_3 \rightarrow 2Mn(CO)_4(PR_3)+2CO$$

$$2Fe_3(CO)_{12}+3py \rightarrow Fe_3(CO)_9(py)_3+3Fe(CO)_5$$

$$2Fe_3(CO)_{12}+3CH_3OH \rightarrow Fe_3(CO)_9(CH_3OH)_3+3Fe(CO)_5$$

$$Cr(CO)_6 \xrightarrow{+py} \underset{\substack{\text{yellow brown}\\ \text{solid}}}{Cr(CO)_4(py)_2} \xrightarrow{+py} \underset{\substack{\text{yellow red}\\ \text{solid}}}{Cr_3(CO_7(py)_5} \xrightarrow{+py} \underset{\substack{\text{bright red}\\ \text{solid}}}{Cr(CO)_3(py)_3}$$

Bidentate ligands like *diars*, o-phen, NO_2 etc replace two or more CO groups, at a time. For example :

$$Mo(CO)_6+diars \rightarrow Mo(CO)_4\ (diars)+2CO$$

$$Fe(CO)_5+diars \rightarrow Fe(CO)_3\ diars+2CO$$

$Ni(CO)_4 + o\text{-}phen \rightarrow Ni(CO)_2\,(o\text{-}phen) + 2CO$

$Ni(CO)_4 + diars \rightarrow Ni(CO)_2\,(diars) + 2CO$

$Cr(CO)_6 + 2diars \rightarrow Cr(CO)_2\,(diars)_2 + 4CO$

$Ni(CO)_4 + 2NO_2 \rightarrow Ni(NO_2)_2 + 4CO$

(*ii*) *Action of NaOH or Na metal*: *Formation of carbonylate anion* (*Reduction*). Aqueous or alcoholic solution of NaOH reacts with $Fe(CO)_5$ to form carbonylate anion, $[HFe(CO)_4]^-$

$$Fe(CO)_5(Fe=0) + 3NaOH \rightarrow Na^+[H^+Fe^{2-}(CO)_4]^- + Na_2CO_3 + H_2O$$

H-atom in $[H^+Fe^{2-}(CO)_4]^{--}$ ion is acidic which means that Fe-atom in this ion is in -2 oxidation state.

Na-metal in liquid NH_3 converts $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Cr(CO)_6$, $Mn_2(CO)_{10}$ etc. into carbonylate anions and in this conversion these carbonyls are reduced.

$$\underset{(Fe=0)}{Fe_2(CO)_9} + 4Na \longrightarrow 2Na_2^+[Fe^{2-}(CO)_4]^{2-} + CO$$

$$\underset{(Co=0)}{Co_2(CO)_8} + 2Na \longrightarrow 2Na^+[Co^-(CO)_4]^-$$

$$\underset{(Fe=0)}{Fe_3(CO)_{12}} + 3Na \longrightarrow 3Na^+[Fe^-(CO)_4]^-$$

$$\underset{(Cr=0)}{Cr(CO)_6} + 2Na \longrightarrow Na_2^+[Cr^{2-}(CO)_5]^{2-} + CO$$

$$\underset{(Mn=0)}{Mn_2(CO)_{10}} + 2Na \longrightarrow 2Na^+[Mn^-(CO)_5]^-$$

(*iii*) *Action of halogens*. Most of the carbonyls react with halogens to form carbonyl halides. For example :

$$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO$$

$$Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4Cl_2 + 2CO$$

$$Mn_2(CO)_{10} + X_2 (X=Br,\ I) \rightarrow 2Mn(CO)_5X$$

$Co_2(CO)_8$ and $Ni(CO)_4$ both get decomposed into metallic halides and CO when treated with halogens.

$$Co_2(CO)_8 + 2X_2 \rightarrow 2CoX_2 + 8CO$$

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO$$

(*iv*) *Action of NO*. Many carbonyls react with nitric oxide (NO) to form metal carbonyl nitrosyls. For example :

$$Fe(CO)_5 + 2NO \xrightarrow{95^\circ C} Fe(CO)_2\,(NO)_2 + 3CO$$

$$3Fe_2(CO)_9 + 4NO \longrightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6\,CO$$

$$Fe_3(CO)_{12} + 6NO \xrightarrow{85^\circ C} 3Fe(CO)_2(NO)_2 + 6CO$$

$$Co_2(CO)_8+2NO\xrightarrow{40°C}2Co(CO)_3(NO)+2CO$$

Moist NO gives a blue-coloured compound, Ni(NO)(OH) with $Ni(CO)_4$ while dry NO gives a blue solution of the composition, $Ni(NO)(NO_2)$

$$2Ni(CO)_4+2NO+2H_2O\rightarrow 2Ni(NO)(OH)+8CO+H_2$$

$$Ni(CO)_4+4NO\rightarrow Ni(NO)(NO_2)+4CO+N_2O$$

(u) *Action of H_2 : Formation of carbonyl hydrides* (*Reduction*). When $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ react with H_2, they are reduced to carbonyl hydrides, $Mn(CO)_5H$ and $Co(CO)_4H$ respectively.

$$Mn_2(CO)_{10}+H_2\xrightarrow{200°C,\ atm.\ pressure}2[Mn^-(CO)_5H^+]^0$$

$$Co_2(CO)_8+H_2\xrightarrow{165°C,\ 200\ atm.\ pressure}2[Co^-(CO)_4H^+]$$

(*vi*) *Action of heat*. Different carbonyls give different products when heated. For example :

$$Fe(CO)_5\xrightarrow{250°C}Fe+5CO$$

$$\underset{\text{(in toluence)}}{3Fe_2(CO)_9}\xrightarrow{70°C,\ Cool}3Fe(CO)_5+Fe_3(CO)_{12}$$

$$Fe_3(CO)_{12}\xrightarrow{140°C}3Fe+12CO$$

$$2Co_2(CO)_8\xrightarrow{50°C\ \text{(inert atmosphere)}}Co_4(CO)_{12}+4CO$$

$$Ni(CO)_4\xrightarrow{180°C}Ni+4CO$$

$$3Fe_2(CO)_9\xrightarrow{50°C}2Fe_3(CO)_{12}+3CO$$

Structure and Nature of M–CO Bonding in Carbonyls

1. **Mononuclear carbonyls.** The structure of mononuclear carbonyls *viz.* $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ have been studied by X-ray diffraction, infrared spectroscopy and [except for $V(CO)_6$] electron-diffraction. The last method has also been used for $Mo(CO)_6$ and $W(CO)_6$. All the mono-nuclear carbonyls have *linear* M–CO bonds in which CO group is linked to the metal atom through the carbon atom, since oxygen atom is more electronegative than carbon.

All the mononuclear carbonyls have the expected shapes, *e.g.* hexacarbonyls, $M(CO)_6$ (M=V, Cr, Mo, W) with M having coordination number (C.N.) equal to 6 have octahedral shape, pentacarbonyls, $M(CO)_5$ (M=Fe, Ru, Os) with C.N. of M=5 have trigonal bipyramidal shape and $Ni(CO)_4$ (C.N. of Ni=4) has tetrahedral shape. Octahedral trigonal bipyramidal and tetrahedral shapes arise due to d^2sp^3, dsp^3 and sp^3 hybridisation of the metallic atom. Each of the empty hybrid orbitals on metal atom overlaps with the filled *sp* hybrid orbital on C-atom of CO molecule [According to Coulson the molecular orbital cofiguration of CO molecule is $(sp)O^2$, $(\sigma_{sp}{}^b)^2$, $(\pi_y{}^b)^2=(\pi_z{}^b)^2$, $(sp)c^2$, $(\pi_y{}^*)^0=(\pi^*{}_z)^0$, $(\sigma_{sp}{}^*)^0$ and forms M←CO σ bond. [in getting the molecular orbital configuration, *x*-axis has been assumed to be the molecular axis and *sp* hybrid orbitals have been obtained by the combination of 2*s* and $2p_x$ orbitals]. For example the formation of Ni←COσ bond in $Ni(CO)_4$ molecule takes place by the overlap between empty sp^3 hybrid orbital on Ni atom and filled *sp* hybrid orbital on C-atom of CO molecule as shown in Fig. 19·1. Other three Ni←CO σ-bonds are formed in a similar manner.

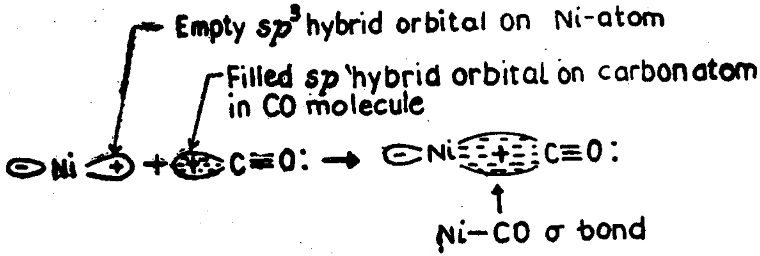


Fig. 19·1. Formation of one Ni←CO σ-bond in $Ni(CO)_4$ molecule.

In case of $M(CO)_5$ and $M(CO)_6$ type carbonyls M←CO σ bond results by the overlap between the vacant dsp^3 and d^2sp^3 hybrid orbital on metal atom and filled *sp* hybrid orbital an C-atom of CO molecule. In the formation of M←CO σ-bond, metal atom acts as an *acceptor* while CO molecule acts as a *donor*.

Since the metal atom in metal carbonyls is in zero oxidation state, the formation of M←CO σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counterbalanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a M→CO π bond by the overlap between an appropriate filled orbital on the metal atom and empty $\pi_y{}^*$ or $\pi_z{}^*$

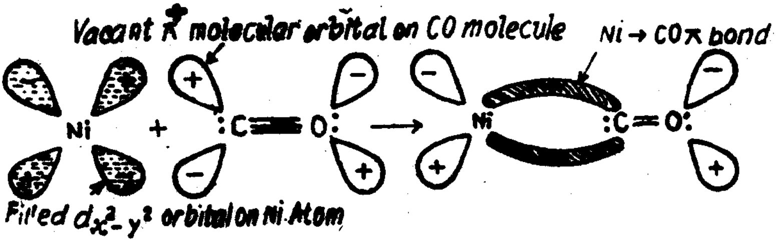


Fig. 19·2. Formation of one Ni → CO π bond in Ni $(CO)_4$

molecular orbital on CO molecule (See the molecular orbital configuration of CO molecule given by Coulson). For example Ni→CO π-bond in $Ni(CO)_4$ molecule results by the overlap between the filled $d_z{}^2$ or $d_{x^2-y^2}$ orbital on Ni-atom [Note that in $Ni(CO)_4$ valence-shell configuration of Ni-atom is $3d_{xy}{}^2$, $3d_{yz}{}^2$ $3d_{zx}{}^2$ $3d_{x^2-y^2}$ $3d_z{}^2$. $4s^0$ and not $3d_{xy}{}^2$ $3d_{yz}{}^2$ $3d_{zx}{}^2$ $3d_{x^1-y^2}$ $3d_z{}^1$. $4s^2$] and empty $\pi_y{}^*$ or $\pi_z{}^*$ molecular orbital on CO molecule (Fig. 19·2.)

When we consider the formation of both the types of bonds in $Ni(CO)_4$, we find that in this molecule two CO molecules are linked with Ni atom exclusively by Ni ← CO σ-bond while the remaining two CO molecules are linked to Ni atom by Ni←CO σ as well as by Ni → CO π bonds. Through resonance an average bond order of 1·5 between Ni and CO is established.

In the formation of M → CO π-bonds in $M(CO)_6$ carbonyls it is filled d_{xy}, d_{yz} and d_{zx} orbitals of M atom which are used to overlap with *vacant* $\pi_y{}^*$ and $\pi_z{}^*$ molecular orbitals of CO molecules to form M → CO π-bonds, since $d_z{}^2$ and $d_{x^2-y^2}$ orbitals of M atom have already been used in the formation of six d^2sp^3 hybrid orbitals. It can be shown that in $M(CO)_6$ carbonyls three out of six CO molecules are linked with M atom exclusively by M←CO σ bonds while the remaining three CO molecules are attached by M ← CO σ and M → CO π-bonds. An average bond order of 1·92A° for Cr—CO bond has been established in $Cr(CO)_6$ molecule.,

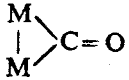
In the formation of M→CO π-bond metal atom acts as a *donor* (Lewis base) while CO molecule acts as an *acceptor* (Lewis acid or π-acid), since CO molecule receives back-donated electrons from the metal atom in low or zero oxidation state into its empty $\pi_y{}^*$ or $\pi_z{}^*$ molecular orbital. M→CO π bond stabilises the low oxidation state of the metal atom in carbonyls. We have already said that CO in carbonyls functions as a poor donor, but on the formation of M → CO π bond the poor donor CO ligand becomes a substantially better donor. M → CO π bond is also called *back donation*, *back-bonding* or *back coordination.*

Since the formation of M → CO π-bond takes place in the opposite direction of M ← CO σ-bond formation, the formation of M → CO π bond decreases the electron density (negative charge) accumulated on the metal atom during the formation of M ← CO σ-bond. The net result is that metal atom in left almost uncharged.

Thus we see that in carbonyls we have a double bond between the metal atom and CO molecule. One of these bonds is a M ← CO σ-bond and the other is a M → CO π bond. The presence of both the bonds in carbonyls strengthens the M — CO bonds and hence the stability of the carbonyls is increased.

It is also clear from the mode of the formation of M ← CO σ-bond and M → CO π-bond that in the former bond metal atom is acting as an acceptor while CO molecule is acting as a donor. On the other hand in the latter bond metal atom is acting as a donor while CO molecule is acting as an acceptor. Consequently *in metallic carbonyls both metal and the ligand* (*i.e.*, CO molecule) *function both as donors and acceptors*.

2. **Dinuclear carbonyls.** (*a*) *$Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ carbonyls.* In all these carbonyls each M atom is directly linked with the other M atom by a σ-bond (M—M σ-bond) and five terminal carbonyl groups (—C≡O) by a co-ordinate bond (M←C≡O). The presence of M—M bond is also supported by the diamagnetic nature of these carbonyls. These carbonyls do not have bridging carbonyl groups (>C=O) in between M atoms. Since the coordination number of each M atom in these carbonyls is six, each M atom is d^2sp^3 hybridised. All the electrons in these carbonyls are paired and hence these carbonyls are diamagnetic. The structure of $Mn_2(CO)_{10}$ has been explained in detail on page 585.

(*b*) *$Co_2(CO)_8$, $Fe_2(CO)_9$ and $Os_2(CO)_9$ carbonyls.* These carbonyls contain both types of carbonyl groups which are bridging carbonyl groups (>C=O) and terminal carbonyl groups (—C≡O). Bridging carbonyl groups exist between two metal atoms. The number of bridging carbonyl groups present in $Co_2(CO)_8$ (only in one isomeric form), $Fe_2(CO)_9$ and $Os_2(CO)_9$ is 2, 3 and 1 respectively while the number of terminal carbonyl groups is 6, 6 and 8 respectively. Each of the bridging carbonyl group is attached with the metal (M) by  bond while each of the terminal carbonyl groups is attached with the metal atom by O≡C→M co-ordinate bond. All these carbonyls have M—M bond. The presence of M—M bond confirms the diamagnetic nature of these carbonyls.

3. **Trinuclear carbonyls.** Here we shall consider the structures of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ carbonyls. The trinuclear corbonyls *viz* $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ have similar structures

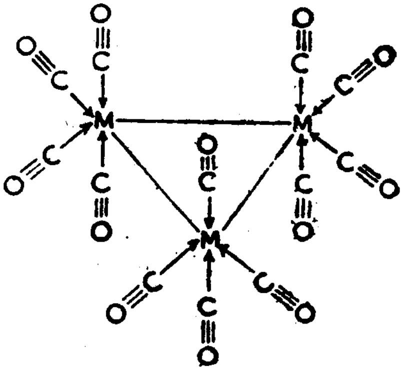


Fig. 19·3. Structure of $M_3(CO)_{12}$ type carbonyls (M=Os, Ru).

while $Fe_3(CO)_{12}$ has a different structure. $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ contain three metal (M) atoms. Each of these is linked with the remaining two M atoms. Thus there are three M—M bonds in each of these carbonyls. All the three M—M bonds lie in an equilateral triangle. Each M atom is attached with four terminal CO groups which make an approximately octahedral configuration around each M atom. These molecules do not have any bridging CO groups (*See* Fig. 19·3.)

For the structure of $Fe_3(CO)_{12}$ see page 590.

Effective Atomic Number (EAN) Rule As Applied to Metallic Carbonyls

(A) Mononuclear carbonyls having the metallic atom with even atomic number. $Cr(CO)_6$, $Mo(CO)_6$ $W(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$ etc. are the examples of such carbonyls. All such carbonyls obey the EAN rule according to which *after CO groups have donated a certain number of electron pairs to the zero valent metal atom through* $OC \rightarrow M$ *σ-bonding, the total number of electrons on the metal atom including those gained from CO molecules becomes equal to the atomic number of the next inert gas.* This is shown in Table 19·1.

Table 19·1. *EAN rule as applied to mononuclear carbonyls having metallic atoms with even atomic number. Note that in all the carbonyls metal atom is in zero oxidaiion state.*

Metal carbonyl	*No. of electrons on the central metal atom =At. No. of the metal atom=Z*	*No. of electrons donated by CO molecules=x*	*EAN of the metal atom in carbonyl =Z+x (symbol of the next inert gas is given in parentheses)*
$Cr(CO)_6$	24	6×2=12	24+12=36 (Kr)
$Mo(CO)_6$	42	6×2=12	42+12=54 (Xe)
$W(CO)_6$	74	6×2=12	74+12=86 (Rn)
$Fe(CO)_5$	26	5×2=10	26+10=36 (Kr)
$Ru(CO)_5$	44	5×2=10	44+10=54 (Xe,
$Os(CO)_5$	76	5×2=10	76+10=86 (Rn)
$Ni(CO)_4$	28	4×2=8	28+8=36 (Kr)

On the basis of EAN rule it can be explained why Ni atom does not form a hexacarbonyl, $Ni(CO)_6$. Non-formation of $Ni(CO)_6$ is because of the fact that EAN of Ni atom in $Ni(CO)_6$ would be equal to 28+2×6=40 which is not the atomic number of any of the noble gases.

(B) Mononuclear carbonyls having the metallic atom with odd atomic number. $V(CO)_6$ and hypothetical carbonyls *viz* $Mn(CO)_5$ and

$Co(CO)_4$ are the examples of such carbonyls. These carbonyls *do not obey* EAN rule as shown below :

$V = 23e^-$	$Mn = 25e^-$	$Co = 27e^-$
$6CO = 12e^-$	$5CO = 10e^-$	$4CO = 8e^-$
$V(CO)_6 = 35e^-$	$Mn(CO)_5 = 35e^-$	$Co(CO)_4 = 35e^-$

(C) **Polynuclear carbonyls.** Now let us see whether or not the polynuclear carbonyls like $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ obey EAN rule. It has been seen that these carbonyls obey EAN rule, if two electrons from each metal—metal bond present in these carbonyls are included in calculating the electrons per metal atom. The structures of $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Co_4(CO)_{12}$ show that these molecules contain *one* Mn—Mn, *one* Co—Co, *one* Fe—Fe, *three* Fe—Fe and *six* Co—Co bonds respectively and hence the EAN per metal atom in these molecules is calculated as follows :

(*i*) $Mn_2(CO)_{10}$: Electrons from 2Mn atoms $= 25 \times 2 = 50$
Electrons from 10CO molecules $= 10 \times 2 = 20$
Electrons from one Mn—Mn bond $= 1 \times 2 = 2$

$Mn_2(CO)_{10} = 72$
$\therefore$ EAN per Mn atom $= 72/2$
$= 36$(Kr)

(*ii*) $Co_2(CO)_8$: Electrons from 2Co atoms $= 2 \times 27 = 54$
Electrons from 8CO molecules $= 8 \times 2 = 16$
Electrons from one Co—Co bond $= 1 \times 2 = 2$

$Co_2(CO)_8 = 72$
$\therefore$ EAN per Co atom $= 72/2$
$= 36$(Kr)

(*iii*) $Fe_2(CO)_9$: Electrons from 2Fe atoms $= 2 \times 26 = 52$
Electrons from 9CO molecules $= 9 \times 2 = 18$
Electrons from one Fe—Fe bond $= 1 \times 2 = 2$
$Fe_2(CO)_9 = 72$
$\therefore$ EAN per Fe atom $= 72/2$
$= 36$(Kr)

(*iv*) $Fe_3(CO)_{12}$: Electrons from 3Fe atoms $= 3 \times 26 = 78$
Electrons from 12CO molecules $= 12 \times 2 = 24$
Electrons from three Fe—Fe bonds $= 3 \times 2 = 6$
$Fe_3(CO)_{12} = 108$
$\therefore$ EAN per Fe atom $= 108/3$
$= 36$(Kr)

(*v*) $Co_4(CO)_{12}$: Electrons from 4CO atoms $=4\times 27=108$

Electrons from 12CO molecules$=12\times 2=$ 24

Electrons from six Co—Co bonds$=2\times 6=$ 12

$Co_4(Co)_{12}=144$

$\therefore$ EAN per Co atom$=144/4$

$=36$(Kr)

18-Electron Rule As Applied to Metallic Carbonyls

The formation of mononuclear carbonyls by transition elements with *even atomic number* can also be explained on the basis of 18-electron rule as shown below in Table 19·2 for $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ carbonyls.

Table 19·2. *Formation of mononuclear carbonyls having metallic atoms with even atomic number on the basis of 18-electron rule*

Metal carbonyls (outer-shell configuration of metal atom is given in parentheses)	No. of outer-shell electrons on the metal atom in zero oxidation state $=a$	No. of electrons donated by CO molecules$=b$	Total number of electrons on the metal atom $=a+b$
$Cr(CO)_6$ ($Cr=3d^5\,4s^1$)	6	$2\times 6=12$	$6+12=18$
$Fe(CO)_5$ ($Fe=3d^6\,4s^2$)	8	$2\times 5=10$	$8+10=18$
$Ni(CO)_4$ ($Ni=3d^8\,4s^2$)	10	$2\times 4=8$	10+8 —18

The formation of binuclear carbonyls having metal atoms with *odd atomic number* can also be explained on the basis of 18-electron rule as shown below for $Co_2(CO)$s and $Mn_2(CO)_{10}$ carbonyls :

$Co_2(CO)_8$ ($Co=3d^7\,4s^2$)

2 Co $=2\times 9e^-=18e^-$

8 CO $=2\times 8e^-=16e^-$

Co—Co bond$=1\times 2e^-=2e^-$

$Co_2(CO)_8=36e^-$

$\therefore$ *Electrons on one Co atom$=18e^-$*

$Mn_2(CO)_{10}$ ($Mn=3d^5\,4s^2$)

2Mn$=2\times 7e^-$ $=14e^-$

10 CO$=10\times 2e^-=20e^-$

Mn—Mn bond$=2e^-$

$Mn_2(CO)_{10}=36e^-$

$\therefore$ *Electrons on one Mn atom$=18e^-$*

Here it may be noted that although Fe has an even atomic number ($=26$), the formation of its binuclear carbonyl, $Fe_2(CO)_9$ can also be accounted for by the 18-electron rule as shown below :

$2Fe(Fe=3d^6\,4s^2)=2\times 8e^-=16e^-$

$9CO=9\times 2e^-=18e^-$

Fe—Fe bond$=1\times 2e^-=2e^-$

$Fe_2(CO)_9=36e^-$

$\therefore$ *Electrons on one Fe atom$=36e^-/2=18e^-$*

SOME CARBONYLS

1. **Nickel tetra carbonyl, Ni $(CO)_4$. Preparation.** It is prepared by :

(*i*) passing CO over finely-divided nickel at 60°C.

$$Ni+4CO \xrightarrow{60^\circ C} Ni(CO)_4$$

(*ii*) by reducing potassium tetracyanonickelate (II), $K_2[Ni(CN)_4]$ with K-Hg amalgam. When $K_2[Ni(CN)_4]$ is reduced with K-Ag amalgam, a red solution of potassium tricyano nickelate (I), $K_2[Ni(CN)_3]$ is obtained. This compound absorbs CO at 90°C, probably forming $K_2[Ni(CN)_3(CO)]$. On treating the solution of this compound with HCl, $Ni(CO)_4$ is obtained.

$$K_2[Ni(CN)_3]+CO \xrightarrow{90^\circ C} K_2[Ni(CN)_3(CO)]$$

$$\underset{(Ni=+1)}{4K_2[Ni(CN)_3(CO)]}+2HCl \longrightarrow \underset{(Ni=0)}{Ni(CO)_4}+\underset{(Ni=+2)}{3K_2[Ni(CN)_4]}+2KCl+H_2$$

(*iii*) by the action of CO on nickel (II) phenyl dithiocarbamate, $Ni(S.SC.NH\,C_6H_5)_2$. (*Laboratory preparation.*)

$$\underset{\substack{\text{Nickel (II) phenyl dithiocarbamate}\\(Ni=+2)}}{2Ni(S.SC.NH\,C_6H_5)_2}+4CO \longrightarrow \underset{(Ni=0)}{Ni(CO)_4}+\underset{\substack{\text{Nickel (IV) phenyl}\\\text{dithiocarbamate}\\(Ni=+4)}}{Ni(S.SC.NH.C_6H_5)_4}$$

(*iv*) by passing CO through an alkaline suspension of $Ni(CN)_2$ or NiS.

$$Ni(CN)_2+4CO \longrightarrow Ni(CO)_4+C_2N_2$$

$$NiS+4CO \longrightarrow Ni(CO)_4+S$$

Properties. (*i*) It is a colourless liquid, boiling at 43° and solidifying at −25°C. It is miscible with benzene and is almost insoluble in water. Nickel carbonyl is highly poisonous.

(*ii*) *Action of H_2SO_4.* H_2SO_4 reacts with it as follows :

$$Ni(CO)_4+H_2SO_4 \longrightarrow NiSO_4+H_2+4CO$$

(*iii*) *Action of NO.* See "*General properties of carbonyls*" discussed on page 571.

(*iv*) *Substitution reactions.* Some or all CO groups can be replaced by monodentate (*e.g.* CNR, PCl_3 etc.) as well as by bidentate (*e.g. o-phen, 'diars, NO_2* etc.) ligands. For the examples see "*General properties of carbonyls*".

(*v*) *Action of heat.* See "*General properties of carbonyls*".

(*vi*) *Action of halogens.* See "*General properties of carbonyls*".

(*vii*) *Action of gaseous HCl.* Gaseous HCl decomposes the solution of $Ni(CO)_4$, evolving H_2 and CO.

$$Ni(CO)_4+2HCl\ (g) \longrightarrow NiCl_2+H_2+4CO$$

Uses. (*i*) Since $Ni(CO)_4$, on heating, is decomposed to metallic nickel, it is used in the production of nickel by Mond's process. (*ii*) It is also used in gas planting and also as a catalyst.

Structure. The vapour density of nickel tetra carbonyl and the freezing point of its solution in benzene has shown that the molecular formula of this compnud is $Ni(CO)_4$.

Electron diffraction studies made on this compound in the vapour state and X-ray diffraction studies made on this compound in the solid state have shown that $Ni(CO)_4$ molecule has tetrahedral shape with Ni—C—O linear units (Fig 19·4). The Ni—C bond length in this molecule has been found to be equal to 1·50 A° which is shorter by 0·32 A° in comparison to Ni—C single bond length (=1·82 A°) found in carbonyls. The C—O bond length in this carbonyl has been found to be equal to 1·15 A° which is larger than the C—O bond length in CO molecule (=1·128 A°).

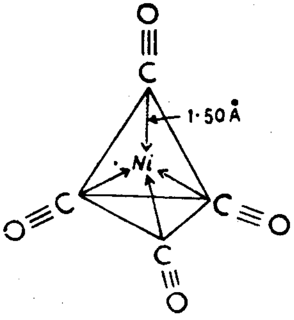
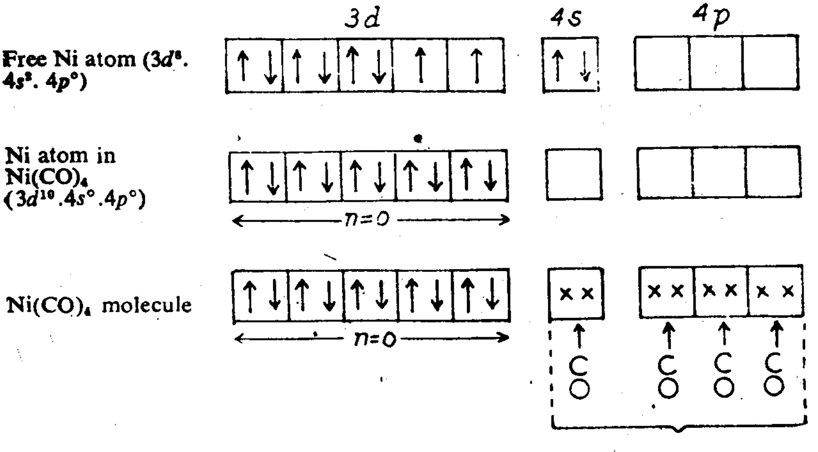


Fig. 19·4 Tetrahedral structure of $Ni(CO)_4$ molecule.

Tetrahedral shape of $Ni(CO)_4$ results from sp^3 hybridisation of Ni-atom. Since $Ni(CO)_4$ molecule is diamagnetic, all the ten electrons present in the valence shell of Ni-atom ($Ni = 3d^8\,4s^2$) get paired in 3*d* orbitals. Thus the valence-shell configuration of Ni-atom in $Ni(CO)_4$ molecule becomes $3d^{10}.\ 4s^0$. OC → Ni-bond results by the overlap between the empty sp^3 hybrid orbital on Ni-atom and doubly-filled *sp* hybrid orbital on C-atom in CO molecule.(Fig 19.5.)



sp^3 hybridisation—tetrahedral shape of $Ni(CO)_4$ molecule

Fig. 19.5. sp^3 hybridisation of Ni atom in tetrahedral $Ni(CO)_4$. × × indicate the electron pair donated by CO molecules. These electrons are in opposite spin.

It is to be pointed out here that, due to the formation of four OC→M bonds, a large negative charge is accumulated on the central Ni atom. This is most unlikely. In such a situation, Pauling suggested that the double bonding takes place with the back donation of *d*-electron from Ni atom to CO ligands to such an extent that electroneutrality principle is obeyed. According to this principle the electron pair is not shared equally between Ni and C-atoms of CO ligands but is attracted more strongly by C-atom which prevents the accumulation of negative charge on Ni-atom and is in keeping with the greater electronegativity of C-atom compared to Ni atom (C=2·5, Ni=1·8).

2. **Iron pentacarbonyl, $Fe(CO)_5$. Preparation.** It is prepared :

(*i*) by the direct combination of CO and iron metal.

$$Fe+5CO \xrightarrow{200°C,\ 100\ atm.\ pressure} Fe(CO)_5$$

(*ii*) by carbonylating FeI_2 or FeS with CO in presence of Cu-metal which acts as a reducing agent.

$$FeI_2+5CO+2Cu \xrightarrow{200°C,\ 200\ atm.\ pressure} Fe(CO)_5+Cu_2I_2$$

$$2FeS+10CO+2Cu \xrightarrow{200°C,\ 200\ atm.\ pressure} 2Fe(CO)_5+Cu_2S$$

Properties. (*i*) $Fe(CO)_5$ is a yellow liquid which is soluble in methyl alcohol, ether, acetone and C_6H_6. It is insoluble in H_2O.

(*ii*) *Decomposition.* On thermal decomposition at 250°C, it gives pure Fe.

$$2Fe(CO)_5 \xrightarrow{250°C} Fe+5CO$$

(*iii*) *Action of ultra-violet light.* When cooled solution of $Fe(CO)_5$ in glacial CH_3COOH is irradiated with ultra violet light, $Fe_2(CO)_9$ is formed.

$$2Fe(CO)_5 \xrightarrow{\text{ultra-violet light}} Fe_2(CO)_9+CO$$

The above reaction is reversed in darkness.

(*iv*) *Hydrolysis.* $Fe(CO)_5$ is hydrolysed by H_2O and acids.

$$Fe(CO)_5+H_2SO_4 \longrightarrow FeSO_4+5CO+H_2$$

(*v*) *Action of alkalies.* When heated with aqueous or alcoholic solution of NaOH, carbonylate anion, $[Fe^{2-}(CO)_4H+]^-$ is formed. The hydrogen atom in this anion is acidic which means that Fe is in −2 oxidation state.

$$\underset{(Fe=0)}{Fe(CO)_5}+3NaOH \longrightarrow Na^+[\underset{(Fe=-2)}{Fe^{2-}(CO)_4}H+]^-+Na_2CO_3+H_2O$$

(*vi*) *Action of NH_3.* With NH_3 it gives $Fe(CO)_4H_2$ and carbamic acid, NH_2COOH

$$Fe(CO)_5+H_2O+NH_3 \longrightarrow Fe(CO)_4H_2+NH_2COOH$$

(*vii*) *Reaction with halogens.* It reacts with halogens in non-aqueous solvents to form the stable tetra-carbonyl halides, $Fe(CO)_4X_2$.

$$Fe(CO)_5+X_2 \longrightarrow Fe(CO)_4X_2+CO$$

The velocities of these reactions follow the order $Cl<Br<I$.

(*viii*) *Reactions with ethylene diamine* (*en*) *and pyridine* (*py*). When $Fe(CO)_5$ reacts with ethylene diamine (*en*), an addition product, $Fe(CO)_5$ (*en*) is formed. Pyridine (*py*) reacts with it to give $[Fe(py)_6]$ $[Fe_4(CO)_{13}]$.

$$Fe(CO)_5+en \longrightarrow Fe(CO)_5(en)$$

$$5Fe(CO)_5+6py \longrightarrow [Fe(py)_6]\,[Fe_4(CO)_{13}]+12CO$$

(*ix*) *Reaction with NO.* Iron carbonyl nitrosyl, $Fe(CO)_2(NO)_2$ is formed when $Fe(CO)_5$ reacts with NO at 95°C.

$$Fe(CO)_5+2NO \xrightarrow{95^\circ C} Fe(CO)_2(NO)_2+3CO$$

(*x*) *Action on metallic and non-metallic halides.* The reactions between $Fe(CO)_5$ and metallic or non-metallic halides can be divided into two categories :

(*a*) When $Fe(CO)_5$ reacts with the halides like CCl_4, SO_2Cl_2, $SnCl_4$ $SbCl_5$ and $CuCl_2$, halides or carbonyl halides of Fe (II) are formed. Thus the oxidation state of Fe increases from zero to +2. For example :

$$Fe(CO)_5+2CCl_4 \longrightarrow Fe^{2+}Cl_2+C_2Cl_6+5CO$$

$$Fe(CO)_5+SO_2Cl_2 \longrightarrow Fe^{2+}Cl_2+SO_2+5CO$$

$$Fe(CO)_5+SnCl_4 \longrightarrow Fe^{2+}(CO)_4Cl_2+SnCl_2+CO$$

$$Fe(CO)_5+SbCl_5 \longrightarrow Fe^{2+}(CO)_4Cl_2+SbCl_3+CO$$

$$Fe(CO)_5+2CuCl_2 \longrightarrow Fe^{2+}Cl_2+2CuCl+5CO$$

(*b*) When $Fe(CO)_5$ reacts with WCl_6 or $MoCl_6$, all the CO groups present in $Fe(CO)_5$, being labile, are replaced by Cl-atoms. Thus in this reaction, $Fe(CO)_5$ acts as a dehalogenating and carbonylating agent. Oxidation state of Fe is increased from zero to +2 (in $FeCl_2$).

$$MCl_6(M=W,\ Mo)+Fe(CO)_5 \xrightarrow{100^\circ C,\ ether} M(CO)_6+3FeCl_2+9CO$$

(*xi*) *Action of air.* When $Fe(CO)_5$ is burnt in air, Fe_2O_3 is obtained.

$$4Fe(CO)_5+3O_2 \xrightarrow{Burn} 2\,Fe_2O_3+20CO$$

Structure. The vapour density and freezing point depression of iron pentacarbonyl in C_6H_6 solution has shown that the molecular formula of this compound is $Fe(CO)_5$. Electron diffraction, Raman and infra-red studies of this compound have shown that $Fe(CO)_5$ molecule has trigonal bipyramidal shape (Fig. 19·6) Electron diffraction study of $Fe(CO)_5$ in the vapour state has shown that Fe—C axial bond and Fe—C basal bond lengths are equal to 1·797A° and 1·842A° respectively while X-ray study has shown that these bond lengths are almost the same. Trigonal bipyramidal shape of $Fe(CO)_5$ results from *dsp^3* hybridisation of Fe-atom. (See Fig. 19·7)

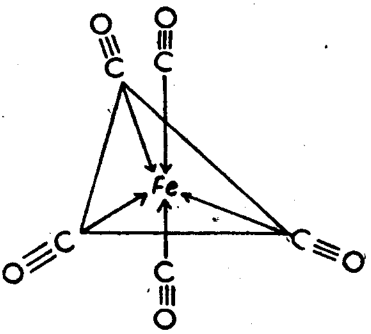
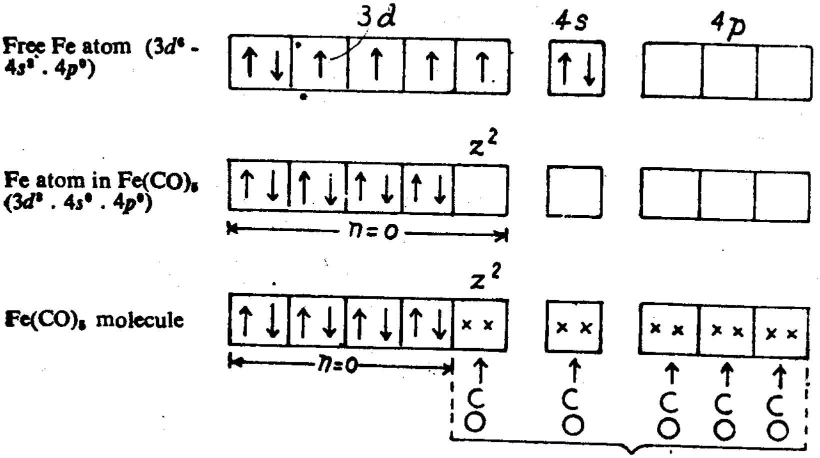


Fig. 19·6 Trigonal bipyramidal structure of $Fe(CO)_5$.

In this molecule Fe is in zero oxidation state and since $Fe(CO)_5$ is diamagnetic, all the eight electrons in the valence-shell of Fe atom ($Fe=3d^6 . 4s^2$) get paired in 3*d* orbitals. Thus the valence-shell configuration of Fe-atom in $Fe(CO)_5$ becomes $3d^8 . 4s^0$. OC → Fe σ-bond results by the overlap between empty *dsp^3* hybrid orbital on Fe-atom and doubly-filled *sp* hybrid orbital on C-atom in CO molecule.



dsp^3 hybridisation—trigonal bipyramidal shape of $Fe(CO)_5$ molecule

Fig. 19·7. *dsp^3* hybridisation of Fe atom in trigonal bipyramidal $Fe(CO)_5$ molecule.

3. **Chromium hexacarbonyl, $Cr(CO)_6$. Preparation.** (*i*) By carbonylating $CrCl_3$ with CO in presence of a reducing agent like lithium aluminium hydride, $LiAlH_4$.

$$CrCl_3+CO+LiAlH_4 \xrightarrow{175°C,\ 70\ atm.\ pressure} Cr(CO)_6+LiCl+AlCl_3$$

(*ii*) by treating $CrCl_3$ with CO in presence of C_6H_5MgBr (*Job's Grignard reaction*) under appropriate conditions.

Properties. (*i*) Chromium hexacarbonyl is a white solid. Crystals of $Cr(CO)_6$ are soluble in ether, chloroform, CCl_4 and C_6H_6.

(*ii*) It is resistant to chemical attack. For example it does not react with air, cold aqueous alkalies and acids (except conc. HNO_3).

(*iii*) *Decomposition.* It is decomposed by F_2 at —75°C to form CrF_6.

(*iv*) *Action of Na-metal or $NaBH_4$ in liquid NH_3 : Formation of carbonylate anion (Reduction).* When $Cr(CO)_6$ is treated with Na-metal or $NaBH_4$ in liq. NH_3, carbonylate anion is formed. In these reactions the carbonyl is reduced.

$$\mathrm{Cr(CO)_6\ (Cr=0)+2Na \xrightarrow{\text{liq. NH}_3} Na_2{}^+{}_2[Cr^{2-}(CO)_5]^{2-}+CO}$$

$$\mathrm{Cr(CO)_6(Cr=0) \xrightarrow{\text{NaBH}_4\text{/liq. NH}_3} Na_2{}^+[Cr^{2-}(CO)_{10}]^{2-}+2CO}$$

(*v*) *Substitution reactions.* Some CO groups present in $Cr(CO)_6$ can be replaced by pyridine (*py*) to get a number of products.

$$\mathrm{Cr(CO)_6 \xrightarrow{+py} \underset{\text{yellow brown solid}}{Cr(CO)_4(\mathit{py})_2} \xrightarrow{+py} \underset{\text{yellow red solid}}{Cr_2(CO)_7(\mathit{py})_5} \xrightarrow{+py} \underset{\text{bright red solid}}{Cr(CO)_3(\mathit{py})_3}}$$

Structure. The elecron diffraction study of $Cr(CO)_6$ molecule in vapour state has shown that the molecule has octahedral shape. (See Fig. 19·8). Cr—C and C—O bond lengths are 1·92 Å and 1·16 Å respectively. Octahedral shape results from d^2sp^3 hybridisation of Cr-atom as shown in Fig. 19·9. In this molecule Cr-atom is in zero oxidation state and since $Cr(CO)_6$ is diamagnetic, all the six electrons in the valence-shell of Cr-atom ($Cr = 3d^5 . 4s^1$) get paired in $3d$-orbitals. Thus the valence shell configuration of Cr-atom in $Cr(CO)_6$ becomes $3d^6\ 4s^0$. OC→Cr σ-bond results from the overlap between an empty d^2sp^3 hybrid orbital on Cr-atom and doubly-filled *sp* hybrid orbital on C-atom in CO molecule.

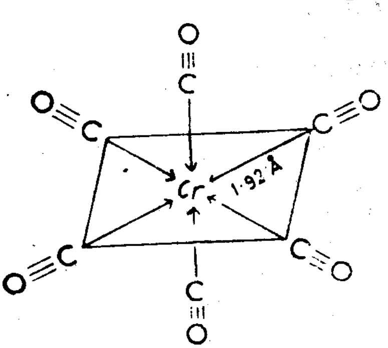
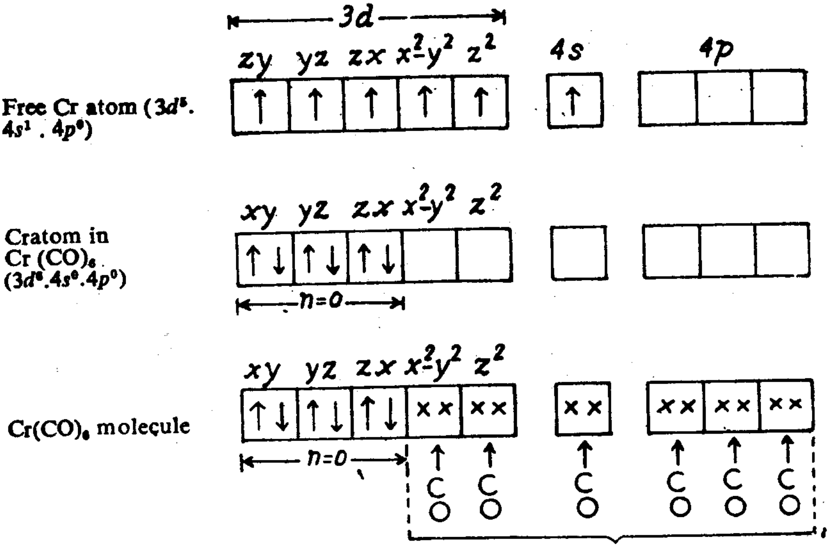


Fig. 19·8. Octahedral structure of $Cr(CO)_6$ molecule.



d^2sp^3 hybridisation—octahedral shape of Cr(CO)$_6$ molecule

Fig. 19·9. d^2sp^3 hybridisation of Cr-atom in $\dot{C}r(CO)_6$ molecule.

4. Dimanganese deca carbonyl, $Mn_2(CO)_9$. Preparation. (*i*) By carbonylating MnI_2 with CO in presence of Mg (in diethyl ether) which acts as a reducing agent.

$$2MnI_2 + 10\,CO + 2Mg\ (\text{in diethyl ether}) \xrightarrow{25^\circ C,\ 210\ \text{atm. pressure}} Mn_2(CO)_{10} + 2MgI_2$$

(*ii*) By carbonylating $MnCl_2$ with CO in presence of $(C_6H_5)_2CONa$.

$$2MnCl_2 + 10CO + 4(C_6H_5)_2CONa \xrightarrow[\text{pressure}]{165^\circ C,\ 140\ \text{atm.}} Mn_2(CO)_{10} + 4(C_6H_5)_2CO + 4NaCl$$

Properties. (*i*) It is a golden yellow crystalline substance. It has m.pt.=155°C and sublimes in vacuo It is soluble in organic solvents. It is slowly oxidised in air, especially in solution.

(*ii*) *Action of hologens.* $Mn_2(CO)_{10}$ reacts with halogens to form carbonyl halides, $Mn(CO)_5X$.

$$Mn_2(CO)_{10} + X_2 (X = Br, I) \longrightarrow 2Mn(CO)_5X$$

(*iii*) *Action of Na-metal.* Na-metal in liquid NH_3 converts $Mn_2(CO)_{10}$ into carbonylate anion. In this reaction the oxidation state of Mn decreases from zero to −1.

$$Mn_2(CO)_{10}(Mn=0) + 2Na \xrightarrow{\text{liq. } NH_3} 2Na^+[Mn^-(CO)_5]^-$$

(*iv*) *Action* H_2. $Mn_2(CO)_{10}$ gives carbonyl hydride, $Mn(CO)_5H$. In the formation of this compound the oxidation state of Mn decreases from zero to -1.

$$Mn_2(CO)_{10}(Mn=0)+H_2 \xrightarrow{200°C,\ 200\ atm.\ pressure} 2[Mn^-(CO)_5H^+]^0$$

(*v*) *Substitution reaction.* $Mn_2(CO)_{10}$ reacts with PR_3 to form $Mn(CO)_4(PR_3)$.

$$Mn_2(CO)_{10}+PR_3 \longrightarrow 2Mn(CO)_4(PR_3)+2CO$$

(*vi*) *Diamagnetic nature.* $Mn_2(CO)_{10}$ is a diamagnetic substance. Diamagnetic character confirms the facts that all the electrons in $Mn_2(CO)_{10}$ are paired and Mn—Mn bond is also present in it.

Structure. The molecular weight of this compound indicates that this compound has dimeric formula, $Mn_2(CO)_{10}$. The infrared absorption spectral and X-ray diffraction studies made on $Mn_2(CO)_9$ molecule have shown that in this molecule each Mn-atom is directly linked with the other Mn-atom by a σ-bond (Mn—Mn σ-bond) and to five terminal carbonyl groups (—C≡O) by a co-ordinate bond (Mn←CO co-ordinate bond). The presence of Mn—Mn σ-bond is also supported by the diamagnetic character of $Mn_2(CO)_9$ molecule. Mn—Mn bond distance has been found to be equal to 2·79 A° (Fig. 19·10). It may be seen that co-ordination number of each Mn-atom in this molecule is six and the molecule has no bridging carbonyl groups (>C=O) in between two Mn-atoms.

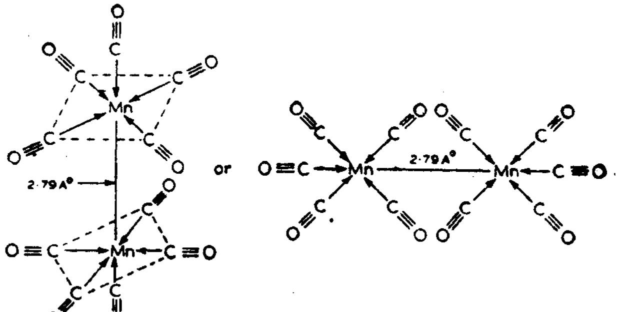


Fig. 19·10. Structure of $Mn_2(CO)_{10}$ molecule. This structure in its simplified form is shown at the right hand side.

Since the co-ordination number of both Mn-atoms is six, both Mn-atoms are d^2sp^3 hybridised as shown in Fig. 19·11. Mn—Mn bond results by the overlap of one singly-filled d^2sp^3 hybrid orbital on one Mn-atom with the d^2sp^3 hybrid orbital on the other Mn-atom. Five vacant d^2sp^3 hybrid orbitals on each Mn-atom accepts a lone pair of electrons donated by the C-atom of the five terminal carbonyl groups and form five Mn←CO co-ordinate bonds. Such ten bonds are formed. Thus we see that all the electrons in $Mn_2(CO)_{10}$ become paired and hence the molecule has diamagnetic character. Note that the valence-shell configuration of Mn-atom in $Mn_2(CO)_{10}$ is $3d^7 . 4s^0$ and not $3d^5 . 4s^2$.

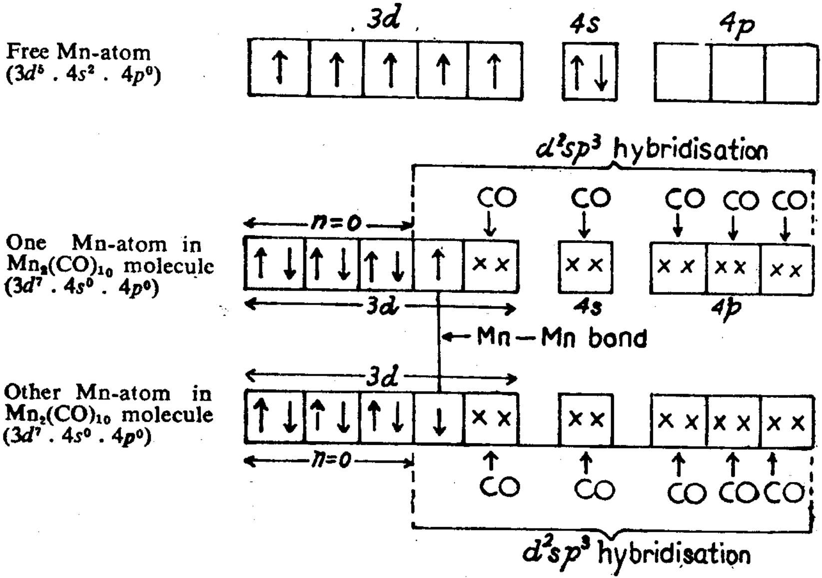


Fig. 19·11. d^2sp^3 hybridisation of each Mn-atom in $Mn_2(CO)_{10}$ molecule.

5. Dicobalt octacarbonyl, $Co_2(CO)_8$. Preparation. It is prepared : (*i*) by the direct combination of CO with cobalt metal.

$$2Co + 8CO \xrightarrow{200°C,\ 100\ atm.\ pressure} Co_2(CO)_8.$$

(*ii*) by carbonylating CoS or CoI_2 with CO in presence of Cu-metal or by carbonylating $CoCO_3$ with CO in presence of H_2. Here Cu-metal and H_2 both act as reducing agent.

$$2CoS\ (or\ 2CuI_2) + 8CO + 4Cu \xrightarrow{200°C,\ 200\ atm.\ pressure} Co_2(CO)_8 + 2Cu_2S\ (or\ 4CuI)$$

$$2CoCO_3 + 8CO + 2H_2 \xrightarrow{120\text{-}200°C,\ 250\text{-}300\ atm.\ pressure} Co_2(CO)_8 + 2H_2O$$

Properties. (*i*) $Co_2(CO)_8$ is an orange brown crystalline substance having m pt.$=51°C$. It is soluble in alcohol, ether and CCl_4. The carbonyl is air sensitive both in the solid and solution states.

(*ii*) *Action of heat.* It is thermally decomposed at 50°C in an inert atmosphere to give tetra cobalt dodeca carbonyl, $Co_4(CO)_{12}$.

$$2Co_2(CO)_8 \xrightarrow{50°C} Co_4(CO)_{12} + 4CO$$

(*iii*) *Action of air.* On exposure to air, dicobalt octacarbonyl is converted into deep violet basic carbonate of cobalt.

(*iv*) *Action of H_2 : Formation of cobalt carbonyl hydride (Reduction).* When $Co_2(CO)_8$ reacts with H_2 at 165°C and 200 atm. pressure, it gets reduced to cobalt carbonyl hydride, $[Co^-(CO)_4H^+]^0$.

$$Co_2(CO)_8+H_2 \xrightarrow{165^\circ C,\ 200\ \text{atm. pressure}} 2[Co^-(CO)_4H^+]^0$$

(*v*) *Action of Na-metal in liq. NH_3 : Reduction.* When $Co_2(CO)_8$ reacts with Na-metal in liq. Na-metal below —75°C, it gets reduced to carbonylate anion, $[Co^-(CO_4)]^-$.

$$Co_2(CO)_8+2Na \xrightarrow{\text{liq. } NH_3} 2Na^+[Co^-(CO)_4]^-$$

(*vi*) *Disproportionation reactions.* There are two types of such reactions in case of $Co_2(CO)_8$.

(*a*) Strong bases having nitrogen or oxygen donor atoms cause disproportionation into Co(+2) and Co(−1). For example :

$$\underset{(Co=0)}{2Co_2(CO)_8}+12NH_3\longrightarrow\underset{(Co=+2)}{2[Co(NH_3)_6]}\ \underset{(Co=-1)}{[Co(CO)_4]_2}+8CO$$

(*b*) With isocyanides, phosphines, arsines and stibines, however, the disproportionation reaction gives penta-coordinate cobalt (I) cation.

$$\underset{(Co=0)}{Co_2(CO)_8}+5CNR\longrightarrow\underset{(Co=+1)}{[Co(CNR)_5]}\ \underset{(Co=-1)}{[Co(CO)_4]}+4CO$$

(*vii*) *Action of NO.* $Co_2(CO)_8$ reacts with NO at 40°C to form cobalt carbonyl nitrosyl, $[Co^-(CO)_3(NO)^+]^0$. Thus in this reaction the oxidation state of cobalt decreases from zero (in corbonyl) to −1 (in nitrosyl).

$$\underset{(Co=0)}{Co_2(CO)_8}+2NO\longrightarrow\underset{(Co=-1)}{[Co^-(CO)_3(NO)^+]^0}+2CO$$

(*viii*) *Action of halogens.* The halogens (X_2) decompose $Co_2(CO)_8$ into CoX_2 and CO according to the following equation.

$$Co_2(CO)_8+2X_2\longrightarrow 2CoX_2+8CO$$

Structure. Infra-red study of the solution of this compound has shown that in solution, this compound exists in two isomeric forms. One of these forms has a bridged structure while the other form has a non-bridged structure. The bridged structure has two bridging carbonyl groups, six terminal carbonyl groups and one Co—Co bond. Each of the two Co-atoms is directly linked with the other Co-atom by a Co—Co bond, with two bridging carbonyl groups and with three terminal carbonyl groups. Co—Co bond distance in this structure has been found to be equal to 2·52 Å. In this structure the coordination number of each Co-atom is six and hence both Co-atoms are d^2sp^3 hybridised as shown in Fig. 19·12. Three d^2sp^3 hybrid orbitals on each Co-atom (which are vacant) accept a lone pair of electrons donated by the C-atom of the three terminal carbonyl groups and form three $Co \leftarrow CO$ co-ordinate bonds. Such six bonds are formed. One d^2sp^3 hybrid orbital on one Co-atom (singly-filled) overlaps with the d^2sp^3 hybrid orbital on the other Co-atom (singly-filled) and forms one Co—Co bond. Two d^2sp^3 hybrid orbitals on each Co-atom (singly-filled) overlap with the appropriate orbital (singly-filled) on C-atom of the two bridging carbonyl groups and form Co—Co bonds. Thus we see that all the electrons in $Co_2(CO)_8$ become paired and hence the molecule has diamagnetic character. Note that the valence-shell configuration of each Co-atom in $Co_2(CO)_8$ is $3d^8 . 4s^1$ and not $3d^7 . 4s^2$.

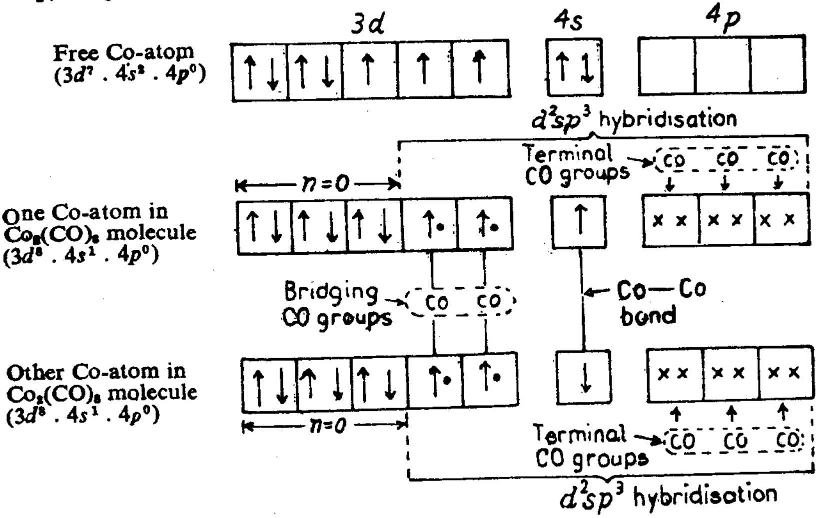
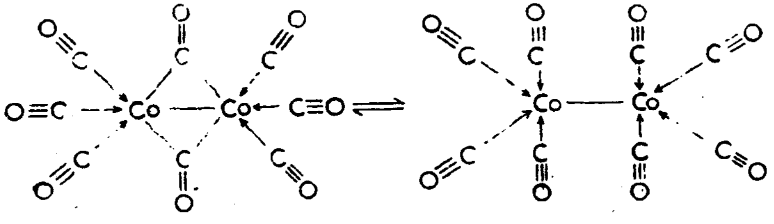


Fig. 19·12. d^2sp^3 hybridisation of Co-atom in $Co_2(CO)_8$ molecule. × × represents the electron pair donated by carbon atom of terminal carbonyl groups while the dot (.) represents an electron on carbon atom of bridging carbnoyl groups. ↓ ↑ represents the electron pair on Co-atom.

The non-bridged structure has one Co—Co bond and eight terminal carbonyl groups. Each of the two Co-atoms is directly linked with the other Co-atom by a Co—Co bond and with four terminal carbonyl groups. The presence of Co—Co bond in both the forms is also supported by the diamagnetic character of Co$_2$'CO)$_8$ molecule. The two isomeric forms have little difference in their energies and exist in equilibirium with each other in a given solution (See Fig. 19·13).



Bridged structure Non-bridged structure

Fig. 19·3. Two isomeric forms of $Co_2(CO)_8$ existing in equilibirium with each other in a given solution. One form has bridged structure while the other form has a non-bridged structure.

At very low temperature the bridged structure predominates and as the temperature is raised, the non-bridged structure appears.

X-ray study of the crystal of $Co_2(CO)_8$ has shown that the molecule in the solid state has bridged structure which is similar to that of one of the isomeric forms of this molecule in solution. On the basis of electron diffraction study various bond lengths are : Co—Co=2·52 Å, Co—C (*bridging*)=1·92 Å, C—O (*bridging*)=1·21 Å, Co—C (*terminal*)=0·80 Å and C—O (*terminal*)=1·17 Å.

6. Di-iron ennea carbonyl, $Fe_2(CO)_9$. Preparation. $F_2(CO)_9$ is obtained as golden crystals when the cooled solution of $Fe(CO)_5$ in glacial CH_3COOH is irradiated with ultra-violet light for six hours.

$$2Fe(CO)_5 \xrightarrow{\text{ultra-violet light}} Fe_2(CO)_9 + CO$$

Properties. (*i*) $Fe_2(CO)_9$ forms triclinic crystals which are diamagnetic. It is slightly soluble in alcohol and acetone and more so in toluene and pyridine and almost insoluble in water, ether, C_6H_6 and many other organic solvents. It is non-volatile.

(*ii*) *Action of heat.* When warmed to 50°, it gives $Fe_3(CO)_{12}$.

$$3Fe_2(CO)_9 \xrightarrow{50°C} 2Fe_3(CO)_{12} + 3CO$$

When its solution in toluene is heated at 70°C and then cooled, green crystals of $Fe_3(CO)_{12}$ are obtained.

$$3Fe_2(CO)_9 \text{ (toluene solution)} \xrightarrow{70°C,\ \text{cool}} 3Fe(CO)_5 + Fe_3(CO)_{12}$$

(*iii*) *Action of NO.* With NO it gives $Fe(CO)_2(NO)_2$ together with $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

$$3Fe_2(CO)_9 + 4NO \rightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6CO$$

(*iv*) *Action of phen.* In acetone or benzene solution at 80°C $Fe_2(CO)_9$ reacts with *phen* to form $[Fe(phen)_3][Fe_2(CO)_8]$. In pyridine, with *phen* it gives $[Fe(phen)_3][Fe_4(CO)_{13}]$.

(*v*) *Action of akali metals.* Carbonylate anion is obtained in its reaction with Na in NH_3 solution

$$Fe_2(CO)_9(Fe=0) + 4Na \xrightarrow{\text{liq. } NH_3} 2Na_2^{+}\ [Fe^{2-}(CO)_4]^{2-} + CO$$

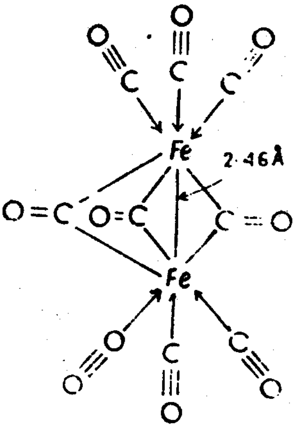


Fig. 19·14. Structure of $Fe_2(CO)_9$ molecule.

Structure. Infra-red and X-ray crystal studies made on $Fe_2(CO)_9$ molecule have shown that in this molecule each Fe atom is directly linked with the other Fe-atom by a δ-bond (Fe—Fe δ-bond), to three bridging carbonyl groups (>C=O) by a σ-bond (Fe—C σ-bond) and to three terminal carbonyl groups (—C≡O) by a co-ordinate bond (Fe←C co-ordinate bond). The presence of Fe—Fe bond is also supported by the diamagnetic character of $Fe_2(CO)_9$ molecule. Fe—Fe bond distance has been found to be equal to 2·46 Å (see Fig. 19·14). The terminal C—O bond distances are smaller than the bridging C—O bond distances. From the structure given in Fig. 19·14 it may be seen that the coordination number of each Fe atom is not equal to 6 but equal to 7.

7. Tri-iron dodeca carbonyl, $Fe_3(CO)_{12}$. Preparation. It is prepared (*i*) by heating toluence solution of $Fe_2(CO)_9$ to 70°C and then cooling the solution.

$$3Fe_2'CO)_9 \text{ (toluene solution)} \xrightarrow{70^\circ C,\ \text{cooling}} 3Fe(CO)_5 + Fe_3(CO)_{12}$$

(*ii*) by the oxidation of $Fe(CO)_4H_2$ with H_2O_2 or MnO_2.

$$3Fe(CO)_4H_2 + 3H_2O_2 \longrightarrow Fe_3(CO)_{12} + 6H_2O$$

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \longrightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$

Properties. (*i*) $Fe_3(CO)_{12}$ forms deep green crystals which are soluble in organic solvents like toluene, alcohol, ether and pyridine.

(*ii*) *Action of heat.* When heated to 140°C, $Fe_3(CO)_{12}$ decomposes to give metallic iron and CO.

$$Fe_3(CO)_{12} \xrightarrow{140^\circ C} 3Fe + 12CO$$

(*iii*) *Reaction with Na.* Carbonylate anion is obtained when $Fe_3'CO)_{12}$ reacts with Na metal in liq. NH_3

$$Fe_3(CO)_{12} + 6Na \xrightarrow{\text{liq. } NH_3} 3Na_2^+[Fe^{2-}(CO)_4]^{2-}$$

(*iv*) *Substitution reactions.* These reactions occur with pyridine (*py*) and methyl alcohol as shown below :

$$2Fe_3(CO)_{12} + 3py \longrightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5$$

$$2Fe_3(CO)_{12} + 3CH_3OH \longrightarrow Fe_3(CO)_9(CH_3OH)_3 + 3Fe(CO)_5$$

(*v*) *Action of NO.* At 85° it reacts with NO to form iron dicarbonyl dinitrosyl, $Fe(CO)_2(NO)_2$.

$$Fe_3(CO)_{12} + 6NO \longrightarrow 3Fe(CO)_2(NO)_2 + 6CO$$

Structure. The molecular weight determination of this compound corresponds to the molecular formula, $Fe_3{\cdot}CO)_{12}$. X-ray study made on $Fe_3(CO)_{12}$ molecule has shown that in this molecule (*a*) Each of the two Fe-atoms is linked with three terminal carbonyl groups, two bridging carbonyl groups and to the third Fe-atom (*b*) The remaining third Fe-atom is linked with four terminal carbonyl groups and to each of the two Fe-atoms (*c*) Three Fe—Fe bonds are also present. Each Fe—Fe bond distance has been found to be equal to 2·8Å (Fig. 19·15).

$\begin{matrix}Fe\\Fe\end{matrix}\!\!>C=O$ bridges are unsymmetrical.

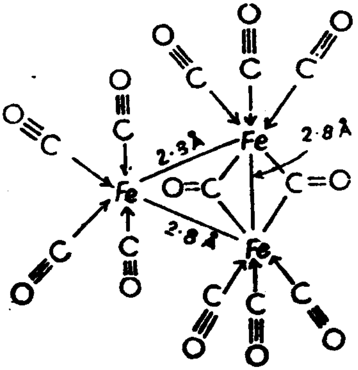


Fig. 19·15. Structure of $Fe_3(CO)_{12}$ molecule.

When we compare the structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, we find that the structure of $Fe_3(CO)_{12}$ can be obtained by replacing one bridging carbonyl group ($>C=O$) present in $Fe_2(CO)_9$ by $Fe(CO)_4$.

$$Fe_2(CO)_9 \xrightarrow{->C=O} Fe_2(CO)_8 \xrightarrow{+Fe(CO)_4} Fe_3(CO)_{12}$$

METALLIC NITROSYLS

Metal nitrosyls are coordination compounds in which NO molecule is attached as NO^+ ion to metal atom or ion. In these compounds the attachment of NO^+ ion to the metal atom or ion takes place through N-atom. In these compounds NO^+ ion which is called nitrosonium or nitrosyl cation acts as a ligand. The co-ordination compounds of transition metals containing NO^+ ion as ligand are called metal (or metallic) nitrosyls. Examples of metal nitrosyls are given below :

(*i*) *Metal nitrosyl carbonyls.* Important examples of this type of co-ordination compounds are $[Co^-(NO^+)(CO)_3]^\circ$, $[Fe^{2-}(NO^+)_2(CO)_2]^\circ$, $[Mn^{3-}(NO^+)_3(CO)]^\circ$, $[Mn^-(NO^+)(CO)_4]^\circ$, $[V^-(NO^+)(CO)_5]^\circ$ etc.

(*ii*) *Metal nitrosyl halides.* These compounds are represented by $[Fe^-(NO^+)_2I]_2$, $[Fe^-(NO^+)_2I]^\circ$, $[Fe^\circ(NO^+)I]^\circ$, $[Fe^{2-}(NO^+)_3Cl]^\circ$, $[Co^-(NO^+)_2X]^\circ$, $[Ni^\circ(NO^+)X]^\circ$ ($X=Cl$, Br, I), $[M^\circ(NO^+)_2Cl_2]^\circ$ ($M=$ Mo or W).

(*iii*) *Metal nitrosyl thio complexes.* These coordination compounds are given by only Fe, Co and Ni. Examples are $M^+[Fe^-(NO^+)_2S]^-$, $[M^+Co^-(NO^+)_2S]^-$, $M^+[Ni^-(NO^+)_2S]^-$ ($M=Na^+$, K^+, NH_4^+

(*iv*) *Metal nitrosyl cyano complexes.* Examples of this type of complexes are $[Mn^+(NO^+)(CN)_5]^{3-}$, $[Fe^{2+}(NO^+)(CN)_5]^{2-}$, $[Mn^+(NO^+)(CN)_5]^{3-}$, $[Mo^\circ(NO^+)(CN)_5]^{4-}$. Among these complexes, pentacyano nitrosyl ferrate (II) ion, $[Fe^{2+}(NO^+)(CN)_5]^{2-}$ is the most important.

(*v*) *Miscellaneous metal nitrosyl complexes.* Nitrosyl complexes like $[Co^+(NO^+)(NH_3)_5]^{2+}$, $[Co^+(NO^+)(NO_2)_5]^{3-}$, $[Fe^+(NO^+)]^{2+}$, $[Ru^{2+}(NO^+)(NH_3)_4Cl]^{2+}$, $[Ru^{2+}(NO^+)Cl_5]^{2-}$, $[Fe^{2-}(NO^+)_2(PR_3)_2]^\circ$ etc. Among these complexes, $[Fe^+(NO^+)]^{2+}$ is the most important.

Preparation. (*i*) *Metal nitrosyl carbonyls* can be obtained by the action of NO on metal carbonyls, *e.g.*,

$$Fe(CO)_5+2NO \xrightarrow{95^\circ C} Fe(CO)_2(NO)_2+3CO$$

$$3Fe_2(CO)_9+4NO \longrightarrow 2Fe(CO)_2(NO)_2+Fe(CO)_5 +Fe_3(CO)_{12}+6CO$$

$$Fe_3(CO)_{12}+6NO \xrightarrow{85^\circ C} 3Fe(CO)_2(NO)_2+6CO$$

$$Co_2(CO)_8+2NO \xrightarrow{40^\circ C} 2Co(CO)_3(NO)+2CO$$

(*ii*) *Metal nitrosyl halides* can be prepared : (*a*) by the action of NO on metal halides in the presence of a suitable metal (*e.g.* Co, Zn etc.) which acts as a halogen acceptor, *e.g.*,

$$CoX_2+4NO+Co \longrightarrow 2[Co(NO)_2X]$$

$$2NiI_2+2NO+Zn \longrightarrow 2[Ni(NO)I]+ZnI_2$$

(*b*) by the action of hologen on nitrosyl carbonyls, *e.g.*,

$$2[Fe(CO)_2(NO)_2]+I_2 \longrightarrow [Fe(NO)_2I]_2+4CO$$

Properties of metal nitrosyl carbonyls (*i*) *Substitution reactions.* In metal carbonyl nitrosyls, NO^+ ions are more firmly attached with the metal ion than the CO groups. It is for this reason that when metal carbonyl nitrosyls are treated with ligands like PR_3, CNR, *phen* etc., it is only CO groups that are replaced by these ligands, *e.g.*,

$$Fe(CO)_2(NO)_2+2L(L=PR_3,\ CNR) \rightarrow Fe(L)_2(NO)_2+2CO$$

$$Fe(CO)_2(NO)_2+phen \rightarrow Fe(phen)(NO)_2+2CO$$

(*ii*) *Action of halogens.* Many metal carbonyl nitrosyls, when treated with halogens, are converted into metal nitrosyl halides, *e.g.*,

$$2[Fe(CO)_2(NO)_2]+I_2 \rightarrow [Fe(NO)_2I]_2+4CO$$

Properties of metal nitrosyl halides. (*i*) Metal nitrosyl halides react with other ligands to form mono-nuclear complexes, *e.g.*,

$$[Fe(NO)_2X]_2+2L \rightarrow 2[Fe(NO)_2XL]$$

(*ii*) Iron nitrosyl halide, $[Fe(NO)_2I]_2$ reacts with K_2S and CH_3Cl to form dark red compounds which have the composition, $K_2[Fe(NO)_2S]_2$ and $[Fe(NO)_2(SCH_3)]_2$ and are called *Roussin's salts.* In these compounds Fe is in −1 oxidation state.

$$[Fe(NO)_2I]_2 \xrightarrow[-2KI]{+K_2S} K_2[Fe(NO)_2S]_2 \xrightarrow[-2KCl]{+CH_3Cl} [Fe(NO)_2(SCH_3)]_2$$

SOME METALLIC NITROSYLS

Now let us make study of sodium nitroprusside, $Na_2[Fe^{2+}(CN)_5(NO^+)]$ and nitrosoforrous sulphate, $FeSO_4.NO$ or $[Fe^+(NO^+)]SO_4$ which are important metallic nitrosyls.

1 Sodium nitroprusside, $Na_2[Fe^{2+}(CN)_5(NO^+)]$. *Preparation.* It is prepared (*i*) by the action of $NaNO_2$ on $Na_4[Fe^{2+}(CN)_6]$.

$$Na_4[Fe^{2+}(CN)_6]+NaNO_2+H_2O \longrightarrow Na_2[Fe^{2+}(CN)_5(NO^+)]+2NaOH+NaCN$$

(*ii*) by passing nitric oxide (NO) into acidified solution of $Na_4[Fe(CN)_6]$.

$$2Na_4[Fe(CN)_6]+H_2SO_4+3NO \rightarrow 2Na_2[Fe(NO)(CN)_5]+2NaCN+Na_2SO_4+1/2\ N_2+H_2O$$

Properties. (*i*) Sodium nitroprusside forms beautiful ruby red rhombic crystals which are soluble in water.

(*ii*) When freshly prepared sodium nitroprusside is added to a solution containing sulphide ion (*i.e.*, Na_2S but not H_2S), a purple or violet colour is produced. The production of this colour is due to the formation of $Na_4[Fe^{2+}(CN)_5(NO^+)(S)]$. The production of this purple or violet colour is used to confirm the presence of S^{2-} ion in a given mixture.

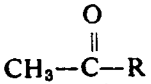
$$Na_2S+Na_2[Fe^{2+}(CN)_5(NO^+)]\longrightarrow Na_4[Fe^{2+}(CN)_5(NO^+)(S^{2-})]$$
(Violet or purple colour)

(*iii*) Alkali sulphites give a rose red colour due to the formation of $Na_4[Fe(CN)_5(NO)(SO_3)]$. This reaction can be used to distinguish sulphites from thiosulphates which do not show this reaction.

$$Na_2SO_3+Na_2[Fe(CN)_5(NO)]\longrightarrow Na_4[Fe(CN)_5(NO)(SO_3)]$$

(*iv*) With silver nitrate a flesh coloured $Ag_2[Fe(CN)_5(NO)]$ is produced.

$$2AgNO_3+Na_2[Fe(CN)_5(NO)]\longrightarrow Ag_2[Fe(CN)_5(NO)]+2NaNO_3$$

(*v*) Aldehydes and ketones containing  $CH_3-\overset{\overset{O}{\|}}{C}-R$ group give deep red colour with sodium nitroprusside and excess of NaOH.

(*vi*) It is converted into sodium ferrocyanide, $Na_4[Fe(CN)_6]$ on treatment with an alkali.

$$6Na_2[Fe(CN)_5(NO)]+14NaOH \longrightarrow 5Na_4[Fe(CN)_6]+Fe(OH)_2 +6NaNO_2+6H_2O$$

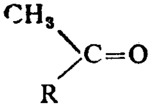
According to another view NO^+ group present in nitroprusside is oxidised to NO_2 and thus a nitro complex is obtained.

$$Na_2[Fe(CN)_5(NO)]+2NaOH \longrightarrow Na_4[Fe(CN)_5(NO_2)]+H_2O$$

(*vii*) $[Fe(CN)_5(NO)]^{2-}$ ion has diamagnetic character. Its diamagnetic character confirms the fact that NO is present as NO^+ ion in this complex ion.

Structure. $[Fe(CN)_5(NO)]^{2-}$ was formerly supposed to contain Fe(+3) ion but Pauling in 1931 and Sidgwick in 1934 suggested that the odd electron of NO group enters the valence-shell of Fe (+3) ion making Fe in +2 oxidation state. Thus NO radical acquires one positive charge and gets coordinated to Fe(+2) ion as NO^+ radical. This view is supported by the fact that $Na_2[Fe(CN)_5(NO)]$ is diamagnetic whereas $K_3[Fe(CN)_6]$ is paramagnetic. Thus in $[Fe(CN)_5(NO)]^{2-}$ there are total three positive charges (Fe=+2, NO=+1] and five negative charges due to the presence of five CN- groups. Hence total charges acquired by $[Fe(CN)_5(NO)]$ is −2. In other words the formula of sodium nitro-prusside is $Na_2[Fe^{2+}(CN)_5(NO^+)]$. $[Fe^{2+}(CN)_5(NO^+)]^{2-}$ has octahedral structure with Fe^{2+} ion located at the centre of the octahedron.

Uses. It is used as a reagent in qualitative analysis for the detection of sulphides, sulphites, aldehydes and ketones containing


group.

2. Nitroso ferrous sulphate, $FeSO_4.NO$ or $[Fe^+(NO^+)]SO_4$. When, to the aqueous solution of a metallic nitrate (say $NaNO_3$) is added freshly prepared solution of $FeSO_4$ and a few drops of conc. HNO_3 along the sides of the test tube, a brown ring of nitroso ferrous sulphate, $[Fe^+(NO^+)]SO_4$ is obtained at the junction of the two liquids in the test tube. The formation of nitroso ferrous sulphate takes place through the following equations :

(*a*) $6NaNO_3+H_2SO_4 \longrightarrow NaHSO_4+HNO_3$
[*or* $NO_3^-+H^+ \longrightarrow HNO_3$]

(*b*) $6FeSO_4+2HNO_3+3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3+2NO+4H_2O$
[*or* $3Fe^{2+}+NO_3^-+4H^+ \longrightarrow 3Fe^{3+}+NO+2H_2O$]

(*c*) $FeSO_4+NO \longrightarrow FeSO_4 . NO$ *or* $[Fe^+(NO^+)]^{2+}SO_4^{2-}$
[*or* $Fe^{2+}+NO \longrightarrow [Fe^+(NO^+)]^{2+}$]

In aqueous solution $[Fe^+(NO^+)]^{2+}$ ion is better expressed as $[Fe(NO)(H_2O)_5]^{2+}$. It is a paramagnetic substance corresponding to the presence of three unpaired electrons, since solution magnetic measurements give 3·90 B.M. as the value of its magnetic moment. This value supports the fact that Fe is in +1 oxidation state in this complex ion *i.e.* it is a high spin complex of Fe (+1) ($3d^7$ system) with NO^+. The complex has N—O stretching frequency at 1745 cm^{-1} which indicates the presence of strong π bonding and the intense brown colour strongly suggests Fe^+—NO^+ charge transfer.

The formation of $[Fe^+(NO^+)]^{2+}$ ion has been utilised in the detection of NO_3^- ion in a given inorganic salt.

Structure and nature of M—NO bonding in nitrosyls. According to Coulson the molecular orbital configuration of NO molecude is $(sp)^2_O$, $(\sigma_{sp}^b)^2$, $(\pi_y^b)^2=(\pi_z^b)^2$, $(sp)^2_N$, $(\pi_y^*)^1=(\pi_z^*)^0$, $(\sigma_{sp}^*)^0$ [in getting this configuration x-axis has been assumed to be the molecular axis and sp hybrid orbitals have been obtained by the combination of $2s$ and $2p_x$ orbitals]. Now when NO molecule co-ordinates with metal atom to form metallic nitrosyls, the single electron present in π_y^* molecular orbital is transfared to metal atom M so that NO molecule is converted into NO^+ cation (called *nitrosonium* or *nitrosyl* cation) and M atom becomes M^- ion Each of the atoms *viz* N and O in NO^+ ion contains one lone pair of electrons in $(sp)_O$ and $(sp)_N$ hybrid orbitals respectively. Now since NO^+ ion is iso-electronic with CO molecule, this ion co-ordinates with M^- ion as a *two-electron-donor* in metal nitrosyls in the same way as CO co-ordinates to M atom in metal Carbonyls Note that NO molecule is a *three-electron-donor*. Since O-atom is more electro negative than N-atom, it is N-atom of NO^+ ion which coordinates to M^- ion in metal nitrosyls. In other words we say that coordination of NO^+ ion to M^- ion metal nitrosyls takes place through the lone pair residing in $(sp)_N$ hybrid orbital on N-atom. The coordinate bond formed in metal nitrosyls can be shown as $M^- \leftarrow NO^+$. Thus we see that the nature of bonding between NO^+ and M^- in nitrosyls is the same as that between CO molecule and M atom in carbonyls.

On the basis of molecular orbital theory the hybrid orbital on N atom *containing* a lone pair [*i.e.* $(sp)^2_N$ lone pair] overlaps with a suitable *vacant* hybrid orbital on M^- ion (sp^3 in tetrahedral case or d^2sp^3 in octahedral case) to form $ON^+ \rightarrow M^-$ σ bond.

Now the *empty* π_x^* or π_y^* molecular orbital can overlap with the *filled* *d*-orbitals (d_{xy}, d_{yz}, d_{zx} orbitals in octahedral case and $d_{x^2-y^2}$ and d_{z^2} orbitals in tetrahedral case) to form $M^- \rightarrow NO^+$ π bond. This type of overlap transfers some charge from M^- ion to NO^+ ion.

Structural studies have shown that the M—N bond in nitrosyls is extremely short (=1·57 to 1·67A°) indicating substantial double bond character.

Effective atomic number (EAN) rule as applied to metallic nitrosyls. Metallic nitrosyls also obey the EAN rule as shown below for certain nitrosyls. In these cases NO has been assumed to be a unipositive ion, NO^+ and hence acts as a two-electron donor. Metal atoms are, therefore, in negative oxidation state.

(*i*) $[Co^-(CO)_3(NO^+)]^0$

$$\begin{aligned} Co^- &= 27e^- + 1e^- = 28e^- \\ 3CO &= 3 \times 2e^- = 6e^- \\ NO^+ &= 1 \times 2e^- = 2e^- \\ \hline [Co^-(CO)_3(NO^+)] &= 36e^- \text{ (Kr)} \end{aligned}$$

(*ii*) $[Fe^{2-}(CO)_2(NO^+)_2]^0$

$$\begin{aligned} Fe^{2-} &= 26e^- + 2e^- = 28e^- \\ 2CO &= 2 \times 2e^- = 4e^- \\ 2NO^+ &= 2 \times 2e^- = 4e^- \\ \hline [Fe^{2-}(CO)_2(NO^+)_2] &= 36e^- \text{ (Kr)} \end{aligned}$$

(*iii*) $[Fe^{2-}(NO+)_2(PR_3)_2]^0$

$$\begin{aligned} Fe^{2-} &= 26e^- + 2e^- = 28e^- \\ 2NO^+ &= 2 \times 2e^- = 4e^- \\ 2PR_3 &= 2 \times 2e^- = 4e^- \\ \hline [Fe^{2-}(NO+)_2(PR_3)_2] &= 36e^- \text{ (Kr)} \end{aligned}$$

(*iv*) $[Mn^{3-}(CO)(NO^+)_3]^0$

$$\begin{aligned} Mn^{3-} &= 25e^- + 3e^- = 28e^- \\ CO &= 1 \times 2e^- = 2e^- \\ 3NO^+ &= 3 \times 2e^- = 6e^- \\ \hline [Mn^{3-}(CO)(NO^+)_3] &= 36e^- \text{ (Kr} \end{aligned}$$

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Basic Properties of Iodine, Interhalogen Compounds, Polyhalides and Pseudohalogens

BASIC PROPERTIES OF IODINE

The tendency of a halogen atom to form compounds in which it is present as a cation is called is basic property. Among halogens iodine shows this tendency to the maximum extent, *i.e.*, iodine gives much more number of well established compounds in which it is present as a monovalent cation (I^+) or as a trivalent cation (I^{3+}). Examples of such compounds are given below.

Compounds containing monovalent iodine cation (I^+). Compounds containing monovalent iodine cation or unipositive iodine (I^+) are :

1. *ICl and IBr interhalogen compounds.* For the preparation, properties, uses and structure of these compounds see "*Interhalogen Compounds*" discussed on the subsequent pages.

2. *Iodine nitrate* (*INO_3*) *and iodine sulphate* (*I_2SO_4*). Solutions of these compounds are obtained by passing a solution of HNO_3 and of H_2SO_4 respectively in absolute alcohol through exchanger containing sorbed I^+ ion.

$$I^+R^- + HNO_3 \longrightarrow INO_3 + HR$$

$$2I^+R^- + H_2SO_4 \longrightarrow I_2SO_4 + 2HR$$

When the aqueous solutions of these compounds are electrolysed, iodine is liberated at cathode, showing that both of these salts contain unipositive iodine, I^+.

3. *Complex compounds of* $[Ipy_2]^+X^-$ *type* ($X^- = NO_3^-$, ClO_4^-). In these compounds I^+ ion gets stabilised by coordination. These compounds are obtained by treating Ag (I) salt with I_2 in chloroform in presence of excess of pyridine (*py*). For example :

$$AgNO_3 + I_2 + 2py \longrightarrow AgI(ppt) + [Ipy_2]NO_3$$

Complexes of this type have the following properties. We shall consider $[Ipy_2]NO_3$ as an example.

(*a*) When $[Ipy_2]\,NO_3$ reacts with acidified KI solution, I_2 is liberated.

I^+ (From complex compound) $+I^-$ (from KI)$\rightarrow I_2$

I_2 liberated in the above reaction can be quantitatively estimated with sod. thiosulphate, $Na_2S_2O_3$

$$2Na_2S_2O_3+I_2\rightarrow Na_2S_4O_6+2NaI$$

(*b*) Electrolysis of $[Ipy_2]\,NO_3$ in chloroform liberates iodine at cathode.

$2I^-$ (From the complex compound)$+2e^-\rightarrow I_2$ (At cathode)

Reactions (*a*) and (*b*) show the presence of I^+ ion in the complex compound, $[Ipy_2]NO_3$.

(*c*) $[Ipy_2]NO_3$ is hydrolysed by water as follows :

$$5[Ipy_2]NO_3+3H_2O\rightarrow 5HNO_3+10py+HIO_3+2I_2$$

(*d*) Treatment of $[Ipy_2]\,NO_3$ with NaOH gives the base $[Ipy_2]$ (OH) which is converted into its anhydride.

$$[Ipy_2]\,NO_3+NaOH\rightarrow[Ipy_2]^+(OH)^-\text{ (base)}+NaNO_3$$

$$2[Ipy_2](OH)\text{(base)}\rightarrow Ipy-O-Ipy\text{ (anhydride of the base)}+H_2O+2py$$

(*e*) Reaction of $[Ipy_2]NO_3$ with phenol, C_6H_5OH gives triiodophenol, $C_6H_2I_3\,OH$.

$$C_6H_5OH+3[Ipy_2]NO_3\rightarrow C_6H_2I_3OH+3HNO_3+6py$$

(*f*) Noble metals like Au get dissolved in chloroform solution of the complex compound.

$$3[Ipy_2]NO_3+Au\rightarrow Au^{3+}+3NO_3^-+\tfrac{3}{2}I_2+6py$$

In $[Ipy_2]\,NO_3$ and other similar compounds, I^+ appears to be two-coordinate and hence $[Ipy_2]^+NO_3^-$ should be formulated as $[pyIpy]^+NO_3^-$.

Compounds containing trivalent iodine cation (I^{3+}). Compounds containing trivalent iodine cation (I^{3+}) are :

1. *Iodine perchlorate, $I(ClO_4)_3\cdot 2H_2O$.* It is formed as yellowish-green needles by the action of O_3 on a cooled solution of I_2 in anhydrous $HClO_4$.

$$I_2+6HClO_4+O_3\rightarrow 2I(ClO_4)_3+3H_2O$$

When aqueous solution of this compound is electrolysed, I_2 gets liberated at cathode.

$$I(ClO_4)_3\rightarrow I^{3+}+3ClO_4^-$$

$$2I^{3+}+6e^-\rightarrow I_2\text{ (At cathade)}.$$

2. *Iodine triacetate, $I\,(CH_3COO)_3$.* It is obtained by oxidising I_2 in acetic anlydride, $(CH_3CO)_2O$ with fuming HNO_3.

It is a crystalline colourless substance, stable in cold but decomposes at 100°C. The saturated solution of the compound in acetic anhydride conducts electricity and during electrolysis I_2 is liberated at the cathode (of silver), forming AgI

$$(CH_3COO)_3I=I^{3+}+3CH_3COO^-$$

$$I^{3+}+3e^-+Ag\rightarrow AgI\text{ (At silver cathode)}$$

3. *Iodine trichloride, ICl_3.* For this see "*Interhalogen Compounds*"

4. *Iodine phosphate, IPO_4.* It is prepared by adding HNO_3 to I_2 and H_3PO_4 dissolved in acetic anhydride.

It is a yellow crystalline solid. It is not stable above room temperature and undergoes hydrolysis with H_2O.

$$5IPO_4+9H_2O \rightarrow I_2+3HIO_3+5H_3PO_4$$

On electrolysis of aqueous solution of IPO_4, I_2 is liberated at cathode.

$$IPO_4 \rightarrow I^{3+}+PO_4^{3-}$$

$$2I^{3+}+6e^- \rightarrow I_2 \text{ (At cathode).}$$

5. *Iodine trinitrate, $I(NO_3)_3$.* It is made by oxidising I_2 with conc. HNO_3.

$$I_2+6HNO_3 \rightarrow 2I(NO_3)_3+3H_2$$

When the aqueous solution of this salt is electrolysed, I_2 is collected of cathode.

6. *Iodyl sulphate, $(IO)_2SO_4$.* It is obtained by the action of hot concentrated H_2SO_4 on iodic acid, HIO_3

$$H_2SO_4+2HIO_3 \longrightarrow (IO)_2SO_4+2H_2O+O_2$$

It is a yellow-coloured compound. On treatment with fuming H_2SO_4, it forms a compound of the composition, $[IO]^+[HSO_4]^-$ This compound in 65% oleum ($H_2S_2O_7$) gives a salt, $[IO]^+[HS_2O_7]^-$

$$[IO]_2SO_4+H_2SO_4 \rightleftharpoons 2[IO]^+[H\ SO_4]^-$$

$$[IO]^+[HSO_4]^-+H_2S_2O_7 \rightleftharpoons [IO]^+\ [HS_2O_7]^-+H_2SO_4$$

When treated with water, it gets hydrolysed to form I_2O_4.

7. *Chloro iodic acid, $H[ICl_4]$. $4H_2O$.* This acid is obtained by passing Cl_2 through a suspension of iodine in conc. HCl. It forms orange-yellow plates and gives salts like $K[ICl_4]$, $Na[ICl_4]$ etc. In this compound iodine is present as I^{3+}.

Evidences proving the existence of cationic iodine. When the compounds like ICl, IBr, ICN, INO_3, I_2SO_4, $[Ipy_2]^+X^-$ ($X^-=NO_3^-$, ClO_4^-), $I(ClO_3)_3$. $2H_2O$, $I(CH_3COO)_3$, ICl_3, IPO_4, $I(NO_3)_3$, $(IO)_2SO_4$, $H[ICl_3]$. $4H_2O$ in their molten state or as their aqueous solution are electrolysed, iodine is liberated at cathode. The liberation of iodine at cathode proves the existence of cationic iodine in these compounds.

The following additional facts also confirm the existence of cationic iodine.

(*i*) When iodine is dissolved in an inert solvent and the solution thus obtained is passed down a cationic exchange resin (H^+R^-), some iodine is retained on the resin as I^+

$$H^+R^-+I_2 \longrightarrow I^+R^-+HI$$

The positive iodine retained on the resin may be recovered by eluting it with aqueous KI or by allowing it to react with various reagents like anhydrous H_2SO_4, alcoholic HNO_3, etc.

$$I^+R^- + KI \longrightarrow K^+R^- + I_2$$

$$2I^+R^- + H_2SO_4 \text{ (anhydrous)} \longrightarrow I_2SO_4 + 2H^+R^-$$

$$I^+R^- + HNO_3 \text{ (alcoholic)} \longrightarrow INO_3 + H^+R^-$$

(*ii*) When I_2 is dissolved in H_2O, a variety of reactions take place. Two of such reactions are :

(*a*) $I_2 + H_2O \rightleftharpoons [I(H_2O)]^+ + I^-$

(*b*) $[I(H_2O)]^+ + H_2O \rightleftharpoons [I(OH)]^\circ + H_3O^+$

The formation of $[I(H_2O)]^+$ and $[I(OH)]^\circ$ in these reactions also confirms the existence of I^+ ion.

INTERHALOGEN COMPOUNDS

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity, the halogen atoms combine with each other and give rise to the formation of binary covalent compounds which are called *interhalogen compounds*. These compounds are of four types : (*i*) *AB type* (+1), *e.g* ClF, BrF, IF (detected spectroscopically), BrCl, ICl, IBr (*ii*) *AB_3 type* (+3), *e.g.* ClF_3, BrF_3, IF_3, ICl_3 (*iii*) *AB_5 type* (+5), *e.g.* ClF_5, BrF_5, IF_5 (*iv*) *AB_7 type* (+7), *e.g.* IF_7. The number given in the bracket indicates the oxidation number of A atom. A halogen atom is larger than B halogen atom, *i.e.* A atom is less electronegative than B atom. In interhalogen compounds, the halogen atom having less electronegativity shows positive oxidation state while that having greater electronegativity shows negative oxidation state. It is for this reason that interhalogen compounds are named as the halides of less electronegative halogen atom. Thus ClF is called *chlorine monofluoride* and not *fluorine monochloride*, since the electronegativity of Cl atom is less than that of F atom.

Halogen atom A acts as the central atom with which odd number of B atoms are covalently bonded. The central atom A may be Cl, Br or I but never F, since F atom seldom achieves a positive oxidation state and also it can not expand its coordination number beyond 4.

With the exception of BrCl, ICl, IBr and ICl_3, all the remaining interhalogen compounds are *halogen flourides*. Greater is the electronegativity difference, $(x_F - x_A)$ (A may be I or Br), greater is the number of fluorides given by atom A. For example iodine $(x_F - x_I = 4{\cdot}0 - 2{\cdot}5 = 1{\cdot}5)$ gives four fluorides *viz.* IF, IF_3, IF_5, and IF_7 while Br atom $(x_F - x_{Br} = 4{\cdot}0 - 2{\cdot}8 = 1{\cdot}2)$ gives only three fluorides namely BrF, BrF_3 and BrF_5. The formation of three fluorides by Cl-atom $(x_F - x_{Cl} = 4{\cdot}0 - 3{\cdot}0 = 1{\cdot}0)$ is taken to be an exception. Actually Cl-atom should give less than three fluorides.

It has not been possible to prepare the inter-halogen compounds containing more than two halogen atoms (*ternary inter-*

halogen compounds). The non-formation of ternary interhalogen compounds is due to the fact that these compounds so formed get decomposed into a mixture of stable binary interhalogen compounds and/or elemental halogens. Polyhalides such as MIBrF, MIClBr, $MIFCl_3$ etc. which contain three different halogen atoms have, however, been prepared.

General Methods of Preparation. Following are the imortant general methods by which interhalogen compounds can be prepared.

1. *By the direct combination of halogens.* All the interhalogens, except IF_7, can be prepared by the direct combination of the halogens under appropriate conditions. The following examples are noteworthy. For the preparation of AB_3 and AB_5 interhalogen compounds excess of B atom must be used in the reaction mixture.

$$Cl_2+F_2 \text{ (equal volumes) } \xrightarrow{250^\circ} 2ClF$$

$$Cl_2+3F_2 \text{ (excess) } \xrightarrow{250^\circ} 2ClF_3$$

$$I_2+Cl_2 \text{ (liquid) (in equimolecular amount) } \rightarrow 2ICl$$

$$I_2+3Cl_2 \text{ (liquid and in excess) } \longrightarrow 2ICl_3$$

$$Br_2 \text{ (vapour) } +3F_2 \text{ (diluted with } N_2) \longrightarrow 2BrF_3$$

$$I_2+3F_2 \text{ (in freon) } \xrightarrow{-78^\circ C} 2IF_3$$

$$Br_2+5F_2 \text{ (excess) } \longrightarrow 2BrF_5$$

2. *From lower interhalogens.* Higher interhalogens can be prepared by the interaction of lower interhalogens with halogens. This method is particularly used for the preparation of *halogen-fluorides*. The following examplss illustrate the method.

$$ClF+F_2 \longrightarrow ClF_3$$

$$ClF_3+F_2 \text{ (excess) } \xrightarrow{350^\circ} ClF_5$$

$$BrF_3+F_2 \xrightarrow{200^\circ} BrF_5$$

$$IF_5+F_2 \xrightarrow{270^\circ} IF_7$$

3. *Miscellaneous methods.* Some miscellaneous methods have been illustrated by the following examples :

$$6HCl+KIO_3+2KI \longrightarrow 2KCl+3H_2O+3ICl$$

$$Cl_2+ClF_3 \xrightarrow{250-350^\circ} 3ClF$$

$$KCl+3F_2 \xrightarrow{200^\circ} KF+ClF_5$$

$$3I_2+5AgF \longrightarrow 5AgI+IF_5$$

$$8F_2+PbI_2 \longrightarrow PbF_2+2IF_7$$

***General Properties**. 1. *Physical state*. The interhalogen compounds may be covalent gases (*e.g.* ClF, BrF, ClF_3, IF_7), liquids (*e.g.* BrF_3, BrF_5, IF_5) or solids (*e.g* ICl, IBr, IF_3, ICl_3).

2. *Colour*. Although many of the interhalogen compounds containing fluorine are *colourless*, yet those made up of heavier halogens are *coloured*. The colour becomes deeper with the increase of the molecular weight of the compound. In this behaviour these compounds resemble the halogens themselves.

3. *Dimagnetic nature*. Since all the valence electrons in interhalogen compounds are present as bonding or non-bonding (*i.e.* lone pairs) electron pairs, these compounds are diamagnetic in nature.

4. *Heats of formation*. All these compounds have low heats of formation. For example, these values for IBr and BrCl are −2·5 and −0·34 kcal/mole respectively. These are extremely volatile compounds. In general, compounds containing fluorine are more volatile than those containing chlorine, bromine or iodine.

5. *Boiling points*. For each type of interhalogen compounds, the boiling points increase with the increase in the electronegativity difference between A and B atoms.

6. *Thermal stability*. Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. Thus the order of stability of some AB compounds is as :

IF (=1·5) > BrF(1·2) > ClF (1·0) > ICl (0·5) > IBr (0 3) > BrCl(0·2)

In parentheses are given the electronegativity difference between A and B atoms. The above order is also explained by saying that greater is the difference between the electronegativity values of A and B, the more polar is the A−B bond and hence greater is the thermal stability of AB compound.

7. *Reactivity*. AB type compounds are more reactive than A_2 and B_2 molecules, since A−B bond in AB compounds is weaker than A−A and B−B bonds in A_2 and B_2 molecules respectively. Thus AB type compounds convert the metals into a mixture of two halides. For example :

$$ICl + 2Na \longrightarrow NaI + NaCl$$

The order of reactivity of some interhalogen compounds has been found as $ClF_3 > BrF_3 > IF_7 > BrF_5 > IF_5 > BrF$.

8. *Hydrolysis*. Hydrolysis gives halogen acid and oxy-halogen acid. The oxy-halogen acid is of larger (*i.e.* central) halogen atom. Examples are :

$BrCl + H_2O \longrightarrow HCl$ (*Halogen acid*) $+ HOBr$ (*Oxy-halogen acid*)
$ICl + H_2O \longrightarrow HCl + HIO$
$ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$
$IF_5 + 3H_2O \longrightarrow 5HF + HIO_3$
$BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$
$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$

It may be noted that the oxidation state of A atom does not change during hydrolysis.

9. *Reaction with non-metallic and metallic oxides.* Non-metallic and metallic oxides are fluorinated by halogen fluorides to give the corresponding fluorides.

$$4BrF_3 + 3SiO_2 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$$
$$4BrF_3 + 2WO_3 \longrightarrow 2WF_6 + 2Br_2 + 3O_2$$

10. *Addition reactions.* The diatomic interhalogens (AB type compounds) add at olefinic double bond sites.

$$-CH{=}CH- + ICl \longrightarrow -CHI-CHCl-$$
$$CH_2{=}CH_2 + BrCl \longrightarrow CH_2Br-CH_2Cl$$

11. *Reaction with alkali metal halides.* Reaction with alkali metal halides gives polyhalides like $NaIBr_2$, $CsIBrCl$, $KICl_4$ etc.

$$IBr + NaBr \longrightarrow NaIBr_2;\quad ICl + KCl \longrightarrow KICl_2$$
$$BrCl + CsI \longrightarrow CsIBrCl;\quad ICl_3 + KCl \longrightarrow KICl_4$$

12. *Self-ionisation and acid-base (neutralisation) reactions.* The available evidence suggests that the liquid interhalogen compounds undergo self-ionisation which involves the halide ion transfer. Following examples illustrate how the self-ionisation of liquid interhalogen compounds takes place.

(*i*) *Liquid ICl.* The self-ionisation of liquid ICl can be represented in the form of conjugate acid-base pair as :

$$\underset{(\text{Acid}_1)}{ICl} + \underset{(\text{Base}_2)}{ICl} \rightleftharpoons \underset{(\text{Acid}_2)}{I^+} + \underset{(\text{Base}_1)}{ICl_2^-}$$

Thus the compounds which produce I^+ ions in liquid ICl act as solvo-acids in this solvent while those which produce ICl_2^- ions act as solvo-bases. For example the covalent halides like $AlCl_3$, $SbCl_5$, $SiCl_4$, $TiCl_4$ etc. give I^+ ions in liquid ICl and hence act as acids in this solvent while the ionic halides like RbCl, KCl, NH_4Cl etc. produce ICl_2^- ions in this solvent and hence act as bases in this solvent. Thus :

$$\left.\begin{array}{l} \underset{\text{Acid}}{AlCl_3} + ICl(l) \rightarrow I^+ + [AlCl_4]^- \rightarrow I^+[AlCl_4]^- \\ \underset{\text{Acid}}{SbCl_5} + ICl(l) \rightarrow I^+ + [SbCl_6]^- \rightarrow I^+[SbCl_6]^- \end{array}\right\} \text{Solvo-acids}$$

$$\left.\begin{array}{l} \underset{\text{Base}}{RbCl} + ICl(l) \rightarrow Rb^+ + [ICl_2]^- \rightarrow Rb^+[ICl_2]^- \\ \underset{\text{Base}}{KCl} + ICl(l) \rightarrow K^+ + [ICl_2]^- \rightarrow K^+[ICl_2]^- \end{array}\right\} \text{Solvo-bases}$$

Thus the solvo-acids and solvo-bases in liquid ICl will interact as follows to form the solvent and a salt (*neutralisation reactions*).

$$\underset{\text{Solvo-acid}}{I^+[SbCl_6]^-} + \underset{\text{Solvo-base}}{Rb^+[ICl_2]^-} \rightarrow \underset{\text{Salt}}{Rb^+[SbCl_6]^-} + \underset{\text{Solvent}}{2ICl}$$

The end point in acid-base reactions taking place in ICl can be followed conductometrically.

(*ii*) *Liquid IBr*. The self-ionisation of liquid IBr is represented as :

$$\underset{(\text{Acid}_1)}{\text{IBr}} + \underset{(\text{Base}_2)}{\text{IBr}} \rightleftharpoons \underset{(\text{Acid}_2)}{\text{I}^+} + \underset{(\text{Base}_1)}{\text{IBr}_2^-}$$

Acid-base reactions taking place in liquid IBr are represented as :

$$\underset{\text{Acid}}{\text{I}_2^+[\text{SnBr}_6]^{2-}} + \underset{\text{Base}}{2\text{M}^+[\text{IBr}_2]^-} \rightarrow \underset{\text{Salt}}{\text{M}_2^+[\text{SnBr}_6]^{2-}} + \underset{\text{Solvent}}{4\text{IBr}}$$

The end point in acid-base reactions occurring in IBr solvent is followed conductometrically.

(*iii*) *Liquid BrF₃*. The self-ionisation of liquid BrF_3 can be represented as :

$$\text{BrF}_3(\text{Acid}_1) + \text{BrF}_3(\text{Base}_2) \rightleftharpoons \text{BrF}_2^+(\text{Acid}_2) + \text{BrF}_4^-(\text{Base}_1)$$

Thus the substances like SnF_4, AuF_3, VF_5, SbF_5 and TaF_5 which produce BrF_2^+ ions in liquid BrF_3 act as acids while those like KF, AgF, BaF_2 etc. which produce BrF_4^- ions in liquid BrF_3 act as bases. Thus :

$$\left.\begin{array}{l} \underset{(\text{Acid})}{\text{SnF}_4} + 2\text{BrF}_3(l) \rightarrow 2[\text{BrF}_2]^+[\text{SnF}_6]^- \\ \underset{(\text{Acid})}{\text{AuF}_3} + \text{BrF}_3(l) \rightarrow [\text{BrF}_2]^+[\text{AuF}_4]^- \end{array}\right\} \quad \text{Solvo-acids}$$

$$\left.\begin{array}{l} \underset{(\text{Base})}{\text{AgF}} + \text{BrF}_3(l) \rightarrow \text{Ag}^+[\text{BrF}_4]^- \\ \underset{(\text{Base})}{\text{BaF}_2} + 2\text{BrF}_3(l) \rightarrow \text{Ba}^{2+}[\text{BrF}_4]_2^- \end{array}\right\} \quad \text{Solvo-bases}$$

Thus the solvo-acids and solvo-bases in liquid BrF_3 will interact as follows (*Neutrilisation reactions*) :

$$\underset{\textit{Solvo-acid}}{[\text{BrF}_2]^+[\text{AuF}_4]^-} + \underset{\textit{Solva-base}}{\text{Ag}^+[\text{BrF}_4]^-} \rightleftharpoons \underset{\textit{Salt}}{\text{Ag}^+[\text{AuF}_4]^-} + \underset{\textit{Solvent}}{2\text{BrF}_3}$$

$$[\text{BrF}_2]^+[\text{MF}_6]^- + \text{K}^+[\text{BrF}_4]^- \rightleftharpoons \text{K}^+[\text{MF}_6]^- + 2\text{BrF}_3$$

In the above equation M=Sb, V, Nb, Ta. The end point in the above acid-base reactions can be determined either with the help of suitable indicator or are followed conductometrically.

Acid base reactions in liquid BrF_3 involving acidic or basic anhydrides have also been reported.

$$\underset{\textit{Acid}}{\text{VF}_5(\text{acidic anhydride})} + \underset{\textit{Base}}{\text{Ag}^+[\text{BrF}_4]^-} \rightleftharpoons \underset{\textit{Salt}}{\text{Ag}^+[\text{VF}_6]^-} + \underset{\textit{Solvent}}{\text{BrF}_3}$$

$$[\text{BrF}_2]^+[\text{TaF}_6]^- + \text{LiF}(\text{basic anhydride}) \rightleftharpoons \text{Li}^+[\text{TaF}_6]^- + \text{BrF}_3$$

(*iv*) *Liquid IF₅*. The self-ionisation of liquid IF_5 can be represented as :

$$\text{IF}_5(\text{Acid}_1) + \text{IF}_5(\text{Base}_2) \rightleftharpoons \text{IF}_4^+(\text{Acid}_2) + \text{IF}_6^-(\text{Base}_1)$$

Thus the compounds like SbF_5, BF_3 etc. which produce IF_4^+ ions in liquid IF_5 act as acids while those like KF which produce IF_6^- ions in liquid IF_5 act as bases. Thus :

$$\left.\begin{array}{l} \underset{\text{Acid}}{SbF_5}+IF_5(l) \rightleftharpoons SbF_6^-+IF_4^+ \rightarrow [IF_4]^+[SbF_6]^- \\ \underset{\text{Acid}}{BF_3}+IF_5(l) \rightleftharpoons BF_4^-+IF_4^+ \rightarrow [IF_4]^+[BF_4]^- \end{array}\right\} \text{Solvo-acids}$$

$$\underset{\text{Base}}{KF}+IF_5(l) \rightleftharpoons K^++IF_6^- \rightarrow K^+[IF_6]^- \qquad \text{Solvo-base}$$

Consequently neutralisation reactions occurring in liquid IF_5 can be represented as :

$$\underset{\text{Solvo-acid}}{[IF_4]^+[SbF_6]^-}+\underset{\text{Solvo-base}}{K^+[IF_6]^-} \rightleftharpoons \underset{\text{Salt}}{K^+[SbF_6]^-}+\underset{\text{Solvent}}{2IF_5}$$

$$[IF_4]^+[BF_4]^-+K^+[IF_6]^- \rightleftharpoons K^+[BF_4]^-+2IF_5$$

13. *Lewis acid strength.* Lewis acid strength of some AB type interhalogens decreases in the order : (Halogens have also been included in the series for the sake of comparison) $ICl >> BrCl > IBr > I_2 > Br_2 > Cl_2$

14. ***Halogenation reactions.*** BrF_3, IF_5 and ICl have been found to be good halogenating agents. For example :

(*a*) When Au and Ag are dissolved in liq. BrF_3 in correct molar proportions, these metals are converted into AuF_3 and AgF respectively (*Fluorination*). These salts react together to produce the fluorinated complex, $Ag^+[AuF_4]^-$.

$$Ag \xrightarrow{\text{Liq. } BrF_3} AgF \; ; \; Au \xrightarrow{\text{Liq. } BrF_3} AuF_3$$

$$AgF+AuF_3 \longrightarrow Ag^+[AuF_4]^-$$

(*b*) Sulphur is converted into SF_4 by IF_5 (*Fluorination*)

$$IF_5+S \xrightarrow[100-300^\circ]{12 \text{ hours}} SF_4+IF$$

(*c*) C_6H_6 is converted into C_6H_5I by ICl (*Iodonation*).

15. *Oxidising power.* The oxidising power of the fluorides of bromine (BrF, BrF_3 and BrF_5) increases with the increase of the oxidation number of Br atom in these fluorides. Thus the oxidising power of these fluorides is in the order : $Br^+F < Br^{3+}F_3 < Br^{5+}F_5$.

Oxidising power of ClF_3, BrF_3 and IF_5 is in the order :

$$ClF_3 > BrF_3 > IF_5$$

Uses of interhalogen compounds. For the uses of ICl, BrF_3, ClF_3, ICl_3 and BrF_5 compounds see the individual study of these compounds on the subsequent pages.

SOME IMPORTANT INTERHALOGEN COMPOUNDS

1. **Iodine monochloride, ICl.** This compound was discovered by Davy and Gay Lussac in 1814 and is obtained as a dark red liquid by passing Cl_2 over I_2 or by heating I_2 with $KClO_3$.

$$I_2+Cl_2 \longrightarrow 2ICl$$

$$KClO_3+I_2 \longrightarrow KIO_3+ICl$$

Properties. (*i*) It solidifies on standing even at room temperature (15—25°). From this solid two forms of the compound may be obtained. These are (*a*) α-form which is ruby-red. It is a stable form (m.pt.=27·2°) (*b*) β-form which is red rhombic. It is a meta stable form (m.pt.=14·0°, b.pt.=97·4°). These two forms are identical in the gaseous state. These can be separated by cooling the liquid ICl below 14° and by adding to the liquid a crystal of either of the two forms.

(*ii*) ICl is soluble in water and gets hydrolysed by it.

$$5ICl+3H_2O \longrightarrow 2I_2+HIO_3+5HCl$$

(*iii*) It also dissolves in alkalies to form I_2, iodate and chloride

$$5ICl+6NaOH \longrightarrow 2I_2+NaIO_3+5NaCl+3H_2O$$

(*iv*) ICl is an electrical conductor when in the molten state. Thus when ICl is in the molten state, it ionises as :

$$2ICl \rightleftarrows I^+ + ICl_2^- \quad (\textit{Ionisation})$$

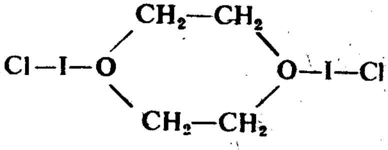
$$2I^+ + 2e^- \longrightarrow I_2 \quad (\textit{At cathode})$$

$$2ICl_2^- \longrightarrow I_2+2Cl_2+2e^- \quad (\textit{At anode})$$

The liberation of I_2 at cathode and both I_2 and Cl_2 at anode shows that ICl is an ionic compound and in it iodine is present as I^+ ion (*unipositive iodine*).

(*v*) ICl forms charge-transfer type complexes with organic bases like pyridine (I) and dioxane (II)

(I)



(II)

Uses. (*i*) A solution of ICl in glacial acetic acid is used for the determination of iodine number which measures the unsaturation of oils and fats. (*ii*) It is also used to iodate and chlorinate organic compounds. (*iii*) The solution of ICl is used as a catalyst in oxidising As_2O_3 by $Ce(SO_4)_3$. (*iv*) It is also used to prepare polyhalides (*v*) Because of the formation of I^+ cation, ICl is also used as an electrophilic iodinating agent. For example, it converts salicylic acid into 3, 5-diodosalicylic acid in nitrobenzene.

2. Iodine monobromide, IBr. It is obtained by the direct combination of the elements.

$$I_2+Br_2 \longrightarrow 2IBr$$

Properties. (*i*) It is a hard, crystalline solid of grey-violet colour.

(*ii*) Its vapour dissociates to a small extent on heating.

$$2IBr_2 \rightleftharpoons I_2 + Br_2$$

(*iii*) IBr is an electrical conductor when in the molen state. It ionises as :

$$IBr \longrightarrow I^+ + Br^-$$

$$2I^+ + 2e^- \longrightarrow I_2 \text{ (At cathode)}$$

$$2Br^- \longrightarrow Br_2 + 2e^- \text{ (At anode)}$$

Thus in IBr, iodine is present as I^+.

3. Chlorine monofluoride, ClF. Preperation. It is formed by the action of Cl_2 on HF at the temperature of liquid air. It is also formed when F_2 and Cl_2 are heated together in a copper vessel at 50°.

Properties. It is a colourless gas. It dissociates when heated strongly.

$$2ClF \longrightarrow Cl_2 + F_2$$

It reacts with a number of metals, even more vigorously than F_2. It inflames cotton-wool and filter paper in the same way as F_2.

4. Bromine monofluoride, BrF. Preparation. It is formed by the action of BrF_3 on Br_2.

$$BrF_3 + Br_2 \longrightarrow 3BrF$$

Properties. It is a reddish-brown liquid (b.pt. = 23°C). It is unstable and decomposes on heating into the elements.

It undergoes disproportionation as :

$$2BrF \longrightarrow BrF_3 + Br_2$$

5. Boromine chloride, BrCl. Preparation. It is prepared by passing Cl_2 gas into liquid Br_2 cooled below 10°C.

$$2Br_2 + Cl_2 \rightleftharpoons 2BrCl$$

Properties. It is a reddish-yellow liquid which decomposes at 10°C into Cl_2 and Br_2. It is soluble in water, ether and CS_2.

6. Bromine trifluoride, BrF_3. This compound was discovered by Lebean in 1905.

Preparation. It is formed (*i*) by mixing Br_2 vapour and F_2 in nitrogen.

$$Br_2 \text{ (Vapour)} + 2F_2 \rightarrow 2BrF_3$$

(*ii*) by the action of ClF_3 on Br_2 at 10°C.

$$ClF_3 + Br_3 \xrightarrow{10^\circ C} BrF_3 + BrCl$$

(*iii*) by the action of F_2 on HBR.

$$3F_2 + 2HBr \longrightarrow 2BrF_3 + H_2$$

(*iv*) when BrF undergoes disproportionation.

$$3BrF \longrightarrow BrF_3 + Br_2$$

Properties. (*i*) It is a colourless fuming liquid with b pt = 127·6° and is exceedingly reactive.

(*ii*) It is violently decomposed by H_2O and organic materials.

(*iii*) It reacts with glass and silica materials and sets fire to wood, paper etc. It displaces O_2 from oxides like SiO_2, CuO etc.

$$3SiO_2+4BrF_3 \longrightarrow 3SiF_4+2Br_2+3O_2$$

(*iv*) It reacts with Br_2 to form BrF

$$BrF_3+Br_2 \longrightarrow 3BrF$$

(*v*) It has high electrical conductivity and ionises as :

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

(*vi*) *Action on metal fluorides.* It dissolves certain metal fluorides into it to form tetra fluoroborites, $M^+[BrF_4]^-$ or hexafluoroborates, $M^{3+}[BrF_6]^{3-}$. For example :

$$KF+BrF_3 \longrightarrow K^+[BrF_4]^{3-} \quad \text{(Pot. tetrafluoroborate)}$$

$$SbF_3+BrF_3 \longrightarrow Sb^{3+}[BrF_6]^{3-} \quad \text{(Antimony hexafluoroborate)}$$

(*vii*) *Action on metals, their oxides and chlorides.* It converts metals, their oxides and chlorides into their fluorides. For example :

$$6M+2BrF_3 \longrightarrow 6MF+Br_2$$

$$3MCl+BrF_3 \longrightarrow 3MF+BrCl_3$$

Uses. (*i*) Due to the fact that BrF_3 converts many metals, their oxides and chlorides into their fluorides, it is used as a fluorinating agent. Many metal fluorides have also been converted into complex fluorides.

(*ii*) BrF_3 is used to prepare polyhalides.

7. **Iodine trichloride, ICl_3. Preparation.** (*i*) It is obtained by the action of excess of Cl_2 on I_2 or on ICl at 100°C.

$$3Cl_2(\textit{Excess}) + I_2 \longrightarrow 2ICl_3$$

$$Cl_2(\textit{Excess}) + ICl \longrightarrow ICl_3$$

(*ii*) It is also formed when dry HCl gas reacts with heated I_2O_5.

$$I_2O_5\text{ (heated)} + 10HCl\text{ (dry gas)} \longrightarrow 2ICl_3 + 5H_2O + 2Cl_2$$

(*iii*) It is also formed along with ICl by the action of HI on Cl_2.

$$4HI + 4Cl_2 \longrightarrow 4HCl + I_2 + ICl + ICl_3$$

Properties. (*i*) It is a lemmon-yellow crystalline solid which fumes readily. It is soluble in organic solvents, liq. NH_3 and liq. SO_2.

(*ii*) It forms crystalline addition compounds with metallic chlorides. These compounds dissociate on exposure to air, giving ICl_3 and MCl.

$$MCl + ICl_3 \quad ICl_3.MI \text{ (Addition compound)} \xrightarrow{\text{Expose to}} ICl_3 + MC$$

(*iii*) With fluorides of K, Rb, Cs, it gives polyhalides of $MICl_3F$ type.

(*iv*) ICl_3 is completely hydrolysed by H_2O.

$$2ICl_3 + 3H_2O \longrightarrow 5HCl + HIO_3 + ICl$$

(*v*) ICl_3 dissociates on heating at 68°C giving ICl and Cl_2.

$$ICl_3 \longrightarrow ICl + Cl_2$$

(*vi*) It reacts with CS_2 as :

$$4ICl_3 + 3CS_2 \longrightarrow CCl_4 + 2CSCl_2 + 2S_2Cl_2 + 2I_2$$

(*vii*) Like ICl, ICl_3 is also decomposed by KOH solution

$$3ICl_3 + 12KOH \longrightarrow 9KCl + KI + 2KIO_3 + 6H_2O$$

(*viii*) Molten ICl_3 has a high conductivity ($=8{\cdot}4\times10^{-3}$ ohm^{-1} cm^{-1}). The liberation of I_2 and Cl_2 at both electrodes indicates that ICl_3 is ionised into $[I^{3+}Cl_2]^+$ and $[I^{3+}Cl_4]^-$ ions.

$$2ICl_3 \rightleftharpoons [ICl_2]^+ + [ICl_4]^- \quad (\textit{Ionisation})$$

$$2[ICl_2]^+ + 2e^- \longrightarrow I_2 + 2Cl_2 \quad (\textit{At cathode})$$

$$2[ICl_4]^- - 2e^- \longrightarrow I_2 + 4Cl_2 \quad (\textit{At anode})$$

Uses. ICl_3 is used in medicines. It is also used in the preparation of polyhalides.

8. Chlorine trifluoride, ClF_3. Preparation. It is prepared when Cl_2 is heated with excess of F_2 in copper vessel at 250°C.

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3$$

Properties. It is a colourless gas which condenses to give a pale-green liquid (b.pt. = −12°C). It is exceedingly reactive and attacks a number of metals. It also attacks glass vigorously. It reacts with water to give a red liquid which crystallises at −70°C. The compound formed is ClFO.

Uses. (*i*) ClF_3 has been used as a fluorinating agent, as an incendiary and in cutting oil well tubes. (*ii*) It is also used as an oxidiser for propellants (*iii*) It is also used for the preparation of polyhalides.

9. Iodine pentafluoride, IF_5. Preparation. It is formed by the direct combination of the elements or by the action of F_2 on heated I_2O_5.

$$I_2\ (\text{Excess}) + 5F_2 \longrightarrow 2IF_5$$

$$2I_2O_5\ (\text{heated}) + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

It may also be prepared by heating together I_2 and AgF.

$$5AgF + 3I_2 \xrightarrow{\text{Red heat}} IF_5 + 5AgI$$

or

$$10AgF + I_2 \longrightarrow 2IF_5 + 10Ag$$

Properties. It is a colourless liquid (b.pt = 98°). Its vapours attack the respiratory organs. It is a very poor conductor. It decomposes on heating to I_2 and IF_7.

$$7IF_5 \longrightarrow I_2 + 5IF_7$$

When heated with H_2O, it is hydrolysed giving successively IOF_3, IO_2F and finally I_2O_5.

$$2IF_5 + 5H_2O \longrightarrow I_2O_5 + 10HF$$

Sulphur is converted to SF_6. Phosphorus in an atmosphere of IF_5 forms I_2 and PF_3. I_2O_5 when boiled with IF_5 gives white crystals of iodine oxy-fluoride, IOF_3 which decompose at 100°C to give black IF_5 and a white solid IO_2F.

$$3IF_5 + I_2O_5 \longrightarrow 5IOF_3$$

$$2IOF_3 \xrightarrow{100°C} IF_5 \text{ (black)} + IO_2F \text{ (white solid)}$$

I_2O_4 dissolves in IF_5 to give IOF_3 and some I_2.

The oxides P_2O_5, V_2O_5, Sb_2O_5, Cr_2O_3 and WO_3 dissolve in hot IF_5 to form POF_3, VOF_3, $SbF_5.IO_2$, CrO_2F_2 and $WO_3.2IF_5$ respectively. Nitrogen (IV) oxide, NO_2, dissolves in IF_5 to give a cream coloured crystalline compound, $IF_5.NO_2$.

It is a good conductor of electricity and ionises as :

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

10. Bromine pentafluoride, BrF_5. Preparation. It is obtained : (*i*) by the action of excess of F_2 on Br_2 (*ii*) by passing F_2 through BrF_3 at 90°C.

Properties. (*i*) It is a colourless liquid. It is highly reactive and hence is generally diluted with N_2 whenever required for the preparation of fluorides.

(*ii*) Many metals and non-metals catch fire when dropped into it.

(*iii*) It is hydrolysed by H_2O with the formation of an oxy-fluoride, $BrOF_3$.

$$BrF_5 + H_2O \longrightarrow 2HF + BrOF_3$$

(*iv*) It dissociates into Br_2 and F_2 at 400—500°

$$2BrF_5 \longrightarrow Br_2 + 5F_2$$

Uses. It is used (*i*) for the preparation of fluorides (*ii*) in organic synthesis (*iii*) as an oxidiser for propellants.

11. Iodine heptafluoride, IF_7. It may be prepared by direct combination of F_2 (excess) and I_2 at 300°C or by refluxing IF_5 in a current of excess of F_2 through a tube of Pt heated to 270°.

$$7F_2 \text{ (Excess)} + I_2 \xrightarrow{300°C} 2IF_7$$

$$IF_5 + F_2 \xrightarrow{270°C} IF_7$$

When iodine reacts with excess of F_2 at 300°C, IF_7 is formed.

Properties. It is a colourless gas having mustly odour. It can be condensed to a colourless liquid or to a colourless crystalline solid. It reacts with most metals (except the platinum group), non-metals including Cl_2 and I_2, water to give periodate and fluoride ions, many inorganic compounds and a variety of organic materials.

It explodes when heated with H_2. It is slowly decomposed by water. Two of fluorine atoms present in IF_7 can easily be removed.

Structure and shape of AB type interhalogen molecules. (*Examples : ICl, BrF, ClF, BrCl*). In AB type molecules A halogen atom is less electronegative than B halogen atom. The Lewis structure of AB molecule, $\overset{\times\times}{\underset{\times\times}{{}^{\times}_{\times}A\times}}\ \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}:$ *or* $\overset{\times\times}{\underset{\times\times}{{}^{\times}_{\times}A}}—\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}:$ shows that the central atom A (central atom is that which is less electronegative) is surrounded by one σ-bonding electron pair and three lone pairs of electrons, *i.e.* σ-*bps*+*lps*=1+3=4. Consequently the central atom A is sp^3 hybridised in AB molecule. The occurrence of sp^3 hybridisation in AB type interhalogen molecules can be understood by taking the example of ICl molecule. sp^3 hybridisation undergone by I-atom has been shown as follows :

$5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1$ (*I-atom in its ground state*) $\xrightarrow{sp^3\ hybridisation}$

$(sp^3)^2(sp^3)^2(sp^3)^2(sp^3)^1$ [*Four sp^3 hybrid orbitals three of which contain a lone pair of electrons while the fourth hybrid orbital is singly-filled*].

sp^3 hybridisation scheme shown above makes it evident that three of the four sp^3 hybrid orbitals contain one lone pair (*lp*) each while the fourth sp^3 hybrid orbital contains one electron. This singly-filled sp^3 hybrid orbital makes a *head-to-head* (*linear*) overlap with the singly-filled $3p_x$ orbital on Cl-atom and forms one sp^3 (I)—p_x(Cl) σ-bond as shown in Fig. 20.1.

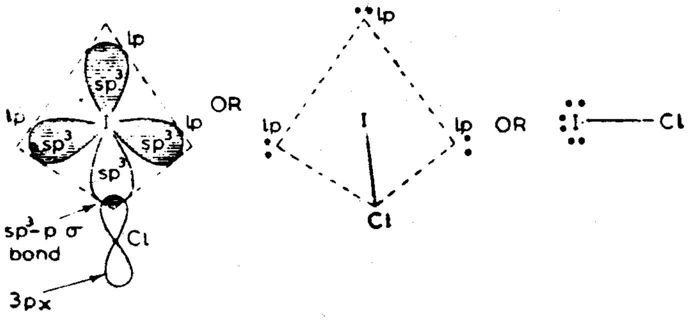


Fig. 20.1. Pictorial representation of the formation of one σ-bond in ICl molecule (*bp*=1, *lps*=3) which has linear shape.

Although the spatial arrangement of the four electron pairs (*bp*=1 and *lps*=3) round I atom is tetrahedral, due to the presence of three lone pairs of electrons in three sp^3 hybrid orbitals, the shape of ICl molecule gets distorted and becomes *linear*. Similarly other molecules like BrF, ClF, BrCl etc. also have linear shape.

A—B bond lengths in various AB type interhalogen molecules are as : BrF=1·750 A°, ClF=1·628 A°, BrCl=2·138 A°, IBr=2.470 A°, ICl=2·321 A°.

ICl molecule forms *zig-zag* chains in both of its α and β forms (Fig. 20·2). These two forms differ only whether the Cl branches are *cis* (α) or *trans* (β).

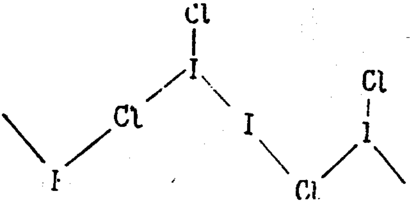


Fig. 20.2. zig-zag chains in both forms (α and β) of ICl molecule.

Structure and shape of AB$_3$ type interhalogen molecules (*Examples : ClF$_3$, BrF$_3$, ICl$_3$*). Lewis structure of AB$_3$ molecule,

$B-\overset{\overset{B}{|}}{\underset{\cdot\cdot\cdot\cdot}{A}}-B$ shows that the central atom A is surrounded by three σ-bonding electron pairs and two lone pairs of electrons, *i.e.* σ-*bps*+*lps*=3+2=5. Consequently the central atom, A is sp^3d hybridised in AB$_3$ molecule. The occurrence of sp^3d hybridisation in AB$_3$ type interhalogen molecules can be understood by taking the following examples :

(*i*) *Structure and shape of ClF$_3$ molecule.* In this molecule Cl atom is the central atom which undergoes sp^3d hybridisation as shown below :

$3s^2 . 3p_x^2 3p_y^2 3p_z^1 . 3d^0$ *(Cl-atom in its ground state)* $\longrightarrow 3s^2 . 3p_x^2 3p_y^1 3p_z^1 . 3d^1$ *(Cl-atom in its excited state)* $\xrightarrow{sp^3d \text{ hybridization}}$ *Five sp^3d hybrid orbitals. Two basal hybrid orbitals contain a lone pair of electrons while the remaining three contain one electron each.*

Each of the three singly-filled sp^3d hybrid orbitals makes a *head-to-head* (*linear*) overlap with the singly-filled 2*p* orbital on each F atom and forms sp^3d(Cl)—*p*(F) σ bond or Cl—F σ bond as shown in Fig. 20.3.

Although the spatial arrangement of five-electron pairs (*bps* =3, *lps*=2) round the central Cl atom in space is trigonal bipyramidal, due to the presence of two lone pairs of electrons, the shape of ClF$_3$ molecule gets distorted and becomes *slightly bent T-shape*, and the repulsion between the two lone pairs of electrons reduces F_aClF_b bond angle from 90° to 87·5°. Both F_a—Cl bond lengths are equal (=1·70 A°) while Cl—F_b bond length (=1·60 A°) is different from these two bond lengths. The difference in bond lengths is in accordance to our expectations, since a trigonal bipyramid is not a regular shape. The two lone pairs of electrons

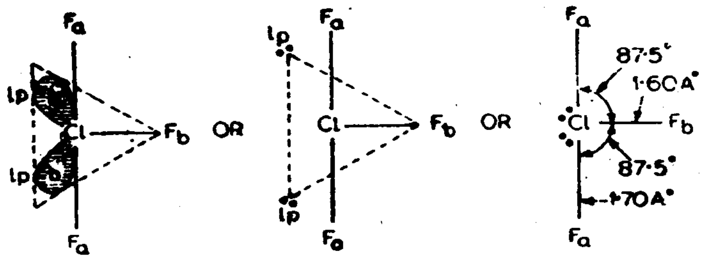


Fig. 20.3. Pictorial representation of the formation of three Cl—F σ-bonds in ClF_3 molecule ($bps=3$, $lps=2$) which has T-shaped geometry. Fa are F atoms which make σ-bonds with the hybrid orbitals occupying the axial positions of the trigonal bipyramid while F_b is the F atom making σ-bond with hybrid orbital occupying the basal position.

occupy the basal positions of the trigonal bipyramid as discussed below.

Theoretically the two lone pairs of electrons can occupy any of the three positions of the five positions of the trigonal bipyramid and thus give three drifferent structures (*a*), (*b*) and (*c*) to ClF_3 molecule as shown in Fig. 20.4.

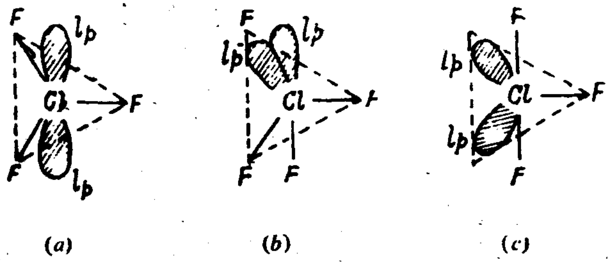


Fig. 20.4. Different structures of ClF_3 molecule showing three different positions occupied by two *lps* in trigonal bipyramid. Structure (*a*) has six (*lp—bp*) repulsions, structure (*b*) has three (*lp—bp*) repulsions and one (*lp—lp*) repulsion while structure (*c*) has four (*lp—bp*) repulsions.

The consideration of (*lp—bp*) and (*lp—lp*) repulsions [(*lp—bp*) represents the repulsion between one *lp* and one *bp*, and (*lp—lp*) represents the repulsion between two *lps*] in these structures makes it evident that the most stable of these three structures is that in which the *lps* occupy the basal positions of the trigonal bipyramid.

(*ii*) *Structure and shape of* BrF_3. Like ClF_3, BrF_3 molecule also has bent T-shaped structure as shown in Fig. 20.5. In this molecule Br-atom is the central atom and is sp^3d hybridised. Here also, lone pairs occupy the basal positions of the trigonal bipyramid.

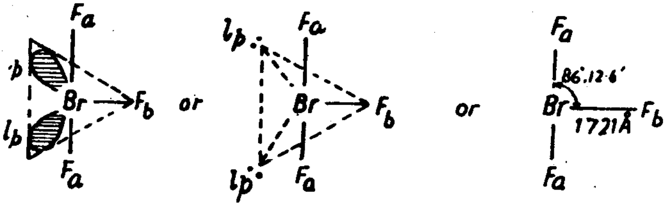


Fig. 20.5. Bent T-shaped geometry of BrF_3 molecule. Lone pairs of electrons (*lp*) occupy the basal positions of the trigonal bipyramid.

(*iii*) *Structure and shape of* ICl_3 *molecule*. Whereas ClF_3 and BrF_3 are monomeric T-shaped molecules, ICl_3 in the solid state is dimeric with a chlorine-bridged structure shown in Fig. 20.6. The dimer, $(ICl_3)_2$ is formed by joining two T-shaped ICl_3 molecules and is flat. Each I-atom is sp^3d hybridised and is bonded to two bridging Cl-atoms and two terminal Cl-atoms. Each I-atom has two lone pairs of electrons due to which $(ICl_3)_2$ molecule does not have the expected regular trigonal bipyramidal shape but has a square planar shape.

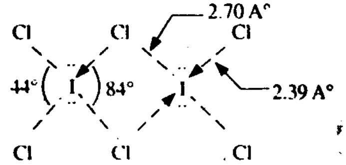
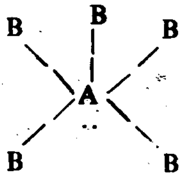


Fig. 20.6. Chlorine-bridged square planar shape of dimerised $(ICl_3)_2$ molecule. In this structure Cl (terminal)—I—Cl (terminal) bond angle=94°, Cl (bridging)—I—Cl (bridging) bond angle=84°, Cl (bridiging)—I bond length=2·70 A° and Cl (terminal)—I bond length=2·39 A°

Structure and shape of AB_5 type interhalogen molecules. (*Examples* : IF_5, ClF_5, BrF_5). The Lewis structure of AB_5 molecule,



shows that the central atom A is surrounded by five σ-bonding electron pairs and one lone pair of electrons, *i.e.* σ-*bps*+*lps*=5+1

=6. Consequently the central atom, A is sp^3d^2 hybridised in AB_5 molecule. The occurrence of sp^3d^2 hybridisation in AB_5 type interhalogen molecules can be understood by considering the following examples :

(*i*) *Structure and shape of IF_5 molecule.* In this molecule I-atom is the central atom which undergoes sp^3d^2 hybridisation as shown below :

$5s^2. 5p_x^2 5p_y^2 5p_z^1. 5d^0 5d^0$ (I-atom in its ground state) ⟶ $5s^2.$

$5p_x^1 5p_y^1 5p_z^1. 5d^1 5d^1$ (I-atom in its second excited state)

$\xrightarrow{sp^3d^2 \text{ hybridisation}}$ *Six sp^3d^2 hybrid orbitals. One axial hybrid orbital contains a lone pair of electrons.*

sp^3d^2 hybridisation scheme shown above makes it evident that one of the six hybrid orbitals containts a lone pair while the remaining hybrid orbitals have one electron each. The hybrid orbital containing the lone pair is the axial hybrid orbital because in this case ($lp-bp$) repulsion is minimum. Each of the five singly-filled sp^3d^2 hybrid orbitals makes a *head-to-head* (*linear*) overlap with the singly-filled $2p$ orbital on each F atom and forms sp^3d^2 (I) $-p$(F) σ-bond or I$-$F σ-bond.

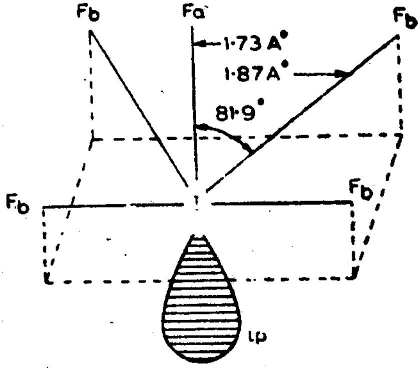
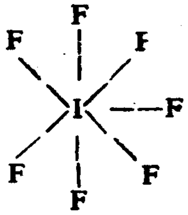


Fig. 20.7. Square pyramidal structure of IF_5 molecule.

Although the spatial arrangement of six electron pairs (σ-bps=5 and lp=1) round the central I-atom is octahedral, due to the presence of one lone pair of electrons in the axial hybrid orbital, the shape of IF_5 gets distorted and becomes *square pyramidal.* A recent single crystal structure study of this molecule made by Burbank and James has shown that the basal F-atoms (F_b atoms) are slightly displaced upwards from the base of the square pyramid and hence IF_5 molecule assumes the structure as shown in Fig. 20 7. F_aIF_b bond angle has been found to be equal to 81·9°. I$-F_a$ bond length (=1·73 A°) is shorter than the I$-F_b$ bond length (=1·87A°).

(*ii*) *Structure and shape of ClF_5 and BrF_5 molecules.* Like IF_5, ClF_5 and BrF_5 molecules also have square pyramidal shape which results due to sp^3d^2 hybridisation of Cl and Br atoms respectively.

Structure and shape of IF_7 molecule. IF_7 is the only interhalogen of AB_7 type. Lewis structure of IF_7 molecule,



shows that the central I atom is surrounded by seven σ-bonding electron pairs and no lone pair of electrons is there on I-atom. Thus σ-*bps*+*lps*=7+0=7 and hence I atom (central atom) is sp^3d^3 hybridised in this molecule as shown below :

$5s^2.\ 5p_x^2\ 5p_y^2\ 5p_z^1.\ 5d^0\ 5d^0\ 5d^0$ (*I-atom in its ground state*)$\longrightarrow$

$5s^1.\ 5p_x^1\ 5p_y^1\ 5p_z^1.\ 5d^1\ 5d^1\ 5d^1$ (*I-atom in its third excited state*)

$\xrightarrow{sp^3d^3\text{ hybridisation}}$ *Seven sp^3d^3 hybrid orbitals each of which contains one electron.*

sp^3d^3 hybridisation scheme shown above makes it evident that each of the seven hybrid orbitals is singly-filled with electrons. Each of these hybrid orbitals makes a *head-to-head* (*linear*) overlap with the singly-filled $2p_x$ orbital on F atom and forms seven I—F σ bonds as shown in Fig. 20.8 and IF_7 molecule has *pentagonal bipyramidal shape* which has two axial I—F_a bonds and five basal I—F_b bonds. I—F_b bonds are lying in the pentagonal plane and are directed at an angle of 72° to each other while the remaining two I—F_a bonds are inclined at an angle of 90° to the pentagonal plane. The angle between two I—F_a bonds is equal to 180°. Thus F_a—I—F_b=90°, F_b—I—F_b=72° and F_a—I—F_a=180°. Both I—F_a bond lengths which are equal to each other are greater than both I—F_b bond lengths which are again equal to each other.

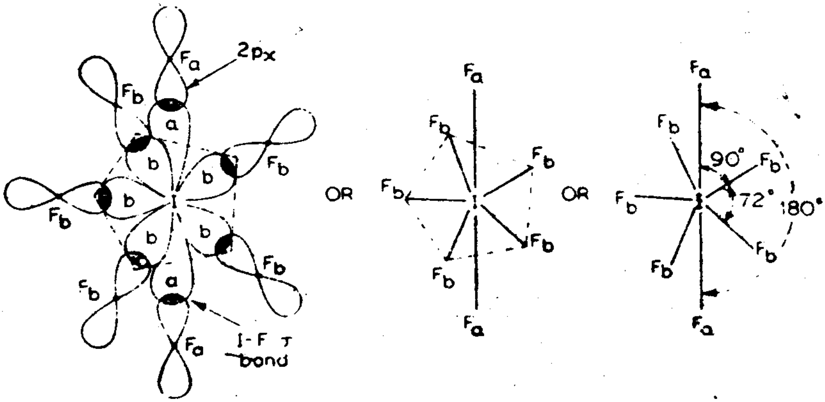


Fig. 20.8 Pentagonal bipyramidal shape of IF_7 molecule.

POLYHALIDE IONS AND POLYHALIDES

What are polyhalide ions and polyhalides ? The ions like I_3^-, IBr_2^-, $IBrF^-$, ICl_4^-, I_7^-, I_9^- (anions), ICl_2^+, BrF_2^+, ClF_2^+ (cations) etc which contain more than two same or different halogen atoms are called *polyhalide ions.* The ionic compounds like $Cs^+[IBr_2]^-$, $K^+[ICl_4]^-$, $[N(CH_3)_4]^+[ICl_4]^-$, $[ICl_2]^+[SbCl_6]^-$, $[BrF_2]^+[SbF_6]^-$ etc. which contain polyhalide cations or anions are called *polyhalides.* As in case of interhalogens, here too the heavier halogen atom plays the role of central atom.

Classification of polyhalide ions. The best way of classifying polyhalide ions is that they are classified on the basis of the total number of halogen atoms present in a particular polyhalide ion. Thus these ions are classified as : (*i*) *Trihalide ions* : I_3^-, ICl_2^-, $IBrF^-$, BrF_2^+, ICl_2^+, ClF_2^+ etc. (*ii*) *Pentahalide ions* : ICl_4^-, BrF_4^-, I_5^-, IF_4^+ etc. (*iii*) *Heptahalide ions* : I_7^-, IF_6^- etc (*iv*) *Other odd polyhalide ions* : I_9^-, I_{11}^-, Br_9^- etc. (*v*) *Other even polyhalide ions* : I_4^-, I_8^- etc.

Solvated polyhalides. Many crystalline polyhalides contain molecules of the solvent or other foreign materials which are essential for the stability of the polyhalides because the whole substance decomposes into a monohalide and a halogen or interhalogen when these foreign molecules are removed. Such polyhalides are called *solvated polyhalides.* Examples are : $KI_3 \cdot H_2O$, $KI_3 \cdot 2H_2O$, $KI_7 \cdot H_2O$, $CsI_{10} \cdot 2C_6H_6$, $Be(ICl_4)_2 \cdot 8H_2O$.

Preparation. (*i*) Simple polyhalides like $K^+Cl_3^-$, $NH_4^+I_5^-$ etc. can be prepared by the action of halogen on metallic halides. For example :

$$Cl_2+KCl \longrightarrow K^+Cl_3^-$$
$$2I_2+NH_4I \longrightarrow NH_4^+I_5^-$$

In some cases the reaction is carried out in a solvent. The solvent used must not react with the reactants, must dissolve the halide and must not solvolyse. For example :

$$[(CH_3)_4N]^+I^-+\left(\frac{n-1}{2}\right)I_2 \xrightarrow{CH_3COOH} [(CH_3)_4N]^+I_n^-$$

The value of n depends on the amount of I_2 used in the reaction.

(*ii*) Mixed polyhalides like $Cs^+[ClF_4]^-$, $K^+[ICl_2]^-$ etc. can be prepared by the action of an appropriate gaseous halogen or interhalogen on a solid metallic halide in the absence of a solvent. Examples are :

$$Cl_2+KI \longrightarrow K^+[ICl_2]^-;\quad 2F_2+CsCl \longrightarrow Cs^+[ClF_4]^-$$
$$ICl+KCl \rightarrow K^+[ICl_2]^-;\quad ICl+KBr \longrightarrow K^+[BrICl]^-$$
$$ICl_3+KCl \rightarrow K^+[ICl_4]^-;\quad BrF_3+KF \longrightarrow K^+[BrF_4]^-$$

Here too, in some cases a suitable solvent is needed for the reaction. For example :

$$Br_2 + CsI(g) \xrightarrow{C_2H_5OH} Cs^+[IBr_2]^-$$

$$ICl + [(CH_3)_4N]Br \xrightarrow{CH_3COOH} [(CH_3)_4N]^+[BrICl]^-$$

(*iii*) Polyhalides of the type namely $M^+[ICl_4]^-$, $M^+[ICl_2]^-$ ($M^+ = Li^+$, Na^+ etc.) and $M^{2+}[ICl_4]_2^-$ ($M^{2+} = Mg^{2+}$, Ca^{2+} etc.) can be prepared by adding I_2 to the solution of metallic chloride in HCl followed by saturation with Cl_2. For Example :

$$2M^+Cl^- \text{ (\textit{solution in HCl})} + I_2 + 3Cl_2 \longrightarrow 2M^+[ICl_4]^-$$

$$M^{2+}Cl_2^- \text{ (\textit{solution in HCl})} + I_2 + 3Cl_2 \longrightarrow M^{2+}[ICl]_2^-$$

$$2Rb^+Cl^- \text{ (\textit{solution in HCl})} + I_2 + Cl_2 \longrightarrow 2Rb^+[ICl_2]^-$$

(*iv*) Polyhalides of one type can be converted into the other type by the action of halogens or interhalogens on them. For example :

$$K[ICl_2] + Cl_2 \longrightarrow K[ICl_4];\ CsBr_3 + I_2 \longrightarrow Cs[IBr_2] + IBr$$

$$K[IBr_2] + Cl_2 \longrightarrow K[ICl_2] + Br_2;\ K[ClIBr] + ICl \longrightarrow K[ICl_2] + IBr$$

(*v*) In a few cases polyhalide acids like $H^+[ICl_4]^-$, $H^+[ICl_2]^-$, $H^+[IBr_2]^-$ and $H^+[IBrCl]^-$ can be formed by adding a halogen or an interhalogen to an acid. $H^+[ICl_4]^-$ is obtained as a tetrahydrate, $H^+[ICl_4]^-.4H_2O$ which becomes dehydrated only on decomposition. The polyhalide acids namely $H^+[ICl_2]^-$, $H^+[IBr_2]^-$ and $H^+[IBrCl]^-$ exist only in solution.

Properties. (*i*) *Colour*. All the polyhalides are coloured compounds. The intensity of the colour increases with the increase of the atomic number of the halogen atoms present. Thus the bromoiodides are red and chlorobromides are yellow.

(*ii*) *Dissociation in aqueous solution*. The polyhalides are usually very soluble in water from which they can often be crystallised. Some of them get dissociated in water to free halogen and halide ion (metallic monohalide). For example :

$$I_3^- \longrightarrow I^- + I_2$$

The stablility of metallic trihalides of MX_3 type having the same cation in the same oxidation state and different trihalide anions in aqueous solution towards dissociation to free halogen and metallic monohalide (MX halide) is in the order : $MI_3 > MBr_3 > MCl_3$.

For the metallic trihalides having the same trihalide anion and different cations in the same oxidation state, the stability increases with the increase of the size of the cation. For example : $NaI_3 < KI_3 < RbI_3 < CsI_3$. Note that the size of Na^+, Rb^+ and Cs^+ cations increases from Na^+ to Cs^+.

The polyhalides containing ICl_4^- anion dissociate in aqueous solution to metal chloride and ICl_3; the latter then hydrolyses to iodate, IO_3^-.

$$M^+[ICl_4]^- \longrightarrow MCl+ICl_3]\times 5$$

$$\underline{5ICl_3+9H_2O \longrightarrow 3HIO_3+15HCl+I_2}$$

$$5M^+[ICl_4]^-+9H_2O \longrightarrow 5MCl+3HIO_3+15HCl+I_2$$

or $$5ICl_4^-+9H_2O \longrightarrow 20Cl^-+3IO_3^-+18H^++I_2$$

(*iii*) *Formation of complexes.* Some of the polyhalide ions form complexes with organic donor molecules. Some examples of such complexes are : $LiI_3 . 4C_6H_5CN$,. $MI_3 . 2C_6H_5CN$(M=Na or K).

(*iv*) *Effect of heat : Thermal decomposition.* When the solid polyhalides are heated, they dissociate more or less readily. The ease of dissociation of a given polyhalide decreases with the increase of the size of the cation with which the polyhalide anion is associated. This means that *the stability of the solid polyhalide towards dissociation is maximum when the cation with which the polyhalide anion is associated is large.*

On thermal dissociation the polyhalides give the metal monohalides and halogen molecule or interhalogen molecule. For example :

$$CsI_3 \xrightarrow{\Delta} CsI+I_2$$

When a polyhalide containing more than one type of halogen atoms undergoes thermal dissociation, the metal monohalide formed is always that which *has highest lattice energy.* Thus when $Cs^+[ICl_2]^-$ undergoes thermal dissociation, the products formed are $CsCl+ICl$ and not $CsI+Cl_2$, since CsCl has higher lattice energy than CsI.

For trihalide ions formed by the same metal, the order of thermal stability is : $I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_3^- > BrCl_2^- > BrCl^-$.

(*v*) ***Reaction with halogens.*** **Sometimes when a polyhalide is allowed to react with a halogen molecule, one or two atoms of halogen present in the polyhalide are substituted by one or two atoms of the reacting halogen, as the case may be.**

$$KIBr_2+Cl_2 \longrightarrow KICl_2+Br_2; \quad CsBr_3+I_2 \longrightarrow CsIBr_2+IBr$$

Sometimes a higher polyhalide is formed.

$$KICl_2+Cl_2 \longrightarrow KICl_4$$

(*vi*) ***Dissolution in liq. halogen or interhalogen.*** Polyhalides may dissolve in liquid halogen or interhalogen to give solution from which the original polyhalide may be crystallised on evaporation. The polyhalides like $K^+[IBr_2]^-$, $NH_4^+[IBr_2]^-$ and $Rb^+[IBr_2]^-$ form solution in bromine.

Structure and shape of trihalide anions. (*Examples : ICl_2^-, I_3^-, ICl_3^-, $IBrF^-$ etc.*) The tri-halide anions like ICl_2^-, I_3^-, $IBrF^-$ etc. have *symmetrical linear shape* while the trihalide anions like IBr^- have *unsymmetrical linear shape.* The structures of ICl_2^- and I_3^- ions have been considered as follows :

(*i*) ***Structure and shape of*** ICl_2^- ***ion.*** This ion has symmetrical linear shape which results from sp^3d hybridisation of I-atom (central atom). Due to the presence of one unit of negative charge on ICl_2^- ion, I-atom (central atom) can be regarded as having eight electrons (instead of seven) in its valence-shell. The Lewis structure of ICl_2^- ion, $[\mathrm{Cl}-\overset{\cdot\cdot}{\underset{\cdot\cdot\cdot\cdot}{\mathrm{I}}}-\mathrm{Cl}]^-$ shows that I-atom is surrounded by two *σ-bps* and the remaining six electrons remain as three *lps* on I-atom. Thus, since $\sigma\text{-}bps + lps = 2+3 = 5$, I-atom is sp^3d hybridised in ICl_2^- ion as shown below :

$$5s^2 \,.\, 5p_x^2 5p_y^2 5p_z^1 \,.\, 5d^0 \text{ (I-atom in its ground state)} \xrightarrow{+e^-}$$

$$5s^2 \,.\, 5p_x^2 5p_y^2 5p_z^2 \,.\, 5d^0 \text{ (I-atom after having gained one electron)}$$

$$\longrightarrow 5s^2 \,.\, 5p_x^2 5p_y^2 5p_z^1 \,.\, 5d^1 \text{ (I-atom in its excited state)}$$

$$\xrightarrow[\text{}]{sp^3d \text{ hybridisation}}$$ *Five* sp^3d *hybrid orbitals. All the three basal hybrid orbitals contain lone pairs of electrons.*

Now the two axial hybrid orbitals, each of which has one electron, overlaps with the $3p_\alpha$ orbital (singly-filled) of two Cl-atoms to form two I—Cl σ-bonds. Due to the presence of *lps*, ICl_2^- ion assumes *linear* (symmetrical) *shape* (See Fig 20.9).

The three lone pairs of electrons (*lps*) occupy the basal positions of the trigonal bipyramid. Theoretically three *lps* can occupy

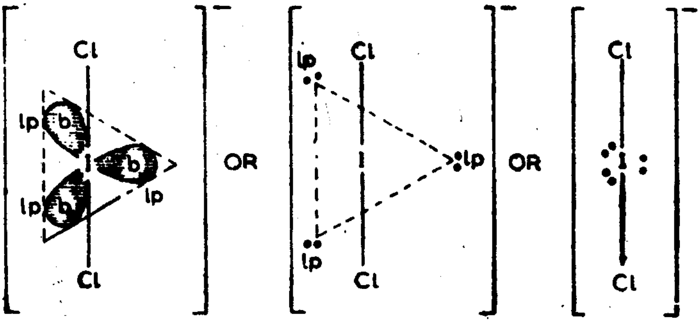
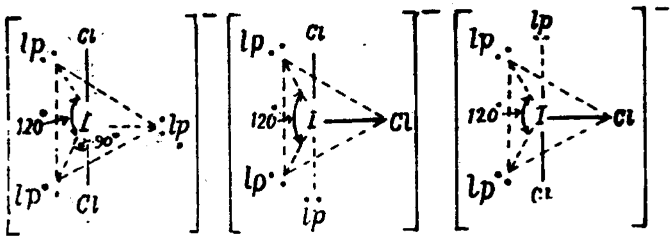


Fig. 20:9. Linear (symmetrical) shape of ICl_2^- ion with $bps=2$ and $lps=3$.

any three positions of the trigonal bipyramid and thus give rise to three different structures namely (*a*), (*b*) and (*c*) to ICl_2^- ion as shown in Fig. 20.10. The most stable structure is that in which the angle between two *lps* is the largest angle. Now since in structure (*a*) the angle between two *lps* is 120° which is the largest angle, this structure is the most stable, *i.e.*, ICl_2^- ion has linear shape.



(a) Linear shape (b) Angular shape (c) Angular shape

Fig- 20.10. Different structures of ICl_2^- ion showing three different positions occupied by three *lps* in trigonal bipyramid. The angle between two *lps* in different structures is as (*a*) =120° ; (*b*) =120°, 90° ; (*c*) =120°, 90°.

(*ii*) ***Structure and shape of*** I_3^- ***ion.*** Like ICl_2^- ion, I_3^- ion also has linear shape as shown in Fig. 20·11.

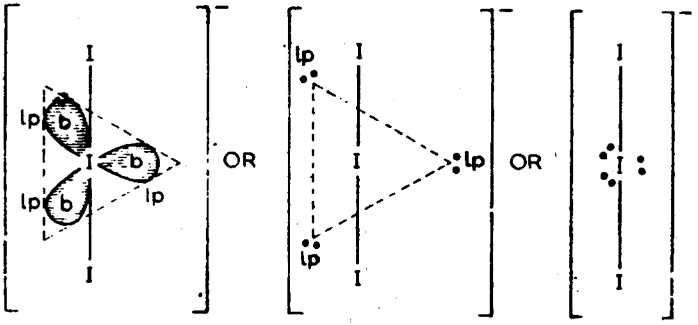
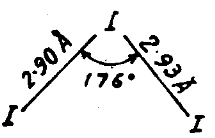
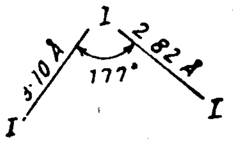


Fig. 20.11 Linear shape of I_3^- ion with *bps*=2 and *lps*=3.

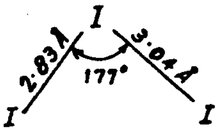
In some cases I—I—I bond angle in I_3^- ion is not equal to 180° and the two I—I bond lengths are unequal (unsymmetrical structure) as shown below in some ionic salts.



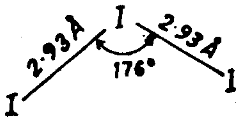
$[(C_6H_5)_4As] + I_3^-$



$[NH_4]^+I_3^-$



$Cs^+I_3^-$



$[N(C_2H_5)_4]^+I_3^-$ (symmetrical form)

$[N(C_2H_5)_4]^+I_3^-$ (unsymmetrical form)

Structure and shape of trihalide cations (*Examples* : ICl_2^+, BrF_2^+, ClF_2^+). The trihalide cations like ICl_2^+, BrF_2^+, ClF_2^+ have angular shape which results from sp^3 hybridisation of the central atom. As an example we can consider the structure of ICl_2^+ ion. In this ion I-atom is the central atom. Due to the presence of one unit of positive charge on ICl_2^+ ion, I-atom (central atom) can be regarded as having six electrons (instead of seven) in its valence-shell. The Lewis structure of ICl_2^+ ion, $[\mathrm{Cl}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{I}}}-\mathrm{Cl}]^+$ shows that I-atom has *σ-bps*=2 and *lps*=2, and, since *σ-bps*+*lps*=4, I-atom is supposed to be sp^3 hybridised as shown below :

$5s^2 . 5p_x^2 5p_y^2 5p_z^1$ (*I-atom in its ground state*) $\xrightarrow{-e^-}$

$5s^2 . 5p_x^2 5p_y^2 5p_z^0$ (*I-atom after having lost one electron*)

$\longrightarrow 5s^2 . 5p_x^2 5p_y^1 5p_z^1$ (*I-atom in its excited state*)

$\xrightarrow{sp^3 \text{ hybridisation}} (sp^3)^2 (sp^3)^2 (sp^3)^1 (sp^3)^1$ (*Four sp^3 hybrid orbitals two of which contain lps and the remaining two are singly-filled*).

It is evident from sp^3 hybridisation scheme shown above that two sp^3 hybrid orbitals have *lps* while each of the remaining two sp^3 hybrid orbitals has one electron. These two singly-filled sp^3 hybrid orbitals make a *head-to-head* (linear) overlap with singly-filled $3p_x$ orbitals on each of the two Cl-atoms ($Cl = 3s^2 . 3p_x^1 3p_y^2 3p_z^2$) and form two $sp^3(I)-3p_x(Cl)$ σ-bonds.

Although the spatial arrangement of four electron pairs round I-atom is tetrahedral, due to the presence of two lone pairs of electrons, the shape of ICl_2^+ ion gets distorted and becomes *angular* or *V-shape* as shown in Fig. 20.12.

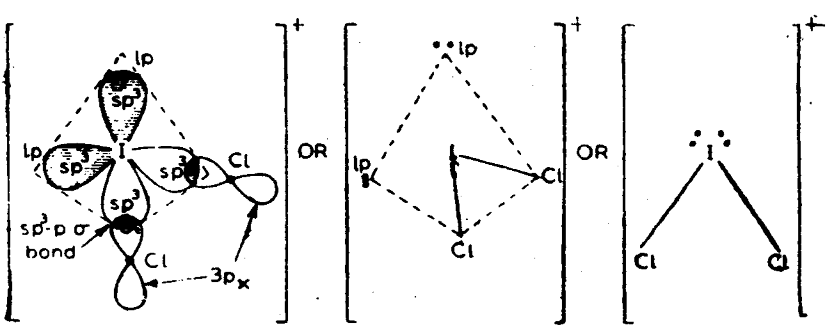
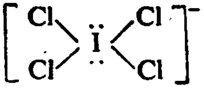


Fig. 20·12. Angular or V-shape of ICl_2^+ ion (*σ-bps*=2, *lps*=2)

The I—Cl bond length and ClICl bond angle found in ICl_2^+ ion depends on the nature of the anion attached to this cation. For example the values of bond angle and bond length in $[ICl_2]^+[SbCl_6]^-$ are 92·5° and 2·31Å respectively while these values in $[ICl_2]^+[AlCl_4]^-$ are 96·7° and 2·28Å respectively.

Structure and shape of pentahalide anions. (*Examples* : I_5^-, ICl_4^-, BrF_4^-). The pentahalide anions like I_5^-, ICl_4^-, BrF_4^- etc. have square planar shape which results from sp^3d^2 hybridisation of the central atom. As an example we can consider the structure of ICl_4^- ion. In this ion I-atom is the central atom. Due to the presence of one unit of negative charge on ICl_4^- ion, I-atom (central atom) can be regarded as having eight electrons (instead of seven) in its valence-shell. The Lewis structure of this ion,



shows that I-atom is surrounded by four σ-*bps* and two *lps*. Thus since σ-*bps*+*lps*=4+2=6, I-atom is assumed to be sp^3d^2 hybridised as shown below :

$5s^2 \cdot 5p_x^2 5p_y^2 5p_z^1 \cdot 5d^0 5d^0$ (*I-atom in its ground state*) $\xrightarrow{+e^-}$ $5s^2 \cdot 5p_x^2 5p_y^2 5p_z^2 \cdot 5d^0 5d^0$ (*I-atom after having gained one electron*) $\longrightarrow$ $5s^2 \cdot 5p_x^2 5p_y^1 5p_z^1 \cdot 5d^1 5d^1$ (*I-atom in its second excited state*) $\xrightarrow{sp^3d^2 \text{ hybridisation}}$ *Six* sp^3d^2 *hybrid orbitals. The two lps occupy the axial hybrid orbitals of the octahedron.*

sp^3d^2 hybridisation shown above makes it evident that out of the six hybrid orbitals two axial hybrid orbitals contain two *lps*, because in order to have minimum lone pair repulsion, the lone pairs must be as far from each other as possible. Other four hybrid orbitals (equatorial hybrid orbitals) which are singly-filled overlap with the singly-filled $2p_x$ orbitals on four Cl-atoms and form four I—Cl σ-bonds.

Although the spatial arrangement of six electron pairs round I-atom is octahedral, due to the presence of two lone pairs of electrons in the axial hybrid orbitals, the shape of ICl_4^- ion gets distorted and becomes square planar as shown in Fig. 20.13.

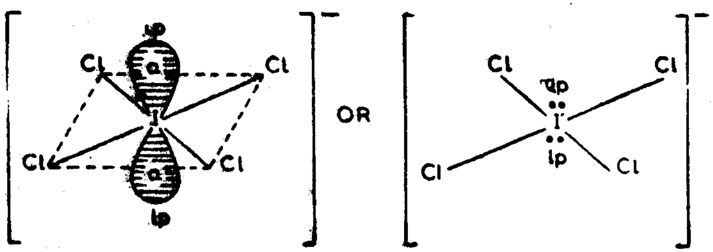


Fig. 20·13 Square planar shape of ICl_4^- ion.

I_5^- ion in $[(CH_3)_4N]^+I_5^-$ has planar V-shaped geometry as shown in Fig. 20·14

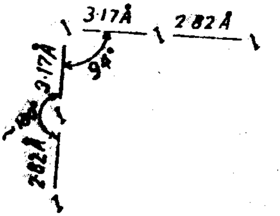
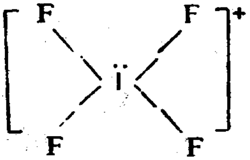


Fig. 20.14. Planar V-shaped geometry of I_5^- ion in $[(CH_3)_4N]^+I_5^-$.

Structure and shape of pentahalide cations. (*Example* : *IF_4^+*). In $[IF_4]^+[SbF_6]^-$, IF_4^+ cation has *distorted tetrahedral* or *sea-saw geometry* with one lone pair of electrons occupying one of the equatorial (*i.e.* basal) positions of the trigonal bipyramid.

Due to the presence of one unit of positive charge on IF_4^+ ion, I-atom (central atom) may be regarded as having six electrons (instead of seven) in its valence shell. Lewis structure of IF_4^+ ion,



shows that the central atom (*i.e.* I-atom) is surrounded by four *σ-bps* and one *lp*, *i.e.* *σ-bps+lp*=4+1=5. Thus, since *σ-bps+lps*=5, I-atom in IF_4^+ ion is *sp^3d* hybridised. Due to the presence of one lone pair of electrons which occupies one of the basal hybrid orbitals, the shape of IF_4^+ ion gets distorted and becomes *distorted tetrahedral* or *sea-saw* as shown in Fig. 20.15.

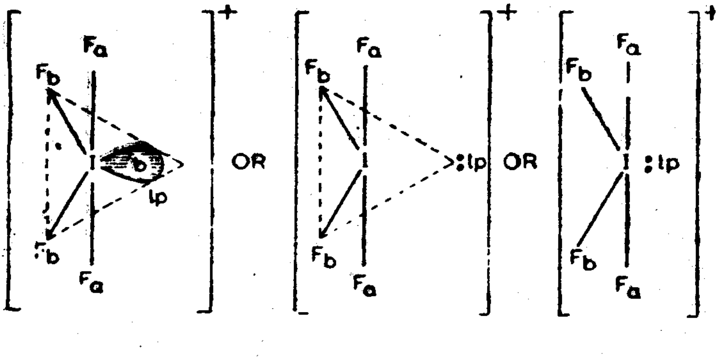
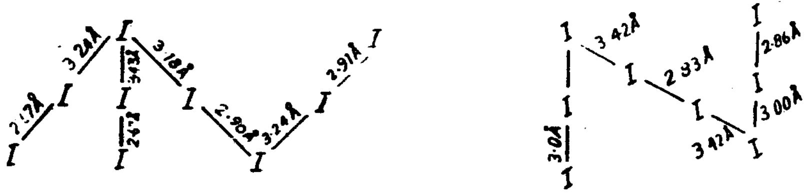


Fig. 20.15. Distorted tetrahedral or sea-saw shape of IF_4^+ ion. F_a are the F-atoms occupying the axial positions of the trigonal bipyramid while F_b are F-atoms occupying the basal positions.

Structure and shape of higher polyhalide ions (*Examples* : I_7^-, I_9^-, I_8^{2-} *etc.*). The structure of hepta-iodine ion, I_7^- in $[(C_2H_5)_4N]^+I_7^-$ does not consist of discrete I_7^- ions but rather consists of three-dimensional array of a linear I_3^- ion and two I_2 molecules in the ratio 1 : 2 ($I_3^- - I_2$). The structure of I_9^- ion in $[(CH_3)_4N]^+I_9^-$ consists of one I_5^- unit linked with two I_2 molecules. The structure of I_8^{2-} ion in Cs_2I_8 consists of two I_3^- units linked with one I_2 molecule (See Fig. 20·16).



Structure of I_9^- ion in $[(CH_3)_4N]^+I_9^-$ Structure of I_8^{2-} in $Cs_2^+ I_8^{2-}$

Fig. 20·16. Structure of I_9^- and I_8^{2-} ions.

PSEUDOHALIDE IONS, PSEUDOHALIDES AND PSEUDOHALOGENS

There are certain uninegative ions (*e.g.* CN^-, OCN^-, N_3^- etc.) which are made up of two or more electronegative atoms and resemble halide ions in some respects. These uninegative ions are called *pseudohalide ions*. Examples of some important pseudohalide ions are : cyanide ion (CN^-), isocyanide ion (NC^-), fulminate ion (ONC^-), cyanate or oxycyanite ion (OCN^-), isocyanate ion (NCO^-), thiocyanate ion (SCN^-), isothiocyanate ion (NCS^-), tellurocyanate ion ($TeCN^-$), selenocyanate ion ($SeCN^-$), isoselenocynate ion ($NCSe^-$), azide ion (N_3^-), azidothiocarbonate ion or azido carbondisulphide ion ($SCSN_3^-$). The salts (ionic compounds) given by the pseudohalide ions [*e g.* AgCN, $Pb(CNS)_2$ etc.] are called *pseudohalides*.

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called *pseudohalogens* or *halogenoids*. So far only a limited number of pseudohalogens have been isolated and characterised. Examples of some pseudohalogens or halogenoids are : cyanogen, $(CN)_2$; oxy cyanogen, $(OCN)_2$, thiocyanogen, $(SCN^-)_2$; tellurocyanogen, $Te(CN)_2$; selenocyanogen, $(SeCN)_2$; azidocarbon disulphide, $(SCSN_3)_2$.

Similarities between halide ions and pseudohalide ions : (*i*) *Formation of ionic as well as covalent compounds.* Like halide ions, pseudohalide ions also form ionic as well as covalent compounds. Examples of ionic compounds formed by halide ions are AgCl, PbI_2 etc. and the analogous ionic compounds given by pseudohalide ions are AgCN, $Pb(CNS)_2$ etc. Similarly the examples of covalent compounds formed by halide ions are ICl, $SiCl_4$, $COCl_2$, SO_2Cl_2 etc. and the analogous covalent compounds given by pseudohalide ions are ICN, $Si(NCS)_4$, $CO(N_3)_2$, $SO_2(N_3)_2$.

(*ii*) *Oxidation of hydracids.* HX acids ($X=Cl^-, Br^-, I^-$) can be oxidised to free halogen (X_2). Similarly HY acids ($Y=SCN^-$, CN^- etc.) can also be oxidised to free pseudohalogen (Y_2). For example :

$$4HCl+MnO_2 \longrightarrow MnCl_2+2H_2O+Cl_2$$

$$4HSCN+MnO_2 \longrightarrow Mn(SCN)_2+2H_2O+(SCN)_2$$

(*iii*) *Thermal decomposition of Pb(IV) salts.* On heating some of the Pb(IV) salts of halide ions (*e.g.* $PbCl_4$) decompose to give Pb (II) salts and free halogen molecule. Similarly some Pb(IV) salts of pseudohalide ions [*e.g.* $Pb(SCN)_4$, $Pb(SeCN)_4$] decompose to give Pb(II) salts and free pseudohalogens. For example :

$$PbCl_4 \xrightarrow{\Delta} PbCl_2+Cl_2 ;$$

$$Pb(SCN)_4 \xrightarrow{\Delta} Pb(SCN)_2+(SCN)_2$$

(*iv*) *Formation of complex ions.* Like halide ions, pseudohalide ions also form complex ions with transition metal ions. Examples of complex ions formed by halide ions with transition metals are $[FeF_6]^{3-}$, $[CoCl_4]^{2-}$, $[HgI_4]^{2-}$ etc. and the analogous complex ions given by pseudohalide ions are $[Fe(CN)_6]^{3-}$, $[Co(SCN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$ etc.

(*v*) *Formation of inter-pseudohalogen and inter-halogen compounds.* Halide ions can combine together to form interhalogen compounds like ClF, ICl, IBr etc. Similarly pseudohalide ions can also combine together to form inter-pseudohalogen compounds like $CN.N_3$, CN.SCN etc.

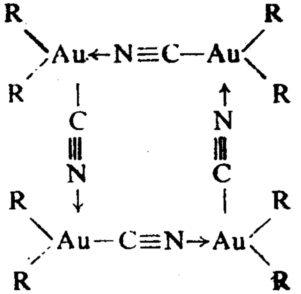
(*vi*) *Formation of monobasic hydracids.* Like halide ions, pseudohalide ions also combine with H_2 to form monobasic hydracids.

$$H_2+2Cl^- \longrightarrow 2HCl+2e^-$$

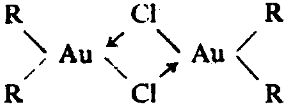
$$H_2+2CN^- \longrightarrow 2HCN+2e^-$$

(*viii*) *Formation of insoluble salts.* Like halide ions, pseudohalide ions also give insoluble salts with Ag^+ Pb^{2+} and Hg^+ cations. Examples of insoluble salts formed by halide ions are AgCl, $PbCl_2$, HgCl etc. and the analogous insoluble compounds given by pseudohalide ions are AgCNS $Pb(CNS)_2$, HgCN. etc.

(*viii*) *Acting as bridging ligands.* Like halide ions, pseudohalide ions also have more than one pair of electrons and hence can coordinate with two metal ions simultaneously. Consequently like halide ions, pseudohalide ions also can act as bridging ligands. For example in $[R_2Au(CN)]_4$ which is a tetrameric compound, four CN^- ions act as bridging ligands. Similarly in $[R_2AuCl]_2$ which is a dimeric compound, two Cl^- ions act as bridging ligands.



[R$_2$Au(CN)]$_4$ compound
(Tetrameric)



[Ru$_2$AuCl]$_2$ compound
(Dimeric)

Note that in each of the above compounds the geometry of Au atoms is square planar.

Dissimilarities between halide ions and pseudohalide ions. (*i*) The hydracids formed by the pseudohalide ions on combination with hydrogen are relatively weaker than the analogous hydracids formed by the halide ions. For example HCN is a very weak acid while HCl is a very strong acid in aqueous medium. The weak nature of hydracids given by pseudohalide ions may be due to the poor electronegativity of the pseudohalogens.

(*ii*) Pseudohalide ions are stronger coordinating ligands than the halide ions and hence the complexes formed by pseudohalide ions are *low spin* (*i.e.* inner-orbital involving d^2sp^3 hybridisation) while those formed by halide ions are *high spin* (outer-orbital involving sp^3d^2 hybridisation). For example $[Fe(CN)_6]^{3-}$ is a low spin complex while $[FeF_6]^{3-}$ is a high spin complex.

That the pseudohalide ions are stronger ligands than the halide ions is due to the ability of the electron deficient pseudohalides to form σ bond (from the pseudohalide to the metal) as well as π-bond (from the metal to the pseudohalide).

(*iii*) Pseudohalide ions, being made up of two hetro atoms, can function as *ambidentate* ligands. For example class *a* metals form isothiocyanate complex like $[Co(NCS)_4]^{2-}$ in which N atom is coordinated to Co^{2+} ion while class *b* metals form thiocynate complexes like $[Pd(SCN)_4]^{2-}$ in which S atom is bonded to Pd^{2+} ion. Halide ions have no tendency to act as ambidentate ligands.

Similarities between halogens and pseudohalogens. Following are the points showing the similarities between the two classes of compounds.

(*i*) *Volatile and dimeric nature.* Like halogens, pseudohalogens are also dimeric and fairly volatile (with the exception of polymeric thiocynogen) in the free state.

(*ii*) *Isomorphous nature.* Pseudohalogens, are isomorphous to halogens when in the free or solid state. For example Cl_2 is isomorphous to $(CN)_2$ and similarly Br_2 is isomorphous with $(SCN)_2$.

(*iii*) *Addition to ethylenic double bond.* Like halogens, pseudohalogens also add to ethylenic double bond linkage. For example :

$$H_2C{=}CH_2+Cl_2 \longrightarrow H_2C(Cl)-CH_2(Cl)$$

$$H_2C{=}CH_2+(SCN)_2 \longrightarrow H_2C(SCN)-CH_2(SCN)$$

(*iv*) *Reaction with alkalies.* Like halogens, pseudohalogens also react with alkalies. For example :

(*a*) $(SCN)_2+2KOH$ (*cold and dilute*) $\longrightarrow KSCN+KOSCN+H_2O$

Cl_2+2KOH (*cold and dilute*) $\longrightarrow KCl+KOCl+H_2O$

(*b*) $3(SCN)_2+6KOH$ (*hot and concentrated*) $\longrightarrow 5KSCN+KSCNO_3+3H_2O$

$3Cl_2+6KOH$ (*hot and concentrated*) $\longrightarrow 5KCl+KClO_3+3H_2O$

(*v*) *Formation of monobasic hydracids.* Like halogens, pseudohalogens also combine with H_2 to form monobasic hydracids.

$$Cl_2+H_2 \longrightarrow 2HCl$$

$$(CN)_2+H_2 \longrightarrow 2HCN$$

Dissimilarity between halogens and pseudohalogens. Pseudohalogens undergo polymerisation and form polymerised species. For example :

$$n(CN)_2 \xrightarrow{500°C} 2(CN)_n$$

$$n(SCN)_2 \xrightarrow{\text{Room temp.}} 2(SCN)_n$$

$$n(SeCN)_2 \xrightarrow{\text{On standing}} 2(SeCN)_n$$

Halogens have no tendency to undergo polymerisation.

Oxidising power of halogens and pseudohalogens. The oxidising power of halogens and pseudohalogens decreases in the following order : $F_2>Cl_2>Br_2>(CN)_2>(SCN)_2>I_2>(SCSN_3)_2>(SeCN)_2$ This order of oxidising power is also supported by the standard reduction potential values (E° values) for the following reduction half-reactions :

$$\tfrac{1}{2}Br_2+e^- \rightarrow Br^- \; ; \; E°=+1{\cdot}07 \text{ V}$$

$$\tfrac{1}{2}(SCN)_2+e^- \rightarrow SCN^- \; ; \; E°=+0{\cdot}77 \text{ V}$$

$$\tfrac{1}{2}I_2+e^- \rightarrow I^- \; ; \; E°=+0{\cdot}535 \text{ V}$$

$$\tfrac{1}{2}(SCSN_3)_2+e^- \rightarrow SCSN_3^-, \; E°=+0{\cdot}275 \text{ V}$$

These values show that with the decrease of E° values from Br_2 to $(SCSN_3)_2$, the oxidising power of these species also decreases in the same direction. Thus :

(*a*) Br_2 oxidises SCN^- ions to $(SCN)_2$

$$Br_2+2SCN^- \rightarrow (SCN)_2+2Br^-$$

(*b*) $(SCN)_2$ oxidises I^- ions to I_2

$$(SCN)_2+2I^- \rightarrow 2SCN^-+I_2$$

(*c*) I_2 oxidises $SeCN^-$ ions to $(SeCN)_2$

$$I_2+2SeCN^- \rightarrow (SeCN)_2+2I^-$$

SOME PSEUDOHALOGENS

1. Cynogen, $(CN)_2$ or C_2N_2. This compound was discovered by Gay-Lussac in 1815.

Preparation. (*i*) It is formed by heating the cyanides of Hg (II), Ag (I) and Au (III). $Hg(CN)_2$ is heated to dull redness in a hard glass tube to get $(CN)_2$ gas which is collected over Hg.

$$Hg(CN)_2 \xrightarrow{\text{dull redness}} Hg+(CN)_2$$

The yield of $(CN)_2$ obtained in this way is not quantitative, since $(CN)_2$ formed polymerises (at 500°) to insoluble paracynogen, $(CN)_x$.

$$x(CN)_2 \xrightarrow[500°C]{\text{Polymerisation}} 2(CN)_x$$

$(CN)_2$ is set free at a lower temperature and is obtanied in better yield by heating a mixture of Hg $(CN)_2$ and $HgCl_2$.

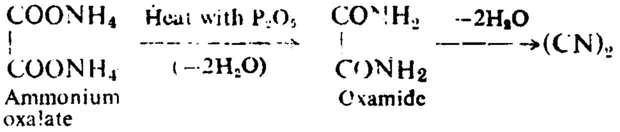
$$Hg(CN)_2+HgCl_2 \rightarrow Hg_2Cl_2+(CN)_2$$

(*ii*) $(CN)_2$ can also be prepared by the action of KCN on $CuSO_4$ solution. The reaction proceeds as :

$$CuSO_4\ (\textit{solution})+2KCN \rightarrow K_2SO_4+Cu(CN)_2$$

$$2Cu(CN)_2 \xrightarrow{\text{decomposes}} 2\,CuCN+(CN)_2$$

(*iii*) $(CN)_2$ can also be prepared by heating ammonium oxalate with P_2O_5.



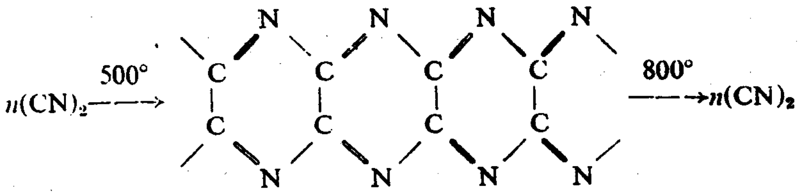
$$\begin{array}{l}COONH_4\\ |\\ COONH_4\end{array} \xrightarrow[(-2H_2O)]{\text{Heat with }P_2O_5} \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} \xrightarrow{-2H_2O} (CN)_2$$

Properties. (*i*) It is a colourless, extremely poisonous, flamable gas (b. pt.$=-21{\cdot}2°$) and freezes to a solid (m. pt.$=-27{\cdot}9°$). It has a smell of bitter almonds.

(*ii*) *Burning in air.* It burns in air with a violet coloured flame to give CO_2 and N_2. During this reaction explosoin takes place.

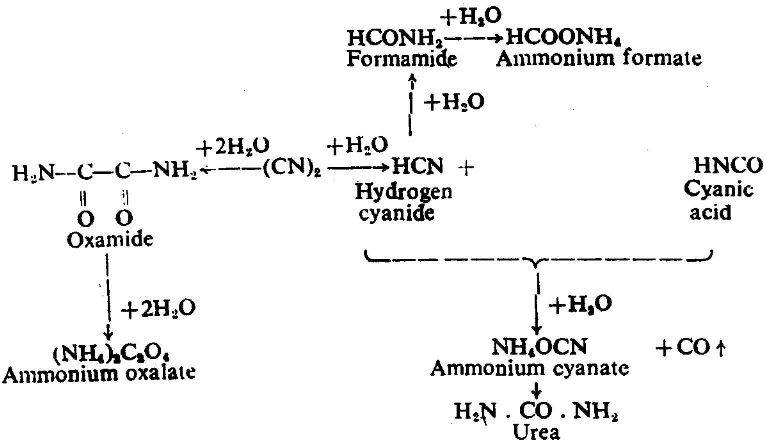
$$(CN)_2+2O_2 \rightarrow 2CO_2+N_2$$

(*iii*) *Polymerisation.* Although pure $(CN)_2$ is stable, the pure gas undergoes polymerisation on heating to 500° to an insoluble solid, *paracyanogen*, $(CN)_n$ which, at 800°, regenerates $(CN)_2$ but decomposes above this temperature.



Paracynogen, $(CN)_n$

(*iv*) *Hydrolysis*. It is soluble in water and undergoes slow hydrolysis to give a number of products, the main products being ammonium formate, urea, oxamide and ammonium oxalate.



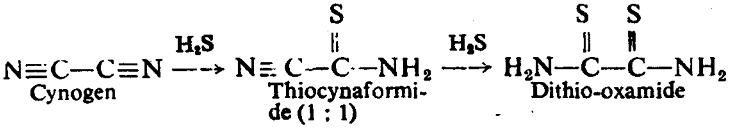
(*v*) *Action of alkalies*. It dissolves in alkalies (*e.g.* KOH) to form the cyanide (KCN) and oxy-cyanide (KCNO).

$$(CN)_2 + 2KOH \rightarrow KCN + KCNO + H_2O$$

(*vi*) *Action of alkali metals*. It combines directly with alkali metals to form their cyanides.

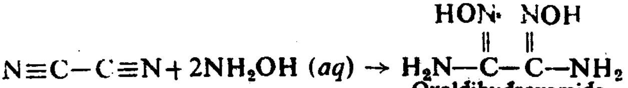
$$2K + (CN)_2 \rightarrow 2KCN$$

(*vii*) *Addition reactions*. A number of reactions of $(CN)_2$ involve addition across one or both of the multiple bonds in its molecule. Thus H_2S gives thiocynaformide and dithio-oxamide while aqueous NH_2OH gives oxaldihydroxamide.



$$N{\equiv}C{-}C{\equiv}N \xrightarrow{H_2S} N{\equiv}C{-}\overset{\overset{S}{\|}}{C}{-}NH_2 \xrightarrow{H_2S} H_2N{-}\overset{\overset{S}{\|}}{C}{-}\overset{\overset{S}{\|}}{C}{-}NH_2$$

Cynogen Thiocynaformide (1 : 1) Dithio-oxamide



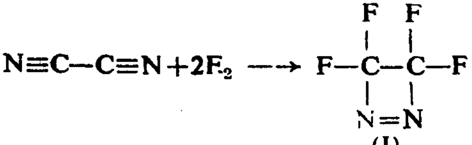
$$N{\equiv}C{-}C{\equiv}N + 2NH_2OH\ (aq) \rightarrow H_2N{-}\overset{\overset{HON}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}NH_2$$

Oxaldihydroxamide.

(*viii*) *Reduction by hydrogen.* When $(CN)_2$ is reduced by H_2, both the triple bonds are converted into single bonds by taking up hydrogen atoms and thus ethylenediamine, $H_2N-CH_2-CH_2-NH_2$ is formed.

$$N\equiv C-C\equiv N+4H_2 \rightarrow H_2N-CH_2-CH_2-NH_2$$

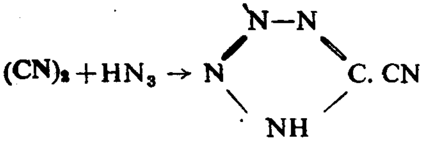
(*ix*) *Fluorination.* When $(CN)_2$ is fluorinated by AgF_2 at ~110°, it gives $(F_2CN)_2$ (I), although other products may also be obtained.



(I)

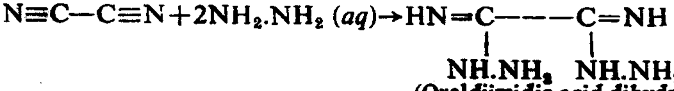
(*x*) *Other reactions.* Some other reactions of $(CN)_2$ are given below :

(*a*)



(5-cyanotetrazole)

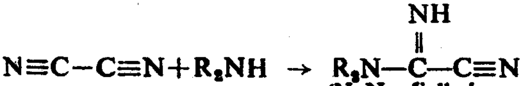
(*b*)



$$N\equiv C-C\equiv N+2NH_2.NH_2\ (aq)\rightarrow HN=\underset{NH.NH_2}{\underset{|}{C}}-\!-\!-\underset{NH.NH_2}{\underset{|}{C}}=NH$$

(Oxaldiimidic acid dihydrazide)

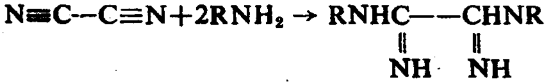
(*c*)



$$N\equiv C-C\equiv N+R_2NH \rightarrow R_2N-\overset{NH}{\overset{\|}{C}}-C\equiv N$$

(N, N—dialkyl cyanoformamidine)

(*d*)



$$N\equiv C-C\equiv N+2RNH_2 \rightarrow RNH\underset{\underset{NH}{\|}}{C}-\!-\!-\underset{\underset{NH}{\|}}{C}HNR$$

(Dialkyl oxamidines)

Uses. It is used in organic synthesis and as poisnous gas in wars.

Structure. The vapour density of the gas is 26 which shows that its formula is C_2N_2. The formation of ethylene diamine, $H_2N-CH_2-CH_2-NH_2$ on reduction and of oxamide, $H_2N-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-NH_2$ during hydrolysis shows that the order of atoms in cyanogen molecule should be N—C—C—N which is linear and symmetrical. Thus the structure of $(CN)_2$ is $\ddot{N}\equiv C-C\equiv\ddot{N}$. The N—C and C—C bond lengths which are equal to 1·16 Å and 1·37 Å respectively show that the true structure of the molecule is best represented as a resonance hybrid of the following three structures, structure (I) being the most contributing form.

$$:N{\equiv}C{-}C{\equiv}N: \leftrightarrow :\overset{+}{N}{=}C{=}C{=}\overset{..\,-}{N}: \leftrightarrow :\overset{..\,-}{N}{=}C{=}C{=}\overset{+}{N}:$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$

In structure (I) both the carbon and both the nitrogen atoms are *sp* hybridised and each carbon and nitrogen pair form two π-bonds in between them. One of the two *sp*-hybrids on each N atom contains a lone pair of electrons and other *sp*-hybrid orbital has one electron. This singly-occupied *sp*-hybrid on each N atom overlaps with *sp*-hybrid on carbon atom to form *sp—sp* N—C σ-bond. *sp* hybrid orbitals on each carbon atom overlap to form *sp—sp* C—C σ-bond. Thus in all we have, *one* C—C *sp—sp* σ-bond, *two* N—C *sp—sp* σ-bonds and four N—C *p—p* π-bonds as shown in Fig. 20.17. Each N atom has a lone pair of electrons residing in one of the two *sp*-hybrid orbitals.

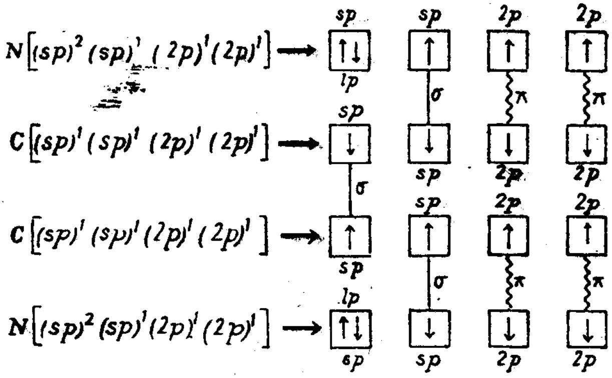


Fig. 20.17. Formation of σ- and π-bonds in cyanogen molecule, $(CN)_2$ [structure (I)] on the basis of sv-hydridisation.

2. **Thiocyanogen, $(SCN)_2$. Preparation.** It may be prepared : (*i*) by treating lead thiocyanate, $Pb(SCN)_2$ or AgSCN with Br_2 in ethereal solution at 0°C.

$$Pb(SCN)_2 + Br_2 \longrightarrow (SCN)_2 + PbBr_2$$

Evaporation of the solvent, after filtering $PbBr_2$, gives free $(SCN)_2$.

(*ii*) by electrolysing an alcoholic solution of NH_4SCN or KSCN.

(*ii*) by the oxidation of HSCN by $Pb(CH_3COO)_4$ or MnO_2.

$$2HSCN + Pb(CH_3COO)_4 \longrightarrow (SCN)_2 + 2CH_3COOH + Pb(CH_3COO)_2$$

$$4HSCN + MnO_2 \longrightarrow (SCN)_2 + 2H_2O + Mn(SCN)_2.$$

Properties. (*i*) It is a yellow solid which polymerises irreversibly at room temperature to a red-brick amorphous solid which is parathiocyanogen, $(SCN)_n$ and insoluble in water.

(*ii*) It is most stable in CCl_4 or CH_3COOH solution in which it exists as NCSSCN.

(*iii*) It is rapidly hydrolysed by water to form thiocyanic acid (HSCN) and hydrocyanic acid (HCN).

(*iv*) Following reactions of $(SCN)_2$ indicate its oxidising property and similarities with halogens.

(*a*) A solution of $(SCN)_2$ in ether or in CS_2 liberates I_2 from an iodide.

$$(SCN)_2 + 2I^- \longrightarrow 2SCN^- + I_2$$

(*b*) It oxidises Cu(I) salts to Cu(II) salts.

$$(SCN)_2 + 2CuSCN \longrightarrow 2Cu^{2+} + 4SCN^-$$

(*c*) It combines with metals to form metallic salts.

$$(SCN)_2 + M(M=0) \longrightarrow M(SCN)_2(M=+2)$$

(*d*) It oxidises thiosulphate ($S_2O_3^{2-}$) into thiosulphate ($S_4O_6^{2-}$)

$$(SCN)_2 + 2S_2O_3^{2-} \longrightarrow 2SCN^- + S_4O_6^{2-}$$

(*e*) Sulphur is precipitated from H_2S.

$$(SCN)_2 + H_2S \longrightarrow 2H^+ + 2SCN^- + S\downarrow$$

(*f*) Arsenite (AsO_3^{3-}) is oxidised to arsenate (AsO_4^{3-}).

$$(SCN)_2 + AsO_3^{3-} + H_2O \longrightarrow 2SCN^- + 2H^+ + AsO_4^{3}$$

(*v*) Some other reactions shown by $(SCN)_2$ can be represented by the following chemical equations :

(*a*) *Cold solution of* $(SCN)_2 + NO \longrightarrow NO.SCN$
(Nitrosyl thiocyanate)

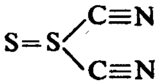
(*b*) *1 M cold solution of* $(SCN)_2 \xrightarrow{+2HCl} (SCN)_2.2HCl$ (*Dihydro chloride*) $\xrightarrow[(-2HCl)]{+H_2O} (SCN)_2.H_2O$ (*Monohydrate*).

Uses. $(SCN)_2$ is used (*i*) as an oxidising agent (*ii*) for the determination of unsaturation in organic compounds.

Structure. $(SCN)_2$ molecule has tautomeric structures namely (*a*) and (*b*) shown below :

$$N\equiv C-S-S-C\equiv N$$

(*a*) Symmetrical structure



(*b*) Unsymmetrical structure

X-ray evidence points to a linear arrangement of S—C—N atoms and hence structure (*a*) is a symmetrical structure.

3. **Selenocyanogen, $(SeCN)_2$. Preparation.** This helegenoid may be prepared as follows :

(*i*) By the reaction of I_2 with silver selenocyanate, AgSeCN dissolved in ether.

$$2AgSeCN + I_2 \longrightarrow (SeCN)_2 + \underset{ppt.}{2AgI\downarrow}$$

(*ii*) When $Pb(CH_3COO)_4$ dissolved in $CHCl_3$ is treated with KSeCN in anhydrous acetone, $Pb(SeCN)_4$ is formed which is unstable and hence decomposes to give $Pb(SeCN)_2$ and $(SeCN)_2$.

$$Pb(CH_3COO)_4 + 4KSeCN \longrightarrow Pb(SeCN)_4 + 4CH_3COOK$$

$$Pb(SeCN)_4 \longrightarrow Pb(SeCN)_2 + (SeCN)_2$$

Properties. It is a yellow crystalline powder which turns red on standing. When kept dry and under pressure, it is quite stable. It is soluble in C_6H_6, $CHCl_3$ or CCl_4. On heating a solution of $(SeCN)_2$ in CS_2 under reflux, polymerisation occurs and crystalline compounds namely $Se_3(CN)_2$ and $Se(CN)_2$ are obtained. These compounds can be separated from each other on cooling. $(SeCN)_2$ reacts with H_2O forming hydroselenic acid, HSeCN.

$$2(SeCN)_2 + 3H_2O \longrightarrow H_2SeO_3 + 3HSeCN + HCN$$

It is slightly weaker in its oxidising properties than I_2.

Structure. Its molecular weight in C_6H_6 agrees with its dimeric formula, $(SeCN)_2$. Its structure is probably the same as that of $(SCN)_2$. Raman spectral studies have shown that $(SeCN)_2$ molecule has a linear structure which can be represented as

$$\ddot{N}\equiv C-\underset{\cdot\cdot}{\ddot{Se}}-\underset{\cdot\cdot}{\ddot{Se}}-C\equiv\ddot{N}$$

4. **Oxycyanogen, $(OCN)_2$. Preparation.** (*i*) Lidov prepared it by the action of H_2O_2, CuO or sodium hypobromite on KOCN.

$$4KOCN + 2H_2O_2 \longrightarrow 2K_2CNO_2 + (OCN)_2 + 2H_2O$$

(*ii*) $(OCN)_2$ can also be prepared by the action of AgOCN on I_2 in CS_2 or CCl_4 solution.

$$2AgOCN + I_2 \longrightarrow 2AgI + (OCN)_2$$

(*iii*) $(OCN)_2$ can also be prepared by the action of cyanogen bromide (CNBr) on Ag_2O.

$$2CNBr + Ag_2O \longrightarrow 2AgBr + (OCN)_2$$

Properties. $(CNO)_2$ shows typical properties of pseudohalogens. It liberates I_2 from an iodide solution, reacts with metals, forms inter-pseudohalogen compounds.

5. **Azido carbon disulphide, $(SCSN_3)_2$. Preparation.** It may be prepared by oxidising potassium azidodithio carbonate, $KSCSN_3$ with H_2O_2, I_2, $FeCl_3$ etc.

$KSCSN_3$ required for the purpose is obtained by the interaction of KN_3 and CS_2 at 40°C.

$$KN_3 + CS_2 \longrightarrow KSCSN_3$$

$$2KSCSN_3 + H_2O_2 \longrightarrow (SCSN_3)_2 + 2KOH$$

$$2KSCSN_3 + I_2 \longrightarrow (SCSN_3)_2 + 2KI$$

$$2KSCSN_3 + 2FeCl_3 \longrightarrow (SCSN_3)_2 + 2FeCl_2 + 2KCl$$

Properties. It is a white crystalline solid and slightly soluble in water. It is unstable and decomposes violently automatically to give N_2, sulphur and $(SCN)_2$.

$$(SCSN_3)_2 \longrightarrow 2N_2 + 2S + (SCN)_2$$

It reacts slowly with dilute acid, and rapidly with concentrated acids to liberate sulphur. However, with HNO_3 no sulphur is precipitated.

In reaction with an alkali it resembles Cl_2.

(*a*) $(SCSN_3)_2 + 2KOH$ (*cold and dilute*) $\longrightarrow KSCSN_3 + KOSCSN_3 + H_2O$

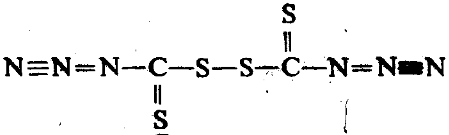
$Cl_2 + 2KOH$ (*cold and dilute*) $\longrightarrow KCl + KOCl + H_2O$

(*b*) $2(SCSN_3)_2 + 6KOH$ (*hot and concentrated*) $\longrightarrow 5KSCSN_3 + KSCSN_3O_3 + 3H_2O$

$3Cl_2 + 6KOH$ (*hot and concentrated*) $\longrightarrow 5KCl + KClO_3 + 3H_2O$

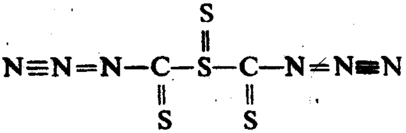
It is a weaker oxidising agent than I_2.

Structure. Following two tautomeric forms have been suggested for the molecule. (I) is probably more likely.



$$N{\equiv}N{=}N{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}{-}N{=}N{\equiv}N$$

(I)



$$N{\equiv}N{=}N{-}\underset{\underset{S}{\|}}{C}{-}\overset{\overset{S}{\|}}{S}{-}\underset{\underset{S}{\|}}{C}{-}N{=}N{\equiv}N$$

(II)

21

Pollution and its Effects on the Living World

Pollution and pollutants

The contamination of air, water and soil with the substances, which have adverse effect on human beings, animals and plants, is called *pollution* of air, water and soil respectively. These substances, whose presence in air, water and soil makes them polluted, are called *pollutants*. Thus a pollutant can be defined as a substance whose contamination with air, water and soil makes them polluted and has adverse effect on living and non-living things.

Types of pollutants

Pollutants may be of the following types :

(*i*) *Gaseous pollutants*. CO, NO, NO_2, CO_2, SO_2, SO_3, O_3 smog gases etc. are most common gaseous pollutants.

(*ii*) *Liquid pollutants*. Liquid wastes include sewage wastes and industrial wastes. The sewage waste contains faecal matter, urine, washings, large number of bacteria etc. Wastes from industry enter the river and affect aquatic life and self- purification system of water is disturbed.

(*iii*) *Solid pollutants*. The solid pollutants include rubbish, ashes, dead animals, wastes sludges, chemicals, paints, sand, pesticides, insecticides, manures, crop residues etc. The solid pollutants may be of two types namely *biodegradeable pollutants* and *non-biodegradeable pollutants*.

(iv) *Pollutants without weight*. The pollutants without weight are radioactive substances, heat and noise. The pollution caused by these pollutants is called *radioactive pollution*, *thermal pollution* and *noise (sound) pollution* respectively.

Types of pollution

Following are the important types of pollution :

(*i*) *Air pollution* - pollution of atmosphere.

(*ii*) *Water pollution* - pollution of river and sea water .

(*iii*) *Industrial pollution*. This pollution is caused by the wastes from industry.

(*iv*) *Noise (sound) pollution*. The adverse affects produced by the excessive noise on human beings is called noise pollution. Excessive noise reduces our hearing capacity.

(*v*) *Thermal pollution.* Excessive of heat affects our health adversely and increase in temperature results in the death of aquatic animals. This is called thermal pollution.

(*vi*) *Radioactive (Radiation) pollution.* The radioactive wastes have adverse effect on water, earth and air. The pollution caused by radioactive wastes is called radio active pollution.

(*vii*) *Soil pollution.* The contamination of soil with acid rain, excess of fertilisers etc. is called *soil pollution.*

AIR POLLUTION

Air, in nature, is never clean, since it is contaminated with poisonous gases (*e.g.*, CO, NO, NO_2, SO_3, O_3 etc.,) unburnt hydrocarbons, etc. *Thus the contamination of air with harmful gases, dust, smoke etc., is called air pollution.* The pollutants like CO, NO, NO_2, SO_2, SO_3, O_3, dust, smoke which pollute air, are called *air pollutants.*

To express the concentration of a gaseous pollutant

The concentration of a gaseous pollutant (*e.g.*, CO, NO, NO_2, SO_2, SO_3, O_3) in air is expressed in terms of the number of molecules of that pollutant present in one million molecules (=1000,000 molecules) of air. Thus the number of molecules of a gaseous pollutant, present in one million molecules of air, is called *ppm* value of that pollutant. For example, if there are 50 molecules of CO in one million molecules of air, the concentration of CO in air is equal to 50 *ppm.* This discussion shows that *ppm* value of a given gaseous pollutant indicates the number of molecules of that pollutant present in 1000,000 molecules of air.

Sources of air pollutants and their bad effects.

In the following paragraphs we shall discuss the sources of some air pollutants and their bad effects on human beings, animals, plants and non-living things. We shall take up the pollutants one by one, as shown below :

1. **Carbon monoxide** (CO) (*a*) *Major sources of CO.* Major sources of CO are given below :

(*i*) CO is produced by the incomplete combustion of all carbon-containing fuels (incomplete combustion is that which takes place in presence of insufficient quantity of O_2) used in automobile engines and defective furnaces. Thus the smoke obtained by the incomplete combustion of petrol in the internal combustion engines of cars, buses, trucks, scooters, aeroplanes etc. (The engines used in these motor vehicles are called internal combustion engines, because the petrol, which is used as a fuel, is burnt inside the engine and not separately) contains a lot of CO.

(*ii*) When coal, wood and oil are burnt, black smoke is produced. This smoke also contains CO.

(*iii*) Cigarette smoke also contains CO.

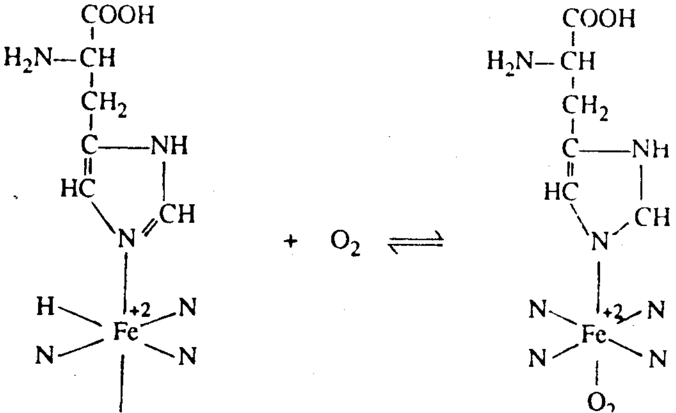
(*iv*) Incomplete combustion of agriculturral and slush matter produces CO.

(*v*) The reactions that take place at high temperature in industrial furnaces, like blast furnace, evolve CO.

(*vi*) Industrial processes involved in steel, paper and petroleum industries also generate CO.

(*vii*) All the above mentioned sources of the production of CO come under human activities. CO is also generated by natural sources like forest fires, volcanic eruptions, seed germination, electric discharge during storms etc.

(*b*) *Toxic effect of CO on human beings and animals.* Before we discuss the toxic effect of CO, it is worthwhile to have an idea about the structure of haemoglobin which is present in the red cells of the blood. Haemoglobin is an octehedral complex of Fe (II). The centre of the octahedron is occupied by Fe (II) and the four corners of the square base are occupied by four N-atoms of the *heme group*. Fifth position (one axial position) is occupied by N-atom of histidine, while the sixth position (*i.e.*, the second axial position) remains unoccupied. Thus the structure of haemoglobin can be represented by (I) or simply by *Hb*. When a human being or an animal inhales O_2 from the atmosphere, this gas combines in lungs with the haemoglobin and forms *oxy-haemoglobin*, HbO_2. In the formation of HbO_2, O_2 occupies the sixth position (which is vacant) of the octahedron of Hb. HbO_2 thus formed, dissociates into Hb and O_2 at the cells of the muscles. Thus, O_2 becomes available to the body muscles or body cells. In other words we can say that HbO_2 acts as an *oxygen-carrier* for blood.



(I) or Hb

HbO_2

$$\text{or } Hb + O_2 \rightleftharpoons Hb\,O_2$$

$$HbO_2 \xrightarrow{\text{Dissociation}} Hb + O_2$$

Now if a human being or an animal inhales CO, instead of O_2, vacant position in the structure of Hb is occupied by CO, since Hb has greater affinity for CO than for O_2 and *carboxyhaemoglobin*, HbCO is formed.

$$Hb + CO \longrightarrow HbCO$$

The formation of HbCO makes Hb unable to take up O_2 from the lungs. This results in that the quantity of O_2 available to the body-cells gets reduced. This is called *anoxia* (*oxygen starvation*). This produces suffocation and may even lead to death.

If a person smokes a packet of cigrettes daily, he inhales CO from the cigarette smoke. This CO produces HbCO in the blood and hence normal body functions are disturbed.

(*c*) *Treatment of CO poisoning*. The most effective treatment of CO poisoning is that the victim is exposed to 2 to 2.5 atm. O_2 under a higher pressure. This results in that CO present in HbCO is substituted by O_2 ($HbCO + O_2 \rightleftharpoons HbO_2 + CO$). When HbO_2 comes in contact with the cells of muscles, O_2 is given up by it ($HbO_2 \rightarrow Hb + O_2$).

(*d*) *Monitoring of CO*. The monitoring of CQ is done by means of *non-dispersive infra-red spectrosmetry*. This technique estimates CO upto a level of 150 ppm and is based on the principle that CO strongly absorbs infra-red radiations at certain specific wavelengths. The amount of infra-red radiations absorbed by CO gas is directly proportional to the concentration of the gas. If the concentration of the gas is near 10 ppm, this gas is estimated by gas-chromatography, in which a flame ionisation detector is used. If the concentration of CO gas is below 10 ppm, the gas is estimated by reducing it with H_2 gas over nickel catalyst at 360°C (*catalytic reduction*) and CH_4 thus obtained ($CO + 3H_2O \xrightarrow{Ni,\ 360\,^{\circ}C} CH_4 + H_2O$) is estimated by flame ionisation detector.

(*e*) *To control the pollution caused by the unburnt hydrocarbons and CO present in the gases released by the vehicle's engine*. The gases released by the vehicle's engine contain various pollutants like CO, CO_2, SO_3, unburnt hydrocarbons (like C_8H_{18}), NO and NO_2. These substances pollute air. In order to control the air pollution caused by hydrocarbons and CO, the following methods are used.

(*i*) *By adding lead tetraethyl, $Pb(C_2H_5)_4$ to the petrol*. Suppose a vehicle uses petrol as fuel. Petrol burns very fast in the vehicle engine, *e.g.*, the rate of combustion (burning) of petrol is very high and hence the time taken by the petrol for its combustion is very short. Due to this short time, the combustion of petrol is incomplete.

$Pb(C_2H_5)_4$ added to the petrol (0.5 to 0.8g per litre) to slow down the rate of the combustion of the petrol $Pb(C_2H_5)_4$ is called *anti-knock*. The addition of $Pb(C_2H_5)_4$ provides more time to the petrol for its combustion and hence enables it to burn more completely. Due to this, the quantity of unburnt hydro- carbons and CO (pollutants) coming out of the engine, with exhaust gases is reduced and hence air pollution is also minimised. $Pb(C_2H_5)_4$ is oxidised to PbO which gets deposited on the spark plugs and valves. In order to prevent the deposition of PbO, suitable amount of $C_2H_4Cl_2$ and $C_2H_4Br_2$ are also added to the petrol, along with $Pb(C_2H_5)_4$. These halides convert PbO into $PbCl_2$ and $PbBr_2$ both of which are volatile and hence come out along with the exhaust gases emitted by the vehicle-engine.

$$Pb(C_2H_5)_4 + O_2 + C_2H_4Cl_2 + C_2H_4Br_2 \longrightarrow CO_2 + H_2O + PbCl_2 + PbBr_2$$

Although the addition of $Pb(C_2H_5)_4$ minimise the air pollution caused by unburnt hydrocarbons and CO, the air gets polluted with dangerous $PbCl_2$ and $PbBr_2$.

(*ii*) *By the catalytic oxidation of CO and hydrocarbons with platinum catalyst.* The pollution of air caused by unburnt hydrocarbons and CO present in the exhaust gases of the vehicle's engine can also be reduced by attaching gasdevice with the vehicle's engine, in which the exhaust gases can be mixed with more air and then burnt completely in the presence of platinum catalyst, before they are discharged into the environment. Hydrocarbons and CO are oxidised by O_2 of the air in presence of platinum catalyst.

$$2C_8H_{18} + 25O_2 \xrightarrow{\text{Pt. catalyst}} 16CO_2 + 18\,H_2O$$

$$2CO + O_2 \xrightarrow{\text{Pt. catalyst}} 2CO_2$$

The disadvantage of this method is that the platinum catalyst gets poisoned by $PbCl_2$ and $PbBr_2$ which are produced by the reaction between $Pb(C_2H_5)_4$, $C_2H_4Cl_2$ and $C_2H_4Br_2$ (these compounds are added to the petrol) in presence of O_2.

2. Carbon dioxide (CO_2). Although *small quantity of CO_2* is not usually considered to be a pollutant, *its excess quantity in the atmosphere* has an adverse effect on our climate. (see green-house effect discussed below) and thus pollutes the air. Thus greater amount of CO_2 in the atmosphere acts as an air pollutant.

(*a*) *Major suppliers of CO_2 to the atmosphere.* Following are the important suppliers of CO_2 to the atmosphere.

(*i*) *Burning of fossil fuels.* The fossil fuels, like coal, natural gas and petroleum, are carbon compounds. When these fuels are burnt, they produce CO_2 which is discharged into the atmosphere. The burning of fossil fuels is releasing about 6000 million tonnes of CO_2 in the atmosphere every year.

(*ii*) *Cultivation of soil.* The cultivation of soil also releases large amount of CO_2 into the atmosphere, which is produced by bacteria. The cultivation of land releases 2000 million tonnes of CO_2 into the air every year.

(*iii*) *Eruption of volcanoes.* CO_2 is also given to the atmosphere through the eruption of volcanoes. This gas comes from the interior of the earth.

(*iv*) *Respiration of living organisms*

(*v*) *Decay of dead organisms*

(*b*) *Major consumers of CO_2 from the atmosphere.* The major consumers of CO_2 gas from the atmosphere are *green plants* and *oceans*. The green plants absorb CO_2 gas from the atmosphere to prepare their food (carbohydrates) through the process of photo-synthesis, while the oceans dissolve CO_2 gas to form carbonate rocks. Thus, we find that green plants and oceans both reduce the quantity of CO_2 in the atmosphere.

(*c*) *Green-house effect.* There is a protective layer of O_3 gas in the atmosphere at a height between 15 km and 60 km. (The thickest layer of O_3 exists at a height of 23 km from the surface of the earth) and then a blanket of CO_2 gas exists in the lower part of the atmosphere (*i.e.* below 15 kms). Now when sunlight, consisting of ultra-violet rays, visible light and infra-red rays falls on the top of the atmosphere, the harmful ultra-violet rays are absorbed by the O_3 layer and hence do not reach the earth's surface. On the other hand, the visible light and infra-red rays pass through the CO_2 layer and fall on the earth. Since the infra-red radiations have heating effect, they heat the earth and its various objects.

Now since the earth and its various objects become hot (of course, less hot than the sun), they start emitting infra-red rays (heat rays), which are of long wavelength (note that the infra-red rays emitted by the extreme hot bodies like sun are of short wavelength). The infra-red radiations of long wavelength emitted by the earth and its objects are absorbed by the CO_2 layer in the atmosphere. Thus we see that the presence of CO_2 in the atmosphere does not allow the infra-red radiations reflected by the earth's surface to go out of the atmosphere. In other words we can say that the layer of CO_2 gas in the atmosphere traps all the infra-red radiations (heat rays) coming from the earth's surface. These trapped infra-red rays heat the earth's atmosphere. *The heating up of earth due to the trapping of infra-red radiations (reflected from the earth's surface) by CO_2 layer in the atmosphere is called "green-house effect"*. Since the infra-red rays coming from the earth cannot pass through the CO_2 layer, the temperature of the earth is raised. The rise in the temperature produced by the "green-house effect" in the earth's atmosphere depends on the amount (proportion) of CO_2 gas present in the atmosphere. The name "green-house effect" comes from the fact that this effect is used in horticulture for the upbringing of green plants in a small house, whose walls and roof are made of glass-sheet. The glass walls and glass roof of the house allow the short wavelength infra-red radiations, contained in sunlight, to go into green-house freely, but do not allow the long wavelength infra-red radiations, reflected by the soil, plants and other contents of the green-house to go out. These trapped infra-red radiations raise the temperature inside the green house. Thus even without the internal supply of heat, the temperature inside the green house-becomes higher than that outside it.

Importance of green-house effect. The green-house effect, produced by the presence of CO_2 layer in the atmosphere is, very necessary for our existence on the earth. We have seen that, due to green-house effect, CO_2 gas in the atmosphere does not allow the long wavelength infra-red radiations (heat-rays) reflected by the earth, to go out of the atmosphere and hence the temperature of the earth's surface and its atmosphere is increased. The rise in temperature of the earth is very necessary for our existence on earth, because without it the whole earth would be converted into extremely cold planet and consequently we shall not be able to have a normal life.

Effect of excess of CO_2 present in the atmosphere. If the atmosphere contains too much quantity of CO_2, the green-house effect is considerably increased, *i.e.*, due to excess quantity of CO_2 present in the atmosphere, the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains) floods the low-lying areas of the earth, changes the biological activity of oceans and the patterns of cropping etc. Thus we see that the presence of the excess of CO_2 in the atmosphere brings about climate changes.

(*d*) *To control the air pollution caused by excess of CO_2.* The best way of preventing the atmosphere from the pollution caused by excess quantity of CO_2, is that a balanced quantity of CO_2 should be maintained in the atmosphere. We have seen above that green plants absorb CO_2 gas from the atmosphere to manufacture their food and also at the same time release O_2 gas into the atmosphere (in the manufacture of their food the plants convert CO_2 into O_2). Thus, if we grow more plants, our atmosphere will get rid of its excess CO_2 gas. We should not cut down the trees.

3. Oxides of nitrogen (NO and NO_2). (*a*) *Sources of the oxides* (*i*) The smoke released by the automobile engines (engines of cars, buses, trucks etc.,) contains NO and NO_2. This smoke results by the combustion of petrol or diesel in the engines.

(*ii*) When coal, oil and natural gas undergo combustion, high temperature produced by the combustion makes N_2 and O_2 present in the atmosphere combine together to form NO and NO_2.

$$N_2 \overset{+\ O_2,\ >\ 110^\circ C}{\rightleftharpoons} 2NO \overset{+\ O_2}{\rightleftharpoons} 2NO_2$$

(*iii*) Many chemical plants, like those which manufacture explosives and nitrogenous fertilisers, also produce NO_2. It is also present in tobacco smoke.

(*iv*) Large amounts of SO_2 and nitrogen oxide are also emitted from power plants and many industrial processes. The mixture containing SO_2 and nitrogen oxides, thus obtained, is called *flue gases mixture.*

(*b*) *Effect of oxides on human beings, animals and vegetables.* Though both NO and NO_2 are toxic, the latter is by far more harmful. Some of the effects caused by these oxides on human beings, animals and vegetables are given below :

(*i*) NO_2 produced as above, reacts with rainy water or moisture, in presence of O_2 or O_3 and produces HNO_3.

$$4NO_2 + H_2O + O_2 \longrightarrow 4HNO_3$$

$$2NO_2 + H_2O + O_3 \longrightarrow 2HNO_3 + O_2$$

HNO_3 formed as above, comes down the atmosphere in the form of *nitric acid rain* or *acid snow.* Acid rain has severe ecological impacts. It makes the lakes so acidic that they can no longer support fish-life. The yield of agricultural crops are also reduced.

Nitric acid rain gradually eats up lime stone and marble of the buildings and corrodes metals. It fades the colour of the fabrics (*e.g.*, cotton, nylon and rayon), leather and paper.

(*ii*) NO_2 causes extensive leaf-drop in the plants.

(*iii*) Nitrogen oxides react with O_2 to produce another pollutant namely ozone.

(*iv*) It has been shown that if monkeys inhale NO_2 of 15-30 ppm concentration for 2 hours, their lungs, heart, liver and kidneys are damaged.

(*v*) NO_2 is very corrosive and attacks skin.

(*vi*) NO_2 helps in the formation of smog (which is a combination of smoke and fog). Smog causes irritation in eyes due to the presence of O_3 in it.

(*c*) (*i*) *To control the pollution caused by nitrogen oxides present in exhaust gases of motor vehicles.* We know that the exhaust gases of motor vehicles contain various pollutants like CO, CO_2, NO, NO_2 etc. These substances cause pollution of the atmosphere when they are discharged into it. The air pollution caused by NO and NO_2 can be controlled by reducing these gases (to N_2 and NH_3) with H_2 in presence of finely-divided platinum metal, before they are allowed to enter the atmosphere.

$$2NO + 2H_2 \xrightarrow{Pt.} N_2 + 2H_2O$$

$$2NO + 5H_2 \xrightarrow{Pt.} 2NH_3 + 2H_2O$$

$$2NO_2 + 4H_2 \xrightarrow{Pt.} N_2 + 4H_2O$$

$$2NO_2 + 7H_2 \xrightarrow{Pt.} 2NH_3 + 4H_2O$$

(*ii*) *To control the pollution caused by NO_2 and SO_2 present in flue gases.* Power plants and many industrial units produce flue gases which contain a mixture of NO_2 and SO_2. Both these gases cause pollution of the atmosphere. The mixture containing NO_2 and SO_2 is treated with H_2SO_4 (called *scrubbing process*) so that the following reactions take place. First of all SO_2 and NO_2 present in the flue gases react in presence of water and produce H_2SO_4 and NO.

$$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$$

NO, thus produced, reacts with NO_2 to form N_2O_3 which reacts with H_2SO_4 to form H(NO) SO_4

$$NO + NO_2 \longrightarrow N_2O_3$$

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2H(NO)SO_4 + H_2O$$

Thus we find that SO_2 and NO_2 present in the flue gases are removed by scrubbing them with H_2SO_4. Flue gases thus freed from SO_2 and NO_2 are then released into the atmosphere.

Since the oxides of nitrogen and SO_2 are acidic in nature, they can be removed by scrubbing them with alkaline solutions of $Ca(OH)_2$ and $Mg(OH)_2$.

(*d*) *Determination of the concentration of the oxides.* The method used for the determination of the concentration of the oxides, consists of making these oxides to react with O_3 to yield electronically excited species. For example when NO reacts with O_3, electronically excited species namely $NO_2{*}$ is produced,

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

NO_2^*, being unstable, quickly returns to the ground state, forming NO_2 and emitting light in the range of 600-3000 nm.

$$NO_2^* \longrightarrow NO_2 + h\nu$$

The intensity of the light emitted is directly proportional to the concentration of NO_2^* and hence of NO molecules. Thus the intensity of light is measured with the help of photo-multipliers and this intensity gives us a measure of the concentration of NO molecules.

4. Oxides of sulphur (*a*) *Sources of the oxides.* The common oxide of sulphur which is the most harmful gaseous pollutant is SO_2. This oxide is released into the atmosphere by volcanic eruptions (natural activity). This oxide is also generated, when coal and oils are burnt in houses and industries. Coal always contains some sulphur as impurity. When coal is burnt, sulphur present in coal is converted into SO_2. Oils also have some sulphur compounds, which give SO_2 on burning.

When sulphite ores, like iron pyrites (FeS_2), copper pyrites (CuS), copper glance (Cu_2S), zinc blende (ZnS), galena (PbS) etc., are roasted in air, SO_2 is produced.

A part of SO_2 present in the atmosphere is oxidised to SO_3 by photolytic and catalytic oxidation processes. Thus SO_2 present in the atmosphere also contains SO_3, although the quantity of SO_3 is not high.

(*b*) *Effects of SO_2 and SO_3 on human beings, animals and plants.* (*i*) We have shown above that SO_2 present in the atmosphere undergoes photolytic and catalytic oxidation to form SO_3. SO_3 thus produced reacts with rainy water or moisture and gives H_2SO_4 ($SO_3 + H_2O \longrightarrow H_2SO_4$) which comes down the atmosphere in the form of *sulphuric acid rain or acid snow*. This acid rain is as dangerous as nitric acid rain (see oxides of nitrogen).

(*ii*) SO_2 irritates the respiratory system of animals and humans. It damamges lungs.

(*iii*) If plants are exposed to SO_2 of high concentration over short periods, brownish colour in the tips of pine needles gets decolourised. If the plants are exposed to SO_2 of low concentration over longer periods, the production of chlorophyl in plants is hampered (*chlorosis*) and hence green colour of the plants is lost.

(*iv*) Due to corrosive nature of SO_2 and H_2SO_4, these pollutants decolourise building materials like lime stone, marble, roof slate and mortar. The corrosion of most metals (*e.g.*, Fe, steels, Zn, Al etc.) is accelerated by SO_2.

(*v*) Fabrics, leather, paper and paints undergo fading of their colour in presence of SO_2.

(*c*) *To control the pollution caused by SO_2 gas.* (*i*) We have already said that power plants and industrial units produce flue gases which contain a mixture of SO_2 and NO_2. Both these gases pollute the atmosphere. The removal of NO_2 from this mixture has already been discussed. SO_2 is removed by treating the flue-gases mixture with a slurry of $CaCO_3$ (lime stone) when SO_2 is absorbed due to the formation of $CaSO_3$ which is removed away.

$$CaCO_3 + \longrightarrow CaSO_3 + CO_2$$

This method is quite economical.

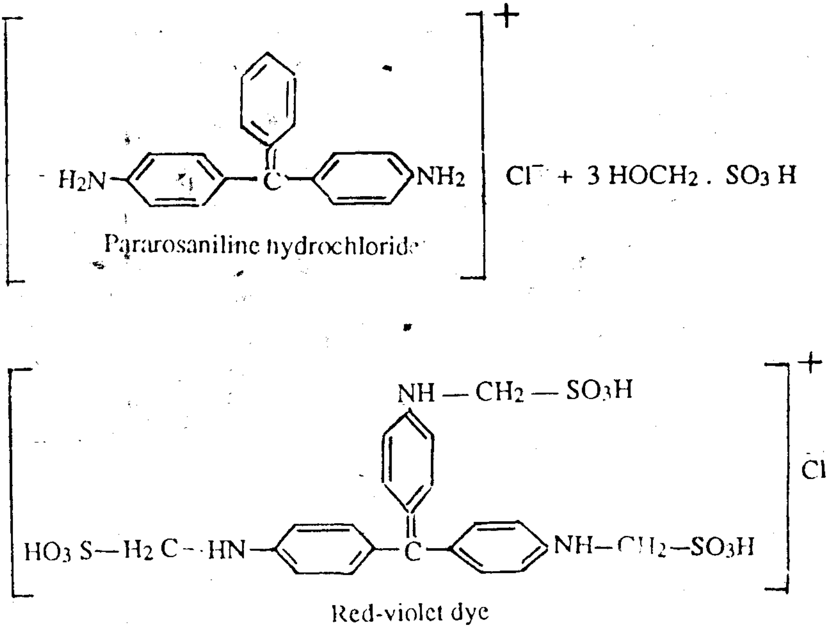
(*ii*) We have said above that coal contains sulphur and hence SO_2 is produced when coal is burnt. SO_2 produced by burning coal causes air pollution. The pollution due to SO_2 can be prevented either by *desulphurisation* of coal or by using natural gas in place of coal for heating purposes. Natural gas does not produce SO_2 on burning.

(*d*) *Monitoring of SO_2 gas.* The method used for monitoring SO_2 gas present in the polluted air in the range of 0.005-5 ppm has been devised by West and Gocke. In this method, the polluted air is pumped through a solution containing $HgCl_4^{2-}$ ions [which are obtained by the action of $HgCl_2$ on KCl solution, $HgCl_2 + 2KCl \rightarrow K_2[HgCl_4]$] when about 95% of SO_2 present in the air, forms the complex ion, $[Hg^{2+}Cl_2(SO_3)]^{2-}$ in solution.

$$[Hg^{2+}Cl_4]^{2-} + SO_2 + H_2O \longrightarrow \underbrace{[Hg^{2+}Cl(SO_3)]^{2-} + 2HCl}_{\text{Solution}}$$

The solution containing complex ion, $[HgCl_2(SO_3)]^{2-}$ is treated with formaldehyde (HCHO) and then with pararosaniline hydrochloride to form a red-violet dye.

$$\underbrace{[HgCl_2(SO_3)]^{2-} + 2\,HCl}_{\text{Solution}} + HCHO \longrightarrow HOCH_2.SO_3H + HgCl_4^{2-}$$



+ $3H_2O$

The absorbance of the red-violet dye is recorded with the help of a spectrophotometer at 548 nm. The extent of absorbance is a measure of the concentration of the dye and hence of SO_2 present in the polluted air.

5. **Ozone (O_3)** (*a*) *Sources of O_3 and its toxic effects.* Some O_3 is produced during various combustion processes taking place in the air around us. Traces of O_3 in the air do not harm but O_3 of concentration more than 0.1 ppm is toxic and harmful to human beings. O_3 also attacks rubber products. O_3 is also produced in the upper part of the atmosphere by the action of sunlight on O_2.

$$3O_2 \xrightarrow{\text{Sunlight}} 2O_3$$

(*b*) *Protective action of ozone layer in the atmosphere.* The region of atmosphere lying between 15 Km. to 60 Km. above the earth's surface is called *stratosphere.* This region contains a stable layer of O_3 whose concentration is between 1 and 5 ppm by volume.

The thickest layer of O_3 exists at a height of 23 Km. from the surface of the earth. This ozone layer is very important for the existence of our life on earth, since O_3 present in this layer absorbs harmful ultra-violet radiations coming from the sun and reaching the earth. If these radiations reach the earth, they will cause skin cancer and will destroy the organic molecules necessary for life.

Thus, we see that O_3 does not allow the ultra-violet-radiations to reach the earth and we are thus saved from the harmful effects caused by these radiations. If O_3 layer in the atmosphere disappears completely, then all the harmful ultra-violet radiations coming from the sun would reach the earth and would cause skin cancer in men and animals and will also damage the plants. All the life on earth would then gradually be destroyed.

(*c*) *Sources of destroying the ozone layer present in stratosphere.* In 1980 scientists showed that there is a hole in the O_3 layer. This hole was detected over the region of Antarctica. Due to the presence of O_3 layer, the ultra-violet rays coming from the sun can pass through the hole and thus can reach the earth's surface. The presence of O_3 hole in the atmosphere is due to the fact that the amount of O_3 present in stratosphere is getting reduced day by day and thus the ozone layer is becoming thinner and thinner. The depletion of the ozone layer is due to the following sources.

(*i*) *Oxides of nitrogen* : The oxides of nitrogen present in the atmosphere decomposes O_3 into O_2 and are themselves regenerated.

$$NO + O_3 \longrightarrow NO_2 + O_2 \,;\, NO_2 + O \longrightarrow NO + O_2$$

Thus we see that the presence of nitrogen oxides in the atmosphere destroyes the ozone layer. These oxides destroy about 70% of O_3 found in the stratosphere. Greater is the amount of the oxides in the atmosphere greater is the percentage of O_3 which is destroyed.

(*ii*) *Nuclear tests.* Nuclear tests being conducted in the world generate high temperature. At high temperature, atmosphereric nitrogen is favourably oxidised to NO.NO thus formed destroys ozone layer, as shown above at (*i*

(*iii*) *Use of fluoro-chloro carbons as aerosol spray propellants* Fluoro-chloro-carbons are the fluoro-chloro methanes like. *Freon-1* ($CFCl_3$) and *Freon-12* (CF_2Cl_2). These are stable compounds. These are chemically inert and hence do not react with the substances. These are used as aerosol spray propellants, refrigrants, firefighting reagents and solvents for cleaning electronic components. When they enter stratosphere, they absorb ultra-violet solar radiations and get broken down into free atomic chlorine. This atomic chlorine decomposes O_3 into O_2 (NO also breaks O_3 into O_2).

$$Cl + O_3 \longrightarrow ClO + O_2 \,;\, ClO + O \longrightarrow Cl + O_2$$

Thus we find that the use of fluoro-chloro carbons (*e.g.*, Freon-1 and Freon-12) as aerosol spray propellants destroys the O_3 layer, as oxides of nitrogen do.

(*iv*) The emissions produced by the supersonic jet aeroplanes also cause the depletion of ozone layer in the atmosphere.

(*d*) *How to protect the ozone layer.* Scientists are worried over the gradual destruction (depletion) of ozone layer by the oxides of nitrogen and fluoro carbons. Nitrogen oxides present in the atmosphere can be removed by the methods discussed under "*Control of pollution caused by nitrogen oxides*". In order to save the destruction of O_3 layer by fluoro-chloro carbons, their used should be banned or some new types of substances should be discovered which may be used as aerosol spray propellants and should not react with O_3 layer, so that it may be saved.

6. Dust. Dust is produced by heavy traffic on the roads and in some industrial operations.

Dust in the air spoils our clothes and causes poor visibility. It provides allergic reactions and aggravates diseases like bronchitis. Dust is deposited on the leaves of plants and thus hinders the process of photo-synthesis taking place in plants. Dust in air reflects back some of the sun's heat rays and thus undue cooling of the earth takes place.

7. Smoke. Smoke is produced during the burning of fuels like coal and oil in homes and factories.

The smoke contains unburnt carbon particles which pollute the air. They spoil our clothes and blacken the buildings. Smoke damages our lungs. Due to cloud of smoke over big industries, the sun's rays are not able to reach every corner of the city and hence infectious diseases in big cities are produced.

The pollution of air due to the presence of carbon particles coming out of a chimney of a factory can be controlled by installation an electrostatic precipitator in the chimney. A high electric potential is applied across the chimney. As the smoke particles (*i.e.* carbon particles) come up the chimney, they are attracted by the charged electrodes. The smoke particles cluster together to form soot, which gets deposited in the chimney. Thus the air is saved from being polluted by carbon particles. The soot can be removed by sweeping the chimney from time to time.

The pollution of air caused by carbon particles can also be prevented by using electrical energy, solar energy, tidal energy etc., as a source of fuel in place of coal energy, since these sources do not produce smoke or carbon particles.

Sources of air pollution.

The various sources which produce air pollution (*i.e.*, atmospheric pollution) are given below :

(*i*) *Burning of coal, wood and oils.* When coal, wood and oils are burnt, black smoke is produced. This smoke contains poisonous gases like CO and SO_2, and black unburnt carbon particles. The smoke is black because of the presence of these carbon particles in it. Coal contains some sulphur as impurity. So, when coal is burnt, sulphur of the coal burns to form SO_2. Oils also contain some sulphur compounds which produce SO_2 on burning. CO, SO_2 and unburnt carbon particles, produced as above, go into the air and make it polluted.

(*ii*) *Gases released by the internal combustion engines of cars, buses, trucks, aeroplanes etc.* The smoke obtained by the incomplete combustion of petrol, used in the internal combustion engines of cars, buses, trucks, scooters, aeroplanes etc. [The engines used in these motor vehicles are called internal combustion engines because the petrol (also called gasoline) which is used as a fuel, is burnt inside the engine and not separately contains CO, NO, NO_2, unburnt carbon particles, some lead compounds, some alcohol and acids. All these substances are poisonous and hence pollute air.

Now let us see how these pollutants are produced in an engine of a car. Petrol is used as a fuel in car engine. The main components of petrol are hydrocarbons. These hydrocarbons have the general formula, C_8H_{18} and hence are called *octanes.* Petrol burns very fast in a car engine. Due to short time available for burning, incomplete combustion of petrol takes place and some CO, unbunt carbon particles, CO_2, water vapour, some alcohol and acids are produced. CO and carbon particles are emitted into the air and thus air is polluted.

When petrol burns in a car engine, a very high temperature is produced. At this high temperature, N_2 and O_2 present in the air in the engine combine together and form NO and NO_2. These gases pollute the air.

In order to control the air polution due to CO, $Pb(C_2H_5)_4$ is added to petrol. The addition of this substance slows down the rate of combustion of petrol [$Pb(C_2H_5)_4$ is called antilock] and also at the same time gives rise to the formation of $PbCl_2$ and $PbBr_2$. Both of these substances are poisonous and hence make the air polluted.

(*iii*) *Chemical industries.* The chemical industries emit various poisonous gases into the air. These gases make the air polluted. An industry poducing bleaching powder emits chlorine gas into the air. Industries working for the extraction of metals (*e.g.*, Fe, Cu, Zn etc.) from sulphide ores produce SO_2 gas which causes air pollution.

(*iv*) *Smoking.* Smoking produces CO and nicotine. Both these chemicals are poisonous and hence make the air polluted.

(*v*) *Dust.* Dust produced by the heavy traffic and various industries pollutes air.

(*vi*) *Radioactive waste materials.* (Nuclear pollution) The radioactive waste materials produced during the enrichment of nuclear fuels and in nuclear reactors, used in hospitals and laboratories, emit high energy gamma radiations, which inhibit cell functions, leading to some serious diseases like leukaemia. The radiations initiate unwanted cell growth which produces cancer etc.

Methods to control air pollution.

We have already said that air is polluted by the presence of CO, CO_2, NO, NO_2, SO_2, SO_3, O_3, unburnt hydrocarbons, dust, smoke etc. The pollution of air by these pollutants can be prevented by the following methods.

(*i*) *By adding lead tetraethyl, $Pb(C_2H_5)_4$ to the petrol or by the catalytic oxidation of CO and hydrocarbons with platinum catalyst.* This method can be used to save the air from pollution caused by the presence of CO and unburnt hydrocarbons in it. These pollutants come in the air from the exhaust gases released by the vehicle's engine.

(*ii*) *By keeping the vehicle properly tuned for the optimum ignition of fuel.* This method also prevents air pollution caused by CO and hydrocarbons present in the exhaust fumes of the vehicles.

(*iii*) *By growing more plants.* This method removes the air pollution cause by CO_2.

(*iv*) *By using electrostatic precipitator.* This method is used for removing carbon particles produced by burning of fuels like coal and oil.

(*v*) *By using smokeless sources of energy.* This method is used for preventing air pollution caused by smoke or carbon particles produced during the burning of coal or oil.

(*vi*) *By using natural gas, in place of coal, for heating purposes.* This method saves air from being polluted by SO_2 gas.

(*vii*) *By using tall chimneys.* The use of tall chimneys in homes and factories can reduce the concentration of pollutants at the ground level.

(*viii*) The air pollution in our homes can be controlled : (*a*) by using liquified petroleum gas (LPG) for cooking, instead of coal, kerosene or wood. Electric heaters and solar cookers can also be used to prevent the air pollution at homes. (*b*) By using a tall chimney in the kitchen. This will minimise the pollution of air of at the ground level. (*c*) By growing more plants in the courtyard. The plants use CO_2 and thus air pollution is reduced.

(*ix*) The pollution caused by the radioactive waste products (nuclear pollution) can be controlled (*a*) by enclosing the radioactive waste products in containers made of concrete and then dumping them in the sea (*b*) by fusing the radioactive waste products into glass and sealing it deep inside hard-rock formations. At the same time, a great vigilance should be kept on the stored radioactive materials and waste products to prevent the leakage of any radioactive materials during storage and disposal.

SMOG

London type smog or classical smog. The word 'smog' was coined to describe the 'smog-fog' which is prevalent in London. The combination of carbon soot particles and gaseous oxides of sulphur present in the atmosphere, gives what is now known as *classical smog*. This smog is also called *London type smog*. This smog is produced by the combustion of industrial and household fuel (coal and petroleum). Carbon particles and SO_2 present in classical smog make it to show reducing character. This smog is formed in the early morning hours in winter months. It causes severe lung and throat irritation.

Los Angeles type or photo-chemical smog. The main constituents of this type of smog are O_3 and oxides of nitrogen (mainly NO_2). Due to the presence of O_3, NO_2 and some other photochemical oxidants, this smog is oxidising in character.

Mechanism of the formation of photochemical smog. Photochemical smog is formed only when the atmosphere contains soot particles, hydrocarbons and oxides of nitrogen (mainly NO_2). When the atmosphere containing the above constituents is exposed to sunlight, NO_2 present in the atmosphere absorbs ultra-violet radiations of the sunlight and undergoes photolysis, giving NO and atomic oxygen (Decomposition of NO_2 into NO and O).

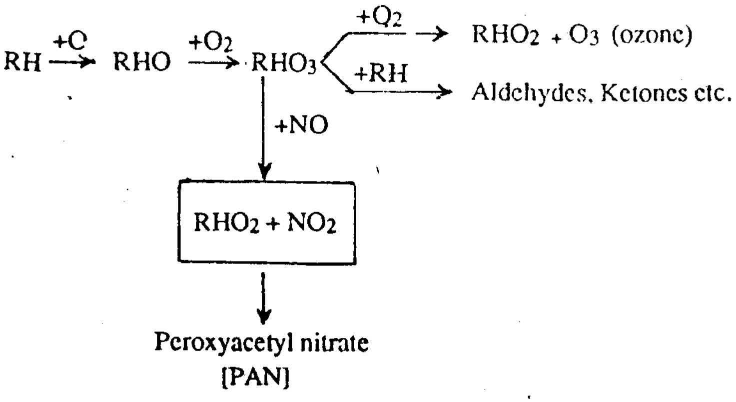
$$NO_2 + \text{U.V. light} \longrightarrow NO + O \quad \text{(atomic oxygen)} \qquad \ldots (i)$$

Atomic oxygen reacts with O_2 (molecular oxygen) in presence of a collisional molecule (M) which conserves energy and O_3 is formed. O_3, thus produced, reacts with NO to regenerate NO_2 and O_2.

$$O + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

If the atmosphere contains hydrocarbons (RH), the atomic oxygen produced in reaction (*i*) reacts with RH to give a variety of free hydrocarbon radicals (*e.g.*, RHO, RHO_2, RHO_3 etc.) which produce O_3 and other secondary pollutants like aldehydes, ketones, peroxyacetyle nitrate (PAN) etc. All these pollutants are called *photo-chemical pollutants*.



O_3, aldehydes ketones etc. present in the photo-chemical smog induce eye-irritation. O_3 adversely affects vegetation and cracks the stretched rubber.

WATER POLLUTION

What is water pollution ?

When insoluble solid particles, soluble salts, sewage (waste water), garbage, low level radioactive substances, industrial wastes, algae, bacteria etc go into water, water gets polluted. This type of pollution is called *water pollution.*

Sources of water pollution and their effects.

1. Industrial wastes and organic sewage wastes. The wastes discharged by industries are called industrial wastes. These wastes contain compounds of metals (*e.g.*, Hg, Cd, Pb etc.), organic compounds, alkalies, phenols etc. which make water polluted. Also see '*Industrial Pollution.*

The sewage is the dirty water which contains human and animal excretions (*e.g.*, urine and faeces). The discharge of large quantities of sewage into rivers and lakes also causes water pollution. This sewage is produced by the every day human activities like bathing, washing clothes and excreting the urine and faeces.

Some of the effects of industrial and sewage wastes are given below :

(*a*) The sewage contains organic compounds. These organic compounds act as food for bacteria present in water of lakes and rivers and hence the population of bacteria in water is rapidly increased. This bacteria oxidises nitrogen and phosphorus present in organic compounds of the sewage to nitrates and phosphates. This oxidation process consumes a large quantity of O_2 gas dissolved in river water. The loss of dissolved O_2 from the river water causes the death of fish and other aquitic living beings.

(*b*) These wastes produce scum and sludge in water.

(*c*) These wastes change the colour of water and produce foul smell.

2. Organic compounds. These include synthetic detergents, herbicides, pesticides, oil and decomposition products. Their effects are given below :

(*i*) *Detergents.* Detergents are *surfactants* (*i.e.*, surface active agents) and *builders.* Surfactants are organic compounds having polar or hydrophilic groups such as -COOH, $-SO_3H_2$, NH_4^+ or non-polar or lyophilic groups soluble in water. Surfactants have the following properties and hence cause water pollution.

(*a*) Bio-micro-organisms (*i.e.*, bacteria present in the water of lakes or rivers) are not able to bio-degrade the surfactants, *i.e.*, surfactants are not decomposed (digested) by the bio-micro-organisms and hence large volumes of detergent foams are collected in the lakes and rivers. These foams make water polluted.

(*b*) Surfactants form a sort of envelope around the organic substances (e.g. phenol). The formation of an envelope results in that these substances do not undergo oxidative de-gradation during the treatment of municipal waste water. Thus, the removal of organic substances from the waste water by the usual treatment methods becomes a problem.

(*c*) Builders are generally sodium salts of phosphoric acid, carbonic acid, sulphuric acid etc. The builders form stable soluble complexes with hardness-producing ions such as Ca^{2+} and Mg^{2+}. These complexes act as plant nutrients and cause a rapid growth of algae and weeds in water. The growth of these plants appears as a green sludge on the surface of the water. These plants bring about de-oxygeneration of water and hence aquatic animals die.

(ii) *Pesticides*. The pesticides (*e.g.*, D.D.T., endrin, dieldrin, B.H.C., polychlorinated diphenyls etc.) are both toxic and persistent. Analysis of polluted water has shown that it contains pesticides which are toxic to fish. Endrin, even in traces, is reported to be toxic for catfish and other varieties of fish. D.D.T. affects the central nervous system of fish and toxaphene has been reported to cause bone degeneration in fish.

3. Chemical fertilisers (Plant nutrients). Nitrate/phosphate salts are generally used as fertilisers, to increase the yield of the crops. When these fertilisers are used in excess, some of their unused quantity is washed away from the agriculture lands into the ponds, lakes and rivers with rain water and thus pollute the water. This water is polluted, since it contains unused nitrate/phosphate salts. Similarly the waste water coming from the fertiliser industries also contains nitrogenous/phosphatic fertilisers which, when washed away into the lakes and rivers with rain water, make the water polluted. The presence of nitrogenous/phosphatic fertilisers in water is harmful to the aquatic life and human beings in the following ways :

(*i*) The presence of the fertilisers in the polluted increases the growth of algae and other aquatic plants which, later on, undergo decomposition and produce disagreeable odour. These plants also deplete the amount of O_2 dissolved in water and hence the survival of aquatic life becomes difficult or impossible.

(*b*) After a long period the lakes and slow moving waters which contains plant noutrients are converted into swamps (A swamp is an area of very wet land with wild plants growing in it) and marshes (A marsh is an area of land which is very wet and muddy).

(*c*) The water containing nitrate salt is not fit for drinking by human beings. Moreover, this polluted water cannot be purified for drinking purposes.

4. Desease producing micro-organisms. If the residents of a municipality are suffering from deseases like dysentry, typhoid, cholera etc., the faeces and urine discharged by such patients contain micro-organisms which are transmitted through water supplies and thus produce disease in other living beings.

5. Petroleum oil. A large quantity of crude petroleum oil is spilled accidently or intentionally into the sea-water from the tankers (ships) or during the drilling and shipping operations. This oil pollutes sea-water. For example the accidental leakage of 118,000 tonnes of crude petroleum oil from the big oil tanker called Torrey Canyon into the waters of English Channel polluted water of the surrounding area in a few hours' time.

Some of the effects of oil pollution are given below :

(*a*) Since oil is lighter than water, oil forms a layer on the surface of water which is called *oil-stick.* This oil- stick checks the oxygenation of water and water eventually becomes devoid of O_2. Thus, the life of aquatic animals and plants is adversely affected.

(*b*) Phyto-plankton (plankton is a layer of tiny animals and plants that live on the surface layer of the sea) on the surface of water absorbs dirt and acts as pollution filter. But the oil film on water surface checks the growth of plankton. This knocking out of plankton by oil film disrupts the entire cycle of marine life.

(*c*) The oil film on water may catch fire and cause harm to the aquatic animals.

(*d*) The life of the people living on sea-shores is also affected due to water polllution caused by petroleum oil.

(*e*) In petroleum drilling, when crude oil is pumped into the surface, NaCl is discharged along with it. NaCl makes the water polluted, since it affects aquatic life.

(*f*) Oil pollution also affects sea-birds. The oil penetrates the feathres and the air which is normally entrapped in the feathers is eliminated. The elimination of entrapped air makes the birds colder and more susceptible to diseases. Due to the elimination of entrapped air, the birds feel difficulty in flyig and swimming. Thus we find that the pollution of sea-water by oil also affects the flight and swimming capability of sea- birds.

Methods of control water pollution

Water polltion can be prevented or minimised by the following methods :

(*i*) The use of excess of nitrate and phosphate fertilisers should be avoided.

(*ii*) The use of synthetic detergents should be minimised or bio-degradeable detergents (bio-degradeable detergents are those which can be decomposed by the bacteria) should be used. Alternatively, a combition of washing soda and soap should be used for washing the clothes.

(*iii*) Before throwing the industrial wastes into the rivers and lakes, they should frst be treated chemically to neutralise the harmful substances present in them.

(*v*) Before dumping the sewage into rivers, it should first be treated chemically to remove the organic compounds present in it.

(*v*) The radio-active waste products obtained in reactors used in hospitals and scientific laboratories should be enclosed in containers made of concrete and then dumped into sea.

SOIL POLLUTION

What is soil pollution ?

The contamination of soil with rain, excess of fertilisers, wrong fertilisers, insecticides (insecticides are the chemical compounds which can kill the insects) and herbicides (herbicides are those chemical compounds which can kill plants) is called soil pollution.

Sources of soil pollution

The main sources which pollute the soil are discussed below :

(*i*) *Acid rain.* We know that air contants SO_2 and NO_2. SO_2 present in air undergoes photolytic and catalytic oxidation to form SO_3 which reacts with rainy water or moisture to form H_2SO_4 ($SO_3 + H_2O \longrightarrow H_2SO_4$. NO_2 reacts with rainy water or moisture in presence of O_2 or O_3 and produces HNO_3.

$$4NO_2 + H_2O + O_2 \longrightarrow 4HNO_3$$
$$2NO_2 + H_2O + O_3 \longrightarrow 2HNO_3 + O_2$$

H_2SO_4 and HNO_3 formed as above come down the atmosphere as acid rain. This acid rain damages the standing crops.

(*ii*) *Repeated use or excess use of the same fertiliser.* Repeated use or excess of the same fertiliser pollutes the soil. For example when $(NH_4)_2SO_4$ is used as a fertiliser into the soil again and again (repeated use of the fertiliser), NH_4^+ ions are used up by the successive crops but SO_4^{2-} ions get accumulated into the soil. Being acidic, SO_4^{2-} ions make the soil highly acidic and hence unfit for plant growth.

If $NaNO_3$ or KNO_3 is used again and again, NO_3^- ions are used up by the successive crops, but Na^+ or K^+ ions get accumulated into the soil. These cations make the soil alkaline and hence the soil canot be used for the crops-growth. The above discussion makes it evident that the repeated use or excesS use of the same fertiliser pollutes the soil.

(*iii*) *Inadequate drainage system in agricultural fields.* We use a lot of water for irrigation, along with fertilisers, but there should be good drainage system for the outlet of the unused water, otherwise the soil will become highly saline (salt containing) and unfit for growing crops. Thus we see that inadequate drainage system in fields is aother source of soil pollution.

(*iv*) *Spraying the vegetable and fruit plants with insecticides and herbicides.* When the standing vegetable and fruit plants are sprayed with insecticides and herbicides, to save them from the harmful insects and herbs etc., the insectices/herbicides enter the living tissues of the growing plants and accumulate in them. When we eat these grains, fruits or vegetables, the insecticides in them may damage our heart. It is, therefore, advised that before eating them, they should be properly washed with sufficient uqantity of water. Since the chemicals like $CaCl_2$ are used for ripening fruits like banana and mangoes, these fruits should be washed with water before they are eaten up bv us.

RADIOACTIVE (RADIATION) POLLUTION

What is radioactive pollution ?

Radioactive substances and nuclear radiations (*i.e.*, α, β and γ-particles) produced during nuclear reactions affect our environment adversely and thus radioactive pollution is created.

Sources of radioactive pollution and its effects.

(*i*) Low level radioactive liquid wastes, radioactive gaseous wastes, and dusts are released during nuclear explosions. The radioactive gaseous wastes are injected into the upper layer of atmosphere where, due to cooling they condense to fine dust particles and thus radioactive cloud is formed. This cloud moves in the direction of the wind, settles down slowly to the surface of the earth and thus pollutes air, water and soil.

(*ii*) The radioactive substances produce energy which is so strong that the living cells are damaged or destroyed.

(*ii*) People working with radioactive elements develop tumours.

(*iv*) Radioactive elements like strontium-90 affects our soil and through this human beings and animals are also affected adversely.

(*v*) Nuclear explosions which are operated in sea make sea water polluted. This affects the aquatic life.

(*vi*) Among the radioactive radiations, γ-radiations (or γ-*rays)* are the most dangerous, since they have high energy and high penerating power. These radiations can, therefore, pass freely in the human body, where they lose energy, which destroys the living cells by converting them into charged particles (ions). These charged particles are chemically very reactive and hence disrupt cell-membranes, reduce the effectiveness of enzymes and even damage genes and chromosomes. All this results in diseases like leakaemania and cancer.

(*viii*) We know that in a nuclear reactor U-235 is used as a nuclear fuel, which undergoes nuclear fission and energy is produced. Nuclear radiations are produced in the processes *viz* mining and enrichment of U-235 taking place in the nuclear reactor. These radiations can leak from the reactor and, therefore, damage the health of the human beings and animals.

Control measures for minimising radioactive pollution

The waste materials produced in the mining, enrichment and fission of U-235 inside the reactor are collectively called *nuclear wastes*. At present, most of the nuclear wastes are being stored in strong leak proof containers. These will be disposed off whenever a safe method of their disposal is found out.

INDUSTRIAL POLLUTION

What is industrial pollution ?

As already said, the waste discharges by industries make water, air and biosphere polluted. This type of pollution is called industrial pollution. The industrial wastes contain compounds of Hg, Na, Cd, As, Pb, Ca etc., inorganic minerals, organic compounds, acids, alkalies, phenols etc. When these wastes are thrown into the lakes and rivers, the water of the lakes and rivers get polluted. These wastes are very harmful, since they injure or kill the fish and other aquatic life and also render the water unfit for drinking and for industrial use.

Hot water discharged from industries also pollutes water, since it is harmful for fish and aquatic life.

Industrial pollutants and their effects

Following are the most important industrial pollutants which affect adversely human, plant and aquatic life.

1. Lead. When leaded gasoline undergoes combustion in automobiles, lead in the form of tetramethyl lead [($Pb(CH_3)_4$] and tetraethyl lead [$Pb(C_2H_5)_4$] is produced. These substances go into the atmosphere. These compounds are brought down on the earth by rain and thus enter into water of lakes and rivers. The compounds like $PbCl_2$, $PbBr_2$, PbBrCl, PbO, PbS, $PbSO_4$ etc. which originate from lead minerals also enter into water. $Pb(OH)_2$ gets its entry into water from lead pipes.

Intake of lead by human beings, animals and plants is harmful as shown below :

(*i*) When rats are exposed to lead polluted air, they die in two-thirds of their average life span.

(*ii*) The birds, which are shot, but recover usually, subsequantly die due to lead-poisonning.

(*iii*) The lead-polluted air has its adverse effects on vegetables, *e.g.* the road-side vegetables are dried up by the exposure of lead-polluted air.

(*iv*) If lead is taken by humans *even in small amounts*, it affects breathing and nervous system.

(*v*) *Excessive intake of lead* causes disruption of synthesis of haemoglobin. It also results in loss of apetite, anaemia, kidney malfunctioning, nervous disorders and brain damage.

(*vi*) Lead can also be absorbed by skin, resulting into many skin diseases.

2. Mercury. Mercury is found in sea due to the weathering of mercury-bearing rocks. Some of the effects of mercury pollution are given below :

(*i*) Monomethyl mercury [CH_3Hg] and dimethyl mercury [$(CH_3)_2Hg$] produce nervous disorders in marine animals.

(*ii*) Contact with Hg produces nervousness, fear, inability to make decisions, heaviness, irritability, headache, pessimism, fatigue, sleeplessness, trembling of limbs, falling teeth and diarrhoea.

(*iv*) Hg brings about genetic changes.

3. Cadmium. Cadmium pollution may arise from soot of zinc, lead and copper processing plants. Cadmium is now used to plate tin containers of canned food. It is easily dissolved in fruit juice. It can remain in the body for a long time. Following are some of the effects of cadmium pollution.

(*i*) It causes vomiting and lung irritation.

(*ii*) If a large quantity of cadmium is absorbed in the kidneys, it causes hypertension and anaemia.

(*iii*) Cadmium is very dangerous for pregnant women.

(*iv*) Cadmium pollution causes a desease called "*Hai Itai*" in which the whole body feels serious pains and the bones begin to fracture very easily.

4. Industrial waste water. Industrial waste water contains a number of metals, organic componds etc., which are very toxic. The nature of the substaces present in the industrial waste water depends on the type of industry from which this waste water has been obtained. When this waste water is discharged into lakes, rivers or oceans as such, it causes severe pollution of water.

(*i*) *Waste water from food processing industry.* Food processing industries which deal with meat and dairy products give waste water. This waste contains a large amount of organic matter which produces oxygen depletion. For example :

(*a*) The beet sugar refining industry produces wastes which have high biochemical oxygen demand (BOD).

(*b*) The breweries and distilleries produce organic solids and fermented starches.

(*c*) The dairy industry produces organic wastes which contain a large amount of protein, fat and lactose.

(*d*) The wastes obtained from meat processing industry contain blood, fats, proteins, feathers and many other organic wastes.

(*ii*) *Waste water from textile industry.* Waste water discharged from the textile industry originates from the impurities in the fibres and from the chemicals used in processing *viz.*, cooking the fibres, desizing the fabrics etc. This waste water is generally alkaline in nature and has high BOD.

(*iii*) *Waste water from paper and pulp industry.* The waste water that comes out of pulp and paper industry contains chemicals used in craft process, bits of barks, wood chips, cellulose fibres and dissolved lignin. This water also contains compounds which are toxic to fish and shell fish.

(*iv*) *Waste water from chemical industry.* Chemical industries manufacturing acids, bases, pesticides, synthetic fibres, detergents and organic and inorganic compounds produce wastes which contain a wide variety of substances. These substances are highly toxic.

(*v*) *Waste water from petroleum industry.* Waste water discharged by oil-drilling process contains drilling muds. Oil refineries and petrochemical plants produce a large amount of hydrocarbons, acids, alkalies, cyanides, numerous sodium salts, phenolic compounds, inorganic and organic sulphur compounds and halogenated hydrocarbons. Many of these compounds produce undesireable odours and tastes. Many of them produce adverse tastes in fish flesh.

(*vi*) *Waste water from metal industry.* Steel plants produce waste water which originates from washing of blast furnace flue gases and pickling of steel. This waste water contains phenol, cyanogen, coke, lime stone, fine suspended solids, metals like Cr, Pb, Ni, Cd, Zn, Cu, Ag etc., acids, alkaline cleaners, grease, oil etc.

(*vii*) *Waste from other industries* (*a*) *Leather industry* yields wastes which contain high amounts of salts, sulphides, chromium, lime etc. These wastes have high BOD.

(*b*) *Nuclear power plants* and *nuclear research laboratories* using radio-active isotopes produce radioactive wastes.

(*c*) *Soft drinking bottling plants* produce highly alkaline wastes which have high BOD wich is received by them when bottles are washed to remove cigatret butts paper and other debris left in the bottles by the previous users.

NOISE POLLUTION

What is noise pollution ?

The unwanted sound in called noise. The sounds of high decibels (decibel is a unit of measuring strength of a sound) like 95, 100, 110, 150, 170 etc. create harmful effect on human health. This is called *noise pollution.*

Sources of noise pollution

(*i*) The increasing speed and length of railway trains increases the volume of noise produced by them during their journey.

(*ii*) In factories the high speed machines create more and more noise. Loud speakers (95 decibels), aeroplanes (100 decibels), motor horn (110 decibels) rockets (170 decibels), siron (150 decibels), motor cycle (110 decibels) etc., create harmful effects on human life.

Effects of noise pollution

(*i*) Excessive noise disturbs the blood pressure modifies rhythm and affects the digestive system.

(*ii*) Prolonged exposure to noise is harmful for nervous system and also affects memory adversely.

(*iii*) Noise leads to gradual loss of learning capacity of human beings.

(*iv*) The sound pollution causes confusion in colour perception and thus may reduce the field of vision.

(*v*) The excessive noise produces psychological effects on human beings, *e.g.*, it increases diastolic blood pressure, irritability, neuro-muscular tension etc.

(*vi*) Excessive sound disturbs sound sleep and proper rest.

(*vii*) It decreases the efficiency of working.

(*viii*) A sound of high decibels (≈ 160 decibels) creates headache.

(*ix*) Noise pollution may increase violence and may cause a state of depression and tiredness.

(*x*) Sound affects human pregnant mothers and increases the rate of their heart beating and has adverse effects on the newly- born child.

22

Electrode Potentials and Their Applications

Electrochemical Cell

We know that whenever an indirect redox reaction takes place, chemical energy is produced. This chemical energy can be converted into electrical energy by a device which is called electrochemical cell. Thus an electrochemical or simply a chemical cell is a device in which energy produced due to indirect redox reaction (which is spontaneous) is converted into electrical energy (electricity). Electrochemical cells are also called **galvanic cells** or **voltaic cells** after the names of the scientists, Luigi Galvani (1780) and Alessandro Volta (1800) who were the first to perform experiments on the conversion of chemical energy into electrical energy.

Table 22.1. Comparison between electrolytic and electrochemical cells.

Electrolytic cells	Electrochemical cells
(*i*) Electric current (electrical energy) is passed through the electrolytic cell. It is this electrical energy that brings about the redox reaction (electrolysis of electrolyte) in the cell. Thus in an electrolytic cell, electrical energy is converted into chemical energy. We can, therefore, say that an electrolytic cell is a device in which electrical energy is converted into chemical energy.	(*i*) Redox reaction taking place in an electrochemical cell produces electrical energy. Thus in electro-chemical cell chemical energy is converted into electrical energy. Thus galvanic cell is a device in which chemical energy is converted into chemical energy.
(*ii*) The redox reaction (*i.e.* electrolysis of the electrolyte) taking place in an electrolytic cell is non-spontaneous, since it takes place only when electrical current is passed through the cell.	(*ii*) The redox reaction taking place in an electrochemical cell is spontaneous, since no electrical current is needed to make it to occur.

(*iii*) Since anode is connected to the positive terminal of the battery (battery acts as source of voltage), it becomes positively charged and hence is also called positive (+) electrode. Similarly, since cathode is connected with the negative terminal of the battery, it becomes negatively charged, and hence is also called negative (–) electrode.	(*iii*) Since electrons (negatively charged particles) are produced on anode, this electrode is rich in electrons and hence is also negative (–) electrode. Since cathode gets electrons from the anode through external circuit, this electrode is deficient in electrons and is also called positive (+) electrode.
(*iv*) Both the electrodes are placed in a single container which contains the single electrolyte in the solution form or in the molten state. In electrolytic cell no salt bridge or porous partition is used.	(*iv*) Both the electrodes are placed in two different containers which contain different electrolytes. These two containers are separated from each other by salt bridge or porous partition. Thus in a galvanic cell salt bridge or porous partition is used.
(*v*) The two electrodes may be of the same or different materials.	(*v*) The two electrodes are of different materials.
(*vi*) In electrolytic cell, the flow of electricity (or current) through the solution is due to the movement (flow) of ions towards their respective electrodes. The flow of current through the solution which is due to the movement of ions is called electrolytic conduction.	(*vi*) In an electrochemical cell, the flow of current is due to the flow of electrons in the external circuit and due to the flow of ions through the solution in the inner circuit.
(*vii*) Oxidation takes place on anode and reduction takes place on cathode.	(*vii*) Oxidation takes place on anode and reduction takes place on cathode.
(*viii*) Electrons are produced by the negative terminal of the external battery. These electrons enter the negative electrode (cathode) of the cell where these are used up in the reduction reaction taking place on	(*viii*) In galvanic cell, electrons are produced on anode because of the oxidation reaction taking place on this electrode. These electrons move to the external circuit and then to cathode where they are consumed in the

cathode. The same number of electrons that are used up in the reduction reaction taking place on cathode are produced on positive electrode (anode) of the cell by oxidation reaction taking place on this electrode. These electrons go to the positive terminal of batter (see Fig. 22.1).	reduction reaction taking place on cathode (see Fig. 22.2).
(*ix*) Cations move towards cathode and anions move towards anode	(*ix*) Cations move towards cathode and anions move towards anode.

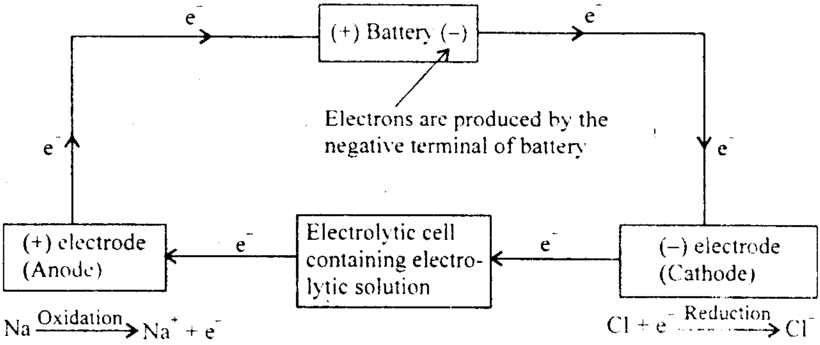


Fig. 22.1. Direction of the movement of electrons in an electrolytic cell.

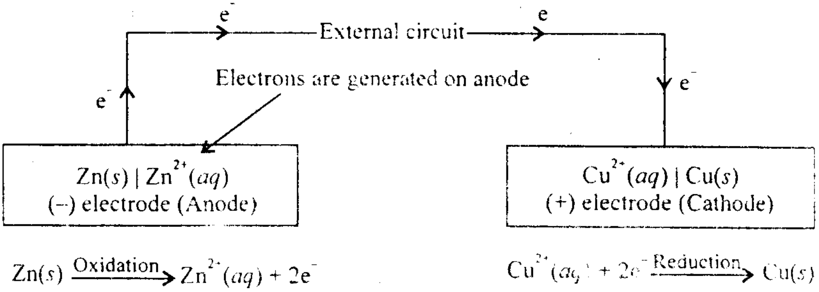


Fig. 22.2. Direction of the movement of electrons in a galvanic cell.

What is electrode potential of an electrode ($E_{electrode}$ or E)?

The electrical potential difference set up between a metal and its ions in solution is called potential of the electrode or simply as electrode potential.

Electrode potential can also be defined as the tendency of an element to lose or gain electrons when it is in contact with its own ions in solution.

Since each electrode represents a half cell, electrode potential is also called potential of the half-cell.

Oxidation and reduction electrode potentials (E_{ox} and E_{red})

When oxidation (loss of electrons) takes place on an electrode w.r.t. SHE, the electrode potential of the electrode is called oxidation electrode potential (E_{ox}). On the other hand when reduction (gain of electrons) takes place on an electrode w.r.t. SHE, the electrode potential of the electrode is called reduction electrode potential (E_{red}). In other words we can say than when an electrode loses electrons, its electrode potential is called oxidation electrode polential and when an electrode gains electrons, its electrode potential is called reduction electrode potential.

Oxidation and reduction potentials of an electrode are just reverse of each other. Thus if oxidation potential of an electrode is x volts, its reduction electrode potential will be equal to $-x$ volts.

What is standard electrode potential (E^0)?

If in a half cell, the metal rode is suspended in a solution of its ions having 1 M concentration and the temperature is 298 K, the electrode potential of the half cell or electrode is called standard electrode potential. Standard oxidation electrode potential is represented as E^0_{ox} while standard reduction electrode potential is represented as E^0_{red} or simply as E^0. According to the present convension, if we say that the value of standard electrode potential of an electrode is x volt, this means that this value is the value of standard reduction electrode potential (*i.e.* $E^0 = x$ volt) and not of standard oxidation electrode potential.

If a gas is involved, the pressure should be 1 atmosphere and the temperature should be 298 K.

Positive and negative values of standard electrode potentials (E^0 values) of electrodes.

Positive value of E^0 of a given electrode implies that, if this electrode is combined with a standard hydrogen electrode (SHE) to form a galvanic cell, this electrode will act as cathode (reduction electrode) in the cell [see Fig. 22.3(*a*)]. On the other hand, negative value of E^0 of a given electrode implies that, if this electrode is combined with a SHE to get a galvanic cell, this electrode will act as anode (oxidation electrode) of the cell [see Fig. 22.3(*b*)].

The above description can also be given in the following words:

An electrode at which reduction takes place w.r.t. SHE has positive value of its E^0 [see Fig. 22.3(*a*)] while the electrode at which oxidation takes place w.r.t. SHE has negative value of its E^0 [see Fig. 22.3(*b*)].

$H^+(aq) \mid H_2(g)$	$\|$	$Cu^{2+}(aq) \mid Cu(s)$
Anode		Cathode
(Oxidation electrode)		(Reduction electrode)
$E^0_{H^+(aq)/H_2(g)} = 0.0 V$		$E^0_{Cu^{2+}/Cu(s)} = +0.34 V$
$\frac{1}{2}H_2(g) \xrightarrow{\text{Oxidation}} H^+(aq) + e^-$		$Cu^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} Cu(s)$

(*a*)

$Zn(s) \mid Zn^{2+}(aq)$	$\|$	$H^+(aq) \mid H_2(g)]$
Anode		Cathode
(Oxidation electrode)		(Reduction electrode)
$E^0_{Zn^{2+}(aq)/Zn(s)} = -0.76 V$		$E^0_{H^+(aq)/H_2(g)} = 0.0 V$
$Zn(s) \xrightarrow{\text{Oxidation}} Zn^{2+}(aq) + 2e^-$		$H^+(aq) + e^- \xrightarrow{\text{Reduction}} \frac{1}{2}H_2(g)$

(*b*)

Fig. 22.3. Electrochemical cell obtained by combining $Cu^{2+}(aq)|Cu(s)$ electrode with SHE (*b*) Electrochemical cell formed by the combination of $Zn^{2+}(aq)|Zn(s)$ electrode and SHE.

Types of electrodes

We know that a galvanic cell consists of two half-cells. Each half-cell has one electrode. The electrodes used in half-cells are broadly classified into the following categories:

I. Metal-metal ion electrodes

These electrodes consist of a metal and metallic ion in solution. $M(s) \mid M^{n+}(aq)$ or $M^{n+}(aq) \mid M(s)$ is the general representation of a metal-metal ion electrode. Half-reaction taking place on this electrode is:

$$\underset{(M = +n)}{M^{n+}(aq)} + ne^- \underset{\text{oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} M(s)$$

$Zn(s) \mid Zn^{2+}(aq)$, $Cu(s) \mid Cu^{2+}(aq)$ etc. are the examples of metal-metal ion electrodes.

$Na(Hg) \mid Na^+(aq)$ is sodium-amalgam electrode. Half-reaction is:

$$Na(Hg) \xrightarrow{\text{oxidation}} Na^+(aq) + e^-$$

II. Gas-gas ion electrodes

In these electrodes, an unreactive metal, usually Pt or Au, is in contact with a gas and its corresponding ion (cation or anion) in solution. Examples of such electrodes are given below:

1. Hydrogen electrode. It is represented as Pt, $H_2(g) \mid H^+(aq)$ or $H^+(aq) \mid H_2(g)$, Pt

$$\underset{(H = +1)}{H^+(aq)} + e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \underset{(H = 0)}{\tfrac{1}{2}H_2(g)}$$

2. Chlorine electrode. It is representated as Pt, $Cl_2(g)$ | $Cl^-(aq)$ or $Cl^-(aq)$ | $Cl_2(g)$, Pt.

$$\underset{(Cl = 0)}{Cl_2(g) + e^-} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \underset{(Cl = -1)}{Cl^-(aq)}$$

3. Oxygen electrode. (*a*) It may be represented as Pt, $O_2(g)$ | $OH^-(aq)$ or $OH^-(aq)$ | $O_2(g)$, Pt

$$\underset{(O = 0)}{O_2(g) + 2H^+(aq) + 4e^-} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \underset{(O = -2)}{2OH^-(aq)}$$

(*b*) It may also be represented as Pt, $O_2(g)$ | $H_2O(l)$ or $H_2O(l)$ | $O_2(g)$, Pt

$$\underset{(O = 0)}{O_2 + 4H^+ + 4e^-} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \underset{(O = -2)}{2H_2O(l)} \ (E^0 = +1.229 \text{ V})$$

III. Metal-metal insoluble salt-anion electrodes.

In these electrodes, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. Examples of such electrodes and half-reactions taking place on these electrodes are given below:

1. Silver-silver chloride electrode. This electrode is obtained by immersing a silver wire coated with solid AgCl in a solution containing Cl^- ions [say $HCl(aq)$ or $KCl(aq)$]. When this electrode acts as an anode, it is represented as:

$$Ag(s) \mid AgCl(s), HCl(aq) \text{ or } KCl(aq)$$

or

$$Ag(s) \mid AgCl(s), Cl^-(aq)$$

On this electrode first of all $Ag(s)$ is oxidised to $Ag^+(aq)$ ions

$$Ag(s) \xrightarrow{\text{oxidation}} Ag^+(aq) + e^-$$

Now since the solution is saturated with $AgCl(s)$, the formation of $Ag^+(aq)$ will upset the equilibrium and $AgCl(s)$ will be precipitated by the combination of $Ag^+(aq)$ with $Cl^-(aq)$ ions.

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Thus the net oxidation half-reaction is obtained by adding the above two reactions

$$\underset{(Ag = 0)}{Ag(s) + Cl^-(aq)} \xrightarrow{\text{Oxidation}} \underset{(Ag = +1)}{AgCl(s) + e^-}$$

This equation shows that $Ag(s)$ is oxidised to $AgCl(s)$. The potential of this electrode depends on the concentration of $Cl^-(aq)$ ions in solution. Thus this electrode is equivalent to $Cl^-(aq)/Cl_2(g)$ electrode.

If silver-silver chloride electrode acts as cathode, it is represented as:

$$Cl^-(aq), AgCl(s)/Ag(s).$$

On this electrode $AgCl(s)$ is reduced to $Ag(s)$

$$\underset{(Ag = +1)}{AgCl(s) + e^-} \xrightarrow{\text{Reduction}} \underset{(Ag = 0)}{Ag(s) + Cl^-(aq)}$$

$Cl^-(aq)$, $AgCl(s)$ | $Ag(s)$ is equivalent to $Cl_2(g)$ | $Cl^-(aq)$ electrode.

2. Calomel electrode. When it acts as an anode, it is represented as:

$$Hg(l)\,|\,Hg_2Cl_2(s), Cl^-(aq)$$

$$\underset{(Hg\,=\,0)}{2Hg + 2Cl^-(aq)} \xrightarrow{\text{oxidation}} \underset{(Hg\,=\,+1)}{Hg_2Cl_2(s) + 2e}$$

When it acts as a cathode, it is represented as:

$$Cl^-(aq), Hg_2Cl_2(s)\,|\,Hg(l)$$

$$Hg_2Cl_2(s) + 2e^- \xrightarrow{\text{Reduction}} 2Hg(l) + 2Cl^-(aq)$$

3. Antimony-antimony trioxide electrode. This electrode is represented as:

$$Sb(s)\,|\,Sb_2O_3(s), OH^-(aq) \text{ or } OH^-(aq), Sb_2O_3(s)\,|\,Sb(s).$$

$$\underset{(Sb\,=\,0)}{2Sb(s) + 6OH^-(aq)} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \underset{(Sb\,=\,+3)}{Sb_2O_3\,(s) + 3H_2O + 6e}$$

4. Mercury-mercuric oxide electrode. It is represented as:

$$Hg(l)\,|\,HgO(s), OH^-(aq) \text{ or } OH^-(aq), HgO(s)\,|\,Hg(l)$$

$$Hg(l) + 2OH^-(aq) \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \underset{(Hg\,=\,+2)}{HgO(s) + H_2O + 2e^-}$$

5. $Cu(s)\,|\,Cu(OH)_2(s), OH^-(aq) \text{ or } OH\ (aq), Cu(OH)_2(s)\,|\,Cu(s).$

$$\underset{(Cu\,=\,0)}{Cu(s) + 2OH^-\,(aq)} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \underset{(Cu\,=\,+2)}{Cu\,(OH)_2(s) + 2e}$$

6. $Zn(s)\,|\,ZnSO_4(s), SO_4^{2-}\,(aq) \text{ or } SO_4^{2-}\,(aq), ZnSO_4(s)\,|\,Zn(s)$

$$\underset{(Zn\,=\,0)}{Zn(s) + SO_4^{2-}\,(aq)} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \underset{(Zn\,=\,+2)}{ZnSO_4(s) + 2e}$$

7. $Pb(s)\,|\,PbSO_4(s),\ SO_4^{2-}\,(aq) \text{ or } SO_4^{2-}\,(aq), PbSO_4(s)\,|\,Pb(s)$

$$\underset{(Pb\,=\,0)}{Pb(s) + SO_4^{2-}} \xrightleftharpoons[\text{Reduction}]{\text{Oxidation}} \underset{(Pb\,=\,+2)}{PbSO_4(s) + 2e^-}$$

IV. Oxidation-reduction electrodes.

In these electrodes, two ions of the same metal in different oxidation state are present in solution and an inert metal like platinum is immersed in the solution. Examples are given below:

(*i*) $Fe^{3+}(aq)\,|\,Fe^{2+}(aq), Pt$

$$Fe^{3+}(aq) + e^- \xrightarrow{\text{Reduction}} Fe^{2+}(aq)$$

(*ii*) $Cr_2O_7^{2-}\,(aq)\,|\,Cr^{3+}(aq), H^+(aq), Pt$

$$\underset{(Cr\,=\,+6)}{Cr_2O_7^{2-}(aq) + 14\,H^+ + 6e^-} \xrightarrow{\text{Reduction}} \underset{(Cr\,=\,+3)}{2\,Cr^3(aq) + 7\,H_2O(l)}$$

(*iii*) $\mathrm{MnO_4^-}(aq)|\mathrm{Mn^{2+}}(aq),\ \mathrm{H^+}(aq),\ \mathrm{Pt}$

$$\underset{(\mathrm{Mn}=+7)}{\mathrm{MnO_4^-}(aq)}+8\mathrm{H^+}(aq)+5e^- \xrightarrow{\text{Reduction}} \underset{(\mathrm{Mn}=+2)}{\mathrm{Mn^{2+}}(aq)}+4\mathrm{H_2O}(l)$$

(*iv*) $\mathrm{Co^{3+}}(aq)\,|\,\mathrm{Co^{2+}}(aq),\mathrm{Pt}$

$$\mathrm{Co^{3+}}(aq)+e^- \longrightarrow \mathrm{Co^{2+}}(aq)$$

To construct a galvanic cell for a given redox reaction

In order to construct a galvanic cell in which the given redox reaction takes place, we should remember the following rule:

Oxidation half-reaction takes place on anode (oxidation electrode) and reduction half-reaction takes place on cathodce (reduction electrode) i.e. the anode of the cell is that electrode on which oxidation takes place and cathode of the cell is that electrode on which reduction takes place.

Study the following example.

Example: *Give the notation of the galvanic cell in which the following redox reaction (cell reaction) takes place:*

(*i*) $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

(*ii*) $Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2(s)$

(*iii*) $Zn(s) + Hg_2SO_4(s) \longrightarrow ZnSO_4(s) + 2Hg(l)$

(*iv*) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(aq)$

(*v*) $K_2Cr_2O_7(aq) + KI(aq) + 14HCl(aq) \longrightarrow 8KCl(aq) + 2CrCl_3(aq) + 3I_2 + 7H_2O(l)$

(*vi*) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O$

(*vii*) $2Ag + Cl_2 \longrightarrow 2AgCl$

(*viii*) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$

Solution: (*i*) On anode oxidation of $\mathrm{FeSO_4}$ (Fe = +2) to $\mathrm{Fe_2(SO_4)_3}$ (Fe = +3) takes place while on cathode reduction of $\mathrm{K_2Cr_2O_7}$ (Cr = +6) to $\mathrm{Cr_2(SO_4)_3}$ (Cr = +3) takes place. This reduction occurs in presence of $\mathrm{H_2SO_4}$. Thus the galvanic cell can be represented as:

$$\mathrm{Pt},\ \underset{\text{Soln.}}{\mathrm{FeSO_4}}\ |\ \underset{\text{Soln.}}{\mathrm{Fe_2(SO_4)_3}}\ \|\ \underset{\text{Soln.}}{\mathrm{K_2Cr_2O_7}}\ |\ \underset{\text{Soln.}}{\mathrm{Cr_2(SO_4)_3}},\ \mathrm{H_2SO_4}(aq),\ \mathrm{Pt}$$

or

$$\underbrace{\mathrm{Pt},\ \mathrm{Fe^{2+}}(aq)\ |\ \mathrm{Fe^{3+}}(aq)}_{\longleftarrow\ \text{Anode}\ \longrightarrow}\ \|\ \underbrace{\mathrm{Cr_2O_7^-}(aq)\ |\ \mathrm{Cr^{3+}}(aq),\ \mathrm{H^+}(aq),\ \mathrm{Pt}}_{\longleftarrow\ \text{Cathode}\ \longrightarrow}$$

(*ii*) Since the given cell reaction does not show which species is oxidised and which species is reduced, it appears that some common terms have been cancelled when oxidation and reduction half-reactions are added to get the given cell reaction. The formation of $\mathrm{Hg_2Cl_2}(s)$ takes place due to the oxidation of Hg(*l*)

$$\underset{(Hg = 0)}{2Hg(l) + 2Cl^-(aq)} \xrightarrow{\text{oxidation}} \underset{(Hg = +1)}{Hg_2Cl_2(s) + 2e^-}$$

$Hg_2^{2+}(aq)$ ions get reduced to Hg(l)

$$Hg_2^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} 2Hg(l)$$

Now since the addition of the oxidation and reduction half-reactions (given above) gives the given cell reaction, the cell contains one metal-insoluble metal salt-anion electrode, Hg(l), $Hg_2Cl_2(s)$, $Cl^-(aq)$ as its LHS electrode (anode) on which oxidation of Hg(l) to $Hg_2Cl_2(s)$ takes place and metal-metal ion electrode, $Hg_2^{2+}(aq) \mid Hg(l)$ as its RHS electrode on which reduction of Hg_2^{2+} (aq) ions to Hg(l) takes place. Thus the cell corresponding to the given cell reaction can be represented as:

$$\underset{\text{LHS electrode (Anode)}}{Hg(l), Hg_2Cl_2(s), Cl^-(aq)} \parallel \underset{\text{RHS electrode (Cathode)}}{Hg_2^{2+}(aq)|Hg(l)}$$

(iii) The given cell reaction shows that Zn(s) is oxidised to $ZnSO_4(s)$ and $Hg_2SO_4(s)$ is reduced to Hg(l). Thus oxidation and reduction half-reactions can be written as:

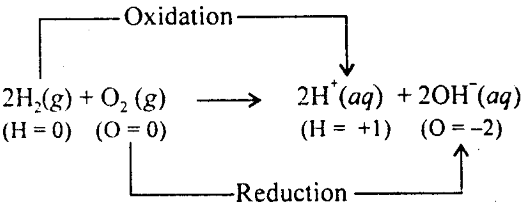
$$\underset{(Zn = 0)}{Zn(s) + SO_4^{2-}(aq)} \xrightarrow{\text{Oxidation}} \underset{(Zn = +2)}{ZnSO_4(s) + 2e^-}$$

$$\underset{(Hg = +1)}{Hg_2SO_4(s) + 2e^-} \xrightarrow{\text{Reduction}} \underset{(Hg = 0)}{2\,Hg(l) + 2e^-}$$

Since SO_4^{2-} (aq) ion is common to both the half-reactions, both the electrodes are metal-insoluble metal salt-anion electrodes. SO_4^{2-} ion (anion) is present in both the insoluble metal salts $viz.$ $ZnSO_4(s)$ and $Hg_2SO_4(s)$. Thus the cell can be represented as:

$$\underset{\text{Anode}}{Zn(s), ZnSO_4(s)}|SO_4^{2-}(aq)|\underset{\text{Cathode}}{Hg_2SO_4(s), Hg(l)}$$

(iv) The given redox reaction can also be written as



$$\underset{(H = 0)}{2H_2(g)} + \underset{(O = 0)}{O_2(g)} \longrightarrow \underset{(H = +1)}{2H^+(aq)} + \underset{(O = -2)}{2OH^-(aq)}$$

Oxidation

Reduction

Thus the redox reaction can be broken into the following half-reactions:

(a) $[\underset{(H = 0)}{H_2(g)} \xrightarrow{\text{Oxidation}} \underset{(H = +1)}{2H^+(aq)} + 2e^-] \times 2$

(b) $\underset{(O = 0)}{O_2(g)} + 2H^+(aq) + 4e^- \xrightarrow{\text{Reduction}} \underset{(O = -2)}{2OH^-(aq)}$

Obviously the given cell reaction can be obtained by adding the above two half-reactions

$$2H_2(g) + O_2(g) + 2H^+(aq) \longrightarrow 4H^+(aq) + 2OH^-(aq)$$

or $$2H_2(g) + O_2(g) \longrightarrow 2H^+(aq) + 2OH^-(aq)$$

or $$2H_2(g) + O_2(g) \longrightarrow 2H_2O(aq)$$

The cell corresponding to this cell reaction can be represented as:

$$\underset{\text{Anode}}{Pt, H_2(g)} \mid \underset{\text{Electrolyte}}{\text{Aqueous solution}} \mid \underset{\text{Cathode}}{O_2(g), Pt}$$

(*v*) The given cell reaction can also be written as:

Oxidation

$$\underset{(Cr = +6)}{K_2Cr_2O_7(aq)} + \underset{(I = -1)}{KI(aq)} + 14HCl(aq) \longrightarrow 8KCl(aq) + \underset{(Cr = +3)}{2CrCl_3(aq)} + \underset{(I = 0)}{3I_2} + 7H_2O(l)$$

Reduction

This reaction shows that on anode $KI(aq)$ $(I = -1)$ is oxidised to $I_2 (I = 0)$ and on cathode $K_2Cr_2O_7\ (aq)$ $(Cr = +6)$ is reduced to $CrCl_3(aq)$ $(Cr = +3)$. This reduction reaction takes place in presence of $HCl(aq)$ or $H^+(aq)$ ions. Thus the galvanic cell can be represented as:

$$Pt, KI(aq) \mid I_2 \parallel K_2Cr_2O_7\ (aq) \mid CrCl_3(aq), HCl(aq), Pt$$

or $$\underset{\text{Anode}}{Pt, I^-(aq) \mid I_2} \parallel \underset{\text{Cathode}}{Cr_2O_7^{2-}(aq) \mid Cr^{3+}(aq), H^+(aq), Pt}$$

(*vi*) The given cell reaction can also be written as:

Reduction

$$\underset{(Mn = +7)}{MnO_4^-} + \underset{(Fe = +2)}{5Fe^{2+}(aq)} + 8H^+(aq) \longrightarrow \underset{(Mn = +2)}{Mn^{2+}(aq)} + \underset{(Fe = +3)}{5Fe^{3+}(aq)} + 4H_2O$$

Oxidation

This reaction shows that on anode $Fe^{2+}(aq)$ ion is oxidised to $Fe^{3+}(aq)$ ion and on cathode $MnO_4^-\ (aq)$ ion $(Mn = +7)$ is reduced to $Mn^{2+}(aq)$ ion $(Mn = +2)$. This reduction takes place in presence of $H^+(aq)$ ions. Thus the galvanic cell can be represented as:

$$\underset{\text{Anode}}{Pt, Fe^{2+}(aq) \mid Fe^{3+}(aq)} \parallel \underset{\text{Cathode}}{MnO_4^-(aq) \mid Mn^{2+}(aq), H^+(aq), Pt}$$

(*vii*) We know that in $Ag(s) \mid AgCl(s), KCl(aq)$ or $Ag(s) \mid AgCl(s), Cl^-(aq)$ electrode, $Ag(s)$ is oxidised to $AgCl(s)$

$$2 \times [Ag(s) + Cl^-(aq) \xrightarrow{\text{oxidation}} AgCl(s) + e^-] \qquad ...(i)$$

We also know that in $Cl_2(g) \mid Cl^-(aq)$ electrode $Cl_2(g)$ is reduced to $Cl^-(aq)$ ion

$$Cl_2(g) + 2e^- \xrightarrow{\text{Reduction}} 2Cl^-(aq) \qquad ...(ii)$$

Since the addition of oxidation and reduction half-reactions (*i*) and (*ii*) given above gives the given cell reaction, the cell corresponding to the given reaction can be represented as:

$$Ag(s) \mid AgCl(s), KCl(aq) \mid Cl_2(g), Pt$$

or $\underbrace{Ag(s) \mid AgCl(s)}_{\text{Anode}} \mid \underbrace{Cl^-(aq) \mid Cl_2(g), Pt}_{\text{Cathode}}$

(*viii*) The given cell reaction shows that on anode $Pb(s)$ ($Pb = 0$) is oxidised to $PbSO_4(s)$ ($Pb = +2$) and on cathode $PbO_2(s)$ ($Pb = +4$) is reduced to $PbSO_4(s)$ ($Pb = +2$). Both the reactions take place in presence of $SO_4^{2-}(aq)$ ion or $H_2SO_4(aq)$

$$Pb(s) + SO_4^{2-}(aq) \xrightarrow{\text{oxidation}} PbSO_4(s) + 2e^-$$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \xrightarrow{\text{reduction}} PbSO_4(s) + 2H_2O$$

Note that both half-reactions take place in presence of $SO_4^{2-}(aq)$ ion. Obviously, cell reaction is obtained by adding the above two half-reactions

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

or $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

Oxidation and reduction half-reactions given above show that the cell corresponding to these half-reactions can be shown as:

$$Pb(s), PbSO_4(s) \mid H_2SO_4(aq) \mid PbO_2(s), Pb$$

or $\underbrace{Pb(s), PbSO_4(s)}_{\text{Anode}} \mid \underbrace{SO_4^{2-}(aq) \mid PbO_2(s), Pb}_{\text{Cathode}}$

Pb shown at cathode is not involved in cell reaction but only serves the purpose of an electrical contact.

To construct a galvanic cell, if two electrodes with their E^0 values are given.

Two electrodes can be combined togetter to get a galvanic cell. While combining them we should remember the following rule:

In a galvanic cell the electrode having higher value of E^0 acts as cathode (RHS electrode) and the electrode having lower value of E^0 acts as anode (LHS electrode)

Illustrative example. *Give the representation of the galvanic cell which is prepared by combining $Cu^{2+} \mid Cu$ and $Zn^{2+} \mid Zn$ electrodes whose standard reduction potentials are 0.34 V and –0.76 V respectively.*

Solution. Since Cu^{2+}/Cu electrode has higher value of E^0 (= 0.34 V) than Zn^{2+}/Zn electrode (= – 0.76 V), Cu^{2+}/Cu electrode acts as cathode (RHS electrode) and Zn^{2+}/Zn electrode acts as anode (LHS electrode). Thus the cell can be represented as:

$Zn \mid Zn^{2+}$	$\parallel$	$Cu^{2+} \mid Cu$
Anode		Cathode
(LHS electrode)		(RHS electrode)
$E^0_{Zn^{2+}/Zn} = -0.76$ V		$E^0_{Cu^{2+}/Cu} = 0.34$ V
(Lower value)		(Higher value)

To write cell reaction (redox reaction) for a given cell.

If we are required to write cell reaction (redox reaction) for a given cell, we should remember that the cell reaction is the sum of oxidation half-reaction and reduction half-reaction. Before adding the two half-reactions, the number of electrons involved in both the half-reactions should be made equal. This method would be clear, if we make the study of the following example

Example. *Write cell reaction (redox reaction) for each of the following galvanic cells:*

(*i*) $Ag(s) \mid AgI(s) \mid KI$ *solution* $(C_1) \parallel AgNO_3$ *solution* $(C_2) \mid Ag(s)$

(*ii*) $Zn(s) \mid ZnO_2^{2-}(C_1), OH\ (C_2) \parallel HgO(s) \mid Hg$

(*iii*) $Pt, H_2(g) \mid HCl$ *solution* $\parallel Hg_2Cl_2(s) \mid Hg$

(*iv*) $Pt, H_2(g) \mid$ *aqueous solution* $\mid O_2(g), Pt$

(*v*) $Fe(s) \mid Fe^{2+}(aq) \parallel H_2SO_4(aq) \mid H_2(g), Pt$

(*vi*) $Pt, H_2(g) \mid HCl(aq) \parallel Cl_2(g), Pt$

(*vii*) $Pt, H_2(g) \mid HCl(solution) \parallel AgCl(s) \mid Ag$

(*viii*) $Pt, H_2(g) \mid HCl(solution) \mid AgNO_3(solution) \mid Ag(s)$

(*ix*) $Hg(l), Hg_2Cl_2(s), KCl$ *solution* $\parallel Hg_2(NO_3)_2(solution) \mid Hg(l)$

Solution. (*i*) LHS electrode (anode) of this cell is a metal-metal insoluble salt-anion electrode, $Ag(s) \mid AgI(s) \mid KI$ solution (C_1) or $Ag(s) \mid AgI(s) \mid I^-(C_1)$ and RHS electrode (cathode) is a metal-metal ion electrode, $Ag^+(C_2) \mid Ag(s)$.

On anode $Ag(s)$ is oxidised to $Ag^+(aq)$ ion which combines with $I^-(C_1)$ ion present in KI solution and forms $AgI(s)$

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

$$Ag^+(aq) + I^-(C_1) \longrightarrow AgI(s)$$

On adding: $$\underset{(Ag = 0)}{Ag(s)} + I^-(C_1) \xrightarrow{\text{oxidation}} \underset{(Ag = +1)}{AgI(s)} + e^-\ (n = 1)\ (\textit{At anode}) \quad ...(a)$$

Equation (*a*) shows that on anode $Ag(s)$ is oxidised to $AgI(s)$.

On cathode $Ag^+(C_2)$ ions are reduced to $Ag(s)$

$$Ag^+(C_2) + e^+ \xrightarrow{\text{Reduction}} Ag(s)\ (n = 1)\ (\textit{At cathode}) \quad ...(b)$$

Cell reaction is obtained by adding (*a*) and (*b*) half-reactions. Thus:

Cell reaction: $Ag^+(C_2) + I^-(C_1) \longrightarrow AgI(s)$

This cell reaction takes place for the passage of one Faradays of electricity ($n = 1$) per mole of $AgI(s)$ formed.

(*ii*) In the given cell, $Zn(s)|ZnO_2^{2-}(C_1), OH^-(C_2)$ and $HgO(s)|Hg$ are anode and cathode respectively. On anode $Zn(s)$ is oxidised to ZnO_2^{2-} ion (C_1) in alkaline medium and on cathode $HgO(s)$ is reduced to Hg. Thus:

$$Zn(s) + 2H_2O \longrightarrow ZnO_2^{2-}(C_1) + 4H^+ + 2e^-$$
$$4H^+ + 4OH^-(C_2) \longrightarrow 4H_2O$$

$$Zn(s) + 4OH^-(C_2) \xrightarrow{\text{Oxidation}} ZnO_2^{2-}(C_1) + 2H_2O + 2e^-\ (n = 2)\ (\text{On anode}) \quad ...(a)$$

$$HgO(s) + 2H^+ + 2e^- \xrightarrow{\text{Reduction}} Hg + 2H_2O\ (n = 2)\ (\text{On cathode}) \quad ...(b)$$

Cell reaction is obtained by adding half-reaction (*a*) and (*b*). Thus:

$$Zn(s) + 4OH^-(C_2) \longrightarrow ZnO_2^{2-}(C_1) + 2H_2O + 2e^-$$
$$HgO(s) + 2H^+ + 2e^- \longrightarrow Hg + H_2O$$

On adding:

$$Zn(s) + 4OH^-(C_2) + HgO(s) + 2H^+ \longrightarrow ZnO_2^{2-}(C_1) + Hg + 3H_2O$$

or $$Zn(s) + 2OH^-(C_2) + 2H^+ + 2OH^-(C_2) + HgO(s) \longrightarrow ZnO_2^{2-}(C_1) + Hg + 3H_2O$$

or $$Zn(s) + 2H_2O + 2OH^-(C_2) + HgO(s) \longrightarrow ZnO_2^{2-}(C_1) + Hg + 3H_2O$$

or $$Zn(s) + 2OH^-(C_2) + HgO(s) \longrightarrow ZnO_2^{2-}(C_1) + Hg + H_2O$$

This reaction takes place for the passage of two faradays ($n = 2$) of electricity per mole of $Zn(s)$.

(*iii*) In the given cell, Pt, $H_2(g)|HCl$ solution or Pt, $H_2(g)|H^+(aq)$ electrode acts as anode and $Hg_2Cl_2(s)|Hg$ electrode acts as cathode. On anode $H_2(g)$ is oxidised to $H^+(aq)$ ion and on cathode Hg_2Cl_2 (mercurous chloride) is reduced to metallic mercury, Hg

$$H_2(g) \xrightarrow{\text{Oxidation}} 2H^+(aq) + 2e^-\ (n=2)\ (\textit{On anode}) \quad ...(a)$$

$$Hg_2Cl_2(s) + 2e^- \xrightarrow{\text{Reduction}} 2Hg + 2Cl^-\ (n=2)\ (\textit{On cathode}) \quad ...(b)$$

Cell reaction is obtained by adding the above two half-reactions:

$$H_2(g) + Hg_2Cl_2(s) \longrightarrow 2H^+(aq) + 2Cl^- + 2Hg$$

This reaction takes place for the passage of two faradays of electricity ($n = 2$) for two moles of $H^+(aq)$ ions formed.

(*iv*) The given cell contains two electrodes *viz.* Pt, $H_2(g)|H^+(aq)$ (anode) and Pt, $O_2(g)|OH^-(aq)$ (cathode). On anode oxidation of $H_2(g)$ to $H^+(aq)$ ions takes place and on cathode $O_2(g)$ is reduced to $OH^-(aq)$ ions.

(*a*) $[H_2(g) \xrightarrow{\text{Oxidation}} 2H^+(aq) + 2e] \times 2$ (*At anode*)

$(H = 0) \qquad (H = +1)$

(*b*) $O_2(g) + 2H^+ + 4e \xrightarrow{\text{Reduction}} 2OH^-(aq)$ (*At cathode*)

$(O = 0) \qquad (O = -2)$

Cell reaction is obtained by adding (*a*) and (*b*) half-reaction. Thus:

Cell reaction: $2H_2(g) + O_2(g) \longrightarrow 2H^+(aq) + 2OH^-(aq)$

or $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$(H = 0) \quad (O = 0) \qquad (H = +1, O = -2)$

This reaction proceeds for the passage of two faradays of electricity ($n = 2$) for the formation of one mole of $H_2O(l)$.

(*v*) Cell representation shows that oxidation and reduction half-reaction are:

$$Fe(s) \xrightarrow{\text{Oxidation}} Fe^{2+}(aq) + 2e$$

$$2H^+(aq) + 2e^- \xrightarrow{\text{Reduction}} H_2(g)$$

Cell reaction: $Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$

(*vi*) Cell representation shows that oxidation and reduction half-reaction are:

$$H_2(g) \xrightarrow{\text{Oxidation}} 2H^+(aq) + 2e$$

$$Cl_2(g) + 2e^- \xrightarrow{\text{Reduction}} 2Cl^-(aq)$$

Cell reaction: $H_2(g) + Cl_2(g) \longrightarrow 2H^+(aq) + 2Cl^-(aq)$

(*vii*) In the given cell, LHS electrode (anode) is a gas-gas ion electrode *viz.* Pt, $H_2(g)|H^+(aq)$ and RHS electrode (cathode) is a metal-metal insoluble salt-anion electrode *viz.* $Cl^-(aq)|AgCl(s)|Ag$.

Oxidation on LHS electrode (anode): $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Reduction on RHS electrode (cathode): $AgCl(s) + e^- \longrightarrow Ag + Cl^-(aq)$

$(Ag = +1) \qquad (Ag = 0)$

Cell reaction: $\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag$

(*viii*) LHS electrode (anode) is a gas-gas ion electrode, Pt, $H_2(g)|H^+(aq)$ and RHS electrode (cathode) is a metal-metal ion electrode, $Ag^+(aq)|Ag(s)$. Thus:

Oxidation on anode: $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

Reduction on cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Cell reaction: $\frac{1}{2}H_2(g) + Ag^+(aq) \longrightarrow H^+(aq) + Ag(s)$

(*ix*) The given cell shows that LHS electrode (anode) is a metal-metal insoluble salt-anion electrode, $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)$ and RHS electrode (cathode) is a metal-metal ion electrode, $Hg_2^{2+}(aq)|Hg(l)$. On anode Hg(*l*) is oxidised to $Hg_2Cl_2(s)$ and on cathode $Hg_2^{2+}(aq)$ ions are reduced to Hg(*l*)

$$\underset{(Hg = 0)}{2Hg(l) + 2Cl^-(aq)} \xrightarrow{\text{Oxidation}} \underset{(Hg = +1)}{Hg_2(Cl_2)(s) + 2e^-}$$

$$\underset{(Hg = +1)}{Hg_2^{2+}(aq) + 2e^-} \xrightarrow{\text{Reduction}} \underset{(Hg = 0)}{2Hg(l)}$$

On adding the oxidation and reduction half-reactions given above, we get:

Cell reaction: $Hg_2^{2+}(aq) + 2Cl^-(aq) \longrightarrow Hg_2Cl_2(s)$

Note that since 2Hg(*l*) are common to both the half-reactions and are present on opposite sides, they have been cancelled.

EMF or e.m.f. (E_{cell}) of an electrochemical cell

We know that an electrochemical cell has two electrodes. One electrode has higher electrode potential than the other. The difference between the electrode potentials of the two electrodes (or two half-cells) of an electrochemical cell, when no current is flowing in the circuit (*i.e.* in an open circuit), is called electromotive force (EMF or e.m.f.) of the cell. EMF of a cell is represent as E_{cell}.

EMF of a cell is the measure of the free energy change (ΔG) which determines the tendency of the cell reaction (redox reaction) to occur. The relation between EMF and ΔG is given by:

$$\Delta G = -nFE_{cell}$$

Here n = No. of electrons involved in the redox reaction

F = 1 Faraday of electricity = 95600 coulombs

E_{cell} = EMF of the galvanic cell

Standard e.m.f. (E^0_{cell}) of a galvanic cell

Standard e.m.f. of a galvanic cell is the difference between the standard electrode potentials of the two electrodes which constitute the cell. It is represented as E^0_{cell}.

To calculate standard e.m.f. (E^0_{cell}) of a given galvanic cell.

Suppose we are given the following galvanic cell whose standard e.m.f. (E^0_{cell}) is to be calculated.

$$Pb(s)|Pb^{2+}(aq)||Ag^+(aq)|Ag(s)$$

Given: $E^0_{Pb^{2+}/Pb} = -0.13$ V and $E^0_{Ag^+/Ag} = +0.80$ V

The given cell can also be written as:

$$\underset{\substack{\text{Anode or oxidation}\\ \text{electrode or left}\\ \text{electrode}}}{\mathrm{Pb}(s)\,|\,\mathrm{Pb}^{2+}(aq)} \quad \| \quad \underset{\substack{\text{Cathode or reduction}\\ \text{electrode or right}\\ \text{electrode}}}{\mathrm{Ag}^{+}(aq)\,|\,\mathrm{Ag}(s)}$$

E^0_{cell} of the galvanic cell can be calculated by using any of the equations from (*i*) to (*iv*).

Since oxidation takes place on anode (oxidation electrode) and reduction takes place on cathode (reduction electrode), E^0_{cell} is given by:

$$\left.\begin{aligned} E^0_{cell} &= (E^0_{ox})_{Anode} + (E^0_{red})_{Cathode} \\ &= (E^0_{ox})_{Left} + (E^0_{red})_{Right} \end{aligned}\right\} \qquad \ldots(i)$$

$$= E^0_{Pb/Pb^{2+}} + E^0_{Ag^+/Ag} = +0.13 + 0.80 = \mathbf{0.93\ V\ (Answer)}$$

Now since $(E^0_{red})_{Cathode} = (-E^0_{ox})_{Cathode}$, equation (*i*) can also be written as:

$$\left.\begin{aligned} E^0_{cell} &= (E^0_{ox})_{Anode} - (E^0_{ox})_{Cathode} \\ &= (E^0_{ox})_{Left} - (E^0_{ox})_{Right} \end{aligned}\right\} \qquad \ldots(ii)$$

$$= E^0_{Pb/Pb^{2+}} - E^0_{Ag/Ag^+}$$

$$= +0.13 - (-0.80) = 0.13 + 0.80 = \mathbf{0.93\ V\ (Answer)}$$

Since $(E^0_{ox})_{Anode} = (-E^0_{red})_{Anode}$, equation (*i*) can also be written as:

$$\left.\begin{aligned} E^0_{cell} &= (-E^0_{red})_{Anode} + (E^0_{red})_{Cathode} \\ &= (E^0_{red})_{Cathode} - (E^0_{red})_{Anode} \\ &= (E^0_{red})_{Right} - (E^0_{red})_{Left} \end{aligned}\right\} \qquad \ldots(iii)$$

$$= E^0_{Ag^+/Ag} - E^0_{Pb^{2}/Pb} = +0.80 - (-0.13)$$

$$= \mathbf{0.93\ V\ (Answer)}$$

Now since in a galvanic cell, $(E^0_{red})_{Cathode}$ is always higher than $(E^0_{red})_{Anode}$, equation (*iii*) can be written as:

$$E^0_{cell} = (E^0_{red})_{Higher} - (E^0_{red})_{Lower} \qquad \ldots(iv)$$

$$= E^0_{Ag^+/Ag} - E^0_{Pb^{2+}/Pb} = +0.80 - (-0.13)$$

$$= \mathbf{0.93\ V\ (Answer)}$$

Solved Examples

Example 1. *Calcualte e.m.f. of the following cell.*

$$Pt,\ H_2(g)\,|\,HCl\,(solution)\,|\,AgCl(s)\,|\,Ag(s)$$

Given that $E^0_{AgCl/Ag} = +0.222\ V$

Solution. The given cell shows that since $H_2(g)$ is oxidised to $H^+(aq)$ on $H_2(g)|H^+(aq)$ electrode, this electrode acts as anode. Similarly since AgCl(s) is reduced to Ag(s) on AgCl/Ag electrode, this electrode is cathode. Thus e.m.f. the given cell

$$= [E^0_{\text{red}}]_{\text{cathode}} - [E^0_{\text{red}}]_{\text{anode}} = E^0_{\text{AgCl/Ag}} - E^0_{\text{H}_2/2\text{H}^+}$$

$$= +0.222 - 0.0 = \mathbf{+0.222\ V}$$ **(Answer)**

Example 2. *The e.m.f. of the following two cells are given as:*

(i) $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu;\quad E^0_{cell} = +1.10\ V$

(ii) $Ag|Ag^+(1M)||Cu^{2+}(1M)|Cu;\quad E^0_{cell} = -0.46\ V$

Calculate e.m.f. of the following cell

$$Zn|Zn^{2+}(1M)||Ag^+(1M)|Ag$$

(A.I.S.B. 1989)

Solution. The redox reactions taking place in cells (*i*) and (*ii*) can be written as:

$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu};\quad E^0_{\text{cell}} = +\ 1.10\ \text{V}$$

$$\text{Ag} + \text{Cu}^{2+} \longrightarrow \text{Ag}^+ + \text{Cu};\quad E^0_{\text{cell}} = -\ 0.46$$

On subtracting we get:

$$\text{Zn} - \text{Ag} \longrightarrow \text{Zn}^{2+} - \text{Ag}^+;\quad E^0_{\text{cell}} = 1.10 - (-\ 0.46) = +1.56\ \text{V}$$

or $$\text{Zn} + \text{Ag}^+ \longrightarrow \text{Zn}^{2+} + \text{Ag};\quad E^0_{\text{cell}} = +1.56\ \text{V}$$

This redox reaction is the reaction that takes place in the cell. Obviously e.m.f. of this cell is equal to **1.56 V (Answer).**

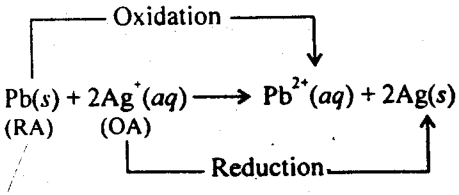
To calculate standard e.m.f. (or $E^0_{\text{redox reaction}}$) of a given redox reaction, if E^0 values of two electrodes or their half-reactions are given

Suppose we are required to determine the value of $E^0_{\text{redox reaction}}$ of the following redox reaction

$$\text{Pb}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Pb}^{2+}(aq) + 2\text{Ag}(s)$$

Given that $E^0_{\text{Pb}^{2+}/\text{Pb}} = -0.13\ \text{V}$ and $E^0_{\text{Ag}^+/\text{Ag}} = +0.80\ \text{V}$

For determining the value of $E^0_{\text{redox reaction}}$, write the given redox reaction as:



$$\text{Pb}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Pb}^{2+}(aq) + 2\text{Ag}(s)$$

$E^0_{\text{redox reaction}}$ can be calculated by using any of the following equations *viz.* (*i*), (*ii*) and (*iii*).

In the given redox reaction, since Pb(s) is being oxidised to $Pb^{2+}(aq)$ and $Ag^+(aq)$ ions are being reduced to Ag(s), Pb(s) acts as a RA and $Ag^+(aq)$ ions act as OA. Thus $E^0_{\text{redox reaction}}$ is given by:

$$E^0_{\text{redox reaction}} = E^0_{\text{OA}} - E^0_{\text{RA}} \qquad ...(i)$$

$$= E^0_{Ag^+/Ag} - E^0_{Pb^{2+}/Pb} = 0.80 - (-0.13) = \mathbf{0.93\ V\ (Answer)}$$

Now since Pb(s) is oxidised to $Pb^{2+}(aq)$ and $Ag^+(aq)$ ions are being reduced to Ag(s) as shown below

$$Pb(s) \xrightarrow{\text{Oxidation}} Pb^{2+}(aq) + 2e^- \ (\textit{Oxidation half-reaction})$$

$$2Ag^+(aq) + 2e^- \xrightarrow{\text{Reduction}} 2Ag(s) \ (\textit{Reduction half-reaction})$$

$E^0_{\text{redox reaction}}$ is given by:

$E^0_{\text{redox reaction}}$ = Standard oxidation potential (E^0_{ox}) for oxidation half--reaction + Standard reduction potential (E^0_{red}) for reduction half-reaction ...(*ii*)

$$= E^0_{Pb/Pb^{2+}} + E^0_{Ag^+/Ag} = +0.13 + 0.80 = \mathbf{0.93\ V\ (Answer)}$$

$E^0_{\text{redox reaction}}$ is also given by:

$$E^0_{\text{redox reaction}} = (E^0_{\text{red}})_{\text{higher}} - (E^0_{\text{red}})_{\text{lower}} \qquad ...(iii)$$

$$= E^0_{Ag^+/Ag} - E^0_{Pb^{2+}/Pb} = +0.80 - (-0.13)$$

$$= +\mathbf{0.93\ V\ (Answer)}$$

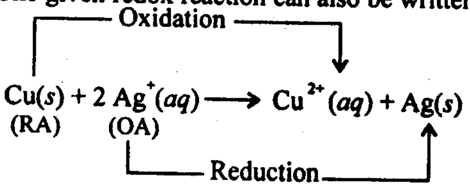
Solved Examples

Example 1. *Calculate e.m.f. of the following redox reaction:*

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + Ag(s)$$

Given that: $E^0_{Cu^{2+}/Cu} = +0.34$ *V and* $E^0_{Ag^+/Ag} = +0.80$ *V.*

Solution. The given redox reaction can also be written as:



Obviously, e.m.f. of the given redox reaction may be calculated by any of the following equations:

(*i*) e.m.f. of the redox reaction = $E^0_{OA} - E^0_{RA} = E^0_{Ag^+/Ag} - E^0_{Cu^+/Cu}$

$= +0.80 - 0.34 = \mathbf{+0.46\ V\ (Answer)}$

(*ii*) e.m.f. of the redox reaction = $E^0_{Cu/Cu^{2+}} + E^0_{Ag^+/Ag}$

$= -0.34 + 0.80 = \mathbf{+0.46\ V\ (Answer)}$

(*iii*) e.m.f. of the redox reaction = $(E^0_{red})_{higher} - (E^0_{red})_{lower}$

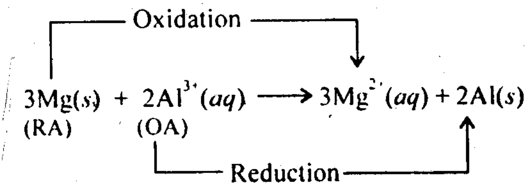
$= 0.80 - 0.34 = \mathbf{+0.46\ V\ (Answer)}$

Example 2. *Calculate e.m.f. of the following redox reaction:*

$$3Mg(s) + 2Al^{3+}(aq) \longrightarrow 3Mg^{2+}(aq) + 2Al(s)$$

Given: $E^0_{Al^{3+}/Al} = -1.66\ V,\ E^0_{Mg^{2+}/Mg} = -2.36\ V.$

Solution. The given redox reaction can also be written as:



Obviously, e.m.f. of the given redox reaction can be calculated by any of the following equations:

(*i*) e.m.f. of the redox reaction = $E^0_{OA} - E^0_{RA} = E^0_{Al^{3+}/Al} - E^0_{Mg^{2+}/Mg}$

$= -1.66 - (-2.36) = -1.66 + 2.36$

$= \mathbf{+0.70\ V\ (Answer)}$

(*ii*) e.m.f. of the redox reaction = $E^0_{Mg/Mg^{2+}} + E^0_{Al^{3+}/Al}$

$= +2.36 + (-1.66)$

$= \mathbf{+0.70\ V\ (Answer)}$

(*iii*) e.m.f. of the redox reaction = $(E^0_{red})_{higher} - (E^0_{red})_{lower}$

$= E^0_{Al^{3+}/Al} - E^0_{Mg^{2+}/Mg}$

$= -1.66 - (-2.36) = \mathbf{+0.70\ V\ (Answer)}$

Example 3. *e.m.f. of the redox reaction (cell reaction),*

$$Ni(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Ni^{2+}(aq)$$

is 0.59 V. Calculate the standard reduction potential of Ni-electrode, if standard reduction potential of Cu-electrode is 0.34 V.

Solution. The redox reaction is:

$$\underset{(RA)}{Ni(s)} + \underset{(OA)}{Cu^{2+}(aq)} \longrightarrow Cu(s) + Ni^{2+}(aq)$$

Obviously, e.m.f. of the redox reaction $= E^0_{\text{OA}} - E^0_{\text{RA}}$

$$= E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Ni}^{2+}/\text{Ni}}$$

or $$+0.59 = 0.34 - E^0_{\text{Ni}^{2+}/\text{Ni}}$$

$\therefore\ E^0_{Ni^{2+}/Ni} = 0.34 - 0.59 = \mathbf{-0.25\ V}$ **(Answser)**

Example 4. *The e.m.f. of the cell in which the reaction,*

$$2Ag^+(aq) + H_2(g) \longrightarrow 2Ag(s) + 2H^+(aq)$$

occurs is 0.80 V. Calculate the standard reduction electrode potential of $Ag^+(aq)/Ag(s)$ *electrode.*

Solution. The given redox reaction can also be written as:

Oxidation

$$\underset{(\text{OA})}{2\text{Ag}^+(aq)} + \underset{(\text{RA})}{\text{H}_2(g)} \longrightarrow 2\text{Ag}(s) + 2\text{H}^+(aq)$$

Reduction

The value of $E^0_{\text{Ag}^+(aq)/\text{Ag}(s)}$ can be calculated by using any of the following three methods.

Method (*i*). e.m.f. of the given redox reaction is given by:

$$\text{e.m.f.} = E^0_{\text{OA}} - E^0_{\text{RA}} = E^0_{\text{Ag}^+/\text{Ag}} - E^0_{2\text{H}^+/\text{H}_2}$$

$$0.80 = E^0_{Ag^+/Ag} - 0.0$$

$$\therefore\quad E^0_{Ag^+/Ag} = \mathbf{+0.80\ V}\ \textbf{(Answer)}$$

Method (*ii*). e.m.f. of the given redox reaction can also be given by:

e.m.f. $= E^0_{\text{ox}}$ for oxidation half-reaction

$+ E^0_{\text{red}}$ for reduction half-reaction

or $$0.80 = E^0_{\text{H}_2/\text{H}^+} + E^0_{\text{Ag}^+/\text{Ag}}$$

or $$0.80 = 0 + E^0_{\text{Ag}^+/\text{Ag}}$$

$\therefore\ E^0_{\text{Ag}^+/\text{Ag}} = \mathbf{+0.80\ V}$ **(Answer)**

Method (*iii*). e.m.f. is also given by:

$$\text{e.m.f.} = \left(E^0_{\text{red}}\right)_{\text{higher}} - \left(E^0_{\text{red}}\right)_{\text{lower}} = E^0_{\text{Ag}^+/\text{Ag}} - E^0_{2\text{H}^+/\text{H}_2}$$

$$0.80 = E^0_{Ag^+/Ag} - 0$$

$\therefore\ E^0_{\text{Ag}^+/\text{Ag}} = \mathbf{+0.80V}$ **(Answer)**

To determine e.m.f. of a redox reaction (cell reaction) formed by combining two electrodes.

Suppose we are given two etectrodes *viz.* Pb^{2+}/Pb and Ag^+/Ag whose standard reduction electrode potentials are -0.13V and $+0.80$V respectively. We are required to calculate e.m.f. of the redox reaction formed by combining the reduction half-reactions corresponding to the given electrodes. e.m.f. of such a redox reaction is given by:

$$\text{e.m.f. of redox reaction or } E^0_{\text{redox reaction}} = E^0_{\text{Higher}} - E^0_{\text{Lower}}$$
$$= E^0_{Ag^+/Ag} - E^0_{Pb^{2+}/Pb}$$
$$= [0.80 - (-0.13)]\text{V}$$
$$= +\mathbf{0.93\ V\ (Answer)}$$

Illustrative Example. *Calculate the standard potential, if standard potentials of Cu^{2+}/Cu and Zn^{2+}/Zn elcetrodes are 0.34 V and – 0.76 V respectively.*

Solution. Standard cell potential $= E^0_{\text{higher}} - E^0_{\text{lower}}$

$$= E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$$
$$= [0.34 - (-0.76)]\text{ V}$$
$$= +\mathbf{1.10V\ (Answer)}$$

Summary of the main points about a galvanic (electro-chemical) cell

A galvanic cell has the following characteristics:

(*i*) The electrode at which oxidation half-reaction takes place is called anode or oxidation electrode while the electrode at which reduction half-reaction occurs is called cathode or reduction electrode. Anode is LHS electrode and cathode in RHS electrode. This discussion can be summarised by saying that oxidation takes place on anode and reduction occurs on cathode.

(*ii*) The two half-reactions always take place simultaneously, *i,e.* half-reactions cannot take place indepedently.

(*iii*) Anode is rich in electrons, since electrons are produced on anode due to oxidation. Anode pushes these electrons into the external circuit and hence acts as negative pole. On the other hand, cathode in deficient in electrons, since it needs electrons to undergo reduction. For bringing about reduction on cathode, cathode pulls the eleclrons from the external circuit. Thus cathode acts as positive pole. This discussion shows that electrons flow from the negative pole (anode) to the positive pole (cathode) in the external circuit. However, current is said to flow in the opposite direction i.e. from cathode to anode. Flow of current (electricity) is due to the flow of electrons in the external circuit and due to the flow of ions through the solution in the inner circuit.

(*iv*) In a galvanic cell, the electrode having higher (*i.e.* more positive or less negative) value of E^0 acts as cathode (RHS electrode) and that having lower (*i.e.* less positive or more negative) value of E^0

acts as anode (LHS elcetrode) *i.e.* in a galvanic cell the value of E^0 of cathode is always higher then the value of E^0 of anode ($E^0_{\text{cathode}} > E^0_{\text{anode}}$). In other words we can say that :

Higher makes cathode and lower makes anode.

(*v*) If, in an electrochemical cell, $\left[E^0_{\text{red}}\right]_{\text{cathode}}$ is not greater than $\left[E^0_{\text{red}}\right]_{\text{anode}}$, the given notation of the cell is wrong. In order to get the correct representation of the cell, the position of electrodes should be interchanged *i.e.* anode of the wrong notation should be made cathode of the correct notation and cathode of the wrong notation shold be made anode of the correct notation.

(*vi*) If E^0 values of two electrodes or reduction half-reactions are given, then the reduction half-reaction having high value of E^0 (more positive or less negative) will occur as reduction half-reaction on cathode (reduction electrode) and reduction half-reaction having lower value of E^0 (less positive or more negative) will occur as oxidatiion half-reaction on anode (oxidation electrode).

(*vii*) The reaction taking place in a galvanic cell in a redox reaction and is called cell reaction . Cell reaction is the sum of oxidation half-reaction taking place on anode and reductiion half- reaction taking place on cathode.

(*viii*) e.m.f. of a galvanic cell is represented as E^0_{cell}. The value of E^0_{cell} can be calculated by using any of the following equations from (*a*) to (*d*)

$$E^0_{\text{cell}} = (E^0_{\text{ox}})_{\text{Anode}} + (E^0_{\text{red}})_{\text{Cathode}} = (E^0_{\text{ox}})_{\text{Left}} + (E^0_{\text{red}})_{\text{Right}} \quad ...(a)$$

$$E^0_{\text{cell}} = (E^0_{\text{ox}})_{\text{Anode}} - (E^0_{\text{ox}})_{\text{Cathode}} = (E^0_{\text{ox}})_{\text{Left}} - (E^0_{\text{ox}})_{\text{Right}} \quad ...(b)$$

$$E^0_{\text{cell}} = (E^0_{\text{red}})_{\text{Cathode}} - (E^0_{\text{red}})_{\text{Anode}} = (E^0_{\text{red}})_{\text{Right}} - (E^0_{\text{red}})_{\text{Left}} \quad ...(c)$$

$$E^0_{\text{cell}} = (E^0_{\text{red}})_{\text{Higher}} - (E^0_{\text{red}})_{\text{Lower}} \quad ...(d)$$

(*ix*) We have shown above that:

$$E^0_{\text{cell}} = (E^0_{\text{red}})_{\text{cathode}} - (E^0_{\text{red}})_{\text{anode}}$$

Now since $[E^0_{\text{red}}]_{\text{cathode}} > [E^0_{\text{red}}]_{\text{anode}}$, the quantity, $[E^0_{\text{red}}]_{\text{cathode}} - [E^0_{\text{red}}]_{\text{anode}}$ is always a positive quantity, *i.e.* E^0_{cell} is always a positive quantity.

(*x*) It the value of E^0_{cell} comes out to be negative, then the cell reaction will not take place spontaneously in the forward direction (from left to right); rather it will take place in the opposite direction (from right to left).

(*xi*) In an electrochemical cell, both the electrodes are placed in two different containers which have different electrolytes separated from each other by salt bridge or porous partition.

(*xii*) The two electrodes that constitute a galvanic cell are of different material.

Illustrative Example. *The Edison storage cell is represented as:*

$$Fe(s)\,|\,FeO(s)\,|\,KOH(aq)\,|\,Ni_2O_3(s)\,|\,NiO(s)$$

The half-cell reactions are:

(*a*) $Ni_2O_3(s) + H_2O(l) + 2e^- \longrightarrow 2NiO(s) + 2OH^-, E^0 = +0.40\ V$

(*b*) $FeO(s) + H_2O(l) + 2e^- \longrightarrow Fe(s) + 2OH^-, E^0 = -0.87\ V$

(*i*) *What is the cell reaction?*

(*ii*) *What is the cell e.m.f.? How does it depend on the concentration of KOH ?*

(*iii*) *What is the maximum amount of electrical energy that can be obtained from one mole of* Ni_2O_3*?* (*I.I.T. 1994*)

Solution. (*i*) We know that in a galvanic cell, the reduction half-reaction having lower value of E^0_{red} will occur as oxidation half-reaction and the reduction half-reaction having higher value of E^0_{red} will occur as reduction half-rection. Now since $[E^0_{red}]_a > [E^0_{red}]_b$, half-reaction (*b*) will occur as oxidation half-reaction and half-reaction (*a*) will take place as reduction half reaction. Thus :

$$Fe(s) + 2OH^- \xrightarrow{\text{oxidation}} FeO(s) + H_2O(l) + 2e^-;\ E^0_{ox} = +0.87\ V$$

$$Ni_2O_3(s) + H_2O(l) + 2e^- \xrightarrow{\text{Reduction}} 2NiO(s) + 2OH^-(aq);\ E^0_{red} = +0.40V$$

On adding we gat :

$$Fe(s) + Ni_2O_3(s) \longrightarrow FeO(s) + 2NiO(s) \quad \text{..................}(i)$$

This is the cell reaction

(*ii*) Cell e.m.f. = $E^0_{ox} + E^0_{red} = +0.87 + 0.40 =$ **1.27 V (Answer)**

Cell e.m.f. does not depend on the concentration of KOH, since KOH is not involved in the cell reaction [reaction (*i*) given above].

(*iii*) The maximum electrical energy (ΔG) obtained per mole of Ni_2O_3 (cell reaction has only one mole of Ni_2O_3) is given by:

$\Delta G = -nF \times$ (e.m.f. the cell) $= -2 \times (96500\ C.mol^{-1}) \times 1.27\ V$

$= \mathbf{-2.4511 \times 10^5\ J\ mol^{-1}}$ **(Answer)**

Electrochemical Series

Etectrochemical series is an arrangement of various electrodes having dissolved ions at 1 M concentration at 298 K or of various reduction half-reactions (half-cell reduction reactions) taking place on the electrodes. These electrodes or reduction half-reactions have their E^0 values in the decreasing order (+ ⟶ 0 ⟶ –). Electrochemical series having E^0 (standard reduction electrode potential) values (in the decreasing order) of some electrodes has been given in Table 22.2)

Table 22.2. Standared reduction electrode potential values (E^0 values) of some electrodes or of some reduction half-reactions.

Reduction half-reactions (Half-cell reduction reactions)			
Oxidised form (OA)		Reduced form (RA)	E^0 values (volts)
$F_2 + 2e^-$	$\rightleftharpoons$	$2F^-$	+2.85
Strongest oxidising agent		*Weakest reducing agent*	
$O_3 + 2H^+ + 2e^-$	$\rightleftharpoons$	$O_2 + H_2O$	+.07
$H_2O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	$2H_2O$	+1.77
$MnO_4^- + 4H^+ + 3e^-$	$\rightleftharpoons$	$MnO_2 + 2H_2O$	+1.69
$Au^+ + e^-$	$\rightleftharpoons$	Au	+1.68
$HClO_3 + 4H^+ + 4e^-$	$\rightleftharpoons$	$HClO + 2H_2O$	+1.64
$2HClO + 2H^+ + 2e^-$	$\rightleftharpoons$	$Cl_2 + 2H_2O$	+1.64
$Ce^{4+} + e^-$	$\rightleftharpoons$	Ce^{3+}	+1.61
$2BrO_3^- + 12H^+ + 10e^-$	$\rightleftharpoons$	$Br_2 + 6H_2O$	+1.52
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	+1.51
$Au^{3+} + 3e^-$	$\rightleftharpoons$	Au	+1.42
$Cl_2 + 2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightleftharpoons$	$2Cr^{3+} + 7H_2O$	+1.33
$2IO_3^- + 12H^+ + 10e^-$	$\rightleftharpoons$	$I_2 + 6H_2O$	+1.20
$Pt^{2+} + 2e^-$	$\rightleftharpoons$	Pt	+1.20
$IO_3^- + 6H^+ + 6e^-$	$\rightleftharpoons$	$I^- + 3H_2O$	+1.09
$Br_2 + 2e^-$	$\rightleftharpoons$	$2Br^-$	+1.06
$Hg^{2+} + 2e^-$	$\rightleftharpoons$	Hg	+0.85
$Ag^+ + e^-$	$\rightleftharpoons$	Ag	+0.80
$Fe^{3+} + e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77
$O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	H_2O_2	+0.68
$H_3AsO_4 + 2H^+ + 2e^-$	$\rightleftharpoons$	$H_3AsO_3 + H_2O$	+0.56
$I_2 + 2e^-$	$\rightleftharpoons$	$2I^-$	+0.53
$Cu^+ + e^-$	$\rightleftharpoons$	Cu	+0.52
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	Cu	+0.34
$Bi^{3+} + 3e^-$	$\rightleftharpoons$	Bi	+0.32
$Cu^{2+} + e^-$	$\rightleftharpoons$	Cu^+	+0.15
$Sn^{4+} + 2e^-$	$\rightleftharpoons$	Sn^{2+}	+0.15
$S_4O_6^{2-} + 2e^-$	$\rightleftharpoons$	$2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^-$	$\rightleftharpoons$	H_2	±0.00 (By definition)
$Pb^{2+} + 2e^-$	$\rightleftharpoons$	Pb	−0.13

E^0 values decreasing ↓

Reduction half-reactions (Half-cell reduction reactions)				
Oxidised form (OA)		Reduced form (RA)	E^0 values (volts)	
$Sn^{2+} + 2e^-$	$\rightleftharpoons$	Sn	-0.14	E^0 values decreasing ↓
$Ni^{2+} + 2e^-$	$\rightleftharpoons$	Ni	-0.24	
$Co^{2+} + 2e^-$	$\rightleftharpoons$	Co	-0.28	
$Cd^{2+} + 2e^-$	$\rightleftharpoons$	Cd	-0.40	
$Cr^{3+} + e^-$	$\rightleftharpoons$	Cr^{2+}	-0.41	
$Fe^{2+} + 2e^-$	$\rightleftharpoons$	Fe	-0.44	
$S + 2e^-$	$\rightleftharpoons$	S^{2-}	-0.51	
$Cr^{3+} + 3e^-$	$\rightleftharpoons$	Cr	-0.71	
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	-0.76	
$Mn^{2+} + 2e^-$	$\rightleftharpoons$	Mn	-1.05	
$Al^{3+} + 3e^-$	$\rightleftharpoons$	Al	-1.67	
$Be^{2+} + 2e^-$	$\rightleftharpoons$	Be	-1.70	
$H_2 + 2e^-$	$\rightleftharpoons$	$2H^-$	-2.24	
$La^{3+} + 3e^-$	$\rightleftharpoons$	La	-2.37	
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	-2.38	
$Na^+ + e^-$	$\rightleftharpoons$	Na	-2.71	
$Ca^{2+} + 2e^-$	$\rightleftharpoons$	Ca	-2.76	
$Sr^{2+} + 2e^-$	$\rightleftharpoons$	Sr	-2.89	
$Ba^{2+} + 2e^-$	$\rightleftharpoons$	Ba	-2.90	
$M^+ + e^-$ (M = K, Rb, Cs)	$\rightleftharpoons$	M	-2.92	
$Li^+ + e^-$	$\rightleftharpoons$	Li	-3.04	
Weakest oxidising agent		*Strongest reducing agent*		

Main features of electrochemical series.

Main features of the electro chemical series given at Table 22.2 are:

1. Oxidising and reducing agents. The species written on LHS of each of the reduction half-reactions accept electons and hence are called oxidised forms or oxidising agents (OAs). These OAs, after accepting electrons, are converted into the species written on RHS. These species are, therefore, called reduced forms or reducing agents (RAs).

2. Variation of E^0 values on moving down the series. If we look at E^0 values given in the electrochemical series, we find that the reduction half-reactions lying above $2H^+ + 2e^- \rightleftharpoons H_2$ have positive E^0 values while the reduction half-reactions lying below $2H^+ + 2e^- \rightleftharpoons H_2$ have negative E^0 values. $2H^+ + 2e^- \rightleftharpoons H_2$ has $E^0 = +0.0$V.

When we consider only those reduction half-reactions which have positive values of E^0, we find that as we move down the series from $F_2 + 2e^- \rightleftharpoons 2F^-$ ($E^0 = +2.85$ V) to $2H^+ + 2e^- \rightleftharpoons H_2$ ($E^0 = +0.0$ V), E^0 values go on becoming less positive, since E^0 value for $F_2 + 2e^- \rightleftharpoons 2F^-$ is the most positive (= +2.85 V) and that for $2H^+ + 2e^- \rightleftharpoons H_2$ is the least positive (= 0.0V). Thus on moving down the series from $F_2 + 2e^- \rightleftharpoons 2F^-$ to $2H^+ + 2e^- \rightleftharpoons H_2$, E^0 values go on decreasing.

Similarly, when we consider only those reduction half-reactions which have negative E^0 values, we find that as we move down the series from $2H^+ + 2e^- \rightleftharpoons H_2$ ($E^0 = -0.0$ V) to $Li^+ + e^- \rightleftharpoons Li$ ($E^0 = -3.04$ V), E^0 values go on becoming more negative, since E^0 values for $2H^+ + 2e^- \rightleftharpoons H_2$ is the least negetive (= – 0.0V) and E^0 value for $Li^+ + 2e^- \rightleftharpoons Li$ is the most negative (= – 3.04 V). Thus on moving down the series from $2H^+ + 2e^- \rightleftharpoons H_2$ to $Li^+ + e^- \rightleftharpoons Li$, E^0 values go on decreasing.

The above discussion shows that as we move down the electrochemical series from $F_2 + 2e^- \rightleftharpoons 2F^-$ to $Li^+ + e^- \rightleftharpoons Li$, E^0 values of the given half-reduction reactions (or electrodes) go on becoming less positive or more negative, *i.e.* E^0 values go on decreasing. The decreasing order of E^0 values has been shown in Fig 22.4.

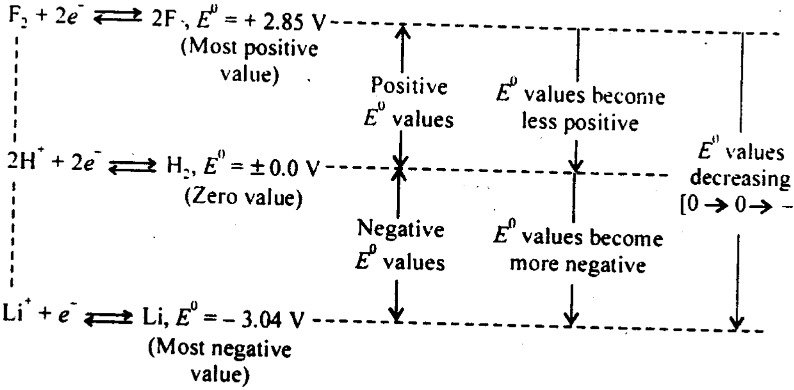


Fig. 22.4. E^0 values decrease down the electrochemical series.

Applications of E^0 values

I.(*a*) To determine the increasing or decreasing order of oxidising/reducing power of elements/ions, if their E^0 values are given

Suppose we are given the following reduction half-reactions along with their E^0 values.

Oxidised form (OA)			Reduced form (RA)	
$2H^+(aq)$	$+ 2e^-$	$\underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}}$	$H_2(g)$,	$E^0 = 0.0$ V
$Zn^{2+}(aq)$	$+ 2e^-$	$\rightleftharpoons$	$Zn(s)$,	$E^0 = -0.76$ V
$Ag^+(aq)$	$+ e^-$	$\rightleftharpoons$	$Ag(s)$,	$E^0 = +0.80$ V
$Cu^{2+}(aq)$	$+ 2e^-$	$\rightleftharpoons$	$Cu(s)$,	$E^0 = +0.34$ V
$Ni^{2+}(aq)$	$+ 2e^-$	$\rightleftharpoons$	$Ni(s)$,	$E^0 = -0.25$ V

In the reduction half-reactions given above the species written on LHS gain electron(s) and hence are reduced to the species (reduced form) written on the RHS. We can also say that the species written on RHS lose electron(s) and hence are oxidised to the species (oxidised form) written on LHS.

Thus the species given on LHS are oxidised forms (*i.e.* oxidising agents which have been abreviated as O.A.) and those given on the RHS are reduced forms (*i.e.* reducing agents, R.A.). The oxiding agents (*i.e.* oxidised forms) have electron-accepting tendency and the reducing agents (*i.e.* reduced forms) have electon-releasing (or electron-losing) tendency.

Now we have to find out how the oxidising power of oxidising agents *viz.* $H^+(aq)$, $Zn^{2+}(aq)$, $Ag^+(aq)$, $Cu^{2+}(aq)$ and $Ni^{2+}(aq)$ and reducing power of reducing agents *viz.* $H_2(g)$, $Zn(s)$, $Cu(s)$ and $Ni(s)$ vary with the decrease in E^0 values. In order to find out this variation, first of all we should write all the given reduction half-reactions in such a way that their E^0 values are in the decreasing order, since these values are also in the decreasing order in the electro-chemical series. Thus the above half-reactions should be written as:

$$\begin{array}{lcll}
\textbf{Oxidised form (OA)} & & \textbf{Reduced form (RA)} & \\
Ag^+(aq) + 2e^- & \xrightarrow{\text{Reduction}} & Ag(s), & E^0 = +0.80\text{ V} \\
Cu^{2+}(aq) + 2e^- & \xrightarrow{\text{Reduction}} & Cu(s), & E^0 = +0.34\text{ V} \\
2H^+(aq) + 2e^- & \xrightarrow{\text{Reduction}} & H_2(g), & E^0 = 0.0\text{ V} \\
Ni^{2+}(aq) + 2e^- & \xrightarrow{\text{Reduction}} & Ni(s), & E^0 = -0.25\text{ V} \\
Zn^{2+}(aq) + 2e^- & \xrightarrow{\text{Reduction}} & Zn(s), & E^0 = -0.76\text{ V}
\end{array}$$

E^0 values decreasing ↓

Before entering into the discussion, we should understand the meaning of stronger and weaker oxidising agent and reducing agent. Stronrger oxidising agent is that which gains electrons more readily while weaker oxidising agent is that which gains electrons less readily. Thus stronger oxidising agent gains electrons more readily than weaker oxidising agent. In other words we say that stronger oxidising agent is more easily reduced than the weaker oxidising agent.

Similarly. stronger reducing agent is that which loses electrons more readily while weaker reducing agent does so less readily. Thus stronger reducing agent loses electrons more readily than weaker reducing agent. In other words we say that stronger reducing agent is more easily oxidised than weaker reducing agent.

Since E^0 value for the reduction half-reaction,

$$\underset{\substack{\text{(Strongest OA)}\\\text{(Oxidised form)}}}{Ag^+(aq)} + e^- \xrightarrow{\text{Reduction}} \underset{\substack{\text{(Weakest R.A)}\\\text{(Reduced form)}}}{Ag(s)} \quad (E^0 = +0.80\text{ V}),$$

is the largest (= + 0.80 V), we can conclude the following :

(*a*) This reduction half-reaction takes place most readily, *i.e.* this reaction has maximum tendency to proceed towards right. However, the reverse of this reaction [*i.e.* $Ag(s) \rightarrow Ag^+(aq) + e^-$ in which Ag(s) is oxidised to $Ag^+(aq)$] takes place least readily.

(*b*) The oxidised form of this reaction, $Ag^+(aq)$ has maximum tendency to gain electron, *i.e.* electron-gaining tendency of the oxidised form in this reaction is maximum.

(*c*) Oxidised form, $Ag^+(aq)$ in this reaction has maximum tendency to get reduced to the reduced form, Ag(*s*), *i.e.* oxidised form, $Ag^+(aq)$ is reduced to the reduced form, Ag(*s*) most readily. This means that the oxidising agent (abbreviated as O.A.) [*i.e* oxidised form, $Ag^+(aq)$] of this reaction is strongest O.A. and hence reducing agent [*i.e.* reduced form, Ag(*s*)] of this reaction is the weakest R.A. Thus $Ag^+(aq)$ in the strongest O.A. and Ag(*s*) is the weakest R.A

Similarly, since E^0 value for the reduction half-reduction,

$$\underset{\substack{\text{(Weakest O.A)}\\ \text{(Oxidised form)}}}{Zn^{2+}(aq)} \quad + \quad 2e^- \xrightarrow{\text{Reduction}} \underset{\substack{\text{(Strongest R.A.)}\\ \text{(Reduced form)}}}{Zn(s)} \qquad (E^0 = -0.76\text{ V}),$$

is the lowest (= – 0.76 V), we can conclude the following :

(*a*) This reduction half-reaction takes place least readily, *i.e.* this reaction has minimum tendency to proceed towards right. However, the reverse of this reaction [*i.e.* $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ in which Zn(*s*) is oxidised to $Zn^{2+}(aq)$] takes place most readily.

(*b*) The oxidised form of this reaction, $Zn^{2+}(aq)$ has minimum tendency to gain electrons, *i.e.* electron-gaining tendency of the oxidised form of this reaction is minimum.

(*c*) Oxidised form, $Zn^{2+}(aq)$ of this reaction has minimum tendency to get reduced to the reduced form, Zn(*s*), *i.e.* the oxidised form is reduced to the reduced form least readily. This means that the O.A. [*i.e.* oxidised form , $Zn^{2+}(aq)$] of this reaction is the weakest O.A. and hence the R.A. [*i.e.* reduced form, Zn(*s*)] of this reaction is the strongest R.A. Thus $Zn^{2+}(aq)$ is the weakest O.A. and Zn(*s*) is the strongest R.A.

The above discussion shows that as the value of E^0 decreases downwards,

(*a*) The tendency of the reduction half-reaction (forward reaction) to proceed from left to right (→)decreases but the tendeney of the oxidation half-reaction (*i.e.* backward reaction) to proceed from right to left (←) increases.

$$Ag^+(aq) + e^- \underset{\substack{\text{Oxidation takes}\\ \text{place least readily.}}}{\overset{\substack{\text{Reduction takes}\\ \text{place most readily}}}{\rightleftarrows}} Ag(s),\ E^0 = +0.80\text{ V } (\textit{Maximum value})$$

$$Zn^{2+}(aq) + 2e^- \underset{\substack{\text{Oxidation takes}\\ \text{place most readily.}}}{\overset{\substack{\text{Reduction takes}\\ \text{place least readily}}}{\rightleftarrows}} Zn(s),\ E^0 = -0.76\text{ V } (\textit{Minimum value})$$

(*b*) Oxidising power of oxidising agents (oxidised forms) decreases and hence reducing power of reducing agents (reduced forms) increases, *i.e.* oxidising power of OAs is directly proportional to the magnitude of E^0 and hence reducing power of RAs is inversely proportional to the magnitude of E^0. Both the above points have been shown in Fig. 22.5 which shows that oxidising power of oxidising agents and reducing power of reducing agents are in the order :

Oxidising power : $Ag^+(aq) > Cu^{2+}(aq) > H^+(aq) > Ni^{2+}(aq) > Zn^{2+}(aq)$

Reducing power : $Ag(s) < Cu(s) < H_2(g) < Ni(s) < Zn(s)$

Oxidised form (OA) — **Reduced form (RA)**

$Ag^+(aq) + e^- \xrightarrow{\text{Reduction}} Ag(s)$, $E^0 = +0.80$ V (Largest value)

(Strongest OA) — (Weakest RA)

Oxdising power decreases ↓ — Reducing power increases ↓ — E^0 values decrease ↓

$Zn^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} Zn(s)$, $E^0 = -0.76$ V (Lowest value)

(Weakest OA) — (Strongest RA)

Fig. 22.5. Variation of oxidising power of oxidising agents and reducing power of reducing agents with the decrease of E^0 values.

(*b*) To explain why among alkali metals, lithium in aqueous solution is the strongest reducing agent

We know that among alkali metals Li has the maximum ionisation energy (Li = 520.3 kJ/mole, Na = 495.8, K = 418.9, Rb = 403.9, Cs = 357.7). Maximum value of ionisation energy suggests that it should be very difficult for Li-atom to lose an electron to get oxidised to Li^+ ion and hence Li-metal should be the weakest reducing agent. However, experiments have shown that in aqueous solution, Li metal can lose its $2s^1$ electron (Li = $1s^2, 2s^1$) quite readily and get oxidised to $Li^+(aq)$. Thus Li metal in aqueous solution is the strongest R.A.

$$\underset{\text{RA}}{Li(s)} \xrightarrow{\text{Oxidation}} \underset{\text{OA}}{Li^+(aq)} + e^-$$

In order to explain this fact let us consider the reduction half-reactions involving alkali metals and their monovalent cations along with their E^0 values as given below:

Oxidised form (OA) — **Reduced form (RA)**

$$Li^+(aq) + e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftarrows}} Li(s) \quad E^0_{Li^+/Li} = -3.040 \text{ V}$$

(Strongest RA) (Most negative value)

$$Na^+(aq) + e^- \longrightarrow Na(s) \quad E^0_{Na^+/Na} = -2.717 \text{ V}$$

$K^+(aq) + e^- \longrightarrow K(s) \qquad E^0_{K^+/K} = -2.925\text{ V}$

$Rb^+(aq) + e^- \longrightarrow Rb(s) \qquad E^0_{Rb^+/Rb} = -2.925\text{ V}$

$Cs^+(aq) + e^- \longrightarrow Cs(s) \qquad E^0_{Cs^+/Cs} = -2.923\text{ V}$

It may be seen from E^0 values that $Li^+(aq) + e^- \rightarrow Li(s)$ reduction half-reaction has the minimum value of E^0 (most negative value) and hence this half-reaction which proceeds from left to right takes place least readily but the oxidation half-reaction which proceeds from right to left [$Li(s) \rightarrow Li^+(aq) + e^-$] takes place most readily, *i.e.* Li(*s*) metal is aqueous solution is most readily oxidised to $Li^+(aq)$ ion by losing an electron and hence this metal in aqueous solution is the strongest RA among alkali metals.

(*c*) Reducing power of alkaline earth metals in aqueous solution

Alkaline earth metals [M(*s*)] can easily lose their ns^2 electrons and get oxidised to $M^{2+}(aq)$ in aqueous solution. Thus alkaline earth metals act as reducing agents in aqueous solution.

$$\underset{(RA)}{M(s)} \xrightarrow{\text{oxidation}} \underset{(OA)}{M^{2+}(aq)} + 2e^-$$

In order to find out the relative order of reducing power of alkaline earth metals like Mg, Ca and Ba, let us consider the reduction half-reactions involving these metals and their divalent cations (Mg^{2+}, Ca^{2+} and Ba^{2+}) along with their E^0 values as given below:

Oxidised form **Reduced form**
(OA) **(RA)**

$Mg^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} Mg(s) \qquad E^0_{Mg^{2+}/Mg} = -2.37\text{ V}$
(Strongest OA) (Weakest RA) (Largest value)

$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s) \qquad E^0_{Ca^{2+}/Ca} = -2.87\text{ V}$

$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s) \qquad E^0_{Ba^{2+}/Ba} = -2.90\text{ V}$
(Weakest OA) (Strongest RA) (Lowest value)

Now since E^0_{red} values decrease as:

$$E^0_{Mg^{2+}/Mg} > E^0_{Ca^{2+}/Ca} > E^0_{Ba^{2+}/Ba},$$

the reducing power of Mg, Ca, and Ba increases as:

$$Mg(s) < Ca(s) < Ba(s)$$

(*d*) To detemine the relative order of oxidising power of halogens (X_2) and reducing power of halide ions (X^-) in aqueous solution

An oxidising agent is a species which can gain one or more electrons quite easily and get reduced to the reduced form readily. Since halogens (X_2) in aqueous solution have a great tendency to gain electrons and are reduced to the halide ions [$X^-(aq)$], halogens act as oxidising agents in aqueous solution.

$$X_2 + 2e^- \xrightarrow{\text{Reduction}} 2X^-(aq)$$

In order to determine the relative order of the oxidising power of halogens in aqueous solution, we make use of E^0 values of reduction half-reactions involving halogens (X_2) and halide ions (X^-)

Oxidised form (OA)				**Reduced form** (RA)	
F_2	+	$2e^-$	$\longrightarrow$	$2F^-(aq)$,	$E^0 = +2.87$ V
(Strongest OA)				(Weakest RA)	(Maximum value)
Cl_2	+	$2e^-$	$\longrightarrow$	$2Cl^-(aq)$,	$E^0 = +1.40$ V
Br_2	+	$2e^-$	$\longrightarrow$	$2Br^2(aq)$,	$E^0 = +1.90$ V
I_2	+	$2e^-$	$\longrightarrow$	$2I^-(aq)$,	$E^0 = +062$ V
(Weakest OA)				(Strongest RA)	(Minimum value)

Since as we move down the given set of reduction half-reactions, E^0 values decrease from $E^0_{F_2/2F^-}$ (= + 2.87 V) to $E^0_{I_2/2I^-}$ (= + 0.62V), the oxidising power of halogens decreases while the reducing power of halide ions increases in the same direction. Thus:

Oxidising power of halogens: $F_2 > Cl_2 > Br_2 > I_2$

Reducing power of halide ions: $F^- < Cl^- < Br^- < I^-$

Solved Examples

Examplel. *Some standard reduction potential values are given as:* $Zn^{2+}/Zn = -0.76$ *V,* $Cu^{2+}/Cu = +0.34$ *V,* $Ni^{2+}/Ni = -0.25$ *V and* $Ag^+/Ag = +0.80$ *V. Name the metals:*

(*i*) *that can be oxidised by Ag*
(*ii*) *that can not be oxidised by Ni*
(*iii*) *that can be oxidised by Zn*
(*iv*) *that can not be reduced by Cu*
(*v*) *that can be reduced by Ag*
(*iv*) *that can not be displaced from their salt solutions by Ni*
(*vi*) *that Zn can displace from their salt solutions*

Solution. Write the reduction half -reactions corresponding to the given electrodes. These reactions should be written in the decreasing order of their E^0 values:

OA				**RA**	
Ag^+	+	e^-	$\longrightarrow$	Ag,	$E^0 = +0.80$ V
(Strongest OA)				(Weakest RA)	
Cu^{2+}	+	$2e^-$	$\longrightarrow$	Cu,	$E^0 = +0.34$ V
Ni^{2+}	+	$2e^-$	$\longrightarrow$	Ni,	$E^0 = -0.25$ V
Zn^{2+}	+	$2e^-$	$\longrightarrow$	Zn,	$E^0 = -0.76$ V
(Weakest OA)				(Strongest RA)	

Since E^0 values are in the decreasing order, the oxidising power of metal ions is in the order:

$$Ag^+ > Cu^{2+} > Ni^{2+} > Zn^{2+}$$

and reducing power of metal atoms is in the reverse order:

$$Ag < Cu < Ni < Zn$$

(*i*) Since Ag^+ ion is the strongest OA, it can oxidise all the remaining metals *viz.* Cu, Ni and Zn to Cu^{2+}, Ni^{2+} and Zn^{2+} ions respectivly. In these reactions Ag^+ ion is reduced to Ag.

(*ii*) Since Ni^+ ion is weaker OA than Cu^{2+} and Ag^+ ions both, this ion (*i.e.* Ni^{2+} ion) cannot oxidise Cu and Ag to Cu^{2+} and Ag^+ ion, *i.e.* Cu and Ag can not be oxidised by Ni^{2+} ion.

(*iii*) Since Zn^{2+} ion is the weakest OA, it cannot oxidise ony of the metal atoms to their respective melal ions. Thus none of the metals can be oxidised by Zn^{2+} ion.

(*iv*) Since Cu is weaker RA than Ni and Zn both, this metal cannot reduce Ni^{2+} and Zn^{2+} ions to their respective melat atoms. Thus Ni^{2+} and Zn^{2+} cannot be reduced by Cu.

(*v*) Since Ag is the weakest RA, this metal cannot reduce any of the metal ions to their respective metallic atoms. Thus none of the metal ions can be reduced by Ag.

(*vi*) The term "*cannot be displaced*" means "*cannot be reduced*". Since Ni is weaker RA than Zn, this metal cannot reduce Zn^{2+} ions to Zn. Thus Zn cannot be displaced from its salt solution.

(*vii*) The term "*can displace*" means "*can reduce*". Since Zn is the strongest RA, this metal can reduce all the metal ions *viz.* Ni^{2+}, Cu^{2+} and Ag^+ ions to their respective metal atoms. Thus Zn can displace all the three metals from their salt solutions.

Example 2. *Reduction half-reactions involving perhalate ions (XO_4^-) and halate ions (XO_3^-) ane given below:*

***Oxidised form* (*O.A.*)** ***Reduced form* (*R.A.*)**

$$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O, E^0 = +1.23\ V$$

Perchlorate ion (*Cl* = + 7) *Chlorate ion* (*Cl* = + 5)

$$BrO_4^- + 2H^+ + 2e^- \longrightarrow BrO_3^- + H_2O, E^0 = +1.80\ V$$

Perbromate ion

$$IO_4^- + 2H^+ + 2e^- \longrightarrow IO_3^- + H_2O, E^0 = +1.64\ V$$

Periodate ion

Arrange perhalate ions is the decreasing order of their oxidising power.

Solution. Since E^0 values decrease as:

$$\underset{+1.80V}{E^0_{BrO_4^-/BrO_3^-}} > \underset{+1.64V}{E^0_{IO_4^-/IO_3^-}} > \underset{+1.23V,}{E^0_{ClO_4^-/ClO_3^-}},$$

the oxidising power of perhalate ions also decreases in the same order, *i.e.* the oxidising power of perhalate ions is in the order:

$$BrO_4^- > IO_4^- > ClO_4^-$$

Example 3. *Reduction of ClO_3^-, BrO_3^- and IO_3^- ions to Cl_2, Br_2 and I_2 has been shown below:*

O.A. ***R.A.***

$$2\,ClO_3^- + 12H^+ + 10e^- \longrightarrow Cl_2 + 6H_2O;\quad E^0_{ClO_3^-/Cl_2} = +1.47\ V$$

$$2\,BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O;\quad E^0_{BrO_3^-/Br_2} = +1.510\ V$$

$$2\,IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O;\quad E^0_{IO_3^-/I_2} = +1.195\ V$$

Arrange XO_3^- *ions in the decreasing order of their oxidising power.*

Solution. The oxidising power of XO_3^- ions is in the order $BrO_3^- > ClO_3^- > IO_3^-$, since E^0 values are in the order:

$$E^0_{BrO_3^-/Br_2}(=+1.510\,V) > E^0_{ClO_3^-/Cl_2}(=+1.470\,V) > E^0_{IO_3^-/I_2}(=+1.195\,V)$$

Example 4. *Cr is strongly reducing but Mn(III) is strongly oxidising. Explain why? Given* $E^0_{Mn^{3+}/Mn} = +1.51\ V$ *and* $E^0_{Cr^{2+}/Cr} = -0.41\ V$.

Solution. Let us write the reduction half-reactions involving Cr and Mn and Cr^{2+} and Mn^{3+} ions

	OA				RA	
(*a*)	Mn^{3+} (Stronger OA)	+	$3e^-$	$\xrightarrow{\text{Reduction}}$	Mn, (Weaker RA)	$E^0_{Mn^{3+}/Mn} = +1.51\ V$
(*b*)	Cr^{2+} (Weaker OA)	+	$2e^-$	$\xrightarrow{\text{Reduction}}$	Cr, (Stronger RA)	$E^0_{Cr^{2+}/Cr} = -0.41\ V$

Now since $E^0_{Mn^{3+}/Mn} > E^0_{Cr^{2+}/Cr}$,

(*i*) Mn^{3+} ion is stronger OA than Cr^{2+}, *i.e.* Mn (III) is strongly oxidising

(*ii*) Being weaker OA, Cr^{2+} ion is not easily reduced to Cr as showen by equation (*b*), but the reverse of this reduction reaction *viz.*,

$$Cr \xrightarrow{\text{Oxidistion}} Cr^{2+} + 2e^-$$

in which Cr is oxidised to Cr^{2+} takes place more easily. Thus Cr is strongly reducing.

Example 5. *With the help of electrochemical series arrange the metals Zn, Cu, Mg and Ag in the increasing order of their electron releasing tendency.*

OR

With the help of electrachemical series arrange the metats Zn, Cu, Mg and Ag in the increasing order of their being oxidised.

Solution. Write the reduction half-reactions involving the given metals and their ions in such a way that their E^0_{red} values should be in the decreasing order:

OA				RA	
Ag^+ Strongest O.A.	+	e^-	$\longrightarrow$	Mg; Weakest R.A.	$E^0_{Ag^+/Ag} = +0.80\ V$
Cu^{2+}	+	$2e^-$	$\longrightarrow$	Cu;	$E^0_{Cu^{2+}/Cu} = +0.34\ V$
Zn^{2+}	+	$2e^-$	$\longrightarrow$	Zn;	$E^0_{Zn^{2+}/Zn} = -0.76\ V$
Mg^{2+} Weakest O.A.	+	$2e^-$	$\longrightarrow$	Mg; Strongest RA.	$E^0_{Mg^{2+}/Mg} = -2.38\ V$

Decreasing ↓

The decreasing order of E^0 values shows that Ag is the weakest R.A. and Mg is the strongest R.A. Thus Ag will lose (release) an electron to get oxidised to Ag^+ least readily and Mg, being the strongest R.A., will do so to get oxidised to Mg^{2+} ion most readily. Thus the electron-releasing tendency of the given metals or their tendency of being oxidised is in the order:

$$Ag < Cu < Zn < Mg.$$

Example 6. *E^0 values of the following two reduction half-reactions are given. Predict whether $Na^+(aq)$ or $H_2O(l)$ will be reduced more easily.*

$$Na^+(aq) + e^- \longrightarrow Na(s);\ E^0_{Na^+/Na} = -2.71\ V$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq);\ E^0_{H_2O/H_2} = -0.83\ V$$

Solution. Since the standard reduction potential of $H_2O(l)$ is higher ($= -0.83$ V) than that of $Na^+(aq)$ ($= -2.71$ V), $H_2O(l)$ is stronger oxidising agent than $Na^+(aq)$. This means that $H_2O(l)$ can be reduced to $H_2(g)$ more easily than $Na^+(aq)$ can be reduced to $Na(s)$.

Example 7. *The following reactions represent the reduction of IO_3^- ion into I^- ion in acidic and basic medium. Predict in which mediun IO_3^- ion will act as a better oxidising agents.*

$$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + H_2O\ ;\ E^0 = +0.907\ V\ (Acidic\ medium)$$

$$IO_3^- + 3H_2O + 6e^- \longrightarrow I^- + 6OH^-\ ;\ E^0 = +0.260V\ (Basic\ medium)$$

Solution. We know that higher is the value of E^0, stronger (better) is the oxidising agent. Now since E^0 value in acidic medium ($= +0.907$ V) $>$ E^0 value in basie medium ($= +0.260$ V), IO_3^- ion in acidie medium acts as stronger (better) oxidising agent.

Example 8. *Standard oxidation potentials of the following two oxidation half-reactions are given. Predict whether $Br^-(aq)$ ion or $H_2O(l)$ will be oxidised more readily ?*

$$2Br^-(aq) \longrightarrow Br_2(g) + 2e^-,\ E^0_{Br^-/Br_2} = -1.08\ V$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-,\ E^0_{H_2O/O_2} = -1.23\ V$$

Solution.

$$\underset{\substack{(Br = -1)\\ \text{(Stronger RA)}}}{2Br^-(aq)} \xrightarrow{\text{Oxidation}} \underset{(Br = 0)}{Br_2(g)} + 2e^-,\ E^0_{ox} = E^0_{Br^-/Br_2} = -1.08\ V$$

$$\underset{\substack{(O = -2)\\ \text{(Weaker RA)}}}{2H_2O(l)} \xrightarrow{\text{Oxidation}} \underset{(O = 0)}{O_2(g)} + 4H^+(aq) + 4e^-,\ E^0_{ox} = E^0_{H_2O/O_2} = -1.23\ V$$

Since $E^0_{ox} = E^0_{Br^-/Br_2}$ ($= -1.08$ V) $>$ $E^0_{ox} = E^0_{H_2O/O_2}$ ($= -1.23$ V), $Br^-(aq)$ ion will be oxidised to $Br_2(g)$ more readily than $H_2O(l)$ gets oxidised to O_2.

Example 9. *Mn is oxidised to divalent state in acidic as well as in basic medium. The values of* $(E^0_{ox})_A$ *and* $(E^0_{ox})_B$ *are given below:*

$$Mn \longrightarrow Mn^{2+} + 2e^-, \qquad (E^0_{ox})_A = +1.19\ V$$

$$Mn \longrightarrow Mn^{2+} + 2e^-, \qquad (E^0_{ox})_B = +1.55\ V$$

State in which medium Mn is oxidised to Mn^{2+} *ion more easily ?*

Solution. $\underset{\substack{(Mn\,=\,0)\\(\text{Weaker RA})}}{Mn} \xrightarrow{\text{Oxidation}} \underset{(Mn\,=\,+2)}{Mn^{2+}} + 2e^-, \qquad (E^0_{ox})_A = +1.19\ V$

$$\underset{\substack{(Mn\,=\,0)\\(\text{Stronger RA})}}{Mn} \xrightarrow{\text{Oxidation}} \underset{(Mn\,=\,+2)}{Mn^{2+}} + 2e^-, \qquad (E^0_{ox})_B = +1.55\ V$$

Now since $(E^0_{ox})_B$ (= + 1.55 V) > $(E^0_{ox})_A$ (= + 1.19 V), Mn in basic medium will lose electrons to get oxidised to Mn^{2+} ion more easily than in acidic medium.

Example10. *E^0 values of the following two reduction half-reactions are given. Predict which of the ions can more easily be oxidised?*

(*a*) $\left[Fe^{3+}(H_2O)_6\right]^{3+} + e^- \longrightarrow \left[Fe^{2+}(H_2O)_6\right]^{2+};\ E^0 = +0.77\ V$

(*b*) $\left[Fe^{3+}(CN)_6\right]^{3-} + e^- \longrightarrow \left[Fe^{2+}(CN)_6\right]^{4-};\ E^0 = +0.36\ V$

Solution. We know that the ion which is stronger R.A. can easily be oxidised to its oxidised form than the ion which is weaker R.A. Again we know that since the value of E^0 for reduction half-reaction (*b*) is lower than that for the reduction half-reaction (*a*), $\left[Fe^{2+}(CN)_6\right]^{4-}$ ion is stronger R.A than $\left[Fe^{2+}H_2O)_6\right]^{2+}$ ion. Thus $\left[Fe^{2+}(CN)_6\right]^{4-}$ ion can more easily be oxidised to $\left[Fe^{3+}(CN)_6\right]^{3-}$ ion in aqueous solution than $\left[Fe^{2+}(H_2O)_6\right]^{2+}$ ion can be oxidised to $\left[Fe^{3+}(H_2O)_6\right]^{3+}$ ion.

Example11. *Standard reduction electrode potentials of some half-reactions at 25°C are given below:*

$$Zn^{2+} + 2e^- \longrightarrow Zn, \qquad E^0 = -0.763\ V$$

$$Pb^{2+} + 2e^- \longrightarrow Pb, \qquad E^0 = -0.126\ V$$

$$Al^{3+} + 3e^- \longrightarrow Al, \qquad E^0 = 1.66\ V$$

$$Cd^{2+} + 2e^- \longrightarrow Cd, \qquad E^0 = -0.402\ V$$

Arrange Zn, Pb, Al and Cd in the increasing strength as reductants.

(*Visva Bharati B.Sc.1988*)

Solution. Write the given reduction half-reactions in such a way that their E^0_{red} value should be in the decreasing order.

$$Pb^{2+} + 2e^- \longrightarrow \underset{(\text{Weakest R.A.})}{Pb}, \qquad E^0 = -0.126\ V$$

$$Cd^{2+} + 2e^- \longrightarrow Cd, \qquad E^0 = -0.402\text{ V}$$
$$Zn^{2+} + 2e^- \longrightarrow Zn, \qquad E^0 = -0.763\text{ V}$$
$$Al^{3+} + 3e^- \longrightarrow \underset{\text{(Strongest R.A.)}}{Al}, \qquad E^0 = -1.660\text{ V}$$

Thus the increasing order of reducing power is : Pb < Cd < Zn < Al.

Example 12. *Predict whether ferrocyanide on, $[Fe(CN)_6]^{4-}$ is stronger or weaker reducing agent than ferrous ion, Fe^{2+} ion. Given that:*

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^-, \quad E^0_{ox} = -0.36\ V$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-, \quad E^0_{ox} = -0.77\ V$$

Solution.

$$(a)\quad \underset{\text{(Stronger OA)}}{Fe^{3+}} + e^- \xrightarrow{\text{Reduction}} \underset{\text{(Weaker RA)}}{Fe^{2+}}, \quad E^0_{red} = +0.77\text{ V}$$

$$(b)\quad \underset{\substack{(Fe = +3)\\ \text{(Weaker OA)}}}{[Fe(CN)_6]^{3-}} + e^- \xrightarrow{\text{Reduction}} \underset{\substack{(Fe = +2)\\ \text{(Stronger RA)}}}{[Fe(CN)_6]^{4-}}, \quad E^0_{red} = +0.36\text{ V}$$

Now since E^0_{red} value for half-reaction (*b*) is lower than that for half-reaction (*a*), $[Fe(CN)_6]^{4-}$ ion is stronger RA than Fe^{2+} ion.

Example 13. *Values for the reduction half-reactions involving 1st transition series elements and their ions in aqueous solution are given below. Answer the following :*

(*a*) *State whether these metals act as oxidising agents or reducing agents.*

(*b*) *Predict the decresing order of oxidising or reducing power of these metals.*

Electrode	*OAs*	*RAs*	
Sc^{3+}/Sc	$Sc^{3+}(aq) + 3e^- \longrightarrow$	$Sc(s)$,	$E^0 = -2.10\ V$
Ti^{2+}/Ti	$Ti^{2+}(aq) + 2e^- \longrightarrow$	$Ti(s)$,	$E^0 = -1.60\ V$
V^{2+}/V	$V^{2+}(aq) + 2e^- \longrightarrow$	$V(s)$,	$E^0 = -1.20\ V$
Mn^{2+}/Mn	$Mn^{2+}(aq) + 2e^- \longrightarrow$	$Mn(s)$,	$E^0 = -1.18\ V$
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow$	$Fe(s)$,	$E^0 = -0.44\ V$
Co^{2+}/Co	$Co^{2+}(aq) + 2e^- \longrightarrow$	$Co(s)$,	$E^0 = -0.28\ V$
Ni^{2+}/Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow$	$Ni(s)$,	$E^0 = -0.24\ V$
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow$	$Cu(s)$,	$E^0 = +0.34\ V$
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow$	$Zn(s)$,	$E^0 = -0.76\ V$

Solution (*a*) Since all the metals, except Cu, have negative values of E^0, *i.e.* less than E^0 value for the reduction half-reaction, $2H^+(aq) + 2e^- \rightarrow H_2(g)$ ($E^0 = 0.0$ V), these metals act as reducing agents. Since Cu has positive value of E^0, Cu does not show reducing property.

(*b*) Since E^0 values increase (*i.e.* become less negative from Sc to Ni), the reducing power of these metals decreases from Sc to Ni.

Example 14. *Explain why H_2O_2 is a better oxidising agent than H_2O?* (*I.I.T. 1986*)

Solution. When H_2O_2 (O = − 1) acts as an OA, it gets reduced to H_2O (O = − 2) and when H_2O (H = +1) acts as an OA, it gets reduced to H_2 (H = 0). Thus the reduction of H_2O_2 to H_2O and that of H_2O to H_2 can be represented by the following reduction half-reactions :

(*a*) $\underset{\substack{(O=-1)\\(\text{Stronger OA})}}{H_2O_2}+2H^++2e^- \xrightarrow{\text{Reduction}} \underset{(O=-2)}{2H_2O}, \quad E^0=+1.77\text{ V}$

(*b*) $\underset{\substack{(H=+1)\\(\text{Weaker OA})}}{2H_2O}+2e^- \xrightarrow{\text{Reduction}} \underset{(H=0)}{H_2}+2OH^-, \quad E^0=-0.83\text{ V}$

Now since E^0 value for reduction half-reaction (*a*) is higher (= + 1.77V) than that for reduction half-reaction (*b*) (= − 0.83V), H_2O_2 is stronger (better) OA than H_2O.

Qnestion 15. *Zn and not Cu is used for the recovery of metallic silver from the complex ion, $[Ag(CN)_2]^-$. Explain.* (*I.I.T. 1987*)

Solution. Recovery of Ag from $[Ag(CN)_2]^-$ ion by the use of Zn or Cu can be represented by the following ionic equations:

$$\underset{(Ag=+1)}{2[Ag(CN)_2]^-} + \underset{\substack{(Zn=0)\\(\text{Stronger RA})}}{Zn} \longrightarrow \underset{(Zn=+2)}{[Zn(CN)_4]^{2-}} + \underset{(Ag=0)}{2Ag}$$

$$\underset{(Ag=+1)}{2[Ag(CN)_2]^-} + \underset{\substack{(Cu=0)\\(\text{Weaker RA})}}{Cu} \longrightarrow \underset{(Cu=+2)}{[Cu(CN)_4]^{2-}} + \underset{(Ag=0)}{2Ag}$$

In both these reactions Zn/Cu acts as RA. Now since $E^0_{Zn^{2+}/Zn}$ (= − 0.76 V) < $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V), Zn is more powerful RA than Cu. Zn is also cheaper than Cu. It is for these reasons that Zn and not Cu is used for the recovery of Ag from $[Ag(CN)_2]^-$ ion.

II.(*a*) To determine the conditions for the feasibility of metal-metal displacement reactions (Redox reactions)

Metal-metal displacement reaction is a redox reaction in which a metal reacts with the aqueous solution of the salt of another metal. This type of displacement reaction can be represented by the following redox reaction.

$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$ (*Molecular equation*)

or $\underset{\substack{\text{Displacing}\\\text{metal or}\\\text{metal being}\\\text{oxidised}\\\text{(RA)}}}{Zn(s)} + \underset{\substack{\text{Metal being}\\\text{displaced}\\\text{or metal being}\\\text{reduced (OA)}}}{Cu^{2+}(aq)} \longrightarrow Zn^{2+}(aq) + Cu(s)$ (*Ionic equation*)

In the above redox reaction :

(*i*) Zn (s) is a metal and $CuSO_4\,(aq)$ is the aqueous solution of sulphate (salt) of another metal, Cu. When Zn(s) reacts with $CuSO_4(aq)$, Cu(s) is percipitated and sulphate of Zn ($ZnSO_4$) is obtained in solution.

(*ii*) Zn(s) displaces Cu(s) from $CuSO_4(aq)$. Thus Zn(s) is the displacing metal and Cu is the metal being displaced.

(*iii*) In the ionic equation, Zn(s) in being oxidised to $Zn^{2+}(aq)$ ion and $Cu^{2+}(aq)$ ion is being reduced to Cu(s). Thus Zn(s) in acting as a reducing agent (RA) and $Cu^{2+}(aq)$ ion is acting as oxidising agent (OA). Thus the ionic equation given above can also be written as shown below:

$$\overbrace{\underset{\substack{\text{Displacing metal}\\ \text{or metal being}\\ \text{oxidised (RA)}}}{Zn(s)} + \underset{\substack{\text{Metal being}\\ \text{displaced or metat}\\ \text{being reduced (OA)}}}{Cu^{2+}(aq)} \longrightarrow Zn^{2+}(aq)}^{\text{Oxidation } (0\rightarrow +2)} + Cu(s)$$

$$\underbrace{Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)}_{\text{Reduction } (+2\rightarrow 0)}$$

Oxidistion and reduction half-reactions for the above redox reaction are:

$$\underset{(Zn = 0)}{Zn(s)} \xrightarrow{\text{Oxidation}} \underset{(Zn = +2)}{Zn^{2+}(aq) + 2e^-}, \; E^0_{ox} = E^0_{Zn/Zn^{2+}}$$

$$\underset{(Cu = +2)}{Cu^{2+}(aq) + 2e^-} \xrightarrow{\text{Reduction}} \underset{(Cu = 0)}{Cu(s)}, \; E^0_{red} = E^0_{Cu^{2+}/Cu}$$

The given redox reaction is feasible [*i.e.* this reaction will take place spontaneously in the forward direction (from left to right)], if the value of e.m.f. of this redox reaction as calculated from any of the equations given at (*i*), (*ii*), (*iii*) and (*iv*) given below is a positive quantity.

(*i*) e.m.f. of the redox reaction

$$= E^0_{\text{Metal being displaced}} - E^0_{\text{Displacing metal}} = \text{A positive quantity}$$

(*ii*) e.m.f. of the redox reaction

$$= E^0_{\text{Metal being reduced}} - E^0_{\text{Metal being oxidised}} = \text{A positive quantity}$$

(*iii*) e.m.f. of the redox reaction

$$= E^0_{OA} - E^0_{RA} = \text{A positive quantity}$$

(*iv*) e.m.f.of the redox reaction

$$= E^0_{ox} \text{ for oxidation half-reaction}$$

$$+ E^0_{red} \text{ for reduction half-reaction} = \text{A positive quantitv}$$

If the value of e.m.f. of the redox reaction as calculated from any of the equations given above comes out to be a negative quantity, the given redox reaction will not proceed in the forward direction, *i.e.* the reaction will not take pleac spontaneously as shown. Rather, it will proceed in the backward direction (from right to left direction).

We have stated above that in order to make a metal -metal displacement reaction feasible, the value of e.m.f. of the reaction, as calculated from equations (*i*) to (*iv*), should be a positive quantity. Obviously, in order to get a positive value of e.m.f. of the reaction or to make the metal -metal displacement reaction feasible, one of the following conditins must be satisfied.

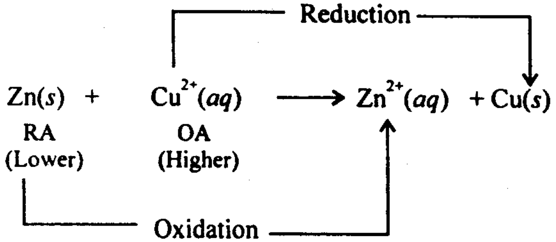
(*a*) $E^0_{\text{Metal being displaced}} > E^0_{\text{Displacing metal}}$

(*b*) $E^0_{\text{Metal being reduced}} > E^0_{\text{Metal being oxidised}}$

(*c*) $E^0_{\text{OA}} > E^0_{\text{RA}}$

Summary

In a redox reaction of the type given below:



(*i*) (*a*) Lower acts as displacing metal
- (*b*) Lower acts as RA
- (*c*) Lower acts as anode in the cell in which this redox reaction occurs.
- (*d*) Lower reduces higher
- (*e*) Lower is oxidised by higher
- (*f*) Lower displaces higher

(*ii*) (*a*) Higher acts as metal being displaced.
- (*b*) Higher acts as OA
- (c) Higher acts as cathode in the cell in which the given redox reaction takes place.
- (*d*) Higher oxidises lower
- (*e*) Higher is reduced by lower
- (*f*) Higher is displaced by lower

(*iii*) $(E^0_{\text{red}})_{\text{OA}} > (E^0_{\text{red}})_{\text{RA}}$ or $(E^0_{\text{ox}})_{\text{OA}} < (E^0_{\text{ox}})_{\text{RA}}$.

(*iv*) Redox reaction is composed of two half-reactions one of which is oxidation half-reaction and the other is reduction half-reaction. The half-reaction having lower value of E^0_{red} is written as oxidation half-reaction and that having higher value of E^0_{red} is written as reduction half-reaction.

(*v*) $E^0_{\text{redox reaction}} = E^0_{\text{ox}}$ of oxidation half-reaction

$+ E^0_{\text{red}}$ of reduction half- reaction

$$= \left[E^0_{ox}\right]_{RA} + \left[E^0_{red}\right]_{OA} = \left[E^0_{red}\right]_{OA} - \left[E^o_{red}\right]_{RA}$$
$$= \left[E^0_{red}\right]_{higher} - \left[E^0_{red}\right]_{lower}$$

(*vi*) e.m.f. or $E^0_{\text{redox reaction}}$ of a redox reaction is always a positive quantity

(*vii*) A redox reaction takes place spontaneously in the forward direction (*i.e.* from left to right), if its e.m.f. or $E^0_{\text{redox reaction}}$ in a positive quantity. If the vlue of e.m.f. is a negative quantity, the redox reaction will take place in the opposite (backward) directiion (from right to left).

Illustrative Example. *Predict whether the following redox reactions will take place spontaneously or not?*

(*i*) $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

(*ii*) $2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^{+}(aq) + Cu(s)$

Given: $Zn^{2+}/Zn = -0.76$ V, $Cu^{2+}/Cu = +0.34$ V *and* $Ag^{+}/Ag = +0.80$ V

Solution. (*i*) In redox reaction (*i*), since Zn(*s*) act as RA and $Cu^{2+}(aq)$ ion act as OA, e.m.f. of redox reaction (*i*)

$$= E^0_{OA} - E^0_{RA} = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} = +0.34 - (-0.76)$$
$$= +1.10 \text{ V} = \text{A positive quantity}$$

Since the value of e.m.f. is a positive quantity (= + 1.10 V), redox reaction (*i*) will occur spontaneously.

(*ii*) In redox reaction (*ii*), since Ag(*s*) acts as RA and $Cu^{2+}(aq)$ ions act as OA, e.m.f. of redox reaction (*ii*)

$$= E^0_{OA} - E^0_{RA} = E^0_{Cu^{2+}/Cu} - E^0_{Ag^{+}/Ag} = +0.34 - 0.80$$
$$= -0.46 \text{ V} = \text{A negative quantity}$$

Since the value of e.m.f. is a negative quantity (= – 0.46 V), redox reaction (*ii*) will not occur in the forward (right) direction. Rather it will proceed in the backwarde (left) direction as shown below:

$$\underset{(RA)}{Cu(s)} + \underset{(OA)}{2Ag^{+}(aq)} \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

e.m.f. of this reaction is a positive quantity as shown below:

$$\text{e.m.f.} = E^0_{OA} - E^0_{RA} = E^0_{Ag^{+}/Ag} - E^0_{Cu^{2+}/Cu}$$
$$= 0.80 - 0.34 = +0.46 \text{ V} = \text{A negative qauantity}$$

Solved Examples

Example 1. *State whether Cu(s) will reduce Zn^{2+} ions in their aqueous solution. Given that $E^0_{Zn^{2+}/Zn} = -0.76$ V and $E^0_{Cu^{2+}/Cu} = +0.34$ V.*

Answer. Answer is NO, *i.e.* Cu(*s*) will not reduce $Zn^{2+}(aq)$ ions.

Explanation 1. We know that: "*Lower reduces higher*"

On the basis of this rule, since the value of $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) is not lower than that of $E^0_{Zn^{2+}/Zn}$ (= – 0.76 V), Cu will not reduce Zn^{2+} ions.

Explanation 2. Suppose Cu(*s*) reduces $Zn^{2+}(aq)$ ions. In this reaction

Cu(*s*) is oxidised to $Cu^{2+}(aq)$ ions and $Zn^{2+}(aq)$ ions are reduced to Zn(*s*). Thus:

$$\underset{\text{RA}}{Cu(s)} + \underset{\text{OA}}{Zn^{2+}(aq)} \longrightarrow Cu^{2+}(aq) + Zn(s)$$

Now, e.m.f of this redox reaction

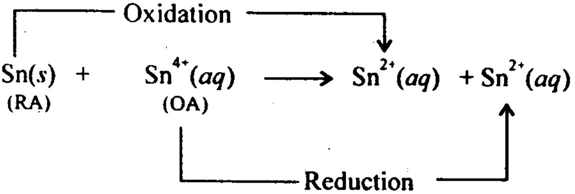
$$= E^0_{OA} - E^0_{RA} = E^0_{Zn^{2+}/Zn} - E^0_{Cu^{2+}/Cu} = -0.76 - 0.34$$
$$= -1.10\text{ V}$$

Since the value of e.m.f. comes out to be negative, the redox reaction is not feasible, *i.e.* Cu(*s*) will not reduce $Zn^{2+}(aq)$ ions.

Example 2. *Will metallic tin reduce* Sn^{4+} *to* Sn^{2+}*? Given that* $E^0_{Sn/Sn^{2+}} = +0.14$ *V and* $E^0_{Sn^{4+}/Sn^{2+}} = 0.15$ *V.*

Answer. Answer is **Yes**, *i.e.* metallic tin will reduce Sn^{4+} to Sn^{2+}.

Explanation. If metallic tin reduces Sn^{4+} to Sn^{2+}, then the following redox reaction should be feasible. In this reaction Sn is oxidised to Sn^{2+}.



$$\underset{\text{(RA)}}{Sn(s)} + \underset{\text{(OA)}}{Sn^{4+}(aq)} \longrightarrow Sn^{2+}(aq) + Sn^{2+}(aq)$$

e.m.f. of this redox reaction is given by:

(*a*) e.m.f. $= E^0_{OA} - E^0_{RA} = E^0_{Sn^{4+}/Sn^{2+}} - E^0_{Sn^{2+}/Sn}$

$= +0.15 - (-0.14) = \mathbf{+0.29\ V}$

(*b*) e.m.f. $= E^0_{ox}$ for the oxidation half-reaction

$+ E^0_{red}$ for reduction half-reaction

$= E^0_{Sn/Sn^{2+}} + E^0_{Sn^{4+}/Sn^{2+}} = +0.14 + 0.15 = \mathbf{+0.29\ V}$

Since e.m.f. is a positive quantity, the redox reaction will occur spontaneously, *i.e.* metallic tin reduces Sn^{4+} to Sn^{2+}.

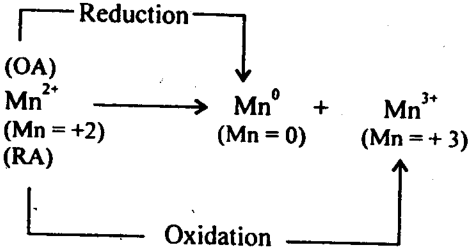
Example 3. *Is* Mn^{2+} *ion stable in aqueous solution? Given that* $E^0_{Mn^{2+}/Mn^{3+}} = -1.51$ *V and* $E^0_{Mn/Mn^{2+}} = +1.19$ *V.*

Answer. Mn^{2+} ion is stable in aqueous solution.

Explanation. Suppose Mn^{2+} ion is not stable in aqueous solution. This means that Mn^{2+} ion disproportionate into Mn^0 and Mn^{3+} ion.

$$\underset{(Mn = +2)}{Mn^{2+}} \longrightarrow \underset{(Mn = 0)}{Mn^0} + \underset{(Mn = +3)}{Mn^{3+}} \quad \textit{(This is not a balanced equation)}$$

This equation shows that some number of Mn^{2+} ions are reduced to Mn^0 and the remaining number of Mn^{2+} ions are oxidised to Mn^{3+} ions. Thus in this reaction Mn^{2+} ions act both as OA as well as RA.



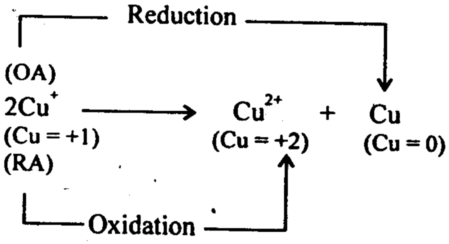
Now since $E^0_{OA} = E^0_{Mn^{2+}/Mn^0}$ (= − 1.19 V) is not greater than $E^0_{RA} = E^0_{Mn^{3+}/Mn^{2+}}$ (= + 1.51 V), the above reaction is not fleasible, *i.e.* Mn^{2+} will not disproportionate into Mn^0 and Mn^{3+} ions. Thus Mn^{2+} ion is stable in aqueous solution.

Example 4. *State whether Cu^+ ion disproportionates to Cu^{2+} ion and elemental Cu in solution. Justify your answer in brief. ($E^0_{Cu^+/Cu} = 0.52$ V, $E^0_{Cu^{2+}/Cu^+} = 0.15$ V)* *(I.I.T. 1991)*

Solution. Suppose that Cu^+ ion undergoes disproportionation into Cu^{2+} ion and Cu metal in solution. This disproportionation reaction can be represented as:

$$\underset{(Cu\,=\,+1)}{2Cu^+} \longrightarrow \underset{(Cu\,=\,+2)}{Cu^{2+}} + \underset{(Cu\,=\,0)}{Cu}$$

This equation shows that Cu^+ ion undergoes oxidation as well as reduction, *i.e.* in this reaction Cu^+ acts both as OA as well as RA. Thus:



Now since $E^0_{OA} = E^0_{Cu^+/Cu}$ (= + 0.52 V) > $E^0_{RA} = E^0_{Cu^{2+}/Cu^+}$ (= + 0.15 V), the above reaction is feasible, *i.e.* Cu^+ ion disproportionates to Cu^{2+} ions and Cu in solution.

Example 5. *Cl_2 can undergo the following two reactions in an alkaline medium*

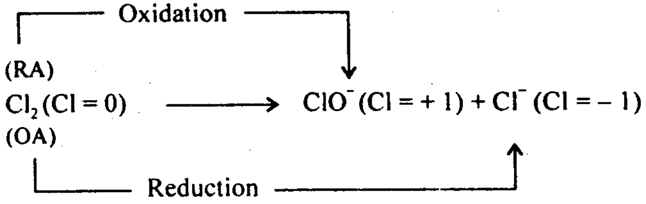
$$Cl_2 + 2e^- \rightleftharpoons 2Cl^-; \quad E^0 = + 1.36\ V$$

$$2ClO^- + 2H_2O + 2e^- \rightleftharpoons Cl_2 + 4OH^-; \quad E^0 = + 0.40\ V$$

Predict whether or not Cl_2 would disproportionate in alkaline medium.

Answer. Yes. Cl_2 would disproportionate in alkaline medium.

Explanation. The disproportionation of Cl_2(Cl = 0) will take place into ClO^-(Cl = +1) and Cl^-(Cl = −1) as shown below:



(*This equations is not balanced*)

Now since $E^0_{\text{OA}} = E^0_{\text{Cl}_2/\text{Cl}^-}$ (= + 1.36 V) > $E^0_{\text{RA}} = E^0_{\text{ClO}^-/\text{Cl}_2}$ (= + 0.40 V), above disproportionation reaction will occur spontaneously. Thus Cl_2 would disproportionate in alkaline medium.

Example 6. *Each of the following redox reactions takes place spontaneously as shown. Arrange Mg, Zn, Cu and Ag in the decreasing order of their standard electrode potentials.*

(*i*) $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

(*ii*) $Mg + Zn^{2+} \longrightarrow Mg^{2+} + Zn$

(*iii*) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

Solution. The given redox reactions can also be written as:

(*i*) $\underset{\text{RA}}{\text{Cu}} + \underset{\text{OA}}{2\text{Ag}^+} \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$

(*ii*) $\underset{\text{RA}}{\text{Mg}} + \underset{\text{OA}}{\text{Zn}^{2+}} \longrightarrow \text{Mg}^{2+} + \text{Zn}$

(*iii*) $\underset{\text{RA}}{\text{Zn}} + \underset{\text{OA}}{\text{Cu}^{2+}} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

Reaction (*i*) is possible, only when:

$$(E^0_{\text{red}})_{\text{OA}} > (E^0_{\text{red}})_{\text{RA}}$$

or $$E^0_{\text{Ag}^+/\text{Ag}} > E^0_{\text{Cu}^{2+}/\text{Cu}} \qquad ...(a)$$

Reaction (*ii*) is possible only when:

$$(E^0_{\text{red}})_{\text{OA}} > (E^0_{\text{red}})_{\text{RA}}$$

or $$E^0_{\text{Zn}^{2+}/\text{Zn}} > E^0_{\text{Mg}^{2+}/\text{Mg}} \qquad ...(b)$$

Reaction (*iii*) is possible only when:

$$(E^0_{\text{red}})_{\text{OA}} > (E^0_{\text{red}})_{\text{RA}}$$

or $$E^0_{\text{Cu}^{2+}/\text{Cu}} > E^0_{\text{Zn}^{2+}/\text{Zn}} \qquad ...(c)$$

From relations (*a*), (*b*) and (*c*) we get,

$$E^0_{\text{Ag}^+/\text{Ag}} > E^0_{\text{Cu}^{2+}/\text{Cu}} > E^0_{\text{Zn}^{2+}/\text{Zn}} > E^0_{\text{Mg}^{2+}/\text{Mg}}$$

This is the required order.

Example 7. *E^0 values for Cr and Fe are $Cr^{3+}/Cr^{2+} = -0.4$ V and $Fe^{3+}/Fe^{2+} = +0.80$ V. Comment on the result of treating a solution of Cr(II) with a solution containing Fe(III) ions.* (*Delhi 1998C*)

Solution. Suppose that when a solution of Cr(II) is treated with a solution containing Fe(III) ions, the following redox reaction takes place.

$$\underset{\text{RA}}{Cr^{2+}(aq)} + \underset{\text{OA}}{Fe^{3+}(aq)} \longrightarrow Fe^{2+}(aq) + Cr^{3+}(aq)$$

This reaction will take place spontaneously only when E^0_{OA} or $E^0_{Fe^{3+}(aq)/Fe^{2+}(aq)} > E^0_{RA}$ or $E^0_{Cr^{3+}(aq)/Cr^{2+}(aq)}$. Now since $E^0_{Fe^{3+}(aq)/Fe^{2+}(aq)}$ $(=+0.80\text{ V}) > E^0_{Cr^{3+}(aq)/Cr^{2+}(aq)}$ $(=-0.40\text{ V})$, above redox reaction will take place as written. Thus when a solution of Cr(II) is treated with a solution containing Fe(III) ions, redox reaction shown above takes place.

Example 8. *Explain why Sn^{2+} and Fe^{3+} ions cannot exist together in the same solution?*

Solution. When Sn^{2+} and Fe^{3+} ions are present in the same solution, Sn^{2+} reduces Fe^{3+} to Fe^{2+} and is itself oxidised to Sn^{4+} because $E^0_{Fe^{3+}/Fe^{2+}}$ $(= 0.77\text{ V}) > E^0_{Sn^{4+}/Sn^{2+}}$ $(= +0.75\text{ V})$. Note that Fe^{3+} ion acts as OA and Sn^{2+} ion acts as RA.

$$\underset{\text{RA}}{Sn^{2+}} + \underset{\text{OA}}{2Fe^{3+}} \longrightarrow Sn^{4+} + 2Fe^{2+} \text{ (\textit{This is a redox reaction})}$$

Thus non-existence of Sn^{2+} and Fe^{3+} ions together in the same solution is due to the occurrence of the above redox reaction.

Example 9. *Can we store (a) copper sulphate solution in a Zn-vessel (b) copper sulphate solution in a silver vessel. Given $E^0_{Cu^{2+}/Cu} = +0.34\text{ V}$, $E^0_{Zn^{2+}/Zn} = -0.76\text{ V}$ and $E^0_{Ag^{+}/Ag} = +0.80\text{ V}$.*

Solution. (*a*) Suppose $CuSO_4$ solution reacts with Zn according to the following equation:

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

or
$$\underset{\text{(RA)}}{Zn(s)} + \underset{\text{(OA)}}{Cu^{2+}(aq)} \longrightarrow Zn^{2+}(aq) + Cu(s) \quad ...(i)$$

e.m.f. of reaction (*i*)

$$= E^0_{OA} - E^0_{RA} = E^0_{Cu^{2+}(aq)/Cu(s)} - E^0_{Zn^{2+}(aq)/Zn(s)}$$
$$= +0.34 - (-0.76) = +1.10\text{ V (Positive quantity)}$$

Since the value of e.m.f. is a positive quantity, reaction (*i*) occurs spontaneously, *i.e.* $CuSO_4$ solution will react with Zn-vessel and hence $CuSO_4$ solution should not be stored in Zn-vessel.

(*b*) Suppose $CuSO_4$ solution reacts with Ag according to the following equation

$$2Ag(s) + CuSO_4(aq) \longrightarrow Ag_2SO_4(aq) + Cu(s)$$

or
$$\underset{\text{(RA)}}{2Ag(s)} + \underset{\text{(OA)}}{Cu^{2+}(aq)} \longrightarrow 2Ag^{+}(aq) + Cu(s) \quad ...(ii)$$

e.m.f. of reaction (*ii*)

$$= E^0_{\text{OA}} - E^0_{\text{RA}} = E^0_{\text{Cu}^{2+}(aq)/\text{Cu}(s)} - E^0_{\text{Ag}^+(aq)/\text{Ag}(s)}$$

$$= +0.34 - 0.80 = -0.46 \text{ V (Negative quantity)}$$

Since the value of e.m.f. is a negative quantity, reaction (*ii*) will not occur spontaneously, *i.e.* $CuSO_4$ solution will not react with Ag-vessel and hence $CuSO_4$ solution can be stored in Ag-vessel.

Example 10. *If e.m.f. of a cell represented by the cell reaction,*

$$A + B^+ \longrightarrow A^+ + B$$

is negative, what is the direction of flow of electrons in the external circuit?

Solution. Negative value of e.m.f. implies the given reaction proceeds in the opposite direction, *i.e.* the actual cell reaction is

$$\underset{\substack{\text{OA}\\\text{(Accepts}\\\text{electrons)}}}{A^+} + \underset{\substack{\text{RA}\\\text{(Releases}\\\text{electrons)}}}{B} \longrightarrow A + B^+$$

Being RA, B releases electrons and A^+ (which acts as OA) accepts electrons. Thus electrons flow from B to A in the external circuit.

(*b*) Metal-metal displacement reactions in electrochemical series

Note the following points:

(*i*) We know that in electrochemical series the reduction half-reactions are written in such a way that their E^0 values are in the decreasing order. Thus an electrode having higher (upper) position in the series has higher value of E^0 than that having lower position in the series.

(*ii*) We know that: *Higher metal oxidises lower metal*

or

Lower metal does not oxidise higher metal

On the basis of this rule, we can conclude that in electrochemical series, a given metal ion can oxidise only those metals which have lower E^0 values or which lie below it in the series but cannot oxidise those metals which have higher E^0 values or which lie above it in the series. Thus from half-reactions given as:

OA	RA	
$Ag^+ + e^- \longrightarrow$	Ag	$E^0_{Ag^+/Ag} = +0.80$ V
$Cu^{2+} + 2e^- \longrightarrow$	Cu	$E^0_{Cu^{2+}/Cu} = +0.34$ V
$Ni^{2+} + 2e^- \longrightarrow$	Ni	$E^0_{Ni^{2+}/Ni} = -0.25$ V
$Zn^{2+} + 2e^- \longrightarrow$	Zn	$E^0_{Zn^{2+}/Zn} = -0.76$ V

We can conclude that

(*a*) Ag^+ ion an oxidise all the metals given below it to their respective cations, *i.e.* each of the following redox reaction is feasible:

$$2Ag^+ + Cu \longrightarrow Cu^{2+} + 2Ag$$

$$2Ag^+ + Ni \longrightarrow Ni^{2+} + 2Ag$$
$$2Ag^+ + Zn \longrightarrow Zn^{2+} + 2Ag$$

(*b*) Cu^{2+} ion can oxidise Ni and Zn both to their respective cations *viz.* Ni^{2+} and Zn^{2+} but cannot oxidise Ag to Ag^+ ion.

$$Cu^{2+} + Ni \longrightarrow Ni^{2+} + Cu$$
$$Cu^{2+} + Zn \longrightarrow Zn^{2+} + Cu$$
$$Cu^{2+} + 2Ag \longrightarrow 2Ag^+ + Cu \quad (\textit{Not feasible reaction})$$

(*c*) Ni^{2+} ion can oxidise only Zn to Zn^{2+} but cannot oxidise Cu and Ag to Cu^{2+} and Ag^+ ions.

$$Ni^{2+} + Zn \longrightarrow Zn^{2+} + Ni$$
$$\left.\begin{array}{l} Ni^{2+} + Cu \longrightarrow Cu^{2+} + Ni \\ Ni^{2+} + 2Ag \longrightarrow 2Ag^+ + Ni \end{array}\right\} \quad (\textit{Not feasible reactions})$$

(*d*) Zn^{2+} ion cannot oxidise any of the metals viz. Ni, Cu and Ag.

$$\left.\begin{array}{l} Zn^{2+} + Ni \longrightarrow Ni^{2+} + Zn \\ Zn^{2+} + Cu \longrightarrow Cu^{2+} + Zn \\ Zn^{2+} + 2Ag \longrightarrow 2Ag^+ + Zn \end{array}\right\} \quad (\textit{Not feasible reactions})$$

(*iii*) We know that: *Lower metal reduces (displaces) higher metal*

or

Higher metal does not reduce lower metal.

On the basis of this rule, we conclude that in electrochemical series, a given metal can reduce (displace) only those metal ions which have higher E^0 values or which lie above it in the series but cannot reduce those metal ions which have lower value of E^0 or which lie below it in the series. Thus from the half-reactions given above we can conclude that:

(*a*) Ag cannot reduce any of the three metallic ions to their corresponding metallic atom, *i.e.* none of the following redox reactions occurs.

$$\left.\begin{array}{l} 2Ag + Cu^{2+} \longrightarrow Cu + 2Ag^+ \\ 2Ag + Ni^{2+} \longrightarrow Ni + 2Ag^+ \\ 2Ag + Zn^{2+} \longrightarrow Zn + 2Ag^+ \end{array}\right\} \quad (\textit{Not feasible reactions})$$

(*b*) Cu can reduce Ag^+ ions to Ag but cannot reduce Ni^{2+} and Zn^{2+} ions to the Ni and Zn respectively.

$$Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$$
$$\left.\begin{array}{l} Cu + Ni^{2+} \longrightarrow Ni + Cu^{2+} \\ Cu + Zn^{2+} \longrightarrow Zn + Cu^{2+} \end{array}\right\} \quad (\textit{Not feasible reactions})$$

(*c*) Ni can reduce Cu^{2+} and Ag^+ ions both to Cu and Ag respectively but cannot reduce Zn^{2+} ion to Zn.

$$Ni + Cu^{2+} \longrightarrow Cu + Ni^{2+}$$
$$Ni + 2Ag^+ \longrightarrow 2Ag + Ni^{2+}$$
$$Ni + Zn^{2+} \longrightarrow Zn + Ni^{2+} \quad (\textit{Not feasible reaction})$$

(*d*) Zn can reduce all the three ions *viz.* Ni^{2+}, Cu^{2+} and Ag^+ to Ni, Cu and Ag respectively. Thus each of the following redox reaction is feasible.

$$Zn + Ni^{2+} \longrightarrow Ni + Zn^{2+}$$
$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$
$$Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$$

Illustrative Example. *We are given the following half-reactions along with their* E^0_{ox} *or* E^0_{red} *values*

$$Ag^+ + e^- \longrightarrow Ag, \qquad E^0_{red} = +0.80\ V$$

$$Zn \longrightarrow Zn^{2+} + 2e^-, \quad E^0_{ox} = +0.76\ V$$

$$Cu \longrightarrow Cu^{2+} + 2e^-, \qquad E^0_{ox} = -0.34\ V$$

$$Ni^{2+} + 2e^- \longrightarrow Ni, \qquad E^0_{red} = -0.25\ V$$

Answer the following:

(i) Name the metals that can be oxidised by Cu.

(ii) Name the metals that cannot be oxidised by Ni.

(iii) Name the metals that can be reduced by Ni.

(iv) Name the metals that cannot be reduced by Ni.

Solution. Write all the half-reactions as reduction half-reactions with their E^0_{red} values in the decreasing order. Thus:

$$\begin{array}{ll} \textbf{OA} & \textbf{RA} \\ Ag^+ + e^- \longrightarrow & Ag,\ E^0_{Ag^+/Ag} = +0.80\ V \\ Cu^{2+} + 2e^- \longrightarrow & Cu,\ E^0_{Cu^{2+}/Cu} = +0.34\ V \\ Ni^{2+} + 2e^- \longrightarrow & Ni,\ E^0_{Ni^{2+}/Ni} = -0.25\ V \\ Zn^{2+} + 2e^- \longrightarrow & Zn,\ E^0_{Zn^{2+}/Zn} = -0.76\ V \end{array} \quad \left| \begin{array}{c} E^0 \text{ values} \\ \text{decreasing} \end{array} \right. \downarrow$$

(*i*) We know that: "*Higher oxidises lower*"

On the basis of this rule, since $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) is higher than both $E^0_{Ni^{2+}/Ni}$ (= – 0.25 V) and $E^0_{Zn^{2+}/Zn}$ (= – 0.76 V), Cu^{2+} ion can oxidise Ni and Zn both to Ni^{2+} and Zn^{2+} ions respectively.

(*ii*) We know that: "*Lower does not oxidise higher*"

On the basis of this rule, Ni^{2+} ion cannot oxidise those metals which have higher value of E^0. Thus since $E^0_{Ag^+/Ag}$ (= 0.80 V) and $E^0_{Cu^{2+}/Cu}$ (= 0.34 V) both are higher than $E^0_{Ni^{2+}/Ni}$ (= – 0.25 V), Ni^{2+} ion cannot oxidise Ag and Cu to Ag^+ and Cu^{2+} ions respectively.

(*iii*) We know that: "*Lower reduces higher*"

On the basis of this rule, since $E^0_{Ni^{2+}/Ni}$ (= – 0.25 V) is lower than both $E^0_{Cu^{2+}/Cu}$ (= 0.34 V) and $E^0_{Ag^+/Ag}$ (= 0.80 V), Ni can reduce (displace) Cu^{2+} and Ag^+ ions both from the aqueous solution of their salts to Cu and Ag respectively.

(*iv*) We know that: "*Higher does not reduce lower*"

On the basis of this rule, Ni cannot reduce the metal ions which have lower E^0 values. Thus since $E^0_{Zn^{2+}/Zn}$ (= – 0.76 V) is lower than $E^0_{Ni^{2+}/Ni}$ (= – 0.25 V), Ni cannot reduce Zn^{2+} ion to Zn metal.

III.(*a*) To determine the conditions of the feasibility of halogen-halogen displacement reactions (Redox reactions)

or

To determine the conditions of the feasibility of a redox reaction involving oxidation of a halide by another halogen

Halogen-halogen displacement reaction is a redox reaction in which a halogen reacts with the aqueous solution of metallic halide (generally potassium halide) containing another halogen. This type of displacement reaction can be represented by the following redox reaction.

$$F_2(g) + 2KCl(aq) \longrightarrow 2KF(aq) + Cl_2(g) \quad \textit{(Molecular equation)}$$

or

$$\underset{\substack{\text{Displacing halogen}\\ \text{or halogen being}\\ \text{reduced (OA)}}}{F_2(g)} + \underset{\substack{\text{Halogen being}\\ \text{displaced or halogen}\\ \text{being oxidised (RA)}}}{2Cl^-(aq)} \longrightarrow 2F^-(aq) + Cl_2(g) \quad \textit{(Ionic equation)}$$

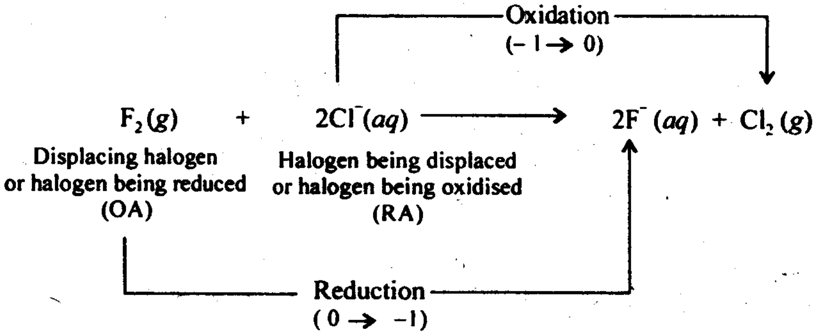
In the above redox reaction:

(*i*) $F_2(g)$ is a halogen and $KCl(aq)$ is the chloride of potassium containing another halogen, Cl. When $F_2(g)$ reacts with the aqueous solution of KCl [*i.e.* $KCl(aq)$], $Cl_2(g)$ is liberated and $KF(aq)$ is formed in solution.

(*ii*) $F_2(g)$ displaces Cl from $KCl(aq)$. Thus $F_2(g)$ is the displacing halogen and Cl is the halogen being displaced.

(*iii*) $F_2(g)$ is being reduced to $F^-(aq)$ ions and $Cl^-(aq)$ ions are being oxidised to $Cl_2(g)$. Thus $F_2(g)$ acts as OA and $Cl^-(aq)$ ions act as RA.

Thus the ionic equation given above can also be written as:



Oxidation and reduction half-reactions for the above redox reaction are:

(*a*) $$\underset{(Cl=-1)}{2Cl^-(aq)} \xrightarrow{\text{Oxidation}} \underset{(Cl=0)}{Cl_2(g)} + 2e^-, \quad E^0_{ox} = E^0_{2Cl^-/Cl_2}$$

(*b*) $$\underset{(F=0)}{F_2(g)} + 2e^- \xrightarrow{\text{Reduction}} \underset{(F=-1)}{2F^-(aq)}, \quad E^0_{red} = E^0_{F_2/2F^-}$$

The given redox reaction is feasible [*i.e.* this reaction will take place spontaneously in the forward direction (from left to right)], if the value of e.m.f. of this redox reaction as calculated from any of the equations given at (*i*), (*ii*), (*iii*) and (*iv*) given below is a positive quantity.

(*i*) e.m.f. of the redox reaction :

$$= E^0_{\text{Displacing halogen}} - E^0_{\text{Halogen being displaced}} = \text{A positive quantity}$$

(*ii*) e.m.f. of the redox reaction

$$= E^0_{\text{Halogen being reduced}} + E^0_{\text{Halogen being oxidised}}$$

$$= \text{A positive quantity}$$

(*iii*) e.m.f. of the redox reaction

$$= E^0_{\text{OA}} - E^0_{\text{RA}} = \text{A positive quantity}$$

(*iv*) e.m.f of the redox reaction

$$= E^0_{\text{ox}} \text{ for oxidation half-reaction } (a)$$

$$+ E^0_{\text{red}} \text{ for reduction half-reaction } (b)$$

$$= \text{A positive quantity}$$

If the value of e.m.f. of the redox reaction as calculated from any of the equations given above comes out to be a negative quantity, the given redox reaction will not proceed in the forward direction, *i.e.* the reaction will not take place spontaneously as shown. Rather, it will proceed in the backward direction (from right to left direction)

We have stated above that in order to make a halogen-halogen displacement reaction feasible, the value of e.m.f. of the reaction, as calculated from any of the equations (*i*) to (*iv*), should be a positive quantity. Obviously, in ordedr to get a positive value of e.m.f. or to make the reaction feasible, one of the following conditions must be satisfied.

(*a*) $E^0_{\text{Displacing halogen}} > E^0_{\text{Halogen being displaced}}$

OR

$$\text{Higher halogen} \underset{\text{is displaced by}}{\overset{\text{displaces}}{\rightleftharpoons}} \text{Lower halogen}$$

OR

(*b*) $E^0_{\text{Halogen being reduced}} > E^0_{\text{Halogen being oxidised}}$

OR

$$\text{Higher halogen} \underset{\text{is oxidised by}}{\overset{\text{is reduced by}}{\rightleftharpoons}} \text{Lower halogen}$$

(*c*) $E^0_{\text{OA}} > E^0_{\text{RA}}$

OR

Higher halogen acts as OA and lower halogen acts as RA.

OR

$$\text{Higher halogen} \underset{\text{reduces}}{\overset{\text{oxidises}}{\rightleftharpoons}} \text{Lower halogen.}$$

Illustrative Example. *Predict whether the following redox reactions will take place spontaneously or not?*

(*a*) $Cl_2(g) + 2F^-(aq) \longrightarrow 2Cl^-(aq) + F_2(g)$

(*b*) $Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2$

Given: $E^0_{Cl_2/2Cl^-} = +1.36\ V$, $E^0_{F_2/2F^-} = +2.87\ V$ *and* $E^0_{I_2/2I^-} = +0.54\ V$.

Solution. (*a*) In redox reaction (*a*), since $Cl_2(g)$ acts as OA and $F^-(aq)$ ions acts as RA, e.m.f. of redox reaction (*a*)

$$= E^0_{OA} - E^0_{RA} = E^0_{Cl_2/2Cl^-} - E^0_{F_2/2F^-} = +1.36 - 2.87 = \mathbf{-1.51\ V}$$

Since the value of e.m.f. is a negative quantity (= – 1.51 V), redox reaction (*a*) will not occur in the forward (right) direction. Rather it will proceed in backward (left) direction as shown below:

$$\underset{(OA)}{F_2(g)} + \underset{(RA)}{2Cl^-(aq)} \longrightarrow 2F^-(aq) + Cl_2(g)$$

e.m.f. of this reaction is a positive quantity as shown below:

$$\text{e.m.f.} = E^0_{OA} - E^0_{RA} = E^0_{F_2/2F^-} - E^0_{Cl_2/2Cl^-}$$
$$= +2.87 - 1.36 = +1.51 = \text{A positive quantity}$$

(*b*) In redox reaction (*b*), since $Cl_2(g)$ acts as OA and $I^-(aq)$ ions act as RA, e.m.f. of redox reaction (*b*)

$$= E^0_{OA} - E^0_{RA} = E^0_{Cl_2/2Cl^-} - E^0_{I_2/2I^-}$$
$$= 1.36 - 0.54 = +0.82\ V = \text{A positive quantity}$$

Since the value of e.m.f. is a positive quantity (= + 0.82 V), redox reaction (*b*) will occur spontaneously.

Solved Examples

Example 1. *I_2 and Br_2 are added to a solution containing I^- and Br^- ions. What reaction would occur, if the concentration of each species is 1 M. Given that:* $E^0_{I_2/I^-} = +0.54\ V$ *and* $E^0_{Br_2/Br^-} = +1.08\ V$.

Solution. Any of the following two reactions can occur

$$(a)\ \underset{\substack{(I = 0)\\ OA}}{I_2} + \underset{\substack{(Br = -1)\\ RA}}{2Br^-} \longrightarrow \underset{(I = -1)}{2I^-} + \underset{(Br = 0)}{Br_2}$$

$$(b)\ \underset{\substack{(I = 0)\\ OA}}{Br_2} + \underset{\substack{(I = -1)\\ RA}}{2I^-} \longrightarrow \underset{(Br = -1)}{2Br^-} + \underset{(I = 0)}{I_2}$$

Now we have to predict which of the above two reactions actually occurs. We know that for the feasibility of a redox reaction, E^0_{OA} should be higher than E^0_{RA}. Now in reaction (*a*), since E^0_{OA} or $E^0_{I_2/I^-}$ (= + 0.54 V) is not higher than E^0_{RA} or $E^0_{Br_2/Br^-}$ (= 1.08 V), this reaction does not occur spontaneously. In reaction (*b*), since E^0_{OA} or $E^0_{Br_2/Br^-}$ (= 1.08 V) is higher than E^0_{RA} or $E^0_{I_2/I^-}$ (= + 0.54 V), this reaction occurs spontaneously. In other words we can say I^- ions will be oxidised to I_2 and Br_2 will be reduced to Br^- ions.

Example 2. *Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction.* (*I.I.T. 2000*)

Solution. The oxidation of I^- ion (I = –1) to I_2 (I = 0) by Cl_2 as represented by the following equation can be cited as an example.

$$\begin{array}{lccccccccc} & 2KI & + & Cl_2 & \longrightarrow & 2KCl & + & I_2 \\ & (I=-1) & & (Cl=0) & & (Cl=-1) & & (I=0) \\ \text{or} & 2I^- & + & Cl_2 & \longrightarrow & 2Cl^- & + & I_2 & . \\ & (RA) & & (OA) \end{array}$$

In this reaction I^- ions acts as RA and Cl_2 molecule acts as an OA. This reaction is feasible, because

$$E^0_{OA} > E^0_{RA}$$

or $$E^0_{Cl_2/Cl^-} (= +1.36\,V) > E^0_{I_2/I^-} (= +0.53\,V).$$

Example 3. *Complete the following chemical equations:*

(*a*) $KI + Cl_2 \longrightarrow$ ....

(*b*) $KClO_3 + I_2 \longrightarrow$ .... (*I.I.T. 1996*)

Solution. (*a*) Suppose the complete equation in its ionic form is:

$$\begin{array}{ccccccc} 2I^- & + & Cl_2 & \longrightarrow & I_2 & + & 2Cl^- \\ (I=-1) & & (Cl=0) & & (I=0) & & (Cl=-1) \\ RA & & OA \end{array}$$

It is a redox reaction in which Cl_2 acts as OA and I^- ions act as RA. This reaction is feasible, if

$$[E^0_{red}]_{OA} > [E^0_{red}]_{RA}$$

or $$E^0_{Cl_2/2Cl^-} > E^0_{I_2/2I^-}$$

or $$+1.36\,V > 0.54\,V$$

Thus the complete equation is:

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

(*b*) Suppose the complete equation in its ionic form is:

$$\begin{array}{ccccccc} ClO_3^- & + & I_2 & \longrightarrow & IO_3^- & + & Cl_2 \\ (Cl=+5) & & (I=0) & & (I=+5) & & (Cl=0) \\ OA & & RA \end{array}$$

It is a redox reaction in which ClO_3^- ion acts as OA and I_2 acts as RA. This redox reaction is feasible only when

$$[E^0_{red}]_{OA} > [E^0_{red}]_{RA}$$

or $$E^0_{ClO_3^-/Cl_2} (= +1.470\,V) > E^0_{IO_3^-/I_2} (= +1.195\,V)$$

Thus the complete equation is

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$

Example 4. *Identify X in the following chemical reaction*

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$$

Solution. The given reaction shows that Cl_2 oxidises X^- to X_2 and is itself reduced to Cl^-. Thus Cl_2 acts as OA and X^- acts as RA.

$$\underset{OA}{Cl_2} + \underset{RA}{2X^-} \longrightarrow 2Cl^- + X_2$$

We know that the given redox reaction is feasible, if

$$[E^0_{red}]_{OA} > [E^0_{red}]_{RA}$$

or $$E^0_{Cl_2/2Cl^-} > E^0_{X_2/2X^-}$$

Obviously X may be Br or I, since these halogens have lower E_{red} values than $E^0_{Cl_2/2Cl^-}$.

(*b*) Halogen-halogen displacement reactions in electrochemical series

Note the following points:

(*i*) We know that in electrochemical series E^0 values corresponding to the electrodes *viz.* $F_2/2F^-$, $Cl_2/2Cl^-$, $Br_2/2Br^-$ and $I_2/2I^-$ are in the decreasing order as shown below:

$$\begin{array}{lll} \text{OA} & \text{RA} & \\ F_2 + 2e^- \longrightarrow & 2F^- & E^0_{F_2/2F^-} = +2.87\,\text{V} \\ Cl_2 + 2e^- \longrightarrow & 2Cl^- & E^0_{Cl_2/2Cl^-} = +1.36\,\text{V} \\ Br_2 + 2e^- \longrightarrow & 2Br^- & E^0_{Br_2/2Br^-} = +1.06\,\text{V} \\ I_2 + 2e^- \longrightarrow & 2I^- & E^0_{I_2/2I^-} = +0.54\,\text{V} \end{array}$$

— E^0 values decreasing ↓

(*ii*) We know that: *Higher halogen oxidises (displaces) lower halogen*

or

Lower halogen does not oxidise (displace) higher halogen

On the basis of this rule, we can conclude that among halogens, a given halogen can oxidise only those halide ions (X^-) to their respective X_2 molecules which have lower E^0 values or which lie below it but cannot oxidise those halide ions which have higher E^0 values or which lie above it. Thus:

(*a*) F_2 can oxidise all the three halide ions *viz.* Cl^-, Br^- and I^- to their respective molecules *viz.* Cl_2, Br_2 and I_2 respectively.

$$F_2 + 2Cl^- \longrightarrow Cl_2 + 2F^-$$
$$F_2 + 2Br^- \longrightarrow Br_2 + 2F^-$$
$$F_2 + 2I^- \longrightarrow I_2 + 2F^-$$

(*b*) Cl_2 can oxidise only Br^- and I^- ions to Br_2 and I_2 respectively but cannot oxidise F^- ion to F_2

$$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$$
$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$
$$Cl_2 + 2F^- \longrightarrow F_2 + 2Cl^- \text{ (\textit{Not feasible})}$$

(*c*) Br_2 can oxidise only I^- ion to I_2 but cannot oxidise F^- and Cl^- ions to F_2 and Cl_2 molecules respectively

$$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$$
$$Br_2 + 2F^- \longrightarrow F_2 + 2Br^- \text{ (\textit{Not feasible})}$$
$$Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^- \text{ (\textit{Not feasible})}$$

(*d*) I_2 cannot oxidise any of the halide ions to their respective halogen molecules.

$$\left.\begin{array}{l} I_2 + 2F^- \longrightarrow F_2 + 2I^- \\ I_2 + 2Cl^- \longrightarrow Cl_2 + 2I^- \\ I_2 + 2Br^- \longrightarrow Br_2 + 2I^- \end{array}\right\} \textit{(Not feasible)}$$

(*iii*) We know that: *Lower halogen reduces higher halogen*

or

Higher halogen does not reduce the lower halogen

On the basis of this rule, we can conclude that among halide ions, a given halide ion (X^-) can reduce only those X_2 molecules to X^- ions which have higher E^0 values or lie above it but cannot reduce those X_2 molecules which have lower E^0 values or lie below it. Thus:

(*a*) F^- ion cannot reduce any of the halogen molecules to its respective halide ion.

$$\left.\begin{array}{l} 2F^- + Cl_2 \longrightarrow F_2 + 2Cl^- \\ 2F^- + Br_2 \longrightarrow F_2 + 2Br^- \\ 2F^- + I_2 \longrightarrow F_2 + 2I^- \end{array}\right\} \textit{(Not feasible)}$$

(*b*) Cl^- ion can reduce only F_2 molecule to F^- ion but cannot reduce Br_2 and I_2 molecules to Cl^- and I^- ions respectively.

$$2Cl^- + F_2 \longrightarrow Cl_2 + 2F^-$$

$$\left.\begin{array}{l} 2Cl^- + Br_2 \longrightarrow Cl_2 + 2Br^- \\ 2Cl^- + I_2 \longrightarrow Cl_2 + 2I^- \end{array}\right\} \textit{(Not feasible)}$$

(*c*) Br^- ion can reduce Cl_2 and F_2 both to Cl^- and F^- ions respectively but cannot reduce I_2 to I^- ion.

$$Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^-$$

$$Br^- + F_2 \longrightarrow Br_2 + 2F^-$$

$$Br^- + I_2 \longrightarrow Br_2 + 2I^- \ \textit{(Not feasible)}$$

IV.(*a*) To determine conditions for the feasibility of metal-hydrogen displacement reactions (Redox reactions)

Metal-hydrogen displacement reaction is a redox reaction in which a metal reacts with an acid and metal salt is formed and H_2 gas is evolved. This type of displacement reaction can be represented by the following redox reaction:

$$Fe(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g) \ \textit{(Molecular equation)}$$

or

$$\underset{\substack{\text{Displacing}\\ \text{metal or metal}\\ \text{being oxidised}\\ \text{(R.A.)}}}{Fe(s)} + \underset{\substack{\text{Hydrogen being}\\ \text{displaced or}\\ \text{being reduced}\\ \text{(O.A.)}}}{2H^+(aq)} \longrightarrow Fe^{2+}(aq) + H_2(g) \ \textit{(Ionic equation)}$$

In the above redox reaction,

(*i*) Fe(*s*) is a metal which reacts with HCl(*aq*) (an acid) to form $FeCl_2(aq)$ (salt) and H_2 gas is evolved.

(*ii*) Fe(*s*) displaces hydrogen from HCl(*aq*). Thus Fe(*s*) acts as a displacing metal.

(*iii*) Fe(*s*) is being oxidised to $Fe^{2+}(aq)$ and $H^+(aq)$ ions are being reduced to $H_2(g)$. Thus Fe(*s*) acts as an oxidising agent (OA) and $H^+(aq)$ ion acts as a reduing agent (RA). Thus the ionic equation given above can also be written as shown below:

Oxidation
$(0 \rightarrow +2)$

$$Fe\,(s) \quad + \quad 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

Displacing metal or metal being oxidised (RA)

Hydrogen being displaced or being reduced (OA)

Reduction
$(+1 \rightarrow 0)$

Oxidation and reduction half-reactions for the above redox reaction are:

$$\underset{(Fe\,=\,0)}{Fe(s)} \xrightarrow{\text{Oxidation}} \underset{(Fe\,=\,+2)}{Fe^{2+}(aq) + 2e^-}, \quad E^0_{ox} = E^0_{Fe/Fe^{2+}}$$

$$\underset{(H\,=\,+1)}{2H^+(aq) + 2e^-} \xrightarrow{\text{Reduction}} \underset{(H\,=\,0)}{H_2(g)}, \qquad E^0_{red} = E^0_{2H^+/H_2}$$

The given redox reaction is feasible [*i.e.* this reaction will take place spontaneously in the forward direction (from left to right)], if the value of e.m.f. of this redox reaction is a positive quantity. In order to get a positive quantity of e.m.f. or to make the redox reaction to proceed in the forward direction, the following condition must be satisfied.

$$E^0_{OA} > E^0_{RA}$$

or
$$E^0_{RA} < E^0_{OA}$$

Now since $E^0_{OA} = E^0_{2H^+/H_2} = 0$, E^0_{RA} or $E^0_{Fe^{2+}/Fe}$ should be less than zero, *i.e.* E^0_{RA} or $E^0_{Fe^{2+}/Fe}$ should be a negative quantity.

This discussion shows that only those metals can displace hydrogen from HCl or only those metals can be oxidised to metal cations which have negative value of their E^0..

Illustrative Example. *Which of the following metals can liberate H_2 gas from dilute mineral acids. Zn, Mg, Cu and Ag. Given that $Zn^{2+}/Zn = -0.76$ V, $Mg^{2+}/Mg = -2.37$ V, $Cu^{2+}/Cu = +0.34$ V, $Ag^+/Ag = +0.80$ V.*

Solution. Since Zn and Mg have negative values of their E^0_{red}, these metals can liberate H_2 gas. On the other hand, Cu and Ag cannot liberate H_2 gas because E^0_{red} values for both these metals are positive.

Alternative solution. Suppose that all the metals can liberate H_2 gas. Thus the reaction of these metals with acids can be represented by following redox reactions:

RA OA

(*a*) $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

(*b*) $Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$

(*c*) $Cu + 2H^+ \longrightarrow Cu^{2+} + H_2$

(*d*) $2Ag + 2H^+ \longrightarrow 2Ag^+ + H_2$

$$\text{e.m.f. of reaction } (a) = E^0_{OA} - E^0_{RA} = E^0_{2H^+/H_2} - E^0_{Zn^{2+}/Zn}$$
$$= 0 - (-0.76) = \mathbf{+0.76\ V}$$

$$\text{e.m.f. of reaction } (b) = E^0_{OA} - E^0_{RA} = E^0_{2H^+/H_2} - E^0_{Mg^{2+}/Mg}$$
$$= 0 - (-2.37) = \mathbf{+2.37\ V}$$

Since e.m.f. of reactions (*a*) and (*b*) both is a positive quantity, these reactions will occur spontaneously, *i.e.* Zn and Mg both react with aqueous solution of mineral acids and liberate H_2 gas

$$\text{e.m.f. of reaction } (c) = E^0_{OA} - E^0_{RA} = E^0_{2H^+/H_2} - E^0_{Cu^{2+}/Cu}$$
$$= 0 - 0.34\ V = \mathbf{-0.34\ V}$$

$$\text{e.m.f. of reaction } (d) = E^0_{OA} - E^0_{RA} = E^0_{2H^+/H_2} - E^0_{Ag^+/Ag}$$
$$= 0 - 0.80 = \mathbf{-0.80\ V}$$

Now since e.m.f. of reactions (*c*) and (*d*) both is a negative quantity, these reactions will not occur spontaneously, *i.e.* Cu and Ag do not react with dilute mineral acids and hence do not liberate H_2 gas.

(*b*) Production of H_2 gas by the action of transition metals on HCl: Reducing property of transition metals

When transition metals (M) of 1st transition series react with an acid (*e.g.* HCl) in aqueous solution, H_2 gas is evolved and metallic chloride (MCl_2) is formed.

$$M(s) + 2HCl(aq) \longrightarrow MCl_2(aq) + H_2(g)$$
$$\text{or} \quad M(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g)$$

In this reaction M(*s*) reduces HCl(*aq*) to $H_2(g)$, *i.e.* transition metal, M(*s*) acts as a reducing agent, since it [*i.e.* M(*s*)] can lose two electrons to get oxidised to $M^{2+}(aq)$. These electrons are accepted by $H^+(aq)$ ions which are reduced to $H_2(g)$.

Now when we look at $E^0_{M^{2+}/M}$ values of transition metals of 1st transition series as given in the margin, we find that, excepting Cu, all the remaining

Metal (M)	$E^0_{M^{2+}/M}$ *value*
Sc	–
Ti	– 1.60 V
V	– 1.20 V
Cr	– 0.91 V
Mn	– 1.81 V
Fe	– 0.44 V
Co	– 0.28 V
Ni	– 0.25 V
Cu	– 0.34 V
Zn	– 0.76 V

metals have negative values of $E^0_{M^{2+}/M}$ and hence can react with HCl to liberate H_2 gas. Since Cu has positive value of $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V), Cu is not able to liberate H_2 gas from HCl.

Solved Examples

Example1. *Will Fe(s) be oxidised to Fe^{2+} ions by reacting with 1.0 M HCl? Given that $E^0_{Fe/Fe^{2+}}$ = + 0.44.* *(I.I.T. 1986)*

Solution. Since $E^0_{Fe/Fe^{2+}}$ = + 0.44 V, $E^0_{Fe^{2+}/Fe}$ = - 0.44 V. Now since the value of $E^0_{Fe^{2+}/Fe}$ (= – 0.44 V) is a negative quantity, Fe(*s*) is able to react with HCl to liberate H_2 gas and to get itself oxidised to Fe^{2+} ion. Thus the following reaction is feasible

$$Fe(s) + 2HCl \longrightarrow FeCl_2 + H_2$$

or

$$Fe(s) + 2H^+ \longrightarrow Fe^{2+} + H_2$$

Alterinative solution. Suppose Fe(*s*) reacts with HCl and gets oxidised to Fe^{2+} ion. Thus:

$$Fe(s) + 2HCl \longrightarrow FeCl_2 + H_2$$

or

$$\underset{(RA)}{Fe(s)} + \underset{(OA)}{2H^+} \longrightarrow Fe^{2+} + H_2$$

Now, e.m.f. of above redox reaction

$$= E^0_{OA} - E^0_{RA} = E^0_{2H^+/H_2} - E^0_{Fe^{2+}/Fe} = 0 - (-0.44\text{ V})$$
$$= +0.44\text{ V}$$

Now since e.m.f. is a positive quantity, the above redox reaction is feasible, *i.e.* Fe(*s*) reacts with HCl and is oxidised to Fe^{2+} ions.

Example 2. *Can H_2 be prepared by the action of H_2SO_4 on Cu and Fe? Explain on the basis of the following date $E^0_{Cu/Cu^{2+}}$ = –0.34 V, $E^0_{Fe/Fe^{2+}}$ = 0.44 V.*

Solution. Since $E^0_{Cu/Cu^{2+}}$ (oxidation potential) = – 0.34 V, $E^0_{Cu/Cu^{2+}}$ (reduction potential) = + 0.34 V. Similarly since $E^0_{Fe/Fe^{2+}}$ (oxidation potential) = 0.44 V, $E^0_{Fe^{2+}/Fe}$ (reduction potential) = –0.44 V. Now since it is only Fe which has negative value of its standard reduction potential, this metal can displace hydrogen from H_2SO_4, *i.e.* H_2 can be prepared by the action of H_2SO_4 only on Fe. Since Cu has positive value of its standard reduction potential, this metal is not able to displace hydrogen from H_2SO_4. Thus H_2 cannot be prepared by the action of H_2SO_4 on Cu.

Example 3. *Give the reason for the following: Although Al is below (negative value) hydrogen in electrochemical series, it is stable in air and water.* *(I.I.T. 1994)*

Solution. Since Al is below hydrogen in the electrochemical series, it has negative value of $E^0_{Al^{3+}/Al}$ (= – 1.67 V) and hence shuold be able to displace H_2 from water (steam)

$$2Al + 6H_2O\,(steam) \longrightarrow Al(OH)_3 + 3H_2$$

When Al is kept in air, it combines with O_2 of the air and forms a protective layer of Al_2O_3 on its surface. This layer prevents Al to react with air and H_2O.

Example 4. *Predict the reaction of 1N H_2SO_4 with the following metals: (a) Cu (b) Pb. Given that $Cu^{2+}/Cu = 0.34$ V and $Pb^{2+}/Pb = -0.13$ V.*

Solution. We know that only those metals which have negative E^0_{red} values can produce H_2 gas by reacting with H_2SO_4. Thus:

(*a*) Since $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) is a positive quantity, Cu cannot evolve H_2 gas from H_2SO_4

(*b*) Since $E^0_{Pb^{2+}/Pb}$ (= – 0.13 V) is a negative quantity, Pb can liberate H_2 gas from H_2SO_4.

(*c*) Metal-hydrogen displacement reactions in electrochemical series

The metals lying below hydrogen in the electrochemical series can displace hydrogen from acids, since these metals have negative values of E^0_{red}. On the other hand the metals lying above lydrogen in the series are not able to displace hydrogen from acids, since these metals have positive vlues of E^0_{red}.

Solved Examlpes

Example 1. *Arrange H, A, B, C, D, and E in electrochemical series in the increasing order of their electrode potentials. Given that:*

(*a*) $A + H_2SO_4 \longrightarrow ASO_4 + H_2$

(*b*) $C + ACl_2 \longrightarrow CCl_2 + A$

(*c*) $C + ECl_2 \longrightarrow$ *No reaction*

(*d*) $D + 2BCl \longrightarrow DCl_2 + 2B$

(*e*) $D + H_2SO_4 \longrightarrow$ *No reaction*

Solution. In reaction (*a*), since A reacts with H_2SO_4 and liberates H_2 gas but in reaction (*e*) D does not react with H_2SO_4, A has negative value of E^0 and D has positive value of E^0, *i.e.*

$$E^0_A < E^0_H \qquad ...(i)$$

and

$$E^0_D > E^0_H \text{ or } E^0_H < E^0_D \qquad ...(ii)$$

In reaction (*b*), since C displaces A from ACl_2,

$$E^0_C < E^0_A \qquad ...(iii)$$

In reaction (*c*), since C is not able to displace E from ECl_2

$$E^0_C > E^0_E \text{ or } E^0_E < E^0_C \qquad ...(iv)$$

In reaction (*d*), since D displaces B from BCl,

$$E^0_D < E^0_B \qquad ...(v)$$

On combining all the relations given above, we can write the increasing order as:

$$E^0_E < E^0_C < E^0_A < E^0_H < E^0_D < E^0_B$$

or

$$E < C < A < H < D < B$$

$$\xrightarrow{\hspace{2em}} E^0 \text{ values increasing} \xrightarrow{\hspace{2em}}$$

Example 2. *Study the following redox reactiosn and arrange H, A and B in the form of electrochemical series in the decreasing order.*

(*a*) $2A + 2HCl \longrightarrow 2ACl + H_2$
(*b*) $B + 2HCl \longrightarrow BCl_2 + H_2$
(*c*) $2A + BCl_2 \longrightarrow 2ACl + B$

Solution. In reactions (*a*) and (*b*), since A and B both replace hydrogen from HCl, both these elements have negative values of E^0 *i.e.*

$$E^0_{\text{A}} < E^0_{\text{H}} \qquad ...(i)$$

$$E^0_{\text{B}} < E^0_{\text{H}} \qquad ...(ii)$$

In reaction (*c*), since A replaces B from BCl_2,

$$E^0_{\text{A}} < E^0_{\text{B}} \qquad ...(iii)$$

On combining (*i*),(*ii*) and (*iii*), we gat:

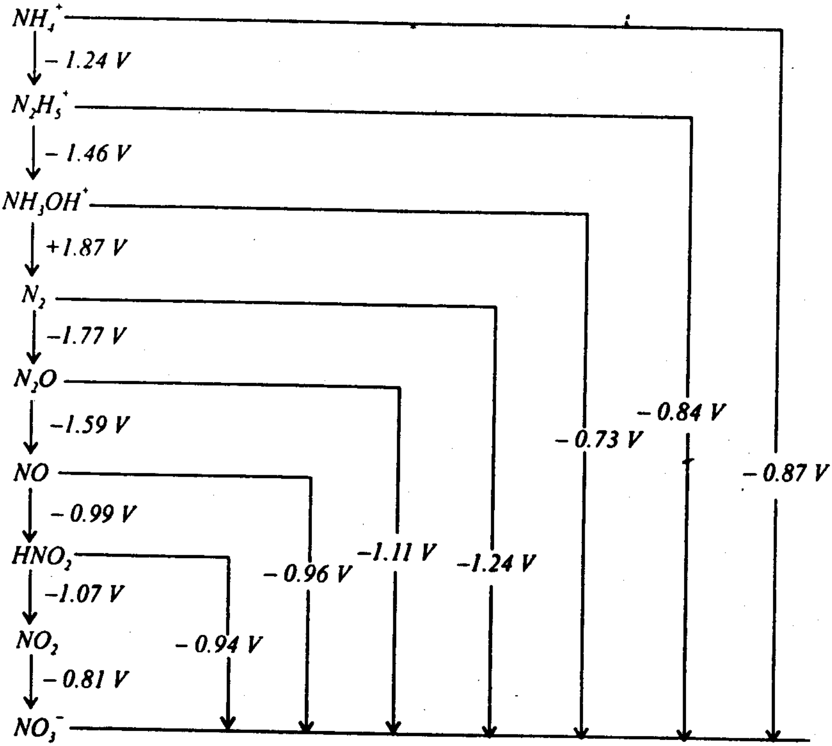
$$E^0_{\text{A}} < E^0_{\text{B}} < E^0_{\text{H}}$$

or $$\text{A} < \text{B} < \text{H}$$

or $$\text{H} > \text{B} > \text{A}$$

—— E^0 values decresing ⟶

Example 3. *Standard oxidation potential values for the compounds of nitrogen in acidic solution are given below:*



(A) Predict whether Cl_2 *(*$E^0_{Cl_2/2Cl^-} = +1.36\ V$*) can oxidise (i)* N_2 *to* N_2O *(ii)* NO_2 *to* NO_3^-

(B) Predict whether hydroxyl ammonium cations (NH_3OH^+) *have a tendency to give* N_2 *and hydrazinium cations* ($N_2H_5^+$)*. Also write the balanced equation.*

(C) Predict whether the following disproportionation reactions take place as written

(i) $4N_2H_5^+ + 2H^+ + 3H_2O \longrightarrow NH_4^+ + NO_3^-$

(ii) $7NH_3OH^+ \longrightarrow 3N_2H_5^+ + 4H_2O + NO_3^- + 5H^+$

(iii) $5N_2O + H_2O \longrightarrow 2NO_3^- + 4N_2 + 2H^+$

(iv) $2N_2O \longrightarrow N_2 + 2NO$

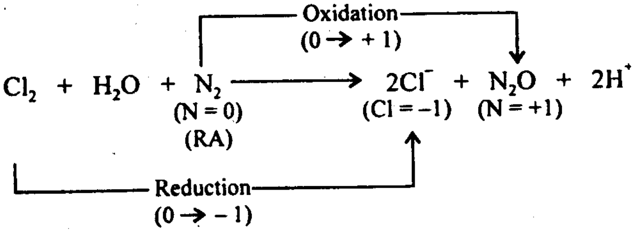
(v) $4NO + H_2O \longrightarrow N_2O + 2HNO_2$

(vi) $8NO + H_2O \longrightarrow 2NO_3^- + 2H^+ + 3N_2O$

(vii) $3HNO_2 \longrightarrow 2NO + NO_3^- + H^+ + H_2O$

(viii) $2NO_2 + H_2O \longrightarrow HNO_2 + NO_3^- + H^+$

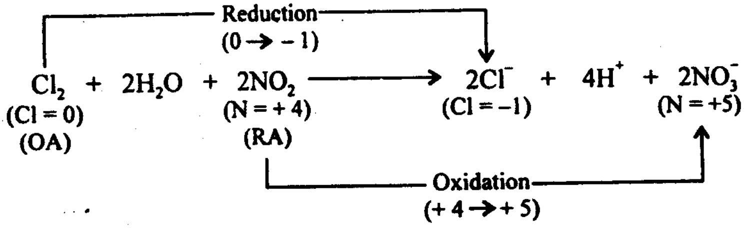
Solution. (A) (*i*) Assume that Cl_2 can oxidise N_2 to N_2O. In this reaction Cl_2 is reduced to Cl^- ions and N_2 is oxidised to N_2O. Thus:



$$Cl_2 + H_2O + \underset{\substack{(N=0)\\(RA)}}{N_2} \longrightarrow \underset{(Cl=-1)}{2Cl^-} + \underset{(N=+1)}{N_2O} + 2H^+$$

Now since $E^0_{OA} = E^0_{Cl_2/Cl^-}$ (= + 1.36 V) is not higher than $E^0_{RA} = E^0_{N_2O/N_2}$ (= + 1.77 V), the above redox reaction is not feasible, *i.e.* Cl_2 cannot oxidise N_2 to N_2O.

(*ii*) When Cl_2 oxidises NO_2 to NO_3^-, it is reduced to Cl^- ions. Thus:



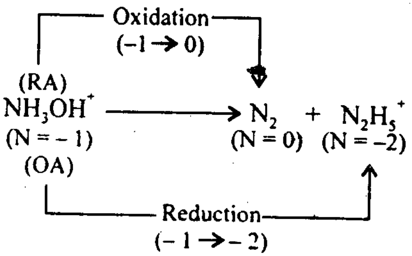
$$\underset{\substack{(Cl=0)\\(OA)}}{Cl_2} + 2H_2O + \underset{\substack{(N=+4)\\(RA)}}{2NO_2} \longrightarrow \underset{(Cl=-1)}{2Cl^-} + 4H^+ + \underset{(N=+5)}{2NO_3^-}$$

Now since $E^0_{OA} = E^0_{Cl_2/Cl^-}$ (= + 1.36 V) is higher than $E^0_{RA} = E^0_{NO_3^-/NO_2}$ (= + 0.81 V), the above redox reaction is feasible, *i.e.* Cl_2 can oxidise NO_2 to NO_3^-

(B) The conversion of hydroxyl ammonium cations (NH_3OH^+) into N_2 and hydrazinium cations ($N_2H_5^+$) is a disproportionation reaction which can be represented by the following unbalanced equation

$$\underset{(N=-1)}{NH_3OH^+} \longrightarrow \underset{(N=0)}{N_2} + \underset{(N=-2)}{N_2H_5^+} \quad (\textit{Unbalanced equation})$$

Above equation can also be written as:



Now since $E^0_{OA} = E^0_{NH_3OH^+/N_2H_5^+}$ (= +1.46 V) in higher than $E^0_{RA} = E^0_{N_2/NH_3OH^+}$ (= − 1.87 V), the above disproportionation reaction is feasible, *i.e.* NH_3OH^+ cations have a tendency to given N_2 and $N_2H_5^+$ cations.

In order to get a balanced equation, we should find out the balanced oxidation and reduction half-reactions and then should add them

$$2NH_3OH^+ \xrightarrow{\text{Oxidation}} N_2 + 2H_2O + 4H^+ + 2e^-$$

$$2NH_3OH^+ + H^+ + 2e^- \xrightarrow{\text{Reduction}} N_2H_5^+ + 2H_2O$$

On Adding: $$4NH_3OH^+ \longrightarrow N_2 + N_2H_5^+ + 4H_2O + 3H^+$$

This is the required balanced equation.

(*C*) (*i*) The reaction,

$$\underset{(N=-2)}{4N_2H_5^+} + 2H^+ + 3H_2O \longrightarrow \underset{(N=-3)}{NH_4^+} + \underset{(N=+5)}{NO_3^-},\ E^0 = ?$$

is a disproportionaton reaction, since $N_2H_5^+$ ion (N = −2) is being oxidised to NO_3^- (N = +5) and in also being reduced to NH_4^+ (N = − 3). This reaction can be broken into the following oxidation and reduction half-reactions (Unbalanced equations)

$$\underset{(N=-2)}{N_2H_5^+} \xrightarrow{\text{Oxidation}} \underset{(N=+5)}{NO_3^-},\ E^0_{ox}\ -0.84\ V$$

$$\underset{(N=-2)}{N_2H_5^+} \xrightarrow{\text{Reduction}} \underset{(N=-3)}{NH_4^+}, \; E^0_{red} = +1.24\text{ V}$$

E^0 value of the given disproportionation reaction is given by:

$$E^0 = E^0_{ox} + E^0_{red} = -0.84 + 1.24 = +\mathbf{0.40\text{ V}}$$

Since E^0 value is positive (= + 0.40 V), the given disproportionation reaction proceeds as indicated by the equation.

(*ii*) $7NH_3OH^+ \longrightarrow 3N_2H_5^+ + 4H_2O + NO_3^- + 5H^+, E^0 = ?$

(N = – 1) (N = – 2) (N = + 5)

$NH_3OH^+ (N = -1) \xrightarrow{\text{Oxidation}} NO_3^- (N = +5) \; E^0_{ox} = -0.73\text{ V}$

$NH_3OH^+ (N = -1) \xrightarrow{\text{Reduction}} N_2H_5^+ (N = -2), \; E^0_{red} = +1.46\text{ V}$

$\therefore E^0 = E^0_{ox} + E^0_{red} = -0.73 + 1.46 = +\mathbf{0.73\text{ V}}$

Thus the given reaction is feasible

(*iii*) $5N_2O + H_2O \longrightarrow 2NO_3^- + 4N_2 + 2H^+, E^0 = ?$

(N= +1) (N= + 5) (N = 0)

$N_2O (N = +1) \xrightarrow{\text{Oxidation}} NO_3^- (N = +5), E^0_{ox} = -1.11\text{ V}$

$N_2O (N = +1) \xrightarrow{\text{Reduction}} N_2 (N = 0), \quad E^0_{red} = +1.77\text{ V}$

$\therefore E^0 = E^0_{ox} + E^0_{red} = -1.11 + 1.77 = +\mathbf{0.66\text{ V}}$

Thus the given reaction proceeds as written.

(*iv*) $2N_2O \longrightarrow N_2 + 2NO, \quad E^0 = ?$

(N = +1) (N = 0) (N = +2)

$N_2O (N = +1) \xrightarrow{\text{Oxidation}} NO (N = +2), \; E^0_{ox} = -1.59\text{ V}$

$N_2O (N = +1) \xrightarrow{\text{Reduction}} N_2 (N = 0), \; E^0_{red} = +1.77\text{ V}$

$\therefore E^0 = -1.59 + 1.77 = \mathbf{0.18\text{ V}}$

Thus the given reaction is feasible.

(*v*) $4NO + H_2O \longrightarrow N_2O + 2HNO_3, \quad E^0 = ?$

(N = +2) (N = +1) (N = +3)

$NO (N = +2) \xrightarrow{\text{Oxidation}} HNO_2 (N = +3), \; E^0_{ox} = -0.99\text{ V}$

$NO (N = +2) \xrightarrow{\text{Reduction}} N_2O (N = +1), \; E^0_{red} = +1.59\text{ V}$

$\therefore E^0 = -0.99 + 1.59 = +\mathbf{0.60\text{ V}}$

Thus the given reaction is feasible.

(*vi*) $\underset{(N=+2)}{8NO} + H_2O \longrightarrow \underset{(N=+5)}{2NO_3^-} + 2H^+ + \underset{(N=+1)}{3N_2O}, \ E^0 = ?$

$NO\,(N=+2) \xrightarrow{\text{Oxidation}} NO_3^-\,(N=+5), \ E^0_{ox} = -0.96\,V$

$NO\,(N=+2) \xrightarrow{\text{Reduction}} N_2O\,(N=+1), \ E^0_{red} = +1.59\,V$

$\therefore E^0 = E^0_{ox} + E^0_{red} = -0.96 + 1.59 = \mathbf{+0.63\,V}.$

Thus the given disproportionation reaction takes place in the forward direction

(*vii*) $\underset{(N=+3)}{3HNO_2} \longrightarrow \underset{(N=+2)}{2NO} + \underset{(N=+5)}{NO_3^-} + H^+ + H_2O, E^0 = ?.$

$\underset{(N=+3)}{HNO_2} \xrightarrow{\text{Oxidation}} \underset{(N=+5)}{NO_3^-}, \quad E^0_{ox} = -0.94\,V$

$\underset{(N=+3)}{HNO_2} \xrightarrow{\text{Reduction}} \underset{(N=+2)}{NO}, \quad E^0_{red} = +0.99\,V$

$\therefore E^0 = E^0_{ox} + E^0_{red} = -0.94 + 0.99\,V = \mathbf{+0.05\,V}$

Thus the given reaction takes place as shown above.

(*viii*) $\underset{(N=+4)}{2NO_2} + H_2O \longrightarrow \underset{(N=+3)}{HNO_2} + \underset{(N=+5)}{NO_3^-} + H^+, E^0 = ?$

$\underset{(N=+4)}{NO_2} \xrightarrow{\text{Oxidation}} \underset{(N=+5)}{NO_3^-}, \ E^0_{ox} = -0.81\,V$

$\underset{(N=+4)}{NO_2} \xrightarrow{\text{Reduction}} \underset{(N=+3)}{HNO_2}, \ E^0_{red} = +1.07\,V$

$\therefore E^0 = E^0_{ox} + E^0_{red} = -0.81 + 1.07 = \mathbf{+0.26\,V}$

The given reaction takes place as shown above.

V. Electropositive and electronegative character of elements

(*a*) The elements which have nagative value of E^0_{red} have a tendency to lose electrons readily to get oxidised to form cations. Such elments are called electropositive elements. Thus the elements having negative value of E^0_{red} show electropositive character. As the value of E^0_{red} becomes more and more negative, the tendency of the element to lose elctrons readily increases and hence electropositive character of the element also increases. Since in the electrochemical series, Li has the most negtative value of $E^0_{Li^+/Li}$, Li metal has the maximum electropositive character.

Illustrative Example. Since all the elements of group II A have negative value of $E^0_{M^{2+}/M}$, all these elements show electropositive character. Since as we proceed from Be to Ba in group IIA, the value of $E^0_{M^{2+}/M}$ becomes more and more negative, the electropositive character of these metals increases from Be to Ba.

$$E^0_{red} \text{ values: } \left\{ \begin{array}{ccccc} E_{Be^{2+}/Be} & E^0_{Mg^{2+}/Mg} & E^0_{Ca^{2+}/Ca} & E^0_{Sr^{2}/Sr} & E^0_{Ba^{2+}/Ba} \\ -1.85\,V & -2.37\,V & -2.87\,V & -2.89\,V & -2.90\,V \end{array} \right.$$

$$\xrightarrow{\hspace{3em}\text{Become more negative}\hspace{3em}}$$

Electropositive character: Be < Mg < Ca < Sr < Ba

$$\xrightarrow{\text{Increases}}$$

(*b*) The elements which have positive value of E^0_{red} have a tendency to gain electrons readily to get reduced to form anions. Such elements are called electronegative elements. Thus the elements having positive value of E^0_{red} show electronegative character. As the value of E^0_{red} becomes more and more positive, the tendency of the element to gain elctrons increases and hence the electronegative character of the element also increases.

Illustrative Example. Since all the halogens have positive value of $E^0_{X_2/2X^-}$, these halogens show elecronegative character. Since as we move from F_2 to I_2 in group VIIA, the value of $E^0_{X_2/2X^-}$ becomes less and less positive, the electronegative character decreases from F_2 to I_2.

$$E^0_{red} \text{ values: } \left\{ \begin{array}{cccc} E^0_{F_2/2F^-} & E^0_{Cl_2/2Cl^-} & E^0_{Br_2/2Br^-} & E^0_{I_2/2I^-} \\ +2.87\,V & +1.35\,V & +1.06\,V & +0.53\,V \end{array} \right.$$

$$\xrightarrow{\hspace{3em}\text{Become more positive}\hspace{3em}}$$

Electronegative character: $F_2 > Cl_2 > Br_2 > I_2$

$$\xrightarrow{\text{Decreases}}$$

(*c*) If we are given two metals out of which one has positive value of E^0 and the other has negative value of E^0, the metal having – *ive* value of E^0 is more electropositive than the metal having +*ive* volue of E^0.

Illustrative Example. Since the value fo $E^0_{Zn^{2+}/Zn}$ (= – 0.763 V) is negative and that of $E^0_{Ag^+/Ag}$ (= + 0.779 V) is postive, Zn is more electropositve than Ag. It is due to greater electropositive character of Zn that this metal can displace Ag from $Na[Ag(CN)_2]$ solution

$$2Na[Ag(CN)_2](aq) + Zn(s) \longrightarrow Na_2[Zn(CN)_4](aq) + 2Ag(s)$$

$$\text{or} \quad 2[Ag(CN)_2]^-(aq) + Zn^0(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2Ag^0(s)$$

The discussion made at (*a*), (*b*) and (*c*) above shows that:

Lower is the value of E^0 of a metal, greater is the electropositive charracter of that metal. Thus the electropositive character of metals increases with the decrease of their E^0 values.

Illustrative Example. ***The electrode potential of four metallic elements A, B, C, and D are + 0.80 V, – 0.76 V, + 0.12 V and + 0.34 V respectively.***

Arrange these elements in the increasing order of their metallic or electropositive character.

Solution. We know that lower is the value of E^0 of a metatlic element, greater is its tendency to lose electrons and hence greater is its electropositive character. Thus since E^0 values decrease as 0.80 V(A) > 0.34 V(D) > 0.12 V(C) and – 0.76 V (B), the electropositive charecter of A, B, C, and D increases as:

A < D < C < B **(Answer)**

VI. Reactivity of metals

We have already said that in a metal-metal displacement reaction (redox reaction), a metal having lower value of E^0_{red} can displace (*i.e.* reduce) the metal having higher value of E^0_{red} from the solution of its salt. Thus a metal having lower (*i.e.* less positive or more negative) value of E^0_{red} is more reactive than the metal having higher value of E^0_{red} (more positive or less negative) in displacing it from the solution if its salt.

Since the value of E^0_{red} of metals decreases down the electrochemical series, the reactivity of metals increases downwards.

Illustrative Example. *Arrange the following metals in the decreasing order of their reactivity: Al, Zn, Sn, and Cu. Given that* $E^0_{Al^{3+}/Al} = -1.60\ V$, $E^0_{Zn^{2+}/Zn} = -0.74\ V$, $E^0_{Sn^{4+}/Sn^{2+}} = +0.15\ V$, $E^0_{Cu^{2+}/Cu} = +0.34\ V$.

Solution. E^0_{red} values can be arranged as:

E^0_{red} *values* :	$E^0_{Al^{3+}/Al}$	$E^0_{Zn^{2+}/Zn}$	$E^0_{Sn^{4+}/Sn^{2+}}$	$E^0_{Cu^{2+}/Cu}$
	$-1.6\ V$	$-0.74\ V$	$+0.15\ V$	$+0.34\ V$

———— Increase ————→

Reactivity of metals: ———— Decreases ————→

Thus the reactivity of the given metals can be arranged as: Al > Zn > Sn > Cu (*Decreasing order*)

VII. Reactivity of halogens

We have already said that in a halogen-halogen displacement reaction (redox reaction), a halogen having higher value (more positive) of E^0_{red} can displace (*i.e.* oxidise) other halogen having lower value of E^0_{red}. Thus a halogen having higher value of E^0_{red} is more reactive than the halogen having lower value of E^0_{red} in displacing it from the aqueous solution of potassium halide. Since the value of E^0_{red} decreases from $E^0_{F_2/2F^-}$ to $E^0_{I_2/2I^-}$, the reactivity of halogens decreases as $F_2 > Cl_2 > Br_2 > I_2$.

VIII. To predict the relative stability of different oxidation states of an element in aqueous solution

If an element exists in more than one oxidation state in aqueous solution, the relative stability of these oxidation states can be known with the help of E^0

values. This point can well be understood by considering the following exomples:

Solved Examples

Example 1. *Explain why* Cu^+ *is less stable than* Cu^{2+} *in aqueous solution. Given that* $E^0_{Cu^{2+}/Cu} = +0.34\ V$ *and* $E^0_{Cu^+/Cu} = +0.52\ V$.

Solution. The reduction of Cu^+ and Cu^{2+} ions in aqueous solution to Cu can be shown by the following reduction half-reactions

O.A. R.A

$Cu^+(aq) + e^- \longrightarrow Cu(s),\quad E^0_{Cu^+/Cu} = +0.52\ V$

Stronger O.A.

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s),\quad E^0_{Cu^{2+}/Cu} = +0.34\ V$

Weaker O.A

In these equations $Cu^+(aq)$ and $Cu^{2+}(aq)$ both act as O.A. and Cu (*s*) acts as R.A.

Now since $E^0_{Cu^+/Cu}$ (= + 0.52 V) > $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V), $Cu^+(aq)$ is stronger O.A. than $Cu^{2+}(aq)$ and hence $Cu^+(aq)$ gets reduced to Cu(*s*) more readily than $Cu^{2+}(aq)$ is reduced to Cu(*s*). Thus $Cu^+(aq)$ is less stable than $Cu^{2+}(aq)$, *i.e.* $Cu^+(aq) < Cu^{2+}(aq)$.

Example 2. (*a*) *Comment on the relative stablity of +2 and +3 oxidiation states of Fe and Mn in 1M aqueous solution.*

(*b*) *Which of the above two metals (Fe and Mn) may be easily oxidised to +2 state.*

Given : $Fe^{2+}/Fe = -0.40\ V$, $Fe^{3+}/Fe^{2+} = +0.80\ V$, $Mn^{2+}/Mn = -1.2\ V$, *and* $Mn^{3+}/Mn^{2+} = +1.5\ V$.

Solution. (*a*) (*i*) The reduction of $Fe^{2+}(aq)$ to Fe(*s*) and that of $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$ can be represented by the reduction half-reactions given below:

OA RA

$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s),\quad E^0_{Fe^{2+}/Fe} = -0.40\ V$

Weaker OA

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq),\quad E^0_{Fe^{3+}/Fe^{2+}} = +0.80\ V$

Stronger OA

Now since $E^0_{Fe^{3+}/Fe^{2+}}$ (= + 0.80 V) > $E^0_{Fe^{2+}/Fe}$ (= – 0.40 V), $Fe^{3+}(aq)$ ion is stronger OA than Fe^{2+} (*aq*) and hence $Fe^{3+}(aq)$ ion will be reduced to $Fe^{2+}(aq)$ ion more readily than $Fe^{2+}(aq)$ can be reduced to Fe(*s*). Thus $Fe^{3+}(aq)$ ion is less stable than $Fe^{2+}(aq)$, *i.e.* Fe in aqueous solution is less stable in +3 oxidation state than it is in +2 oxidation state [$Fe^{3+}(aq) < Fe^{2+}(aq)$]

(*ii*) The reduction of $Mn^{2+}(aq)$ to Mn(*s*) and that of $Mn^{3+}(aq)$ to $Mn^{2+}(aq)$ can be represented by the following reduction half-reactions.

OA RA

$Mn^{2+}(aq) + e^- \longrightarrow Mn(s),\quad E^0_{Mn^{2+}/Mn} = -1.2\ V$

Weaker OA

$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq)$, $E^0_{Mn^{3+}/Mn^{2+}} = +1.5$ V

Stronger OA

Now since $E^0_{Mn^{3+}/Mn^{2+}}$ (= +1.5 V) > $E^0_{Mn^{2+}/Mn}$ (= − 1.2 V), $Mn^{3+}(aq)$ ion is stronger OA than $Mn^{2+}(aq)$ ion and hence $Mn^{3+}(aq)$ will get reduced to $Mn^{2+}(aq)$ more easily than $Mn^{2+}(aq)$ gets reduced to Mn(*s*). Thus $Mn^{3+}(aq)$ is less stable than $Mn^{2+}(aq)$ *i.e.* Mn in aqueous solution is less stable in +3 oxidation state than it is in +2 oxidation state [$Mn^{3+}(aq) < Mn^{2+}(aq)$].

(*b*) The oxidation of Fe(*s*) to $Fe^{2+}(aq)$ and that of Mn(*s*) to $Mn^{2+}(aq)$ can be represented by the following oxidation half-reactions.

RA OA

$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$, $E^0_{Fe^{2+}/Fe} = -0.40$ V

Weaker RA *Stronger OA*

$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$, $E^0_{Mn^{2+}/Mn} = -1.20$ V

Stronger RA *Weaker OA*

Now since $E^0_{Mn^{2+}/Mn}$ (=−1.20 V)< $E^0_{Fe^{2+}/Fe}$ (=+0.40V), Mn(*s*) is stronger RA than Fe(*s*), *i.e.* Mn(*s*) will be oxidised to $Mn^{2+}(aq)$ more easily than Fe(*s*) gets oxidised to $Fe^{2+}(aq)$

Nernst Equation

To calculate electrode potential of a given electrode with the help of Nernst equation

If the concentration of the electrolyle solution is 1 mol L^{-1} or 1 M and the temperature is 298K (25°C), the electrode potential of the given electrode is called standard electrode potential (E^0). However, if the concentration of the electrolyte solution is different from 1M, the electrode potential of the electrode has different value from that of standard electrode potential, E^0. This value can be calculated with the help of Nernst equation. For this purpose *the electrode reaction is always written as reduction reaction.* Suppose we have to determine the electrode potential of $M^{n+}(aq)/M(s)$ electrode.

The reduction reaction corresponding to this electrode is:

$$M^{n+}(aq) + ne^- \longrightarrow M(s) \qquad ...(i)$$

The value of electrode reduction potential, $E_{M^{n+}(aq)/M(s)}$ for the electrode, $M^{n+}(aq)/M(s)$ is given by Nernst equation *viz.*

$$E_{M^{n+}(aq)/M(s)} = E^0_{M^{n+}(aq)/M(s)} - \frac{RT}{nF}\ln\frac{[M(s)]}{[M^{n}(aq)}$$

$$= E^0_{M^{n+}(aq)/M(s)} - \frac{2.303\,RT}{nF}\log\frac{[M(s)]}{[M^{n+}(aq)]}\ (\therefore \ln = 2.303\log) \qquad ...(ii)$$

In this equation:

$E^0_{M^{n+}(aq)/M(s)}$ = Standard electrode potential for the electrode, $M^{n+}(aq)/M(s)$

R = Gas constant = 8.314 JK^{-1} mol^{-1}
T = temperature in Kelvin = 298K
n = No. of electrons involved in the electrode reduction reaction (i).
F = Faraday of electricity (1F = 96500 C. mol^{-1})

Now let us calculate the value of $\dfrac{2.303\,RT}{F}$.

$$\frac{2.303\,RT}{F}=\frac{2.303\times(8.314\,\text{J.K}^{-1}\cdot\text{mol}^{-1})\times(298\,\text{K})}{96500\ \text{C.mol}^{-1}}$$

$$=\frac{2.303\times8.314\times298\,\text{J}}{96500\,\text{C}}=\frac{0.0591\,\text{J}}{\text{C}}=\frac{0.0591\,\text{C.V}}{\text{C}}\qquad(\therefore\ J=C.V)$$

$$=0.0.591\ \text{V}$$

On putting $\dfrac{2.303RT}{F}=0.0591$ V in equation (ii) we get:

$$E_{\text{M}^{n+}(aq)/\text{M}(s)}=E^{0}_{\text{M}^{n+}(aq)/\text{M}(s)}-\frac{0.0591}{n}\log\frac{[\text{M}(s)]}{[\text{M}^{n+}(eq)]}\ V\qquad\ldots(iii)$$

Since molar concentration of pure solids, liquids and gases at atmospheric pressure is taken as unity, [M(s)] = 1. Thus equation (iii) should be written as:

$$\boxed{\begin{aligned}&E_{\text{M}^{n+}(aq)/\text{M}(s)}=E^{0}_{\text{M}^{n+}/\text{M}(s)}-\frac{0.0591}{n}\log\frac{1}{[\text{M}^{n+}(aq)]}\ V\\ \text{or }&E_{\text{M}^{n+}(aq)/\text{M}(s)}=E^{0}_{\text{M}^{n+}(aq)/\text{M}(s)}+\frac{0.0591}{n}\log[\text{M}^{n+}(aq)]\ V\end{aligned}}$$

These equations represent Nernst equation which gives the electrode potential of $\text{M}^{n+}(aq)/\text{M}(s)$ electrode or for the half-cell reduction reaction,

$$\text{M}^{n+}(aq)+ne^{-}\longrightarrow\text{M}(s)$$

taking place at the above electrode at 298 K (or 25°C) and the electrolyte solution may have any molar concentration other than 1 M.

Relation between $E^{0}_{\text{Ag}^{+}/\text{Ag}}$, $E^{0}_{\text{I}^{-}/\text{AgI}/\text{Ag}}$ and $(\text{K}_{sp})_{\text{AgI}}$

Let us consider a silver electrode, Ag^{+}/Ag dipped in a solution of AgNO_3. If to this half-cell, excess of NaI (more than to precipitate whole of AgNO_3) is added, the following equilibrium is established.

$$\underset{(\text{Ag}=+1)}{\text{AgI}}+e^{-}\rightleftharpoons\underset{(\text{Ag}=0)}{\text{Ag}}+\text{I}^{-}\ (n=1)\qquad\ldots(a)$$

This reduction half-reaction correspond to $\text{I}^{-}/\text{AgI}/\text{Ag}$ electrode (it is a metal-insoluble salt-anion electrode). Thus we have two electrodes *viz.* Ag^{+}/Ag (it is a metal-metal ion electrode) and $\text{I}^{-}/\text{AgI}/\text{Ag}$. The equilibrium established for Ag^{+}/Ag electrode can be written as:

$$Ag^+ + e^- \rightleftharpoons Ag\ (n = 1) \qquad \text{...}(b)$$
$$(Ag = +1) \qquad (Ag = 0)$$

It may be seen that in both the reduction half-reactions, Ag^+ ion is reduced to Ag. We can, therefore, assume that:

$$E_{I^-/AgI/Ag} = E_{Ag^+/Ag} \qquad \text{...}(i)$$

Nernst equation for reduction half-reactions (*a*) and (*b*) which take place on $I^-/AgI/Ag$ and Ag^+/Ag electrodes respectively can be written as:

$$E_{I^-/AgI/Ag} = E^0_{I^-/AgI/Ag} - \frac{0.0592}{1}\log[I^-] \qquad \text{...}(ii)$$

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - \frac{0.0592}{1}\log\frac{1}{[Ag^+]} \qquad \text{...}(iii)$$

Now since $E^0_{I^-/AgI/Ag} = E^0_{Ag^+/Ag}$ as indicated by equation (*i*), RHS of equations (*ii*) and (*iii*) must be equal to each other, *i.e.*

$$E^0_{I^-/AgI/Ag} - 0.0592\log[I^-] = E^0_{Ag^+/Ag} - 0.0592\log\frac{1}{[Ag^+]}$$

or $$E^0_{I^-/AgI/Ag} = E^0_{Ag^+/Ag} + 0.0592\log[I^-] + 0.0592\log[Ag^+]$$

or $$E^0_{I^-/AgI/Ag} = E^0_{Ag^+/Ag} + 0.0592\log[Ag^+][I^-] \qquad \text{...}(iv)$$

Since the dissociation of AgI takes place as:

$$AgI \rightleftharpoons Ag^+ + I^-,$$

solubility product of AgI, $(K_{sp})_{AgI}$ is given by:

$$(K_{sp})_{AgI} = [Ag^+][I^-] \qquad \text{...}(v)$$

With the help of equation (*v*), equation (*iv*) becomes:

$$\boxed{E^0_{I^-/AgI/Ag} = E^0_{Ag^+/Ag} + 0.0592\log(K_{sp})_{AgI}} \qquad \text{...}(vi)$$

This equation can be used to calculate the value of $E^0_{I^-/AgI/Ag}$, if the values of $E^0_{Ag^+/Ag}$ in a saturated solution of AgI and $(K_{sp})_{AgI}$ are given.

Now since the solution of AgI is saturated, $[Ag^+] = [Cl^-]$ and hence equation (*v*) can be written as:

$$(K_{sp})_{AgI} = [Ag^+][Ag^+] = [Ag^+]^2$$

or $$[Ag^+] = \sqrt{(K_{sp})_{AgI}} \qquad \text{...}(vii)$$

With the help of equation (*vii*), equation (*iii*) reduces to:

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - 0.0592\log\frac{1}{\sqrt{(K_{sp})_{AgI}}}$$

$$= E^0_{Ag^+/Ag} - 0.0592\left[\log 1 - \log\sqrt{(K_{sp})_{AgI}}\right]$$

$$= E^0_{Ag^+/Ag} - 0.0592\left[0 - \log\sqrt{(K_{sp})_{AgI}}\right]$$

or $$\boxed{E_{Ag^+/Ag} = E^0_{Ag^+/Ag} + 0.0592 \log \sqrt{(K_{sp})_{AgI}}} \quad ...(viii)$$

This equation can be used to calculate the value of $E_{Ag^+/Ag}$ in a saturated solution of AgI, if the values of $E^0_{Ag^+/Ag}$ and $(K_{sp})_{AgI}$ are given.

Solved Examples

Example 1. *At what pH of HCl solution will hydrogen gas electrode show electrode potential of –0.118 V? H_2 gas is bubbled at 298 K and 1 atm. pressure.*

Solution. Reduction half-reaction taking place at hydrogen electrode, $2H^+(aq) \mid H_2(g)$ is:

$$\underset{(\text{Conc.} = ?)}{2H^+(aq)} + 2e^- \xrightarrow{\text{Reduction}} \underset{(p_{H_2} = 1)}{H_2(g)} \ (n = 2), \ E_{2H^+(aq)/H_2(g)} = -0.118 \text{ V}$$

On writing the Nernst equation for the above reduction half-reaction

$$E_{2H^+(aq)/H_2(g)} = E^0_{2H^+(aq)/H_2(g)} - \frac{0.0591}{2} \log \frac{p_{H_2}}{[H^+]^2}$$

or $$-0.118 = 0.0 - \frac{0.0592}{2} \log \frac{1}{[H^+]^2}$$

or $$\frac{0.118 \times 2}{0.0591} = \log 1 - 2 \log [H^+]$$

or $$\frac{0.118 \times 2}{0.0591} = 0 + 2\text{pH} \qquad [\text{pH} = -\log [H^+]]$$

$$\therefore \quad \text{pH} = \frac{0.118 \times 2}{0.0591 \times 2} = 1.99 \approx \mathbf{2.0} \ \textbf{(Answer)}$$

Example 2. *How can the electrode potential of $M(s) \mid M^{n+}(aq)$ electrode be increased?*

Solution. The reduction half-reaction for the given electrode can be written as:

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

From Nerst equation, electrode potential corresponding to the above reduction half-reaction is given by

$$E_{M^{n+}(aq)/M(s)} = E^0_{M^{n+}(aq)/M(s)} - \frac{0.0591}{n} \log \frac{[M(s)]}{[M^{n+}(aq)]}$$

or $$E_{M^{n+}(aq)/M(s)} = E^0_{M^{n+}(aq)/M(s)} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}(aq)]}$$

It is evident from the above Nernst equation that since $[M^{n+}(aq)]$ appears in the denominator, the value of electrode potential *viz.* $E_{M^{n+}(aq)/M(s)}$ is directly proportional to $[M^{n+}(aq)]$. Thus if a small amount of the electrolyte in which the electrode is dipped is added, the concentration of $M^{n+}(aq)$ ion, *i.e.* $[M^{n+}(aq)]$ increases and hence the value of $E_{M^{n+}(aq)/M(s)}$ also increases.

Example 3. *The standard reduction potential for the half-reaction,*

$$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(g) + H_2O \text{ is } 0.78\ V$$

(i) Calculate the reduction potential at 8M H^+.

(ii) What will be the reduction potential of the half-cell is a neutral solution. Assume all other species to be at unit concentration. (*I.I.T. 1993*)

Solution. (*i*)

$$(a)\ \underset{(C=1\ M)}{NO_3^-(aq)} + \underset{(C=1\ M)}{2H^+(aq)} + e^- \longrightarrow \underset{(C=p_{NO_2}=1)}{NO_2(g)} + \underset{(C=1M)}{H_2O},\quad E_a^0 = 0.78\ V$$

This equation shows that all the species involved in this reduction half-reaction are at unit concentration and the value of E^0_{red} is equal to 0.78 V.

We have to find out the value of E^0_{red} for the above half-reaction in which the concentration of $H^+(aq)$ is 8 M (not 1 M) and that of other species is unity (C = 1 M). Thus the reduction half-reaction (*a*) should be written as:

$$(b)\ \underset{(C=1\ M)}{NO_3^-(aq)} + \underset{(C=8\ M)}{2H^+(aq)} + e^- \longrightarrow \underset{(C=p_{NO_2}=1)}{NO_2(g)} + \underset{(C=1\ M)}{H_2O}(n=1),\ E_b = ?$$

E_b has to be calculated. From Nerst equation E_b is given by:

$$E_b = E_a^0 - \frac{0.0591}{n}\log\frac{p_{NO_2}\times[H_2O]}{[NO_3^-][H^+]^2}$$

$$= 0.78 - \frac{0.0591}{1}\log\frac{1\times 1}{1\times 8^2} = 0.78 + 0.0591\times 2\times \log 8$$

$$= 0.78 + 0.0591\times 2\times 0.903 = \mathbf{0.887\ V\ (Answer)}$$

(*ii*) When we say that the solution is neutral, $[H^+] = 10^{-7}$ M. Thus equation (*a*) can be written as:

$$(c)\ \underset{(C=1\ M)}{NO_3^-(aq)} + \underset{(C=10^{-7}\ M)}{2H^+(aq)} + e^- \longrightarrow \underset{(C=p_{NO_2}=1)}{NO_2(g)} + \underset{(C=1\ M)}{H_2O}\ (n=1),\ E_c = ?$$

E_c has to be calculated. From Nerst equation, E_c is given by

$$E_c = E_a^0 - \frac{0.0591}{n}\log\frac{p_{NO_2}\times[H_2O]}{[NO_3^-][H^+]^2}$$

$$= 0.78 - \frac{0.0591}{1}\log\frac{1\times 1}{1\times(10^{-7})^2}$$

$$= 0.78 + 0.0591\times 2\times \log 10^{-7}$$

$$= 0.78 + 0.0591\times 2\times(-7) = 0.78 - 0.0591\times 2\times 7$$

$$= \mathbf{-0.046\ V\ (Answer)}$$

Example 4. *A zinc rod is dropped in 0.1 M solution of $ZnSO_4$. The salt is*

95% dissociated at this dilution at 298 K. Calculate the electrode potential. Given that $E^0_{Zn^{2+}/Zn} = -0.76$ *V.* *(P.S.B. 1994)*

Solution. The electrode can be represented as Zn(*s*) | Zn^{2+}(*aq*) and the reduction reaction taking place at this electrode can be written as:

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \text{ (Here } n = 2)$$

On using Nerst equation, we get the value of $E_{Zn^{2+}/Zn}$ given by:

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0591}{n} \log \frac{[Zn(s)]}{[Zn^{2+}(aq)]}$$

or
$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}(aq)]} \qquad ...(i)$$

Now since $ZnSO_4$ solution is 95% dissociated, the value of [Zn^{2+}(*aq*)] will not be equal to 0.1 M, but it is equal to 95% of 0.1 = $\frac{95}{100} \times 0.1 = \frac{9.5}{100} = 0.095$ M. On putting [Zn^{2+}(*aq*)] = 0.095 M in equation (*i*), we get:

$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$$
$$= -0.76 - 0.02955 \{\log 1 - \log 0.095\}$$
$$= -0.76 - 0.02955 \{0 - (-1.022)\} = -0.76 - 0.0302$$
$$= \mathbf{-0.7902 \text{ V (Answer)}}$$

Example 5. *A zinc electrode is placed in 0.1 M solution of* $ZnSO_4$ *at 25°. Assuming that the salt is dissociated to the extent of 20% at this dilution, calculate the potential of this electrode at this temperature. Given* $E^0_{Zn^{2+}/Zn} = -0.76$ *V* *(Indian School of Mines, Dhanbad 1986)*

Solution. The reduction reaction taking place at the electrode is:

$$Zn^{2+} + 2e^- \longrightarrow Zn \text{ (Here } n = 2)$$

$E_{Zn^{2+}/Zn}$ is given by:

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0591}{n} \log \frac{[Zn]}{[Zn^{2+}]} \qquad ...(i)$$

Now since $ZnSO_4$ solution is dissociated to the extent of 20%, the concentration of Zn^{2+} ions is not equal to 0.1 M, but is equal to $\frac{20}{100} \times 0.1 = 0.02$ M. On putting [Zn^{2+}] = 0.02 M in equation (*i*), we get:

$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.02} = \mathbf{-0.810 \text{ V (Answer)}}$$

Example 6. *The standard reduction potential of* Ag^+/Ag *electrode at 298 K is 0.799 V. Given that for AgI,* $K_{sp} = 8.7 \times 10^{-17}$. *(i) Evaluate the potential of* Ag^+/Ag *electrode in a saturated solution of AgI (ii) Calculate the standard reduction potential of* $I^-/AgI/Ag$ *electrode.* *(I.I.T. 1994)*

Solution. (*i*) We have already shown that $E_{Ag^+/Ag}$ is given by the euqaiton:

$$E^0_{Ag^+/Ag} = E^0_{Ag^+/Ag} + 0.0592 \log \sqrt{(K_{sp})_{AgI}}$$

Now put $E^0_{Ag^+/Ag} = 0.799$ V (given) and $(K_{sp}) = 8.7 \times 10^{-17}$ (given) in the above equation to get:

$$\begin{aligned} E_{Ag^+/Ag} &= 0.799 + 0.0592 \log \sqrt{8.7 \times 10^{-17}} \\ &= 0.799 + 0.0592 \log 9.33 \times 10^{-19} \\ &= 0.799 + 0.0592 \times (-8.030) \\ &= 0.799 - 0.0592 \times 8.030 = 0.799 - 0.474 \\ &= \mathbf{0.325\ V\ (Answer)} \end{aligned}$$

(*ii*) We have already shown that $E^0_{I^-/AgI/Ag}$ is given by:

$$E^0_{I^-/AgI/Ag} = E^0_{Ag^+/Ag} + 0.0592 \log(K_{sp})_{AgI}$$

On putting $E^0_{Ag^+/Ag} = 0.799$ and $(K_{sp})_{AgI} = 8{,}7 \times 10^{-17}$ in the above equation, we get:

$$\begin{aligned} E^0_{I^-/AgI/Ag} &= 0.799 + 0.0592 \log(8.7 \times 10^{-17}) \\ &= 0.799 + 0.0592 \times (-16.0605) \\ &= 0.799 - 0.0592 \times 16.0605 \\ &= 0.799 - 0.949 = -\mathbf{0.150\ V\ (Answer)} \end{aligned}$$

Example 7. *The standard reduction potential for Cu^{2+}/Cu is + 0.34 V. Caucluate the reduction potential at pH = 14 for the above couple, if K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19} M^3.* *(I.I.T. 1996)*

Solution. The electrode reduction reaction is:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)\ (n = 2)$$

The reduction potential of the above electrode reaction is given by:

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{n} \log \frac{[Cu]}{[Cu^{2+}]}$$

$$E^0_{Cu^{2+}/Cu} = 0.34 - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} \qquad \text{...(A)}$$

The value of $[Cu^{2+}]$ which is required in the above equation can be calculated by using the following relations:

We know that

$$pH + pOH = 14$$

Now since $pH = 14$, $pOH = 14 - 14 = 0$

$$\therefore \qquad [OH^-] = 10^{-pOH} = 10^{-0} = 1$$

Since $Cu(OH)_2$ ionises as:

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-,$$

$(K_{sp})_{Cu(OH)_2}$ is given by:

$$(K_{sp})_{Cu(OH)_2} = [Cu^{2+}][OH^-]^2$$

$$1.0 \times 10^{-19} = [Cu^{2+}] \times 1$$

$$\therefore \qquad [Cu^{2+}] = 10^{-9}$$

Put $[Cu^{2+}] = 10^{-19}$ in equation (A) to get the value of $E_{Cu^{2+}/Cu}$

$$\begin{aligned}E_{Cu^{2+}/Cu} &= 0.34 - \frac{0.0591}{2}\log\frac{1}{10^{-19}}\\ &= 0.34 - \frac{0.0591}{2}\times[\log 1 + 19\log 10]\\ &= 0.34 - \frac{0.0591}{\cancel{2}}\times 19 = -\mathbf{0.22\ V}\end{aligned}$$

Example 8. *Why does an electrochemical cell stop working after some time?*

OR

Why does a galvanic cell become dead after some time?

Solution. Let us consider the Daniel cell:

$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

or

$$\underset{\text{Anode}}{Zn(s)\,|\,Zn^{2+}(aq)}\,||\,\underset{\text{Cathode}}{Cu^{2+}(aq)\,|\,Cu(s)}$$

Here the two half-reactions taking place in the cell are:

$$Zn(s) \xrightarrow{\text{Oxidation}} Zn^{2+}(aq) + 2e^- \ (\text{At anode})$$

or $$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \qquad ...(a)$$

$$Cu^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} Cu(s)\ (\text{At cathode}) \qquad ...(b)$$

Cell reaction is:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

As the cell reaction proceeds, the concentration of $Zn^{2+}(aq)$ ions (*i.e.* $[Zn^{2+}(aq)]$) in the solution goes on increasing and that of $Cu^{2+}(aq)$ ions (*i.e.* $[Cu^{2+}(aq)]$) goes on decreasing. Now write Nernst equation for the reduction-half reeactions (*a*) and (*b*).

$$E_{Zn^{2+}(aq)/Zn(s)} = E^0_{Zn^{2+}(aq)/Zn(s)} - \frac{0.0591}{2}\log\frac{[Zn(s)]}{[Zn^{2+}(aq)]} \qquad ...(c)$$

$$E_{Cu^{2+}(aq)/Cu(s)} = E^0_{Cu^{2+}(aq)/Cu(s)} - \frac{0.0591}{2}\log\frac{[Cu(s)]}{[Cu^{2+}(aq)]} \qquad ...(b)$$

Since the concentration of $Zn^{2+}(aq)$ ions increases, the value of $E_{Zn^{2+}(aq)/Zn(s)}$ will also increase as is evident from equation (*c*). Similarly, since the concentration of $Cu^{2+}(aq)$ ions decreases, the value of $E_{Cu^{2+}(aq)/Cu(s)}$ will also decrease as is evident from equation (*d*). Ultimately a stage is reached when the two electrode potentials becomes equal [*i.e.* $E_{Zn^{2+}(aq)/Zn(s)} = E_{Cu^{2+}(aq)/Cu(s)}$] and hence e.m.f. of the cell (E_{cell}) or E of the redox reaction also becomes equal, *i.e.* :

$$E_{cell} = E_{Cu^{2+}(aq)/Cu(s)} - E_{Zn^{2+}(aq)/Zn(s)} = \text{zero}$$

Since E_{cell} is zero, the current stops flowing in the circuit. The point at which the two electrode potentials become equal is called equilibrium point (see Fig. 22.6)

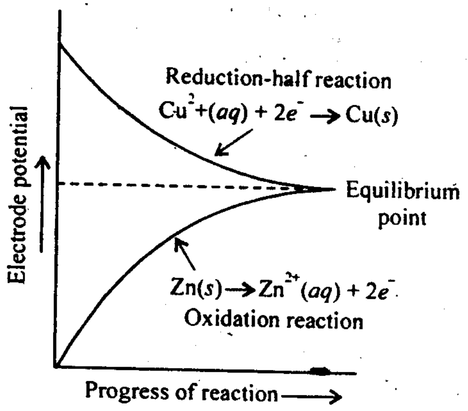


Fig. 22.6. At the equilibrium point in the redox reaction, $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ the two electrode potentials become equal and hence E_{cell} becomes equal to zero.

To calculate the value of electrode potential of hydrogen electrode: To calculate the value of pH of an acid solution

We know that hydrogen electrode is represented as:

$$HCl(aq) \,|\, H_2(g), Pt \quad \text{or} \quad H^+(aq) \,|\, H_2(g), Pt$$

This electrode is obtained by bubbling $H_2(g)$ into $HCl(g)$ solution at 298 K and 1 atm. pressure.

Reduction half-reaction taking place on hydrogen electrode is:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \quad (n = 2)$$

On applying Nernst equation to this reaction, we get:

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{2} \log \frac{pH_2}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2} = -\frac{0.0591}{2}[\log 1 - 2\log[H^+]]$$

$$= -\frac{0.0591}{2}[0 - 2(-\text{pH})] \qquad [\because \log[H^+] = -\text{pH}]$$

$$\therefore \boxed{E_{H^+/H_2} = -\,0.0591\,\text{pH at } 298\text{ K}}$$

This equation can be used to calculate the value of E_{H^+/H_2}, if pH of the acid solution is given. In other words, this equation can be used to calculate pH of an acid solution, if the value of E_{H^+/H_2} is given:

Illustrative Example. *Calculate pH of the following half-cell.*

$$Pt, H_2(g) \,|\, H_2SO_4(aq)$$

The oxidation potential of this electrode is + 0.3V. (*MLNR 1995*)

Solution. We know that electrode potential of hydrogen electrode, $H^+(aq)/H_2(g)$ and pH of acid solution are related as:

$$E_{H^+/H_2} = -0.0591\ \text{pH}$$

or $$-0.3 = -0.0591\ \text{pH}$$

$\therefore$ $$\text{pH} = \frac{0.3}{0.0591} = \mathbf{5.076\ (Answer)}$$

To calculate e.m.f. (E_{cell}) of an electrochemical cell with the help of Nernst equation

If the concentration of each of the electrolyte solutions in an electrochemical cell is 1 M or 1 mol L^{-1} and the temperature is 298 K (25°C), the e.m.f. of the cell is called standard e.m.f. of the cell which is represented as E^0_{cell}. However, if the concentration of the solutions is different from 1 M, the e.m.f. of the cell is represented as E_{cell} which has different value from E^0_{cell}. The value of E_{cell} for a given electrochemical cell working at 298 K can be calculated with the help of Nernst equation.

Let us calcutate the value of E_{cell} of the electrochamical cell represented as:

$$\underset{\text{Anode}}{\underset{(C_1)}{Tl(s) \mid Tl^+(aq)}} \parallel \underset{\text{Cathode}}{\underset{(C_2)}{Cu^{2+}(aq) \mid Cu(s)}} \text{ at 298 K.}$$

Obviously half-reaction taking place on anode and cathode are.

$$2Tl(s) \xrightarrow{\text{Oxidation}} 2Tl^+(C_1) + 2e^-,\ E^0_{ox} = E^0_{Tl/Tl^+}$$

$$Cu^{2+}(C_2) + 2e^- \xrightarrow{\text{Reductioin}} Cu(s),\ E^0_{red} = E^0_{Cu^{2+}/Cu}$$

Cell reaction: $2Tl(s) + Cu^{2+}(C_2) \longrightarrow 2Tl^+(C_1) + Cu(s)\ (n = 2)$ ...(*i*)

E^0_{cell} of cell reaction $= E^0_{ox} + E^0_{red} = E^0_{Tl/Tl^+} + E^0_{Cu^{2+}/Cu}$ ...(*ii*)

The value of E_{cell} for the cell reaction (*i*) (redox reaction) taking place in the cell is given by Nernst equation. Thus:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Tl^+]^2[Cu(s)]}{[Tl(s)]^2[Cu^{2+}]}$$

Now, since Cu(*s*) and Tl(*s*) are solids, [Cu(*s*)] = 1, [Tl(*s*)] = 1, above equation can be written as:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Tl^+]^2}{[Cu^{2+}]}$$

or $$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{C_1^2}{C_2}$$ ...(*iii*)

Equation (*iii*) can be used to calculate the value of E_{cell} by putting the values of E^0_{cell} from equation (*ii*), C_1 and C_2

In general

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{(\text{Concentration of electrolyte in anode})^2}{\text{Concentration of electrolyte in cathode}}$$

This equation shows that the value of E_{cell} is inversely proportional to the magnitude of the concentration of electrolyte in anode (C_1) and directly proportional to the magnitude of the concentration of electrolyte in cathode (C_2). Thus the value of E_{cell} can be increased by decreasing the value of C_1 and by increasing the value of C_2.

To calculate e.m.f. of a given redox reaction taking place at 298 K in electrochemical cell

Suppose we have to calculate e.m.f. of the redox reaction

$$aA + bB \rightleftharpoons cC + dD$$

occuring in an electrochemical cell at 298 K. e.m.f. of this redox reaction is given by Nernst equatiion *viz.*

e.m.f. of redox reaction or $E_{\text{redox reaction}}$

$$= E^0_{\text{redox reaction}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

In this equation:

$E^0_{\text{redox reaction}}$ = Standard e.m.f. of the given redox reaction

n = No of electrons involved in the redox reaction

Solved Examples

Example 1. *The e.m.f. of the following cell is found to be 0.20 V at 298 K*

$$Cd \mid Cd^{2+} (?) \parallel Ni^{2+} (2.0M) \mid Ni$$

What is the molar concentration of Cd^{2+} ions in the solution? Given that:

$$Cd^{2+} \mid Cd = -0.40\ V,\ Ni^{2+}/Ni = -0.25\ V$$

Solution. The redox reaction taking place in the cell is

$$\underset{(2.0\ M)}{Cd + Ni^{2+}} \longrightarrow \underset{(\text{Conc} = ?)}{Cd^{2+}} + Ni\ (n = 2),\ E_{cell} = 0.20\ V \text{ at } 298\ K$$

E_{cell} is given by Nernst equation *viz.*

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Cd^{2+}][Ni]}{[Cd][Ni^{2+}]}$$

or

$$0.20 = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Cd^{2+}] \times 1}{1 \times 2} \quad ..(i)$$

Now E^0_{cell} is given by:

$$E^0_{cell} = E^0_{higher} - E^0_{lower} = -0.25 - (-0.40) = +0.15\ V$$

Put $E^0_{cell} = +0.15$ V in equation (*i*) to get:

$$0.20 = 0.15 - \frac{0.0591}{2} \log \frac{[Cd^{2+}]}{2}$$

$$\therefore \log\frac{[Cd^{2+}]}{2} = -\frac{(0.20-0.15)\times 2}{0.0591} = -1.6920$$

or $\log[Cd^{2+}] - \log 2 = -1.6920$

or $\log[Cd^{2+}] - 0.3021 = -1.6920$

or $\log[Cd^{2+}] = -1.6920 + 0.3021 = -1.3899$

$$[Cd^{2+}] = \text{Antilog}(-1.3899) = 0.0409\text{ M } \textbf{(Answer)}$$

Example 2. *Iron and nickel are used to make an electro-chemical cell by using a salt bridge to join a half-cell containing 1.0 M solution of $Fe^{2+}(aq)$ in which a strip of Fe has been immersed to a second half cell which contains 1.0 M $Ni^{2+}(aq)$ solution in which a strip of Ni has been immersed. A voltmeter is connected between the two metal strips.*

(*i*) *In which half-cell does reduction occur?*

(*ii*) *Write the half-cell reactions.*

(*iii*) *Which metal is anode?*

(*iv*) *In which direction are the electrons passing through the voltmeter?*

(*v*) *What would be the effect on the voltmeter reading, if Fe^{2+} concentration is increased.*

(*vi*) *What will be the voltmeter reading when the ecll reaches equilibirium?*

Given that $F^{2+}/Fe = -0.44$ V and $Ni^{2+}/Ni = -0.25$ V.

Solution. Since Ni^{2+}/Ni $(= -0.25\text{ V}) > Fe^{2+}/Fe$ $(= -0.44\text{ V})$, Ni^{2+}/Ni electrode acts as cathode and Fe^{2+}/Fe electrode acts as anode. Thus the cell can be represented as:

$$\overset{\longrightarrow \text{Electrons} \longrightarrow}{\underset{\text{Anode}}{Fe \mid Fe^{2+}} \quad \| \quad \underset{\text{Cathode}}{Ni^{2+} \mid Ni}}$$

(*i*) Obviously reduction takes place at cathode which is Ni^{2+}/Ni electrode or nikel half-cell.

(*ii*) Half-cell reactions are:

$$Fe \xrightarrow{\text{Oxidation}} Fe^{2+} + 2e^- \textit{ (On anode)}$$

$$Ni^{2+} + 2e^- \xrightarrow{\text{Reduction}} Ni \textit{ (On cathode)}$$

Cell reaction: $\underset{(1.0\text{ M})}{Fe + Ni^{2+}} \longrightarrow \underset{(1.0\text{ M})}{Fe^{2+}} + Ni$

(*iii*) Fe metal is anode.

(*iv*) Electrons are passing from iron (anode) to nikel (cathode)

(*v*) We know from Nernst equation

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[Ni^{2+}]}$$

This equation shows that the value of E_{cell} is inversely proportional to the concentration of Fe^{2+}, $[Fe^{2+}]$. Thus when the concertation of F^{2+} ions is increased, the value of E_{cell} decreases, *i.e.* voltmeter reading decreases (*vi*) When the cell reaches equilibrium, the electrode potentials of both the electrodes become equal and hence E_{cell} becomes zero.

Example 3. *Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell:*

$$Ni \mid Ni^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M) \mid Cu$$

is 0.58 V. Given $E^0_{Cu^{2+}/Cu} = +0.34\ V$ (*D.S.B. 1993*)

Solution. Cell reaction is:

$$\underset{(0.1\ M)}{Ni + Cu^{2+}} \longrightarrow \underset{(0.01\ M)}{Ni^{2+} + Cu} \quad (n = 2)$$

The value of E_{cell} for the cell involving the above cell reactiion is given by Nernst equation *viz.*

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log \frac{[Ni^{2+}]\ [Cu]}{[Cu^{2+}]\ [Ni]}$$

or $$0.58 = E^0_{cell} - \frac{0.0592}{2} \log \frac{0.01 \times 1}{0.1 \times 1}$$

or $$0.58 = E^0_{cell} + 0.0296 \qquad ...(i)$$

Now we know that:

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Cu^{2+}/Cu} - E^0_{Ni^{2+}/Ni}$$

or $$E^0_{cell} = +0.34 - E^0_{Ni^{2+}/Ni} \qquad ...(ii)$$

Put the volue of E^o_{cell} from equation (*ii*) in equation (*i*) to get:

$$0.58 = +0.34 - E^0_{Ni^{2+}/Ni} + 0.0296$$

$$\therefore \quad E^0_{Ni^{2+}/Ni} = \mathbf{-0.2104\ V\ (Answer)}$$

Example 4. *Zinc granules are added in excess to a 500 ml of 1.0 M nikel ntirate solution at 25°C until equilibirium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni elctrodes are $-$ 0.75 V and $-$ 0.24 V respectively, find out the concetration of Ni^{2+} ions in the solution at equitibirium.* (*I.I.T. 1991*)

Solution. The redox reaction occurring in the cell at equilibirium can be written as:

$$Zn + NI^{2+} \longrightarrow Zn^{2+} + Ni \ (n = 2)$$

Nernst equatioin for this reaction is:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Ni^{2+}]} \qquad ...(i)$$

At equilibirum, since $E_{cell} = 0$, $[Zn^{2+}] = [Zn^{2+}]_{eq}$ and $[Ni^{2+}] = [Ni^{2+}]_{eq}$, equation (*i*) should be written as:

$$E^0_{cell} = \frac{0.0591}{2} \log \frac{[Zn^{2+}]_{eq}}{[Ni^{2+}]_{eq}} \qquad ...(ii)$$

Now, $$E^0_{cell} = E^0_{higher} - E^0_{lower} = E^0_{Ni^{2+}/Ni} - E^0_{Zn^{2+}/Zn}$$

$$= -0.24 - (-0.75) = 0.51\ V$$

On putting $E^0_{cell} = 0.51$ V in eqation (*ii*) we get:

$$0.51 = \frac{0.0591}{2} \log \frac{[Zn^{2+}]_{eq}}{[Ni^{2+}]_{eq}}$$

or $$\frac{[Zn^{2+}]_{eq}}{[Ni^{2+}]_{eq}} = \text{Antilog}\left[\frac{2 \times 0.51}{0.0591}\right]$$

or $$\frac{[Zn^{2+}]_{eq}}{[Ni^{2+}]_{eq}} = 1.815 \times 10^{17} \qquad ...(iii)$$

Initial number of moles of Ni^{2+} ions = 0.50 mol

If x moles of Ni^{2+} ions react at equilibirum then:

	$Zn + Ni^{2+}$	$\rightleftharpoons Zn^{2+} + Ni$
No. of moles of Ni^{2+}/Zn^{2+} ions in the begining	0.50 mol	0.0
No. of moles of Ni^{2+}/Zn^{2+} ions at equilibirium	$(0.50 - x)$ mol	x mol
Concentration of Ni^{2+}/Zn^{2+} ions at equilibirium	$2(0.50 - x)$ mol L^{-1}	$2x$ mol L^{-1}

Put $[Zn^{2+}]_{eq} = 2x$ and $[Ni^{2+}]_{eq} = 2(0.50 - x)$ in equation (*iii*) to get

$$\frac{2x}{2(0.50 - x)} = 1.815 \times 10^{17}$$

$\therefore x = 0.5$

$\therefore$ Concentration of Ni^{2+} ions at equilibirium

$$= 2(0.50 - x) = 2(0.50 - 0.50) = \textbf{Zero} \ \textbf{(Answer)}$$

Example 5. *A cell, $Ag \mid Ag^+ \parallel Cu^{2+} \mid Cu$ initially contains 1 M Ag^+ and 1M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65A of current for 1 h.* (*I.I.T 1999*)

Solution. Amount of electrons passed through the cell

$$= \frac{Q}{F} = \frac{A\,t}{F} = \frac{(9.65A) \times (60 \times 60s)}{96500 \text{ C.mol}^{-1}} = 0.36 \text{ mol.}$$

In the initial stage (*i.e.* befroe passing the current) number of moles of Cu^{2+} and Ag^+ ions is 1 but in the final stage (*i.e.* after passing the current) the number of moles of Cu^{2+} and Ag^+ ions changes. Thus:

Cell reaction:	$2Ag + Cu^{2+}$	$\rightleftharpoons Cu + 2Ag^+$ $(n = 2)$
No. of moles of Cu^{2+}/Ag^+ ions in the initial stage	1.0 M	1.0 M
No. of moles of Cu^{2+}/Ag^+ ions in the final stage	$\left(1 + \frac{0.36}{2}\right)$M $= 1.18$M	$(1 - 0.36)$ M $= 0.64$ M

Now let us calculate $(E_{cell})_{initial}$ and $(E_{cell})_{final}$ with the help of Nernst equation

$$(E_{\text{cell}})_{\text{initial}} = E^0_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} = E^0_{\text{cell}} - \frac{0.0591}{2}\log\frac{(1)^2}{1}$$

$$= E^0_{\text{cell}} - \frac{0.059}{2}\times 0 = E^0_{\text{cell}}$$

$$(E_{\text{cell}})_{\text{final}} = E^0_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]}$$

$$= E^0_{\text{cell}} - \frac{0.0591}{2}\log\frac{(0.64)^2}{1.18} = E^0_{\text{cell}} - \frac{0.0591}{2}\log\ 0.3471$$

$$= E^0_{\text{cell}} - 0.01355$$

∴ Change in cell potential, ΔE is given by:

$$\Delta E = (E_{\text{cell}})_{\text{final}} - (E_{\text{cell}})_{\text{initial}} = E^0_{\text{cell}} - 0.01355 - E^0_{\text{cell}}$$

$$= \mathbf{-0.01355\ V}$$ **(Answer)**

Example 6. *Consider the following cell reaction*

$$2Co^{3+}(aq) + Zn(s) \longrightarrow 2Co^{2+}(aq) + Zn^{2+}(aq)$$

Predict the effect of the following changes on the e.m.f. of the cell.

(a) $Co(NO_3)_2$ is added to the cathodic compartment

(b) $Co(NO_3)_3$ is added to the cathodic compartment.

(c) More water is added to cathodic compartment.

(d) The size of Zn electrode is doubled.

Solution. The given cell reaction shows that Zn/Zn^{2+} electrode acts as anode and $\text{Co}^{3+}/\text{Co}^{2+}$ electrode acts as cathode.

$$\text{Zn}(s)\,|\,\text{Zn}^{2+}(aq)\,||\,\text{Co}^{3+}(aq)\,|\,\text{Co}^{2+}(aq)$$

Anode Cathode

From Nernst equation, E_{cell} for the given cell reaction can be written as:

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{\text{n}}\log\frac{[\text{Co}^{2+}(aq)]^2[\text{Zn}^{2+}(aq)]}{[\text{Co}^{3+}(aq)]^2\,[\text{Zn}(s)]}$$

Since in the given cell reaction, the number of electrons (n) involved = 2, the above equation can be written as:

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Co}^{2+}(aq)]^2[\text{Zn}^{2+}(aq)]}{[\text{Co}^{3+}(aq)]^2\,[\text{Zn}(s)]} \quad ...(i)$$

(*a*) Equation (*i*) shows that since [$\text{Co}^{2+}(aq)$] appears in the numerater, the value of E_{cell} is inversely proportional to [$\text{Co}^{2+}(aq)$]. Thus when $\text{Co(NO}_3)_2$ is added to the cathodic compartment, the concentration of $\text{Co}^{2+}(aq)$ ions *i.e.*[$\text{Co}^{2+}(aq)$] increases and hence the value of E_{cell} (or e.m.f. value) decreases.

(*b*) Equation (*i*) shows that since [$\text{Co}^{3+}(aq)$] appears in the denominater, the value of E_{cell} is directly proportional to [$\text{Co}^{3+}(aq)$]. Thus when $\text{Co(NO}_3)_3$ is added to the cathodic compartment, the concentration of $\text{Co}^{3+}(aq)$ ions *i.e.* [$\text{Co}^{3+}(aq)$] increases and hence the value of E_{cell} also increases,

(*c*) Equation (*i*) shows that since [$\text{Zn}^{2+}(aq)$] appears in the numerater, the value of E_{cell} is inversely proportional to [$\text{Zn}^{2+}(aq)$]. Thus when more H_2O is added to the anodic compartment, the concentration of $Zn^{2+}(aq)$ ions *i.e.* $[Zn^{2+}(aq)]$ decreases and hence the value of E_{cell} increases.

(*d*) The doubling of the size of Zn electrode does not affect the magnitude of E_{cell}, since the concentration of Zn(s) *viz.* [Zn(*s*)] is always taken as unity [[Zn(*s*)] = 1] irrespective of the mass of Zn electrode.

Example 7. *The standard reduction potentials of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively.*

(*i*) *Construct the galvanic cell using these electrodes so that the standard e.m.f. of the cell is positive.*

(*ii*) *For what concentration of Ag^+ ions, the e.m.f. of the cell at 25°C is zero, if the concentration of Cu^{2+} ions is 0.01 M.*

Solution. (*i*) Since Ag^+/Ag elecrode has higher value of its standard reduction potential, it will work as cathode and Cu^{2+}/Cu electrode will act as anode. Thus the galvanic cell can be represented as:

$$\underset{\text{Anode}}{Cu(s)\,|\,Cu^{2+}(aq)}\;||\;\underset{\text{Cothode}}{Ag^{+}(aq)\,|\,Ag(s)}$$

(*ii*) The cell reaction as:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)\ (n = 2)$$

$$E^0_{cell} = E^0_{Cu/Cu^{2+}} + E^0_{Ag^+/Ag} = -0.337 + 0.799 = +0.462\ \text{V}$$

On using Nernst equation to the cell reaction, we get:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]\times[Ag]^2}{[Cu]\times[Ag^+]^2}$$

or
$$0.0 = 0.462 - \frac{0.0591}{2}\log\frac{0.01\times 1}{1\times[Ag^+]^2}$$

or
$$\frac{0.462\times 2}{0.0591} = \log\frac{0.01}{[Ag^+]^2}$$

$$15.6345 = \log 0.01 - 2\log[Ag^+]$$

$$15.6345 = -2 - 2\log[Ag^+]$$

or
$$2\log[Ag^+] = -2 - 15.6345$$

or
$$\log[Ag^+] = \frac{-2-15.6345}{2} = -8.8173$$

∴
$$[Ag^+] = \text{Antilog}(-8.8173) = \mathbf{1.523 \times 10^{-9}\ M}\ \textbf{(Answer)}$$

Example 8. *The standard electrode potentials are given as $E^0_{Cu^{2+}/Cu} = 0.34V$ and $E^0_{Ag^+/Ag} = 0.80\ V$. Calculate the cell potential (E_{cell}) for the cell containing 0.1 M Ag^+ and 4.0 M Cu^{2+} at 25°C.* (*A.I.S.B. 1997*)

Solution. We know that the electrode having higher value of E^0 acts as cathode and that having lower value of E^0 acts as anode. Thus the cell can be represented as:

$$\underset{\text{Anode}}{Cu\,|\,Cu^{2+}}\;||\;\underset{\text{Cathode}}{Ag^{+}\,|\,Ag}$$

Oxidation and reduction half-reactions can be written as:

$$Cu \xrightarrow{\text{Oxidation}} Cu^{2+} + 2e^-,\ E^0_{Cu/Cu^{2+}} = -0.34\ V$$

$$2Ag^+ + 2e^- \xrightarrow{\text{Ruduction}} 2\,Ag;\ E^0_{Ag^+/Ag} = 0.80\ V$$

Cell reaction : $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag\ (n=2)$;

$$E^0_{cell} = -0.34 + 0.80 = 0.46\ V$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[Cu^{2+}][Ag]^2}{[Cu]\,[Ag^+]^2}$$

$$= 0.46 - \frac{0.0591}{2}\log\frac{4\times 1^2}{1\times(0.1)^2} = 0.46 - 0.295\log\frac{4}{0.01}$$

$$= 0.46 - 0.0295\log\frac{4\times 100}{0.01\times 100}$$

$$= 0.46 - 0.0295\,[\log 400 - \log 1] = 0.46 - 0.0295\times 2.6020$$

$$= 0.46 - 0.0767 = \mathbf{0.3833\ V\ (Answer)}$$

Example 9. (*a*) *Calculate the potential of the following cell reaction at 298 K.*

$$Sn^{4+}\,(1.50\,M) + Zn(s) \longrightarrow Sn^{2+}\,(0.50\,M) + Zn^{2+}\,(2.0\,M)$$

The standard potential (E^0_{cell}) *of the cell is 0.89 V.*

(*b*) ***Whether the potential of the cell will increase or decrease, if the concentration of*** Sn^{4+} ***is increased in the cell ?*** *(A.I.S.B. 1997)*

Solution (*a*) According to Nernst equation E_{cell} is given by:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[Sn^{2+}]\,[Zn^{2+}]}{[Sn^{4+}]\,[Zn(s)]}$$

$$= 0.89 - \frac{0.0591}{2}\log\frac{0.50\times 2.0}{1.5} = 0.89 - 0.02955\log\frac{0.1}{1.5}$$

$$= 0.89 - 0.02955\log 0.0666 = 0.89 - 0.02955\times 1.176$$

$$= 0.89 - 0.0347 = \mathbf{0.8553\ V\ (Answer)}$$

(*b*) Suppose the concentration of Sn^{4+} is increased to 2.0 M, then

$$E_{cell} = 0.89 - 0.02955\log\frac{0.1}{2.0} = 0.89 - 0.02955\times\log 0.05$$

$$= 0.89 - 0.02955\times(-1.30) = 0.89 + 0.0384 = \mathbf{0.9284}\ V$$

This value of E_{cell} is higher then that obtained at (*a*). Thus if the concentration of Sn^{4+} is increased, the value of E_{cell} increases.

Example 10. *Caculate e.m.f. of the following cell.*

$$Fe\,|\,Fe^{2+}\,||\,Sn^{2+}\,|\,Sn$$

$$a = 0.6 \qquad a = 0.2$$

$$E^0_{Fe} = -0.44\ V,\ E^0_{Sn} = +0.14\ V$$ *(MNLR 1995)*

Solution. The cell reaction can be written as:

$$Fe + Sn^{2+} \longrightarrow Fe^{2+} + Sn\ (n=2)$$

$$E^0_{cell} = E^0_{Fe/Fe^{2+}} + E^0_{Sn^{2+}/Sn} = 0.44 + 0.14 = +0.58$$

$$\therefore E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[Sn^{2+}]} = 0.58 - \frac{0.0591}{2}\log\frac{0.6}{0.2}$$

$$= 0.58 - \frac{0.0591}{2}\log 3 = 0.58 - 0.014 = \mathbf{+0.566\ V\ (Answer)}$$

Example 11. *Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell:*

$$Ni(s)\,|\,Ni^{2+}(0.01\ M)\,||\,Cu^{2+}(0.1\ M)\,|\,Cu(s)$$

is 0.59 V. Given that $Cu^{2+}/Cu = 0.34\ V$ (DSBE 1993)

Solution. The cell reaction of the given cell can be written as:

$$Ni(s) + Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq) + Cu(s)\ (n = 2)$$

$$C = 0.1\ M \qquad C = 0.01\ M$$

Nernst equation for this reaction is:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}(aq)]\,[Cu(s)]}{[Ni(s)]\,[Cu^{2+}(aq)]}$$

$$0.59 = E^0_{cell} - \frac{0.0591}{2}\log\frac{0.01}{0.1}$$

$$0.59 = E^0_{cell} - \frac{0.0591}{2}\log\frac{1}{10}$$

$$0.59 = E^0_{cell} + 0.0295$$

$$\therefore E^0_{cell} = 0.59 - 0.0295 = 0.5605$$

Now we konw that:

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

or $$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{Ni^{2+}/Ni}$$

or $$0.5605 = 0.34 - E^0_{Ni^{2+}/Ni}$$

$$\therefore E^0_{Ni^{2+}/Ni} = 0.34 - 0.5605 = \mathbf{-0.2205\ V\ (Answer)}$$

Example 12. *For the cell reaction*

$$Hg_2Cl_2(s) \longrightarrow 2Hg(l) + Cl_2\,(0.8\ atm)$$

Write the half-cell reactions. Calculate E^0_{cell} and E_{cell} for the above cell reaction.

Given that: $E^0_{Cl^-/Hg_2Cl_2(s)/Hg(l)} = +0.27\ V$ and $E^0_{Cl_2/2Cl^-} = +1.36\ V$

Solution. The given cell reaction shows that Hg_2Cl_2 is reduced to Hg and Cl^- ion is oxidised to Cl_2.

$$Hg_2Cl_2(s) + 2e^- \xrightarrow{\text{Reduction}} 2Hg(l) + 2Cl^-(aq),$$

$$(Hg = +1) \qquad\qquad (Hg = 0)$$

$$E^0_{Cl^-/Hg_2Cl_2(s)/Hg(l)} = +0.27\ V$$

$$2Cl^- \xrightarrow{\text{Oxidiastion}} Cl_2(g) + 2e^-,\ E^0_{2Cl^-/Cl_2} = -1.36\ V$$

$$(Cl = -1) \qquad\qquad (Cl = 0)$$

On adding : $Hg_2Cl_2(s) \longrightarrow 2Hg(l) + Cl_2(g)$ (0.8 atm.) $(n = 2)$

$$E^0_{cell} = +0.27 - 1.36 = \mathbf{-1.09\ V\ (Answer)}$$

E_{cell} is given by the Nernst reqution

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Hg(l)]^2 \times p_{Cl_2}}{[Hg_2Cl_2(s)]}$$

$$= -1.09 - \frac{0.0591}{2} \log \frac{1 \times 0.8}{1} = -1.09 - \frac{0.0591 \times 0.097}{2}$$

$$= \mathbf{-1.09\ V\ (Answer)}$$

Example 13. *An excess of liquid Hg is added to an acidified solution of 1.0 × 10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} ion remains at equilibirium at 25°C. Calculate $E^0(Hg_2^{2+}/Hg)$, assuming that only the reaction that occurs is:*

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

Given that $E^0(Fe^{3+}/Fe^{2+}) = 0.77$ V (*I.I.T. 1995*)

Solution. For the reaction :

$$(a) \qquad \underset{C=0}{2Hg} + \underset{C=1}{2Fe^{3+}} \longrightarrow \underset{C=1}{Hg_2^{2+}} + \underset{C=1}{2Fe^{2+}}, (n=2)$$

E^0 is given by:

$$E^0 = E^0_{ox} + E^0_{red} = E^0_{2\,Hg/Hg_2^{2+}} + E^0_{Fe^{3+}/Fe^{2+}}$$

$$= -E^0_{Hg_2^{2+}/2\,Hg} + E^0_{Fe^{3+}/Fe^{2+}}$$

or

$$E^0 = -E^0_{Hg_2^{2+}/2\,Hg} + 0.77\ V \qquad ...(i)$$

Now we konw that the value of E^0 for the above reaction at equilibirium at 25°C is given by :

$$E^0_{eq} = \frac{0.0591}{n} \log \frac{[Hg_2^{2+}]_{eq} \times [Fe^{2+}]^2_{eq}}{[Hg]^2_{eq} \times [Fe^{3+}]^2_{eq}} \qquad ...(ii)$$

In order to get the value of E^0_{eq} from equation (*ii*) equation (*a*) should be written as:

(*b*)	2Hg +	$2Fe^{3+}$ $\rightleftharpoons$	Hg_2^{2+} +	$2Fe^{2+}$ (*n* = 2)
Concentration of ions in the beginning	0	1.0×10^{-3}M	0	
Concentration of ions at equilibirium	0	$\frac{5}{100} \times (1.0 \times 10^{-3}M)$ $= 5.0 \times 10^{-5}$M	$\frac{10\times10^{-3} - 50\times10^{-5}}{2}$M $= 4.75 \times 10^{-4}$M	$(1.0 \times 10^{-3} - 5.0 \times 10^{-5}$ M) $= 9.5 \times 10^{-4}$ M

$$\therefore \qquad E^0_{eq} = \frac{0.0591}{2} \times \log \frac{[Hg_2^{2+}]_{eq} \times [Fe^{2+}]^2_{eq}}{[Hg]^2_{eq} \times [Fe^{3+}]^2_{eq}}$$

$$= \frac{0.0591}{2} \times \log \frac{(4.75 \times 10^{-4}\ M) \times (9.5 \times 10^{-4}\ M)^2}{1 \times (5.0 \times 10^{-5}\ M)^2}$$

$$= \frac{(0591\ V)}{2} \log 0.1715\ M$$

or $E^0_{eq} = -0.023\text{ V}$ ...(*iii*)

Put $E^0 = E^0_{eq} = -0.023$ V in equation (*i*) to get the value of $E^0_{Hg_2^{2+}/2Hg}$

$$-0.023\text{ V} = -E^0_{Hg_2^{2+}/2Hg} + 0.77\text{ V}$$

$\therefore E^0_{Hg_2^{2+}/2Hg} = 0.77 + 0.023 = \mathbf{0.793\ V\ (Answer)}$

Example 14. *For the galvanic cell :*

Ag | AgCl(s) | KCl(0.2 M) || KBr(0.001 M) | AgBr(s) | Ag,

calculate the e.m.f. generated and assign correctly the polarity to each electrode for a spontaneous process after taking into account the cell at 25°C. Given: $(K_{sp})_{AgCl} = 2.8 \times 10^{-10}$ *and* $(K_{sp})_{AgBr} = 3.3 \times 10^{-13}$ *(I.I.T. 1992)*

Solution. The given cell can also be represented as:

$$\underset{\text{Anode}}{Ag \mid AgCl(s) \mid Cl^-(0.2\text{ M})} \parallel \underset{\text{Cathode}}{Br^-(0.001\text{ M}) \mid AgBr(s) \mid Ag}$$

Oxidiation half-reaction taking place on anode and reduction half-reaction occuring on cathode are:

$$Ag\,(s) + Cl^-\,(aq) \xrightarrow{\text{Oxidation}} Ag\,Cl\,(s) + e^-\ \text{(On anode)}$$

$$Ag\,Br\,(s) + e^- \xrightarrow{\text{Reduction}} Ag\,(s) + Br^-\,(aq)\ \text{(On cathode)}$$

Cell reaction is obtained by adding above two half-reactions; Thus :

Cell reaction : $AgBr(s) + \underset{(0.2\text{ M})}{Cl^-(aq)} \longrightarrow AgCl(s) + \underset{(0.001\text{ M})}{Br^-(aq)}\ (n = 1)$ ...(*a*)

$$\therefore E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log \frac{[Br^-]}{[Cl^-]}$$

or $E_{cell} = E^0_{cell} - 0.0592 \log \dfrac{0.001}{0.2}$ ...(*i*)

Now we know that E^0_{cell} is given by:

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

or $E^0_{cell} = E^0_{Br^-/AgBr/Ag} - E^0_{Cl^-/AgCl/Ag}$ ...(*ii*)

Now we know that

$E^0_{Br^-/AgBr/Ag} = E^0_{Ag^+/Ag} + 0.0592 \log (K_{sp})_{AgBr}$ ...(*iii*)

and $E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + 0.0592 \log (K_{sp})_{AgCl}$ ...(*iv*)

Put the vlues of $E^0_{Br^-/AgBr/Ag}$ and $E^0_{Cl^-/AgCl/Ag}$ from equatiions (*iii*) and (*iv*) respectively in equation (*ii*) to get the value of E^0_{cell}.

$$E^0_{cell} = [E^0_{Ag^+/Ag} + 0.0592\ \log (K_{sp})_{AgBr}] - [E^0_{Ag^+/Ag} + 0.0592 \log (K_{sp})_{AgCl}]$$

$$= 0.0592 \log \frac{(K_{sp})_{AgBr}}{(K_{sp})_{AgCl}} = 0.0592 \log \frac{3.3 \times 10^{-13}}{2.8 \times 10^{-10}}$$

or $E^0_{cell} = -0.1732\text{ V}$ ...(*v*)

Now put $E^0_{cell} = -0.1732$ V in equation (*i*) to get the value of E_{cell}

$$E_{cell} = -0.1732 - 0.0592 \log \frac{0.001}{0.2} = \mathbf{-0.0371\ V\ (Answer)}$$

Since the value of E_{cell} comes out to be a negative quantity. the cell reaction shown above at (*a*) is non -spontaneous. The spontaneous reaction is the following reaction which is the reverse of reaction (*a*)

$$AgCl(s) + Br^-(aq) \longrightarrow AgBr(s) + Cl^-(aq)$$

According to this reaction the cell should be represented as:

$$\underset{\text{Anode (Negative terminal)}}{Ag \mid AgBr(s) \mid Br^-(0.001\ M)} \parallel \underset{\text{Cathode (Positive terminal)}}{Cl^-(0.2\ M) \mid AgCl(s) \mid Ag}$$

Example 15. *The e.m.f. of a cell corresponding to the reaction,*

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1\ M) + H_2(g,\ 1\ atm)$$

is 0.28 V at 25°C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

Given that $E^0_{Zn^{2+}/Zn} = -0.76$ *V and* $E^0_{H^+/\frac{1}{2}H_2} = 0.0$ *V* (*I.I.T. 1986*)

Solution. The two half-reactions are:

$$Zn(s) \xrightarrow{\text{Oxidation}} Zn^{2+}(aq) + 2e^-;\ E^0_{ox} = +0.76\ V$$

$$2H^+(aq) + 2e^- \xrightarrow{\text{Reduction}} H_2(g),\ \ E^0_{red} = 0.0\ V$$

$$\therefore\ E^0_{cell} = E^0_{ox} + E^0_{red} = +0.76 + 0.0 = +0.76\ V$$

Now, according to Nersnt equation, we have :

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}] \times [p_{H_2}]}{[Zn] \times [H^+]^2} \quad \text{(Here } n = 2\text{)}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{0.1 \times 1}{1 \times [H^+]^2}$$

$$0.28 - 0.76 = -\frac{0.0591}{2} \{\log (0.1) - 2 \log [H^+]\}$$

$$\frac{-0.48 \times 2}{-0.0591} = -1 - 2 \times (-pH) \qquad [\because \log [H^+] = -pH]$$

$$= -1 + 2pH$$

$$\therefore \qquad pH = \left[\frac{0.48 \times 2}{0.0591} + 1\right] \times \frac{1}{2} = \mathbf{8.62\ (Answer)}$$

Concentration Cells

Cocentration cells are galvanic cells in which both the electrodes are of the same material but the concentration of the electrolyte ions in them are different. The electrode having smaller concentration of the electrolyte ions in it acts as anode (negative terminal) while that having larger concentration of the electrolyte ions acts as cathode (positive termianal). Some examples of concentration cells are:

(*i*) $\underset{\text{Anode}}{Cu(s) \mid Cu^{2+}(C_1)} \parallel \underset{\text{Cothode}}{Cu^{2+}(C_2) \mid Cu(s)}\ (C_2 > C_1)$

(*ii*) $\underset{\text{Anode}}{\text{Pt, H}_2(g)\,|\,\text{H}^+(\text{C}_1)}\,||\,\underset{\text{Cathode}}{\text{H}^+(\text{C}_2)\,|\,\text{H}_2(g),\text{Pt}}\ (\text{C}_2 > \text{C}_1)$

(*iii*) $\text{Hg}\,|\,\underset{\substack{(\text{C}_1)\\ \text{Anode}}}{\text{Mercurous nitrate solution}}\,||\,\underset{\substack{(\text{C}_2)\\ \text{Cathode}}}{\text{Mercurous nitrate solution}}\,|\,\text{Hg}$

In all the concentration cells $C_2 > C_1$, since C_2 is the concentratioin of electrolyte in cathode and C_1 is the concentration of electrolyte in anode.

To calculate e.m.f. of a given concentration cell at 298 K

As an example let as calculate e.m.f. of the following concentration cell.

$$\underset{\text{Anode}}{\text{Cu}\,|\,\text{Cu}^{2+}(\text{C}_1)}\ ||\ \underset{\text{Cathode}}{\text{Cu}^{2+}(\text{C}_2)\,|\,\text{Cu}}$$

Obviously half-reactions taking place on anode and cathode are:

$$(\text{Cu})_{\text{anode}} \xrightarrow[\text{on anode}]{\text{Oxidation}} \underset{(\text{C}_1)}{\left(\text{Cu}^{2+}\right)_{\text{anode}}} + 2e^-, E^0_{\text{ox}} = \left(E^0_{\text{Cu/Cu}^{2+}}\right)_{\text{anode}}$$

$$\underset{(\text{C}_2)}{\left(\text{Cu}^{2+}\right)_{\text{cathode}}} + 2e^- \xrightarrow[\text{on cathode}]{\text{Reduction}} (\text{Cu})_{\text{cathode}},\ E^0_{\text{red}} = \left(E^0_{\text{Cu}^{2+}/\text{Cu}}\right)_{\text{cathode}}$$

Cell reaction : $(\text{Cu})_{\text{anode}} + \underset{(\text{C}_2)}{\left(\text{Cu}^{2+}\right)_{\text{cathode}}} \longrightarrow \underset{(\text{C}_1)}{\left(\text{Cu}^{2+}\right)_{\text{anode}}} + (\text{Cu})_{\text{cathode}}$

E_{cell} of the above cell reaction is given by Nernst equation *viz.*

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n}\log\frac{[(\text{Cu}^{2+})_{\text{anode}}]}{[(\text{Cu}^{2+})_{\text{cathode}}]}$$

or $$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n}\log\frac{\text{C}_1}{\text{C}_2} \qquad ...(i)$$

The value of E^0_{cell} required in equation (*i*) is given by:

$$E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}} = \left(E^0_{\text{Cu/Cu}^{2+}}\right)_{\text{anode}} + \left(E^0_{\text{Cu}^{2+}/\text{Cu}}\right)_{\text{cathode}} = \text{zero.}$$

Thus for a concentration cell $E^0_{\text{cell}} = 0$. On putting $E^0_{\text{cell}} = 0$ in equation (*i*), we get:

$$E_{\text{cell}} = 0 - \frac{0.591}{n}\log\frac{\text{C}_1}{\text{C}_2}$$

$$\boxed{\begin{aligned} \text{or}\quad & E_{\text{cell}} = -\frac{0.0591}{n}\log\frac{\text{C}_1}{\text{C}_2}\\ \text{or}\quad & E_{\text{cell}} = \frac{0.0591}{n}\log\frac{\text{C}_2}{\text{C}_1}\end{aligned}} \qquad ...(ii)$$

It is evident from equation (*ii*) that to get positive value of E_{cell}, C_2 should be greater than C_1.

Solved Examples

Example 1. *The e.m.f. of the cell Hg | Mercurous nitrate (0.01M) || Mercurous nitrate (0.1 M) | Hg is found to be 0.0591 V at 298 K. What is the valency of the murcurous ion in mercurous nitrate ?*

Sotution. Since the given cell is a concentration cell, its e.m.f. is given by the Nernst equation given below. (For a concentration cell $E^0_{cell} = 0$)

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{\text{Concentration of solution in anode}}{\text{Concentration of solution in cathode}}$$

$$\text{or} \quad 0.0591 = 0 - \frac{0.0591}{n} \log \frac{0.01}{0.10}$$

$$\text{or} \quad 0.0591 = -\frac{0.0591}{n} \log 10^{-1} = -\frac{0.0591}{n} \times (-1) \times \log 10$$

$$\text{or} \quad 0.0591 = -\frac{0.0591}{n} \times (-1) \times 1 = \frac{0.0591}{n}$$

$$\therefore \quad n = 1$$

Thus the valency of mercurous ion in mercurous nitrate = **1 (Answer)**

Example 2. *A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M H^+ ions. The e.m.f. of the cell is 0.118 V at 25°C. Calculate the concentration of H^+ ions at the positive electrode.* *(I.I.T. 1988)*

Solution. Let the concentration of H^+ ions in the positive electrode be C. Thus the cell can be represented as:

$$\underset{\substack{\text{Negative Electrode} \\ \text{(Anode)}}}{\text{Pt}, H_2(g) \mid H^+(10^{-6}\text{M})} \parallel \underset{\substack{\text{Postive Electrode} \\ \text{(Cathode)}}}{H^+(C = ?) \mid H_2(g), \text{Pt}}$$

Obviously the above cell is a concentration cell, since the electrodes of the cell are of the same material. Since the E^0_{cell} of the above cell in,equal to zero, E_{cell} of this cell is given by Nernst equation *viz.*

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{\text{Concentration of } H^+ \text{ions in anode}}{\text{Concentration of } H^+ \text{ ions in cathode}}$$

$$= 0 - \frac{0.0591}{1} \log \frac{10^{-6}}{C}$$

$$\text{or} \quad E_{cell} = -\frac{0.0591}{1} \log \frac{10^{-6}}{C}$$

$$\text{or} \quad 0.118 = -\frac{0.0591}{1} \log \frac{10^{-6}}{C}$$

$$\text{or} \quad \frac{-0.118}{0.0591} = \log \frac{10^{-6}}{C}$$

$$\text{or} - 1.9966 = \log 10^{-6} - \log C$$

$$\text{or} - 1.9966 = -6 - \log C$$

$$\log C = -6 + 1.9966 = -4.0034$$

$\therefore$ C = Antilog (– 4.0034) = **10^{-4} M (Answer)**

Alternative solution. Oxidation and reduction half-reactions taking place in the cell are:

$$(H_2)_{anode} \xrightarrow{\text{Oxidation}} (2H^+)_{anode} + 2e^- \text{ (At anode)}$$

$$(2H^+)_{cathode} + 2e^- \xrightarrow{\text{Reduction}} (H_2)_{cathode} \text{ (At cathode)}$$

Thus cell reaction is:

$$(H_2)_{anode} + \underset{(C=?)}{(2H^+)_{cathode}} \longrightarrow \underset{(C=10^{-6})}{(2H^+)_{anode}} + (H_2)_{cathode} \quad (n=2)$$

E_{cell} of the above cell reaction is given by Nernst equation

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[(H^+)_{anode}]^2}{[(H^+)_{cathode}]^2}$$

$$0.118 = 0 - \frac{0.0591}{2} \log \frac{(10^{-6})^2}{(C)^2}$$

$$0.118 = -\frac{0.0591}{2} \times 2 \times \log \frac{10^{-6}}{C}$$

$$0.118 = -0.0591 \log \frac{10^{-6}}{C}$$

$$\frac{-0.118}{0.0591} = \log \frac{10^{-6}}{C}$$

$$\therefore \quad C = 10^{-4}\,M \text{ (Answer)}$$

Example 3. *Find the solubility product of a saturated solution of Ag_2CrO_4 in water as 298 K, if the e.m.f. of the cell*

$Ag \mid Ag^+$ (saturated solution of Ag_2CrO_4) $\parallel Ag^+$ (0.1 M) $\mid Ag$

is 0.164 V at 298K. (*I.I.T. 1998*)

Solution. Let the concentration of Ag^+ ions in anode be C. Thus the given cell can be represented as:

$$\underset{\text{Anode}}{Ag \mid Ag^+ (C=?)} \parallel \underset{\text{Cathode}}{Ag^+ (0.1\,M) \mid Ag}$$

Obviously the given cell is a concentation cell, since both the electrodes of the cell are of the same material. Since the value of E^0_{cell} of such cells is equal to zero, the value of E_{cell} is given by:

$$E_{cell} = -\frac{0.0591}{n} \log \frac{\text{Concentration of } Ag^+ \text{ions in anode}}{\text{Concentration of } Ag^+ \text{ions in cathode}}$$

$$\text{or} \quad 0.164 = -\frac{0.0591}{1} \log \frac{C}{0.1}$$

$$\text{or} \quad \frac{0.164}{-0.0591} = \log C - \log 10^{-1}$$

$$\text{or} \quad -2.7749 = \log C + 1$$

$$\text{or} \quad -3.7749 = \log C$$

$\therefore C = \text{Antilog}(-3.7749) = 1.6791 \times 10^{-4}\text{M}$

We know that Ag_2CrO_4 ionises as:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$\therefore [K_{sp}]_{Ag_2CrO_4} = [Ag^+]^2 \times [CrO_4^{2-}]$$

Now since the solution of Ag_2CrO_4 is saturated, $[CrO_4^{2-}] = \frac{[Ag^+]}{2}$ and hence:

$$[K_{sp}]_{Ag_2CrO_4} = [Ag^+]^2 \times \frac{[Ag]^+}{2} = \frac{[Ag^+]^3}{2}$$

$$= \frac{(1.6791 \times 10^{-4})^3}{2} = \frac{4.7340 \times 10^{-12}}{2} = \mathbf{2.367 \times 10^{-12}}\ \textbf{(Answer)}$$

Example 4. *For the cell:*

$$Ag(s)\,|\,AgNO_3(0.01\,M)\,||\,AgNO_3(1.0\,M)\,|\,Ag(s)$$

(i) Calculate e.m.f. at 25°C (ii) Write net cell reaction (iii) Will the cell generate e.m.f., if two concentrations become equal? *(A.I. 1994)*

Solution (*i*) Since the given cell is a concentration cell, its e.m.f. is given by:

$$E_{\text{cell}} = -\frac{0.0591}{n}\log\frac{\text{Concentration of the solution in anode}}{\text{Concentration of the solution in cathode}}$$

$$= -\frac{0.0591}{1}\log\frac{0.01}{1.0}\ (\text{Here } n = 1)$$

$$= -0.0591 \times \log 10^{-2}$$

$$= -0.0591 \times (-2) \times 1$$

or $E_{\text{cell}} = +0.0591 \times 2 = \mathbf{0.1182\ V}$ **(Answer)**

(*ii*) Cell reaction is obtained by adding oxidation and reduction half-reactions as shown below:

$$(Ag)_{\text{Anode}} \xrightarrow{\text{Oxidation}} \underset{(C=0.001\,\text{M})}{(Ag^+)_{\text{Anode}}} + e^-$$

$$\underset{(C=1.0\,\text{M})}{(Ag^+)_{\text{Cathode}}} \xrightarrow{\text{Reduction}} (Ag)_{\text{Cathode}}$$

$$(Ag)_{\text{Anode}} + \underset{(C=1.0\,\text{M})}{(Ag^+)_{\text{Cathode}}} \longrightarrow \underset{(C=0.01\,\text{M})}{(Ag^+)_{\text{Anode}}} + (Ag)_{\text{Cathode}}\ (n=1)$$

(*iii*) If the concentration of Ag^+ ions in both the electrodes becomes equal, then

$$E_{\text{cell}} = -\frac{0.0591}{1}\log\frac{C}{C}$$

or $E_{\text{cell}} = -0.0591 \times \log 1 = -0.0591 \times 0.0 = 0.0$

Thus the cell will not generate e.m.f., since the value of e.m.f. becomes equal to zero.

Equilibirium Constant of Redox Reaction s(K_{eq})

To calculate the equilibirium constant (K_{eq}) of a given redox reaction at equilibrium by Nernst equation

Let us calculate the equilibirium constant (K_{eq}) for the following redox reaction at equilibirium

$$\underset{(RA)}{Zn(s)} + \underset{(OA)}{Cu^{2+}(aq)} \rightleftharpoons Zn^{2+}(aq) + Cu(s)\ (n=2) \qquad ...(A)$$

Since the given redox reaction is at equilibirium, the electrode potentials of the two electrodes *viz.* $Zn^{2+}(aq) \mid Zn(s)$ and $Cu^{2+}(aq) \mid Cu(s)$ involved in the reaction are equal *i.e.* $E_{Zn^{2+}(aq)/Zn(s)} = E_{Cu^{2+}(aq)/Cu(s)}$ and hence $E_{\text{redox reaction}}$ or E_{cell} is equal to zero as shown below:

$$E_{\text{redox reaction}} \text{ or } E_{cell} = E_{Cu^{2+}(aq)/Cu(s)} - E_{Zn^{2+}(aq)/Zn(s)} = \text{zero}$$

From Nernst equation E_{cell} of equilibrium (A) is given by:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}(aq)][Cu(s)]}{[Zn(s)][Cu^{2+}(aq)]}$$

or
$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} \qquad ...(i)$$

Now since, $E_{cell} = 0$, $[Zn^{2+}(aq)] = [Zn^{2+}(aq)]_{eq}$ and $[Cu^{2+}(aq)] = [Cu^{2+}(aq)]_{eq}$, equation (*i*) can also be written as:

$$0 = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}}$$

or
$$E^0_{cell} = \frac{0.0591}{2}\log\frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}} \qquad ...(ii)$$

Now since $\frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}}$ is called equilibrium constant of redox reaction (A)

$$K_{eq} = \frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}} \qquad ...(iii)$$

With the help of equation (*iii*), equation (*ii*) can also be written as:

$$\boxed{\begin{aligned} E^0_{cell} &= \frac{0.0591}{2}\log K_{eq} \\ \text{or} \quad E^0_{\text{redox reaction}} &= \frac{0.0591}{2}\log K_{eq} \end{aligned}} \qquad ...(iv)$$

In general, the value of K_{eq} for the redox reaction,

$$aA + bB \rightleftharpoons cC + dD \qquad ...(B)$$

which involves the transfer of *n* electrons, is given by:

$$\boxed{E^0_{\text{cell}} = E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log K_{\text{eq}}} \qquad ...(v)$$

In equation (v)

E^0_{cell} or $E^0_{\text{redox reaction}}$ = Standard cell potential for the given redox reaction

$$= E^0_{\text{cathode}} - E^0_{\text{anode}} = E^0_{\text{OA}} - E^0_{\text{RA}}$$

K_{eq} = Equilibrium constant for redox reaction (B)

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Solved Examples

Example 1. *The standard reduction potential at 25°C of the reaction*

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

is equal to – 0.8277 V. Calculate the equilibrium constant for the reaction,

$$2H_2O \longrightarrow H_3O^+ + OH^- \text{ at } 25°C. \qquad (\textit{I.I.T. 1989})$$

Solution. The reaction,

$$2H_2O \longrightarrow H_3O^+ + OH^- \qquad ...(i)$$

for which the value of K_{eq} is to be calculated is a redox reaction. This reaction can be broken into the following oxidation and reduction half-reactions

$$(a)\ \underset{(H=0)}{2H_2O + H_2} \xrightarrow{\text{Oxidation}} \underset{(H=+1)}{2H_3O^+ + 2e^-}, \quad E^0_{\text{ox}} = ?$$

$$(b)\ \underset{(H=+1)}{2H_2O} + 2e^- \xrightarrow{\text{Reduction}} \underset{(H=0)}{H_2 + 2OH^-}, \quad E^0_{\text{red}} = -0.8277\text{ V (given)}$$

Obviously the given redox reaction (i) can be obtained by adding reactions (a) and (b) as shown below:

$$4H_2O \longrightarrow 2H_3O^+ + 2OH^- (n=2)$$

or $$2H_2O \longrightarrow H_3O^+ + OH^- (n=1)$$

Obviously redox reaction (i) involves the transfer of one electron (n = 1) only. In order to find out the value of E^0_{ox}, write the oxidation half-reaction (a) as:

$$2H_2O + H_2 \longrightarrow 2H_3O^+ + 2e^-$$

or $$2H_2O + H_2 \longrightarrow 2H_2O + 2H^+ + 2e^-$$

or $$H_2 \longrightarrow 2H^+ + 2e^-$$

Obviously this reaction represents hydrogen electrode and hence $E^0_{\text{ox}} = 0$. Thus the value of E^0 for the redox reaction (i) is given by:

$$E^0_{\text{redox reaction}} = E^0_{\text{ox}} - E^0_{\text{red}} = 0 + (-0.8277\text{ V}) = -0.8277\text{ V}$$

The value of K_{eq} for the redox reaction (i) *viz.*

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

which involves the transfer of only one electron (n = 1) and whose $E^0_{\text{redox reaction}} = -0.8277$ V is given by:

$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log\frac{[\mathrm{H_3O^+}]^2[\mathrm{OH^-}]}{[\mathrm{H_2O}]^2}$$

or
$$-0.8277 = \frac{0.0591}{1}\log K_{eq}$$

$$\log K_{eq} = \frac{-0.8277}{0.0591} = -14.0$$

$\therefore$ $K_{eq} = \text{Antilog}(-14.0) = \mathbf{10^{-14}}$ **(Answer)**

Example 2. *Calculate equilibrium constant for the redox reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2F^{2+} + I_3^-$. The standard reduction potentials in acidic medium are 0.77 V and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples.* (*I.I.T. 1998*)

Solution. The given redox reaction is

$$\underset{(\mathrm{Fe}=+3)}{2\mathrm{Fe^{3+}}} + \underset{(\mathrm{I}=-1)}{3\mathrm{I^-}} \rightleftharpoons \underset{(\mathrm{Fe}=+2)}{2\mathrm{Fe^{2+}}} + \underset{(\mathrm{I}=-1/3)}{\mathrm{I_3^-}}\ (n=2) \qquad \ldots(i)$$

The value of K_{eq} for the above redox reaction is given by:

$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log\frac{[\mathrm{Fe^{2+}}]^2[\mathrm{I_3^-}]}{[\mathrm{Fe^{3+}}]^2[\mathrm{I^-}]^3}$$

or
$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log K_{eq} \qquad \ldots(ii)$$

Obviously, in order to find out the value of K_{eq} from equation (*ii*), the value of $E^0_{\text{redox reaction}}$ and n must be known.

It is evident from equation (*i*) that $n = 2$. $E^0_{\text{redox reaction}}$ is given by:

$E^0_{\text{redox reaction}} = E^0_{\text{higher}} - E^0_{\text{lower}} = 0.77 - 0.54 = 0.23\ \text{V}$

On putting $n = 2$ and $E^0_{\text{redox reaction}} = 0.23$ V in equation (*ii*), we get:

$$0.23 = \frac{0.0591}{2}\log K_{eq}$$

or
$$\log K_{eq} = \frac{2 \times 0.23}{0.0591} = 7.7834179$$

$\therefore$ $K_{eq} = \text{Antilog}(7.7834179) = \mathbf{6.26 \times 10^7}$ **(Answer)**

Example 3. *Calculate the equilibrium constant for the reaction $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$. Given that $E^0_{Ce^{4+}/Ce^{3+}} = 1.44\ V$, $E^0_{Fe^{3+}/Fe^{2+}} = 0.68\ V$* (*I.I.T. 1997*)

Solution. The given cell reaction is:

$$\mathrm{Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}}\ (n=1) \qquad \ldots(i)$$

The value of K_{eq} for the above cell reaction is given by:

$$E^0_{\text{cell reaction}} = \frac{0.0591}{n}\log\frac{[\mathrm{Fe^{3+}}][\mathrm{Ce^{3+}}]}{[\mathrm{Fe^{2+}}][\mathrm{Ce^{4+}}]}$$

$$E^0_{\text{cell reaction}} = \frac{0.0591}{n}\log K_{eq} \qquad \ldots(ii)$$

Now $E^0_{\text{cell}} = E^0_{\text{higher}} - E^0_{\text{lower}} = 1.44 - 0.68 = 0.76$ V, and $n = 1$. Put these values in equation (*ii*) go get:

$$0.76 = \frac{0.0591}{1}\log K_{eq}$$

$$\log K_{eq} = \frac{0.76 \times 1}{0.0591} = 12.8552$$

∴ K_{eq} = Antilog (12.8552) = 7.6×10^{12} (Answer)

Example 4. *Calculate the equilibrium constant for the redox reaction, $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$. Given that Cu^{2+}/Cu = 0.337 V and Zn^{2+}/Zn = – 0.763 V. Predict whether the given redox reaction will go to completion.*

Solution. The value of K_{eq} for the given redox reaction for which $n = 2$ is given by:

$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

or $$E^0_{\text{higher}} - E^0_{\text{lower}} = \frac{0.0591}{n}\log K_{eq}$$

or $$0.337 - (-0.763) = \frac{0.0591}{2}\log K_{eq}$$

or $$1.1 = \frac{0.0591}{2}\log K_{eq}$$

∴ $$\log K_{eq} = \frac{2 \times 1.1}{0.591} = 37$$

$$K_{eq} = \text{Antilog}(37) = 10^{37}$$

Thus $$K_{eq} = \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]} = 10^{37}$$

Since the value of K_{eq} is quite high, the reaction between Cu^{2+} ions and metallic Zn (*i.e.* the given redox reaction) will go to completion.

Example 5. *Calculate the equilibrium constant for the redox reaction between Sn(s) and $Pb^{2+}(aq)$ ions. Will this reaction go to completion (Pb^{2+}/Pb = – 0.126 V and Sn^{2+}/Sn = – 0.136 V)?*

Solution. Redox reaction is:

$$\underset{\text{(RA)}}{\text{Sn}(s)} + \underset{\text{(OA)}}{\text{Pb}^{2+}(aq)} \rightleftharpoons \text{Pb}(s) + \text{Sn}^{2+}(aq)\ (n = 2)$$

K_{eq} for this reaction is given by:

$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log\frac{[\text{Sn}^{2+}(aq)]}{[\text{Pb}^{2+}(aq)]}$$

or $$E^0_{\text{OA}} - E^0_{\text{RA}} = \frac{0.0591}{n}\log K_{eq}$$

or $$E^0_{\text{Pb}^{2+}/\text{Pb}} - E^0_{\text{Sn}^{2+}/\text{Sn}} = \frac{0.0591}{n}\log K_{eq}$$

or $$-0.126-(-0.136)=\frac{0.0591}{2}\log K_{eq}$$

$$\therefore \quad \log K_{eq}=\frac{2\times 0.01}{0.0591}=0.3$$

$$\therefore \quad K_{eq}=\mathbf{2}\ \textbf{(Answer)}$$

Since the value of K_{eq} is very small, the reaction between Sn(*s*) and Pb^{2+}(*aq*) will not go to completion, *i.e.* reactants and products both will be found in significant amount at equilibrium.

Example 6. *Determine the equilibrium constant for the following redox reaction at 298 K.*

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

From the calculated value of equilibrium constant, predict whether Sn^{2+} ions can reduce Fe^{3+} ions to Fe^{2+} ions quantitatively or not. Given $E^0_{Fe^{3+}/Fe^{2+}} = +0.771$ V and $E^0_{Sn^{4+}/Sn^{2+}} = 0.15$ V.

Solution. Redox reaction is:

$$\underset{\text{(OA)}}{2Fe^{3+}} + \underset{\text{(RA)}}{Sn^{2+}} \longrightarrow 2Fe^{2+} + Sn^{4+}\ (n=2)$$

K_{eq} for this reaction is given by:

$$E^0_{\text{redox reaction}} = \frac{0.0591}{n}\log\frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$$

or $$E^0_{OA} - E^0_{RA} = \frac{0.0591}{n}\log K_{eq}$$

or $$0.771-0.150=\frac{0.0591}{2}\log K_{eq}$$

or $$\log K_{eq}=\frac{2\times(0.771-0.150)}{0.0591}=21.0$$

$$\therefore \quad K_{eq}=\text{Antilog}(21.0)=\mathbf{1.0\times 10^{21}}\ \textbf{(Answer)}$$

Since the value of K_{eq} is quite high, the given redox reaction will go to completion, *i.e.* Sn^{2+} ions will reduce Fe^{3+} ions to Fe^{2+} ions quantitititatively.

Standard Free Energy Change (ΔG^0)

To calculate free energy change (ΔG) of a redox reaction occuring in an electrochemical cell

When a redox reaction takes place in an electrochemical cell, electrical work is done by the cell on the surroundings, *i.e.* electrical work is obtained from the cell. This work (W) is equal to the free energy change (ΔG) of the redox reaction (cell reaction), *i.e.*

$$W=\Delta G \qquad ...(i)$$

Change in free energy (ΔG) is equal to the product of the quantity of electricity flowing in the circuit and e.m.f. of the cell reaction, E_{cell} or $E_{\text{redox reaction}}$, *i.e.*

$$\Delta G = \text{Quantity of electricity flowing in the circuit} \times E_{\text{cell}}$$

or $$\Delta G = nF \times E_{\text{cell}} \qquad ...(ii)$$

Here nF = Quantity of electricity

n = No. of moles of electrons transferred in the redox reaction

F = Faraday = 96500 C.mol^{-1}

From equations (i) and (ii), we can write

$$W = \Delta G = nFE_{\text{cell}} \qquad ...(iii)$$

Now since work is done by the cell on the surroundings, ΔG is a negative quantity, *i.e.*

$$\Delta G = -nFE_{\text{cell}} \qquad (iv)$$

On combining equations (iii) and (iv), we get:

$$W = \Delta G = -nFE_{\text{cell}} \qquad ...(v)$$

As a matter of fact, W is the maximum work ($W_{\max}$) that can be obtained from the cell or from the redox reaction occurring in the cell. Thus equation (v) should be written as:

$$W_{\max} = \Delta G = -nFE_{\text{cell}} \qquad ...(vi)$$

If we put E^0_{cell} in place of E_{cell} in equation (vi), ΔG is written as ΔG° which is called **standard free energy change**. Thus for standard conditions, equation (vi) becomes

$$W_{\max} = \Delta G^\circ = -nFE^0_{\text{cell}} \qquad ...(vii)$$

Since n, F and E^0_{cell} are expressed by the units *viz.* mol, C mol^{-1} (F = 96500 C mol^{-1}) and volts (V) respectively, equation (vii) can be written as:

$$\Delta G^\circ = (-n\,\text{mol}) \times (96500\,\text{C mol}^{-1}) \times (E^0_{\text{cell}}\ \text{V})$$

$$\Delta G^\circ = (-n \times 96500 \times E^0_{\text{cell}})\,\text{CV}$$

$$\boxed{\Delta G^\circ = (-96500 \times n \times E^0_{\text{cell}})\,\text{J.mol}^{-1} (\because \text{C.V.} = \text{J.mol}^{-1}) \qquad ...(viii)}$$

Now since 96490 J.mol^{-1} = 1 eV.atom^{-1}, equation ($viii$) can also be written as:

$$\Delta G^\circ = \frac{-96500 \times n \times E^0_{\text{cell}}}{96490}\,\text{eV.atom}^{-1}$$

$$\boxed{\Delta G^\circ = -n \times E^0_{\text{cell}}\ \text{eV.atom}^{-1} \qquad ...(ix)}$$

Whenever ΔG° has to be calculated in J.mol^{-1}, equation ($viii$) must be used. If ΔG° is to be calculated in eV.atom^{-1}, equation (ix) should be used.

If a redox reaction occurs spontaneously, its ΔG° would be negative. Thus if ΔG° is positive, the redox reaction would not occur spontaneously.

To calculate standard free energy change (ΔG°) for a given electrode or for its half-cell reaction (electrode reaction)

Let us consider $M^{n+}(aq) \mid M(s)$ electrode. The half-cell reaction corresponding to this electrode is:

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

Obviously this half reaction involves the transfer of n electrons. The value of ΔG° for this half-reaction or for $M^{n+}(aq)/M(s)$ electrode is given by:

$$(\Delta G^\circ)_{M^{n+}/M(s)} = [-96500 \times n \times E^0_{M^{n+}(aq)/M(s)}] \text{ J.mol}^{-1}$$

or $$(\Delta G^\circ)_{M^{n+}(aq)/M(s)} = [-n \times E^0_{M^{n+}(aq)/M(s)}] \text{ eV.atom}^{-1}$$

In general, above equation can also be written as:

$$\boxed{\begin{array}{ll} & (\Delta G^\circ)_{\text{Electrode}} = (-96500 \times n \times E^0_{\text{Electrode}}) \text{ J.mol}^{-1} \\ \text{or} & (\Delta G^\circ)_{\text{Electrode}} = (-n \times E^0_{\text{Electrode}}) \text{ eV.atom}^{-1} \end{array}}$$

Solved Examples

Example 1. *Calculate the standard free energy change for the following cell (redox) reaction*

$$Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$$

Given $Fe^{3+}/Fe^{2+} = +0.77$ V, $Ag^+/Ag = +0.80$ V, $F = 96500$ C.mol^{-1}

Solution. We know that standard free energy change (ΔG°) for the given cell reaction for which $n = 1$ is given by:

$$\begin{aligned} \Delta G^\circ &= (-nFE^0_{\text{redox reaction}}) \text{ Joules} \\ &= [-1 \times 96500 \times (E^0_{Fe^{2+}/Fe^{3+}} + E^0_{Ag^+/Ag})] \text{ Joules} \\ &= [-1 \times 96500 \times (-0.77 + 0.80)] \text{ Joules} \\ &= -0.03 \times 96500 \text{ Joules} = \mathbf{-2859 \text{ Joules (Answer)}} \end{aligned}$$

Alternative solution. Since the given redox reaction is sum of oxidation and reduction half-reactions given below, ΔG° for the given redox reaction is equal to the sum of ΔG° values of the two half-reactions. Thus:

$$(a)\ Fe^{2+}(aq) \xrightarrow{\text{Oxidation}} Fe^{3+}(aq) + e^-, (\Delta G^\circ)_a = -nFE^0_{Fe^{2+}/Fe^{3+}} \text{ Joules}$$
$$= -1 \times F \times (-0.77) \text{ Joules} = +0.77F \text{ Joules}$$

$$(b)\ Ag^+(aq) + e^- \xrightarrow{\text{Reduction}} Ag(s), (\Delta G^\circ)_b = -nFE^0_{Ag^+/Ag} \text{ Joules}$$
$$= -1 \times F \times 0.80 \text{ Joules} = -0.80F \text{ Joules}$$

On adding oxidation [reaction (*a*)] and reduction [reaction (*b*)] half-reactions, we get the redox reaction:

$$\begin{aligned} Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s), \Delta G &= (\Delta G^\circ)_a + (\Delta G^\circ)_b \\ &= (+0.77F - 0.80F) \text{ Joules} = -0.03F \text{ Joules} \\ &= -0.03 \times 96500 \text{ Joules} \\ &= \mathbf{-2895 \text{ Joules (Answer)}} \end{aligned}$$

Example 2. *Calculate the maximum possible electrical work that can be obtained from the following cell under standard conditions at 25°C*

$$Zn(s) \mid Zn^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$$

Given $Zn^{2+}(aq)/Zn(s) = -0.76$ V, $Ni^{2+}(aq)/Ni(s) = -0.25$ V, $F = 96500$ C.mol^{-1}.

Solution. Maximum possible electrical work (W_{max}) that can be obtained from the given cell is equal to the standard free energy change (ΔG°) for the cell reaction, *i.e.*

$$W_{max} = \Delta G^\circ.$$

Now ΔG° for the cell reaction,

$$Zn(s) + Ni^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ni(s)\ (n = 2)$$

is given by:

$$\Delta G^\circ = -nFE^0_{\text{cell reaction}} \text{ Joules}$$

$$= -2 \times 96500 \times (E^0_{Zn/Zn^{2+}} + E^0_{Ni^{2+}/Ni}) \text{ Joules}$$

$$= -2 \times 96500 \times [+0.76 + (-0.25)] \text{ Joules}$$

$$= -2 \times 96500 \times 0.51 \text{ Joules} = -98430 \text{ J}$$

$$= \mathbf{-984.30\ kJ\ (Answer)}$$

Example 3. *On the basis of the concept of free energy predict whether the following reaction would occur spontaneously at 298 K.*

$$Co(s) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe(s)$$

Given $Co^{2+}/Co = -0.28$ *V and* $Fe^{2+}/Fe = -0.44$ *V.*

Solution. ΔG° for the given reaction is given by:

$$\Delta G^\circ = -nFE^0_{\text{reaction}} = -nF \times [E^0_{Co/Co^{2+}} + E^0_{Fe^{2+}/Fe}]$$

$$= -nF \times [0.28 + (-0.44)] = -nF \times (-0.16)$$

or $\Delta G^\circ = +0.16nF$

Since the value of ΔG° comes out to be positive, the given reaction would not occur spontaneously.

Example 4. *For the Daniell cell involving the cell reaction:*

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s),$$

the standard free energies of formation of $Zn(s)$, $Cu(s)$, $Cu^{2+}(aq)$ *and* $Zn^{2+}(aq)$ *are 0, 0, 15.66 and – 35.14 K cal.mol*$^{-1}$ *respectively. Calculate the value of* E^0_{cell}.

Solution. We know that:

$$\Delta G^\circ = -nFE^0_{\text{cell}}$$

or $\Delta G^\circ(\text{products}) - \Delta G^\circ(\text{reactants}) = -nF\,E^0_{\text{cell}}$

or $[(-35.14 + 0) - (0 + 15.66)]\ \text{Kcal} = -nF\,E^0_{\text{cell}}$

or $-50.80\ \text{Kcal} = -(2\ \text{mol}) \times (96500\ \text{C.mol}^{-1}) \times E^0_{\text{cell}}$

or $E^0_{\text{cell}} = \dfrac{50.80\ \text{K cal}}{(2\ \text{mol}) \times (96500\ \text{C.mol}^{-1})}$

$$= \frac{50.80 \times 4.184\ \text{kJ}}{(2\ \text{mol}) \times (96500\ \text{C.mol}^{-1})} \quad (\because 1\ \text{Kcal} = 4.184\ \text{kJ})$$

$$= \frac{50.80 \times 4.184 \times 1000\ \text{J}}{(2\ \text{mol}) \times (96500\ \text{C.mol}^{-1})} = \frac{50.80 \times 4.184 \times 1000\ C.V.}{(2\ \text{mol}) \times (96500\ \text{C.mol}^{-1})}$$

$(\because J = C.V.)$

$$= \frac{50.80 \times 4.184 \times 1000}{2 \times 96500} \text{ V} = \frac{212547.2}{2 \times 96500} \text{ V}$$

$$= \mathbf{1.101 \text{ volts (Answer)}}$$

Example 5. *Calculate standard free energy for the following reeduction half-reaction in kJ.mol^{-1} and eV.atom^{-1}.*

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$$

Given that $MnO_4^- / Mn^{2+} = 1.51 \text{ V}$

Solution. In the units of kJ.mol^{-1}, $\Delta G°$ for the given half-reaction which involves the transfer of 5 electrons ($n = 5$) is given by

$$(\Delta G°)_{MnO_4^-/Mn^{2+}} = [-nFE^0_{MnO_4^-/Mn^{2+}}] \times 10^{-3} \text{ kJ.mol}^{-1}$$

$$= -5 \times 96500 \times 1.51 \times 10^{-3} \text{ kJ.mol}^{-1}$$

$$= \mathbf{-728.575 \text{ kJ.mol}^{-1} \text{ (Answer)}}$$

In units of eV.atom^{-1}, $\Delta G°$ is given by:

$$\Delta G° = -nE^0_{cell} \text{ eV.atom}^{-1} = -5 \times 1.51 \text{ eV.atom}^{-1}$$

$$= \mathbf{-7.55 \text{ eV.atom}^{-1} \text{ (Answer)}}$$

Example 6. *Calculate standard free energy change for the half-reaction:*

$$Sn^{4+} + 2e^- \longrightarrow Sn$$

Given that $Sn^{4+}/Sn^{2+} = +0.150 \text{ V}$, $Sn^{2+}/Sn = -0.136 \text{ V}$.

Solution. The given half-reaction represents Sn^{4+}/Sn electrode. All the three electrodes can be represented as:

$$\begin{tikzcd} Sn^{4+} \arrow[r, "E° = +0.150\text{ V}", "n=2"'] \arrow[rr, bend right] & Sn^{2+} \arrow[r, "E° = -0.136\text{ V}", "n=2"'] & Sn \end{tikzcd}$$

Obviously $(\Delta G°)_{Sn^{4+}/Sn} = (\Delta G°)_{Sn^{4+}/Sn^{2+}} + (\Delta G°)_{Sn^{2+}/Sn}$

$$= -nFE^0_{Sn^{4+}/Sn^{2+}} - nFE^0_{Sn^{2+}/Sn}$$

$$= -2F \times 0.150 - 2F \times (-0.136)$$

$$= -2F \times 0.150 + 2F \times 0.136 = -0.300F + 0.272F$$

$$= \mathbf{-0.028F \text{ Joules (Answer)}}$$

Example 7. *Calculate standard free energy change for* FeO_4^{2-} / Fe^{2+} *electrode, if* E^0 *values for* FeO_4^{2-} / Fe^{3+} *and* Fe^{3+}/Fe^{2+} *electrodes are 2.20 V and 0.77 V respectively.*

Solution. The given electrodes can be shown as given in Fig. 22.7

$$\begin{tikzcd} FeO_4^{2-} \arrow[r, "E° = 2.20\text{ V}", "n=3"'] \arrow[rr, bend right] & Fe^{3+} \arrow[r, "E° = 0.77\text{ V}", "n=1"'] & Fe^{2+} \end{tikzcd}$$

Fig. 22.7. Representation of electrodes of iron.

n shown in Fig. 22.7 indicates the number of electrons involved in the reduction half-reactions corresponding to the electrodes as shown below:

$$FeO_4^{2-} + 8H^+ + 3e^- \longrightarrow Fe^{3+} + 4H_2O \ (n = 3,\ E^0 = 2.20\ V)$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \ (n = 1,\ E^0 = 0.77\ V)$$

Fig. 22.7 shows that:

$$(\Delta G^\circ)_{FeO_4^{2-}/Fe^{2+}} = (\Delta G^\circ)_{FeO_4^{2-}/Fe^{3+}} + (\Delta G^\circ)_{Fe^{3+}/Fe^{2+}}$$
$$= -3 \times 2.20 + (-1 \times 0.77) = -6.60 - 0.77$$
$$= -7.37 \text{ electron volts } \textbf{(Answer)}$$

Relation between ΔG° and K_{eq}

Under the study of "*Equilibirium Constant*" we have shown that, according to Nernst equation, E^0_{cell} of a redox reaction in equilibirium is related to its equilibirium constant (K_{eq}) by the equation:

$$E^0_{cell} = \frac{0.0591}{n} \log K_{eq} \text{ volts at 298 K} \qquad ...(i)$$

Under the study of "*Free Energy*" we have shown that E^0_{cell} of a redox reaction is related to its standard free energy change (ΔG°) by the following equation:

$$\Delta G^\circ = -nFE^0_{cell} \text{ C.mol}^{-1}.\text{V} \qquad ...(ii)$$

In order to find out a relation between ΔG° and K_{eq} we must eliminate E^0_{cell} from the above two equations. Thus the relationship between ΔG° and K_{eq} can be shown by the equation:

$$-\frac{\Delta G^\circ}{nF} = \frac{0.0591}{n} \log K_{eq}$$

or $$-\Delta G^\circ = 0.0591 F \log K_{eq}$$

$$\boxed{\text{or} \qquad \Delta G^\circ = -0.0591 \times F \times \log K_{eq}} \qquad ...(iii)$$

Solved Examples

Example 1. *Calculate the standard free energy change (ΔG°) for the cell reaction (redox reaction)*

$$Fe^{2+}(aq) + Ag^+(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Use the calculated value of ΔG° in calculating equilibirium constant of the reaction. Given Fe^{3+}/Fe^{2+} = +0.77 V, Ag^+/Ag = + 0.80 V and F = 96500 C.mol^{-1}.

Solution. ΔG° for the given redox reaction is given by: (For this redox reaction $n = 1$)

$$\Delta G^\circ = [-nF \times E^0_{\text{redox reaction}}] \text{ Joules}$$
$$= [-1 \times 96500 \times (E^0_{Fe^{2+}/Fe^{3+}} + E^0_{Ag^+/Ag})] \text{ Joules}$$
$$= [-1 \times 96500 \times (-0.77 + 0.80)] \text{ Joules}$$
$$= -0.03 \times 96500 \text{ Joules} = \textbf{-2859 Joules (Answers)}$$

Now we know that:

$$\Delta G^\circ = -0.0591 \times F \times \log K_{eq}$$
$$-2859 = -0.0591 \times 96500 \times \log K_{eq}$$

$$\therefore \quad \log K_{eq} = \frac{2859}{0.0591 \times 96500} = \frac{2859}{5703.15} = 0.5013019$$

$$\therefore \quad K_{eq} = \text{Antilog}(0.5013019) = \mathbf{0.351\ (Answer)}$$

Example 2. *Calculate $\Delta G°$ for the following cell:*

$$Fe(s) \mid Fe^{2+}(aq)(1\ M) \parallel Cu^{2+}(aq)(1\ M) \mid Cu(s)$$

Use the calculated value of $\Delta G°$ for calculating the value of equilibirium constant for the cell reaction. Given $Cu^{2+}/Cu = +\ 0.34\ V$, $Fe^{2+}/Fe = -\ 0.44\ V$ and $F = 96500\ C.mol^{-1}$.

Solution. The redox reaction is:

$$\text{Fe}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Cu}(s)\ (n = 2)$$

$$\Delta G° = -\, nF \times E^0_{\text{redox reaction}}$$

$$= -2 \times 96500 \times [E^0_{\text{Fe/Fe}^{2+}} + E^0_{\text{Cu}^{2+}/\text{Cu}}]$$

$$= -2 \times 96500 \times [+0.44 + 0.34]$$

$$= -\,2 \times 96500 \times 0.78\ \text{Joules} = \mathbf{150540\ Joules\ (Answer)}$$

Now we know that:

$$\Delta G° = -\,0.0591 \times F \times \log K_{eq}$$

$$-\,150540 = -0.0591 \times 96500 \times \log K_{eq}$$

$$\therefore \quad \log K_{eq} = \frac{150540}{0.0591 \times 96500} = \frac{15054}{570.315} = 26.3959$$

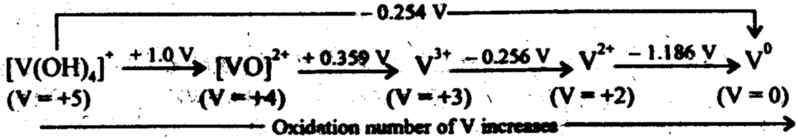
$$\therefore \quad K_{eq} = \text{Antilog}(26.3959) = \mathbf{4.135 \times 10^{-27}\ (Answer)}$$

EMF Diagram

What is EMF diagram of an element?

EMF diagram of an element is a short form in which standard reduction (or oxidation) potential values of the element in its free state or in its compounds in different oxidation states are presented in a condensed manner. In an EMF diagram of an element the species of the element having different oxidation states are arranged from left to right or from top to bottom in the decreasing or increasing order of oxidation number of element and the values of E^0_{red} or E^0_{ox} are inserted between the oxidised and reduced species. In EMF diagram the acidic or alkaline medium [*i.e.* H^+ or OH^- ions] and molecules of the medium (*e.g.* H_2SO_4, KOH, H_2O) are omitted.

Illustrative Example. The standard reduction potential values of vanadium in +5, +4, +3, +2 and 0 (zero) oxidation states can be arranged in a short form given below. This short form is called EMF diagram of vanadium.



The reduction half-reactions given in the above EMF diagram can be written as follows:

$$\underset{(V=+5)}{[V(OH)_4]^+} + 2H^+ + e^- \longrightarrow \underset{(V=+4)}{[VO]^{2+}} + 3H_2O\,(n=1),\ E^0_{red} = 1.0\text{ V}$$

$$\underset{(V=+4)}{[VO]^{2+}} + 2H^+ + e^- \longrightarrow \underset{(V=+3)}{V^{3+}} + H_2O\,(n=1),\ E^0_{red} = +0.359\text{ V}$$

$$\underset{(V=+3)}{V^{3+}} + e^- \longrightarrow \underset{(V=+2)}{V^{2+}}\,(n=1),\ E^0_{red} = -0.256\text{ V}$$

$$\underset{(V=+2)}{V^{2+}} + 2e^- \longrightarrow \underset{(V=0)}{V^0}\,(n=2),\ E^0_{red} = -1.186\text{ V}$$

$$\underset{(V=+5)}{[V(OH)_4]^+} + 4H^+ + 5e^- \longrightarrow \underset{(V=0)}{V} + 4H_2O\,(n=5),\ E^0_{red} = -0.254\text{ V}$$

To calculate the value of E^0 of a given half-cell reaction from the values of E^0 of other given half-cell reactions.

When we are required to calculate the value of E^0 for a given half-cell reaction from the given values of E^0 of other half-cell reactions, we should remember the following points:

(*i*) Free energy change ($\Delta G°$) for a half-cell reaction which may be oxidation half-reaction or reduction half-reaction is given by:

$$(\Delta G°)_{\text{half reaction}} = (-n \times E^0_{\text{half reaction}})\,\text{eV.atom}^{-1}$$

Here n = No. of electrons involved in the half-reaction

$E^0_{\text{half reaction}}$ = Standard reduction potential for the reduction half-reaction or standard oxidation potential for the oxidation half-reaction.

(*ii*) Suppose we have three half-reactions, say 1, 2 and 3 whose E^0 values are E^0_1, E^0_2 and E^0_3 (E^0_3 is to be calculated) and the number of electrons involved in these reactions is n_1, n_2 and n_3 respectively. Suppse we have to determine the value of E^0_3. Now:

(*a*) if half-reaction 3 is the sum of half-reactions 1 and 2, then $\Delta G°$ for reaction 3 will be equal to the sum of $\Delta G°$ values for reactions 1 and 2, *i.e.*

$$(\Delta G°)_3 = (\Delta G°)_1 + (\Delta G°)_2$$

or $$-n_3E^0_3 = -n_1E^0_1 + (-n_2E^0_2)$$

or $$-n_3E^0_3 = -n_1E^0_1 - n_2E^0_2$$

or $$n_3E^0_3 = n_1E^0_1 + n_2E^0_2$$

or $$E^0_3 = \frac{n_1E^0_1 + n_2E^0_2}{n_3}.$$

Now, as said above, since half-reaction 3 is the sum of half-reactions 1 and 2, $n_3 = n_1 + n_2$ and hence above equation becomes

$$\boxed{E_3^0 = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2} \text{ volts}}$$

(*b*) if half-reaction 3 is obtained by subtracting half-reaction 2 from half-reaction 1, then

$$(\Delta G^\circ)_3 = (\Delta G^\circ)_1 - (\Delta G^\circ)_2$$

or $$-n_3E_3^0 = -n_1E_1^0 - (-n_2E_2^0)$$

or $$-n_3E_3^0 = -n_1E_1^0 + n_2E_2^0$$

or $$+n_3E_3^0 = +n_1E_1^0 - n_2E_2^0$$

or $$E_3^0 = \frac{n_1E_1^0 - n_2E_2^0}{n_3}$$

or $$\boxed{E_3^0 = \frac{n_1E_1^0 - n_2E_2^0}{n_1 - n_2} \text{ volts}}$$

Solved Examples

Example 1. *Calculate the value of E^0 for the reaction:*

$$Au^{3+} + 3e^- \longrightarrow Au$$

Given that: $Au^+ + e^- \longrightarrow Au,\ E^0 = 1.7\ V$

$$Au^{3+} + 2e^- \longrightarrow Au^+,\ E^0 = 1.4\ V$$

Solution. Write the given half-reaction as:

(1) $\mathrm{Au^+} + e^- \longrightarrow \mathrm{Au}\ (n_1 = 1),\ E_1^0 = 1.7\ \mathrm{V}$

(2) $\mathrm{Au^{3+}} + 2e^- \longrightarrow \mathrm{Au^+}\ (n_2 = 2),\ E_2^0 = 1.4\ \mathrm{V}$

(*A*) $\mathrm{Au^{3+}} + 3e^- \longrightarrow \mathrm{Au}\ (n_A = 3);\ E_A^0 = ?$ (to be calculated)

Since, Reaction (*A*) = Reaction (1) + Reaction (2),

$$(\Delta G^\circ)_A = (\Delta G^\circ)_1 + (\Delta G^\circ)_2$$

$$-n_AE_A^0 = -n_1E_1^0 + (-n_2E_2^0)$$

$$n_AE_A^0 = n_1E_1^0 + n_2E_2^0$$

$$3 \times E_A^0 = 1 \times 1.7 + 2 \times 1.4 = 4.5$$

$$\therefore \quad E_A^0 = \frac{4.5}{3} = 1.5\ \mathrm{V}\ \textbf{(Answer)}$$

Alternative solution. The given reduction half-reactions can be shown in the form of EMF diagram given in Fig. 22.8.

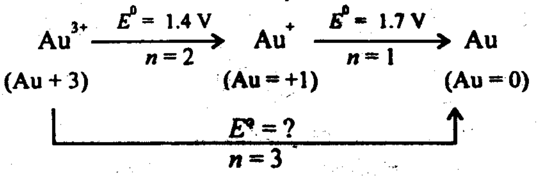


Fig. 22.8. Reduction potential for different electrodes of gold.

Fig. 22.8 show that:

$$(\Delta G^\circ)_{Au^{3+}/Au} = (\Delta G^\circ)_{Au^{3+}/Au^+} + (\Delta G^\circ)_{Au^+/Au}$$

$$-n \times E^0_{Au^{3+}/Au} = -n \times E^0_{Au^{3+}/Au^+} + (-n \times E^0_{Au^+/Au})$$

$$n \times E^0_{Au^{3+}/Au} = n \times E^0_{Au^{3+}/Au^+} + n \times E^0_{Au^+/Au}$$

$$3 \times E^0_{Au^{3+}/Au} = 2 \times 1.4 + 1 \times 1.7 = 4.5$$

$$\therefore \quad E^0_{Au^{3+}/Au} = \frac{4.5}{3} = \mathbf{1.5\,V\ (Answer)}$$

Example 2. *Calculate the value of E^0 for the half-reaction.*

(A) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O (n_A = 3)$, $E_A^0 = ?$

(to be calculated)

Given that:

(1) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ (n_1 = 5)$, $E_1^0 = 1.51\ V$

(2) $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O\ (n_2 = 2)$, $E_2^0 = 1.23\ V$

Solution. Since, Reaction (A) = Reaction (1) – Reaction (2),

$$(\Delta G^\circ)_A = (\Delta G^\circ)_1 - (\Delta G^\circ)_2$$

$$-n_A E_A^0 = -n_1 E_1^0 - (-n_2 E_2^0)$$

$$-n_A E_A^0 = -n_1 E_1^0 + n_2 E_2^0$$

$$n_A E_A^0 = n_1 E_1^0 - n_2 E_2^0$$

$$3E_A^0 = 5 \times 1.51 - 2 \times 1.23$$

$$3E_A^0 = 5.09$$

$$\therefore \quad E_A = \frac{5.09}{3} \approx \mathbf{1.696\,V\ (Answer)}$$

Alternative solution. The given reduction half-reactions can be shown in the form of EMF diagram given in Fig. 22.9.

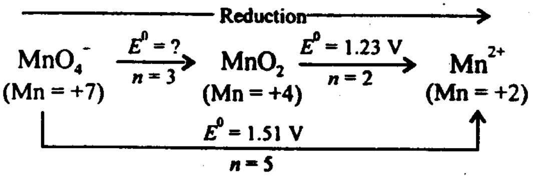


Fig. 22.9. Reduction potentials of different electrodes of Mn.

It is obvious from Fig. 22.9 that:

$$(\Delta G^\circ)_{MnO_4^-/MnO_2} + (\Delta G^\circ)_{MnO_2/Mn^{2+}} = (\Delta G^\circ)_{MnO_4^-/Mn^2}$$

$$-3 \times E^0_{MnO_4^-/MnO_2} + (-2 \times E^0_{MnO_2/Mn^{2+}}) = -5 \times E^0_{MnO_4^-/Mn^{2+}}$$

$$3 \times E^0_{MnO_4^-/MnO_2} + 2 \times 1.23 = 5 \times 1.51$$

$$\therefore \quad E^0_{MnO_4^-/MnO_2} = \frac{5 \times 1.51 - 2 \times 1.23}{3} V = \mathbf{1.696\,V\ (Answer)}$$

Example 3. *Calculate the value of E^0 for the reduction half-reaction:*

(A) $Tl^{3+} + 3e^- \longrightarrow Tl\ (n_A = 3),\ E_A^0 = ?$ *(to be calculated)*

Given that:

(1) $Tl^+ + e^- \longrightarrow Tl\ (n_1 = 1),\ E_1^0 = -0.336\ V$

(2) $Tl^{3+} + 2e^- \longrightarrow Tl^+\ (n_2 = 2),\ E_2^0 = +1.250\ V$

Solution. Since, Reaction (*A*) = Reaction (1) + Reaction (2),

$$(\Delta G^\circ)_A = (\Delta G^\circ)_1 + (\Delta G^\circ)_2$$

$$-n_A E_A^0 = -n_1 E_1^0 + (-n_2 E_2^0)$$

$$-n_A E_A^0 = -n_1 E_1^0 - n_2 E_2^0$$

$$n_A E_A^0 = n_1 E_1^0 + n_2 E_2^0$$

$$3 \times E_A^0 = 1 \times (-0.336) + 2 \times 1.250$$

$$\therefore \quad E_A^0 = \frac{2 \times 1.250 - 1 \times 0.336}{3}\ \text{V} = \mathbf{7.21\ V\ (Ansewer)}$$

Alternative solution. The given reduction half-reactions can be shown in the form of EMF diagram given in Fig. 22.9.

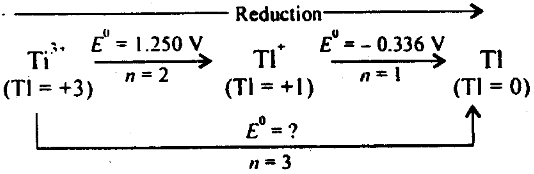


Fig. 22.10. Reduction potentials for different electrodes of thallium.

Fig. 22.10 shows that:

$$(\Delta G^\circ)_{Tl^{3+}/Tl^+} + (\Delta G^\circ)_{Tl^+/Tl} = (\Delta G^\circ)_{Tl^{3+}/Tl}$$

$$-n \times E^0_{Tl^{3+}/Tl^+} + (-n \times E^0_{Tl^+/Tl}) = -n \times E^0_{Tl^{3+}/Tl}$$

$$n \times E^0_{Tl^{3+}/Tl^+} + n \times E^0_{Tl^+/Tl} = n \times E^0_{Tl^{3+}/Tl}$$

$$2 \times 1.250 + 1 \times (-0.336) = 3 \times E^0_{Tl^{3+}/Tl}$$

$$\therefore \quad E^0_{Tl^{3+}/Tl} = \frac{2 \times 1.250 - 1 \times 0.336}{3}\ \text{V} = \mathbf{7.21\ V\ (Answser)}$$

Example 4. *Calculate the value of E^0 for the half-reaction:*

(A) $\frac{1}{2}Cl_2 + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 5e^-$

Given that:

(1) $Cl^- + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 6e^-,\ E_1^0 = -1.45\ V,\ n_1 = 6$

(2) $2Cl^- \longrightarrow Cl_2 + 2e^-,\ E_2^0 = -1.36\ V,\ n_2 = 2$

Solution. Equation (*A*) can also be written as:

(*B*) $Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 10e^-,\ E_B^0 = ?,\ n_B = 10$

Equation (1) can also be written as:

$$(3)\ 2Cl^- + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 12e^-,\quad E_3^0 = -1.45\ V,\quad n_3 = 12$$

Now subtract equation (2) from (3). This gives equation (*B*),

$$(3)\ 2Cl^- + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 12e^-,\quad E_3^0 = -1.45\ V,\quad n_3 = 12$$

$$(2)\qquad 2Cl^- \longrightarrow Cl_2 + 2e^-,\quad E_2^0 = -1.36\ V,\quad n_2 = 2$$

$$(B)\ Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 10e^-,\ E_B^0 = ?,\ n_B = 10$$

Now since, Equation (*B*) = Equation (3) – Equation (2)

$$(\Delta G^\circ)_B = (\Delta G^\circ)_3 - (\Delta G^\circ)_2$$

$$-n_B \times E_B^0 = -n_3 \times E_3^0 - (-n_2 \times E_2^0)$$

$$-10 \times E_B^0 = -12 \times (-1.45) - [-2 \times (-1.36)]$$

$$-10E_B^0 = 12 \times 1.45 - 2 \times 1.36$$

$$E_B^0 = \frac{2 \times 1.36 - 12 \times 1.45}{10}\ V = \frac{2.72 - 17.40}{10}\ V$$

$$= \mathbf{-1.46\ V\ (Answer)}$$

Anternative solution. In order to make the number of Cl-atoms equal in all the species containing this atom in the given oxidation half-reactions, these half-reactions should be written as:

$$Cl_2 + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 10e^-\ (n = 10),\ E^0 = ?$$

$$2Cl^- + 6H_2O \longrightarrow 2ClO_3^- + 12H^+ + 12e^-\ (n = 12),\ E^0 = -1.45\ V$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-\ (n = 2),\ E^0 = -1.36$$

These oxidation half-reactions can also be shown in the form of EMF diagram given in Fig. 22.11.

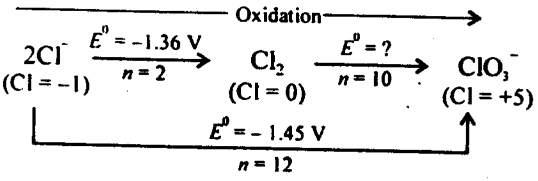


Fig. 22.11. EMF diagram showing the oxidation half-reactions given above.

Fig. 22.11 shows that:

$$(\Delta G^\circ)_{Cl^-/Cl_2} + (\Delta G^\circ)_{Cl_2/ClO_3^-} = (\Delta G^\circ)_{Cl^-/ClO_3^-}$$

$$-n \times E^0_{Cl^-/Cl_2} + (-n \times E^0_{Cl_2/ClO_3^-}) = -n \times E^0_{Cl^-/ClO_3^-}$$

$$-2 \times (-1.36) + (-10 \times E^0_{Cl_2/ClO_3^-}) = -12 \times (-1.45)$$

$$+2.72 - 10 \times E^0_{Cl_2/ClO_3^-} = 17.40$$

$$\therefore\ E^0_{Cl_2/ClO_3^-} = \frac{+2.72 - 17.40}{10}\ V = \mathbf{-1.46\ V\ (Answer)}$$

Example 5. *From the reduction potentials of the following two half-reactiosn:*

$$Fe^{2+} + 2e^- \longrightarrow Fe; \qquad E^0 = -0.44\ V$$
$$Fe^{3+} + 3e^- \longrightarrow Fe; \qquad E^0 = -0.036\ V$$

Determine the reduction potential of $Fe^{3+} + e \longrightarrow Fe^{2+}$.

Solution. 1. $Fe^{3+} + 3e^- \longrightarrow Fe; \quad E_1^0 = -0.036\ V, n_1 = 3$

2. $Fe^{2+} + 2e^- \longrightarrow Fe; \quad E_2^0 = -0.44\ V, n_2 = 2$

When we subtract equation 2 from equation 1, we get:

$$A.\ Fe^{3+} + e^- \longrightarrow Fe^{2+};\ E_A^0 = ?, n_A = 1$$

Now since

$$\text{Equation } A = \text{Equation 1} - \text{Equation 2}$$

$$\therefore \qquad (\Delta G^\circ)_A = (\Delta G^\circ)_1 - (\Delta G^\circ)_2$$
$$-n_A E_A^0 = -n_1 E_1^0 - (-n_2 E_2^0)$$
$$-1 \times E_A^0 = -3 \times (-0.036) - [-2 \times (-0.44)]$$
$$-E_A^0 = +0.108 - 0.880 = -0.772$$
$$\therefore \qquad E_A^0 = \mathbf{+0.772\ V\ (Answer)}$$

Alternative solution. The given reduction half-reactions can be shown in the form of EMF diagram given in Fig. 22.12.

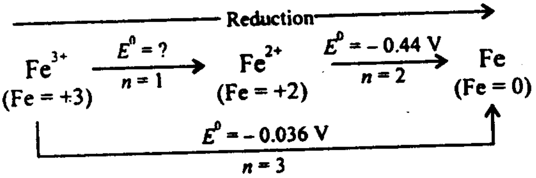


Fig. 22.12. Reduction potentials for different electrodes of iron.

Fig. 22.12 shows that:

$$(\Delta G^\circ)_{Fe^{3+}/Fe^{2+}} + (\Delta G^\circ)_{Fe^{2+}/Fe} = (\Delta G^\circ)_{Fe^{3+}/Fe}$$
$$-n \times E^0_{Fe^{3+}/Fe^{2+}} + (-n \times E^0_{Fe^{2+}/Fe}) = -n \times E^0_{Fe^{3+}/Fe}$$
$$-1 \times E^0_{Fe^{3+}/Fe^{2+}} + [-2 \times (-0.44)] = -3 \times (-0.036)$$
$$-E^0_{Fe^{3+}/Fe^{2+}} + 0.880 = 0.108$$

$$\therefore\ -E^0_{Fe^{3+}/Fe^{2+}} + 0.880 = 0.108 = (0.880 - 0.108)\ V = \mathbf{0.772\ V\ (Answer)}$$

Example 6. *Standard reduction electrode potential values of* MnO_4^- / MnO_4^{2-} *and* MnO_4^- / MnO_2 *couples are 0.56 V and 1.70 V respectively. Find out the standard reduction electrode potential for* MnO_4^{2-} / MnO_2 *couple.*

Solution. Write the half-reactions for the given electrodes so that the number of electrons (n) involved in these half-reactions may be known.

$$\underset{(\mathrm{Mn}=+7)}{\mathrm{MnO_4^-}} + e^- \longrightarrow \underset{(\mathrm{Mn}=+6)}{\mathrm{MnO_4^{2-}}} (n=1,),\quad E^0 = 0.056\text{ V}$$

$$\underset{(\mathrm{Mn}=+7)}{\mathrm{MnO_4^-}} + 4\,\mathrm{H}^+ + 3e^- \longrightarrow \underset{(\mathrm{Mn}=+4)}{\mathrm{MnO_2}} + 2\,\mathrm{H_2O} (n=3),\quad E^0 = 1.70\text{ V}$$

$$\underset{(\mathrm{Mn}=+6)}{\mathrm{MnO_4^{2-}}} + 4\,\mathrm{H}^+ + 2e^- \longrightarrow \underset{(\mathrm{Mn}=+4)}{\mathrm{MnO_2}} + 2\,\mathrm{H_2O} (n=2),\quad E^0 = ?$$

Now the given couples can be shown in the form of an EMF diagram given in Fig. 22.13.

$$\xrightarrow{\qquad\qquad \text{Reduction} \qquad\qquad}$$

$$\begin{tikzcd}
\underset{(\mathrm{Mn}=+7)}{\mathrm{MnO_4^-}} \arrow[r, "E^0=0.56\text{ V}", "n=1"'] \arrow[rr, bend right, "E^0=1.70\text{ V}", "n=3"'] & \underset{(\mathrm{Mn}=+6)}{\mathrm{MnO_4^{2-}}} \arrow[r, "E^0=?", "n=2"'] & \underset{(\mathrm{Mn}=+4)}{\mathrm{MnO_2}}
\end{tikzcd}$$

Fig. 22.13. EMF diagram showing the reduction of manganese.

Fig. 22.13 shows that:

$$(\Delta G^\circ)_{\mathrm{MnO_4^-/MnO_4^{2-}}} + (\Delta G^\circ)_{\mathrm{MnO_4^{2-}/MnO_2}} = (\Delta G^\circ)_{\mathrm{MnO_4^-/MnO_2}}$$

$$-n \times E^0_{\mathrm{MnO_4^-/MnO_4^{2-}}} + (-n \times E^0_{\mathrm{MnO_4^{2-}/MnO_2}}) = -n \times E^0_{\mathrm{MnO_4^-/MnO_2}}$$

$$-1 \times 0.56 + (-2 \times E^0_{\mathrm{MnO_4^{2-}/MnO_2}}) = -3 \times 1.70$$

$$0.56 + 2 \times E^0_{\mathrm{MnO_4^{2-}/MnO_2}} = 3 \times 1.70$$

$$\therefore \quad E^0_{\mathrm{MnO_4^{2-}/MnO_2}} = \frac{3 \times 1.70 - 0.56}{2}\text{ V} = \mathbf{2.27\text{ V}}\ \textbf{(Answer)}$$

Example 7. *The standard reduction potentials of* Cu^{2+}/Cu *and* Cu^+/Cu *couples are 0.337 V and 0.52 V respectively. Calculate the standard potential for the half-reaction,* $Cu^{2+} + e^- \longrightarrow Cu^+$.

Solution. The given couples can be represented by the following reduction half-reactions

Cu^{2+}/Cu couple: $\mathrm{Cu^{2+}} + 2e^- \longrightarrow \mathrm{Cu}\ (n=2, E^0 = 0.337\text{ V})$

Cu^+/Cu couple: $\mathrm{Cu^+} + e^- \longrightarrow \mathrm{Cu}\ (n=1, E^0 = 0.52\text{ V})$

$\mathrm{Cu^{2+}} + e^- \longrightarrow \mathrm{Cu^+}\ (n=1, E^0 = ?)$

EMF diagram corresponding to the above reduction half reactions is given in Fig. 22.14.

$$\xrightarrow{\qquad\qquad \text{Reduction} \qquad\qquad}$$

$$\begin{tikzcd}
\underset{(\mathrm{Cu}=+2)}{\mathrm{Cu^{2+}}} \arrow[r, "E^0=?", "n=1"'] \arrow[rr, bend right, "E^0=0.337\text{ V}", "n=2"'] & \underset{(\mathrm{Cu}=+1)}{\mathrm{Cu^+}} \arrow[r, "E^0=0.52\text{ V}", "n=1"'] & \underset{(\mathrm{Cu}=0)}{\mathrm{Cu}}
\end{tikzcd}$$

Fig. 22.14. EMF diagram for copper.

Fig. 22.14 shows that:

$$(\Delta G^{\circ})_{Cu^{2+}/Cu^{+}} + (\Delta G^{\circ})_{Cu^{+}/Cu} = (\Delta G^{\circ})_{Cu^{2+}/Cu}$$

$$-n \times E^{0}_{Cu^{2+}/Cu^{+}} + (-n \times E^{0}_{Cu^{+}/Cu}) = (-n \times E^{0}_{Cu^{2+}/Cu})$$

$$-1 \times E^{0}_{Cu^{2+}/Cu^{+}} + (-1 \times 0.52) = -2 \times 0.337$$

$$\therefore \quad E^{0}_{Cu^{2+}/Cu^{+}} = 2 \times 0.337 - 0.52 = \mathbf{0.154\ V\ (Answer)}$$

Example 8. *The standard reduction potentials for the half-reactions: $Sn^{2+} + 2e^{-} \longrightarrow Sn$ and $Sn^{4+} + 2e^{-} \longrightarrow Sn^{2+}$ are $-$ 0.136 V and 0.15 V respectively. Calculate the reduction potential of the reduction half-reaction, $Sn^{4+} + 4e^{-} \longrightarrow Sn$. Also comment on the ease of the reduction of Sn^{2+} to Sn and of Sn^{4+} to Sn.*

Solution. EMF diagram corresponding to the given reduction half-reactions is given in Fig. 22.15.

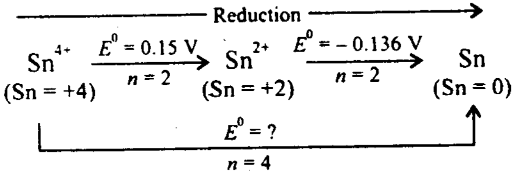


Fig. 22.15. EMF diagram for the half-reactions involving tin.

From EMF diagram it is obvious that:

$$(\Delta G^{\circ})_{Sn^{4+}/Sn^{2+}} + (\Delta G^{\circ})_{Sn^{2+}/Sn} = (\Delta G^{\circ})_{Sn^{4+}/Sn}$$

$$-n \times E^{0}_{Sn^{4+}/Sn^{2+}} + (-n \times E^{0}_{Sn^{2+}/Sn}) = -n \times E^{0}_{Sn^{4+}/Sn}$$

$$-2 \times 0.15 + [-2 \times (-\ 0.136)] = -\ 4 \times E^{0}_{Sn^{4+}/Sn}$$

$$-2 \times 0.15 + 2 \times 0.136 = -4 \times E^{0}_{Sn^{4+}/Sn}$$

$$\therefore \quad E^{0}_{Sn^{4+}/Sn} = \frac{0.300 - 0.272}{4}\ V = \mathbf{0.007\ V\ (Answer)}$$

The reduction of Sn^{2+} to Sn and of Sn^{4+} to Sn can be shown as:

(*i*) $Sn^{2+} + 2e^{-} \longrightarrow Sn, E^{0} = -0.136$ V

(*ii*) $Sn^{4+} + 4e^{-} \longrightarrow Sn, E^{0} = +0.007$ V

Now since E^{0} value for reduction half-reaction (*ii*) is higher than that for reduction half-reaction (*i*), Sn^{4+} is a stronger oxidising agent than Sn^{2+}. In other words we say that it is easier to reduce Sn^{4+} to Sn than Sn^{2+} to Sn.

Example 9. *From the following EMF diagram for Mn, determine the value of E^{0} for $MnO_4^{-} - Mn^{3+}$ couple.*

$$MnO_4^{-} \xrightarrow{+0.56\,V} MnO_4^{2-} \xrightarrow{+2.26\,V} MnO_2 \xrightarrow{+0.95\,V} Mn^{3+}$$

Solution. On incorporating $MnO_4^{-} - Mn^{3+}$ couple in the EMF diagram, we get the diagram given in Fig. 22.16.

$$\xrightarrow{\quad\quad\quad\quad\quad\quad\quad\text{Reduction}\quad\quad\quad\quad\quad\quad\quad}$$

$$\begin{tikzcd}[column sep=huge] \underset{(Mn = +7)}{MnO_4^-} \arrow[r, "E^0 = 0.56\ V", "n = 1"'] \arrow[rrr, bend right, "E^0 = ?", "n = 4"'] & \underset{(Mn = +6)}{MnO_4^{2-}} \arrow[r, "E^0 = +2.26\ V", "n = 2"'] & \underset{(Mn = +4)}{MnO_2} \arrow[r, "E^0 = +0.95\ V", "n = 1"'] & \underset{(Mn = +3)}{Mn^{3+}} \end{tikzcd}$$

Fig. 22.16. EMF diagram for maganese.

n shown in the diagram indicates the number of electrons involved in reduction half-reactions as shown below:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}\ (n = 1),\ E^0 = +0.56\ V$$

$$MnO_4^{2-} + 4\,H^+ + 2e^- \longrightarrow MnO_2 + 2\,H_2O\,(n = 2),\ E^0 = +2.26\,V$$

$$MnO_2 + 4H^+ + e^- \longrightarrow Mn^{3+} + 2H_2O(n = 1),\ E^0 = +0.95\,V$$

$$MnO_4^- + 8\,H^+ + 4e^- \longrightarrow Mn^{3+} + 4\,H_2O\,(n = 4), E^0 = ?$$

EMF diagram shows that:

$$(\Delta G^\circ)_{MnO_4^-/Mn^{3+}} = (\Delta G^\circ)_{MnO_4^-/MnO_4^{2-}} + (\Delta G^\circ)_{MnO_4^{2-}/MnO_2} + (\Delta G^\circ)_{MnO_2/Mn^{3+}}$$

$$-n \times E^0_{MnO_4^-/Mn^{3+}} = (-n \times E^0_{MnO_4^-/MnO_4^{2-}}) + (-n \times E^0_{MnO_4^{2-}/MnO_2}) + (-n \times E^0_{MnO_2/Mn^{3+}})$$

$$-4 \times E^0_{MnO_4^-/Mn^{3+}} = -1 \times 0.56 + (-2 \times 2.26) + (-1 \times 0.95)$$

$$4 \times E^0_{MnO_4^-/Mn^{3+}} = 1 \times 0.56 + 2 \times 2.26 + 1 \times 0.95$$

$$\therefore \quad E^0_{MnO_4^-/Mn^{3+}} = \frac{1 \times 0.56 + 2 \times 2.26 + 1 \times 0.95}{4} = \mathbf{1.74\ V\ (Answer)}$$

Example 10. *From the following EMF diagram for iron, calculate the value of E^0 for (i) $FeO_4^{2-} - Fe^{2+}$, and (ii) $Fe^{2+} - Fe$ couples.*

$$\begin{tikzcd}[column sep=huge] FeO_4^{2-} \arrow[r, "+2.20\ V"] \arrow[rrr, bend right, "+1.08\ V"'] & Fe^{3+} \arrow[r, "+0.77\ V"] & Fe^{2+} \arrow[r] & Fe \end{tikzcd}$$

Solution. If $FeO_4^{2-} - Fe^{2+}$ couple is incorporated in the given EMF diagram, we get the diagram showin in Fig. 22.17.

$$\begin{tikzcd}[column sep=huge] \underset{(Fe = +6)}{FeO_4^{2-}} \arrow[r, "E^0 = +2.20\ V", "n = 3"'] \arrow[rr, bend left, "E^0 = ?", "n = 4"'] \arrow[rrr, bend right, "E^0 = +1.08\ V", "n = 6"'] & \underset{(Fe = +3)}{Fe^{3+}} \arrow[r, "E^0 = +0.77\ V", "n = 1"'] & \underset{(Fe = +2)}{Fe^{2+}} \arrow[r, "E^0 = ?", "n = 2"'] & \underset{(Fe = 0)}{Fe} \end{tikzcd}$$

Fig. 22.17. EMF diagram for iron.

n shown in the EMF diagram indicates the number of electrons involved in the reduction half-reactions corresponding to the electrode couples as shown below:

$$FeO_4^{2-} + 8H^+ + 3e^- \longrightarrow Fe^{3+} + 4H_2O, \quad (n = 3, E^0 = +2.20\,V)$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}, \quad (n = 1, E^0 = +0.77\,V)$$

$$Fe^{2+} + 2e^- \longrightarrow Fe, \quad (n = 2, E^0 = ?)$$

$$FeO_4^{2-} + 8H^+ + 4e^- \longrightarrow Fe^{2+} + 4H_2O, \quad (n = 4, E^0 = ?)$$

$$FeO_4^{2-} + 8H^+ + 6e^- \longrightarrow Fe + 4H_2O \quad (n = 6, E^0 = +1.08\,V)$$

From EMF diagram, we see that:

(*i*) $$(\Delta G^\circ)_{FeO_4^{2-}/Fe^{2+}} = (\Delta G^\circ)_{FeO_4^{2-}/Fe^{3+}} + (\Delta G^\circ)_{Fe^{3+}/Fe^{2+}}$$

$$-n \times E^0_{FeO_4^{2-}/Fe^{2+}} = -n \times E^0_{FeO_4^{2-}/Fe^{3+}} + (-n \times E^0_{Fe^{3+}/Fe^{2+}})$$

$$-4 \times E^0_{FeO_4^{2-}/Fe^{2+}} = -3 \times 2.20 + (-1 \times 0.77)$$

$$\therefore \quad E^0_{FeO_4^{2-}/Fe^{2+}} = \frac{3 \times 2.20 + 1 \times 0.77}{4} = +1.84\ V\ \textbf{(Answer)}$$

(*ii*) $$(\Delta G^\circ)_{FeO_4^{2-}/Fe} = (\Delta G^\circ)_{FeO_4^{2-}/Fe^{3+}} + (\Delta G^\circ)_{Fe^{3+}/Fe^{2+}} + (\Delta G^\circ)_{Fe^{2+}/Fe}$$

$$-n \times E^0_{FeO_4^{2-}/Fe} = -n \times E^0_{FeO_4^{2-}/Fe^{3+}} + (-n \times E^0_{Fe^{3+}/Fe^{2+}}) + (-n \times E^0_{Fe^{2+}/Fe})$$

$$-6 \times 1.08 = -3 \times 2.20 + (-1 \times 0.77) + (-2 \times E^0_{Fe^{2+}/Fe})$$

$$\therefore \quad E^0_{Fe^{2+}/Fe} = \frac{6 \times 1.08 - 3 \times 2.20 - 1 \times 0.77}{2} = -0.445\ V\ \textbf{(Answer)}$$

Example 11. *From the reduction potential of the following sequence of reactions predict whether MnO_4^- or MnO_4^{2-} ion is the better oxident, if the reduction product is Mn^{2+}.*

$$MnO_4^- \xrightarrow{0.564\,V} MnO_4^{2-} \xrightarrow{-2.26\,V} MnO_2 \xrightarrow{0.95\,V} Mn^{3+} \xrightarrow{1.51\,V} Mn^{2+}$$

Solution. In order to answer this question we will have to determine E^0 alues for MnO_4^-/Mn^{2+} and MnO_4^{2-}/Mn^{2+} couples or for their corresponding half-reactions given below:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad (n = 5, E^0 = ?)$$

$$MnO_4^{2-} + 8H^+ + 4e^- \longrightarrow Mn^{2+} + 4H_2O \quad (n = 4, E^0 = ?)$$

Write the sequence of reactions as shown in Fig. 22.17.

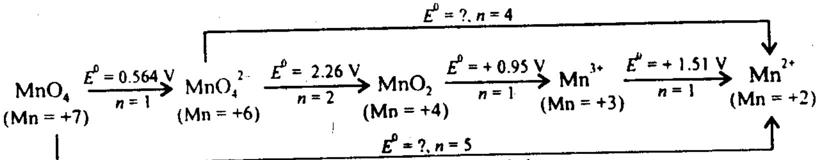


Fig. 22.17. Sequence of reactions involving manganese.

In Fig. 22.17 *n* indicates the number of electrons involved in the reduction-half reactions corresponding to the electrodes shown in the figure.

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}\ (n = 1, E^0 = 0.564\ V)$$
$$MnO_4^{2-} + 4H^+ + 2e^- \longrightarrow MnO_2 + 2H_2O\ (n = 2, E^0 = 2.26\ V)$$
$$MnO_2 + 4H^+ + e^- \longrightarrow Mn^{3+} + 2H_2O\ (n = 1, E^0 = 0.95\ V)$$
$$Mn^{3+} + e^- \longrightarrow Mn^{2+}\ (n = 1, E^0 = 1.51\ V)$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ (n = 5, E^0 = ?)$$
$$MnO_4^{2-} + 8H^+ + 4e^- \longrightarrow Mn^{2+} + 4H_2O\ (n = 4, E^0 = ?)$$

From Fig. 22.17 it is evident that :

(*i*) $5 \times E^0_{MnO_4^-/Mn^{2+}} = 1 \times 0.564 + 2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51$

$$\therefore E^0_{MnO_4^-/Mn^{2+}} = \frac{1 \times 0.564 \times 2 \times 2.26 + 1 \times 0.95 + 1 \times 151}{5}\ V = 1.508\ V$$

Thus for MnO_4^-/Mn^{2+} couple or for the reduction half-reaction,

$$\underset{(OA)}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O, E^0 = 1.508\ V \qquad ...(a)$$

(*ii*) $4 \times E^0_{MnO_4^{2-}/Mn^{2+}} = 2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51$

$$\therefore E^0_{MnO_4^{2-}/Mn^{2+}} = \frac{2 \times 2.26 + 1 \times 0.95 + 1 \times 151}{4}\ V = 1.745\ V$$

Thus for MnO_4^{2-}/Mn^{2+} couple or for the reduction half-reaction,

$$\underset{(OA)}{MnO_4^{2-}} + 8H^+ + 4e^- \longrightarrow Mn^{2+} + 4H_2O, E^0 = 1.745\ V \qquad ...(b)$$

Now since E^0 value for reaction (*b*) is higher than E^0 value for reaction (*a*), MnO_4^{2-} is a better oxidant than MnO_4^-. **(Answer)**

Example 12. *If the standard electrode potential (E^0) for OCl^-/Cl^- and $Cl^-/\frac{1}{2}Cl_2$ electrodes are 0.88 V and −1.36 V respectively. Determine E^0 value for $OCl^-/\frac{1}{2}Cl_2$ electrode.*

Solution. Write the reduction half-reactions for the given electrodes

(*a*) $\underset{(Cl = +1)}{OCl^-} + 2H^+ + 2e^- \longrightarrow \underset{(Cl = -1)}{Cl^-} + H_2O, E^0 = +0.88\ V, n = 2$

(*b*) $\underset{(Cl = 0)}{\frac{1}{2}Cl_2} + e^- \longrightarrow \underset{(Cl = -1)}{Cl^-}, E^0 = +1.36\ V, n = 1$

(*c*) $\underset{(Cl = +1)}{OCl^-} + 2H^+ + 2e^- \longrightarrow \underset{(Cl = 0)}{\frac{1}{2}Cl_2} + H_2O, E^0 = ?, n = 1$

These reactions give the value of *n* for each reaction.

Above reactions can be shown in the form of an EMF diagram given below:

$$\begin{tikzcd}[column sep=large]
\underset{(\mathrm{Cl}=+1)}{\mathrm{OCl}^-} \arrow[r, "E^0=?", "n=1"'] \arrow[rr, bend right, "E^0=0.88\text{ V}", "n=2"'] & \underset{(\mathrm{Cl}=0)}{\frac{1}{2}\mathrm{Cl}_2} \arrow[r, "E^0=1.36\text{ V}", "n=1"'] & \underset{(\mathrm{Cl}=-1)}{\mathrm{Cl}^-}
\end{tikzcd}$$

This diagram shows that

$$(\Delta G^0)_{\mathrm{OCl}^-/\mathrm{Cl}^-} = (\Delta G^0)_{\mathrm{OCl}^-/\frac{1}{2}\mathrm{Cl}_2} + (\Delta G^0)_{\frac{1}{2}/\mathrm{Cl}_2/\mathrm{Cl}^-}$$

or $$0.88 \times 2 = E^0 \times 1 + 1.36 \times 1$$

$\therefore$ $$E^0 = 1.76 - 1.36 = \mathbf{+0.40\ V}$$

Electrolysis

To predict the nature of products obtained by the electrolysis of aqueous solution of electrolytes.

The nature of products obtained by the electrolysis of the aqueous solution of a given electrolyte depends on the follwing factors:

(*i*) The state of electrolyte being electrolysed, *e.g.* the products obtained by the elctrolysis of molten NaCl are difterent from those which are obtained by the electrolysis of aqueous solution of NaCl.

(*ii*) Concentration of the electrolyte solution.

(*iii*) Material used for making electrodes.

(*iv*) Relative E^0_{ox} values of the species being oxidised at anode and relative E^0_{red} values of the species being reduced at cathode, *e.g.*

(*a*) The species having larger value of E^0_{red} is preferentially reduced at cathode than the species having lower value of E^0_{red} value.

(*b*) The species having higher E^0_{ox} value is preferentially oxidised at anode than the species having lower value of E^0_{ox} value.

General discussion of the electrolysis of the aqueous solution of MX salt.

We know that the aqueous solution of MX salt undergoes dissociation (ionisation) and gives $\mathrm{M}^+(aq)$ (cation) and $\mathrm{X}^-(aq)$ (anion) ions.

$$\mathrm{MX}(s) \rightleftharpoons \mathrm{M}^+(aq) + \mathrm{X}^-(aq)$$

When aqueous solution of MX is electrolysed, $\mathrm{M}^+(aq)$ and $\mathrm{X}^-(aq)$ ions obtained as above move towards their respective electrodes on which they undergo reduction (on cathode) and oxidistion (on anode).

While considering the reduction and oxidation of $\mathrm{M}^+(aq)$ and $\mathrm{X}^-(aq)$ ions on their respective electrodes, we should also remember $\mathrm{H_2O}(l)$ also undergoes reduction on cathode and oxidation on anode.

Reduction on cathode. There are two possible reduction reactions that may take place on cathode. We have either reduction of $\mathrm{M}^+(aq)$ to $\mathrm{M}(s)$ or reduction of $\mathrm{H_2O}(l)$ to $\mathrm{H_2}(g)$

$$\mathrm{M}^+(aq) + e^- \longrightarrow \mathrm{M}(s)$$

$$2\mathrm{H_2O}(l) + 2e^- \longrightarrow \mathrm{H_2}(g) + 2\mathrm{OH}^-(aq)$$

Two cases arise:

(*i*) If the standard reduction electrode potential of $M^+(aq)$ ion is higher than that of $H_2O(l)$ [*i.e.* $E^0_{M^+/M} > E^0_{H_2O/H_2}$], $M^+(aq)$ ion gets reduced to $M(s)$ more easily than $H_2O(l)$ gets reduced to $H_2(g)$. Thus in this case metal M (not H_2 gas) is obtained on cathode, *i.e.* the actual reduction reaction taking place on cathode is:

$$M^+(aq) + e^- \longrightarrow M(s)$$

Examples. (*i*) Since the ions viz Ag^+ (Ag^+/Ag = + 0.80 V), Cu^{2+} (Cu^{2+}/Cu = + 0.34 V) etc. have higher E^0_{red} values than H_2O (H_2O/H_2 = – 0.83 V), these ions are more easily reduced to their respective metals than $H_2O(l)$ gets reduced to $H_2(g)$, Thus metal (and not H_2 gas) is obtained on cathode *i.e.* the actual reduction reaction taking place on cathode is:

$$M^+(aq) + e^- \longrightarrow M(s)$$

(*ii*) If the standard reduction electrode potential of $M^+(aq)$ ion is lower than that of $H_2O(l)$ [*i.e.* $E^0_{M^+/M} < E^0_{H_2O/H_2}$], $H_2O(l)$ gets reduced to $H_2(g)$ more easily than $M^+(aq)$ ion gets reducced to $M(s)$. Thus in this case $H_2(g)$ (not metal, M) is obtained on cathode, *i.e.* the actual reduction reaction taking place on cathode is :

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

Example. Since the ions *viz.* Na^+(Na^+/Na = – 2.71 V), Ca^{2+} (Ca^{2+}/Ca = – 2.87 V), K^+(K^+/K = – 2.93 V), Mg^+(Mg^{2+}/Mg = – 2.37 V), Al^{3+} (Al^{3+}/Al = – 1.66 V) etc., have lower E^0_{red} values than H_2O ($E^0_{H_2O/H_2}$ = – 0.83V), $H_2O(l)$ is more easily reduced to given $H_2(g)$ than these metal ions get reduced to give metal on cathode. Thus $H_2(g)$ (not metal) is obtained on cathode.

Oxidation on anode. There are two possible oxidation reactions that may take place on anode. We have either the oxidation of $X^-(aq)$ ion to $X_2(g)$ or of $H_2O(l)$ to $O_2(g)$.

$$2X^-(aq) \longrightarrow X_2(g) + 2e^-$$
$$2H_2O(l) \longrightarrow 2O_2(g) + 2H^+ + 2e^-$$

Two cases arise:

(*i*) If the standard oxidation electrode potential of $X^-(aq)$ ion is higher than that of $H_2O(l)$ [*i.e.* $E^0_{X^-/X_2} > E^0_{H_2O/O_2}$], $X^-(aq)$ ion is more easily oxidised to $X_2(g)$ than $H_2O(l)$ gets oxidised to $O_2(g)$. Thus is this case $X_2(g)$ [and not $O_2(g)$] is obtained on anode, *i.e.* the actual oxidation reaction taking place on anode is :

$$2X^-(aq) \longrightarrow X_2(g) + 2e^-$$

Examples. Since the ions like Br^-(Br^-/Br_2 = – 1.08 V) and I^- (I^-/I_2 = –0.77 V) have higher E^0_{ox} values than H_2O(H_2O/O_2 = – 1.23 V), $X^-(aq)$ ions (X^- = Br^-, I^-) are more easily oxidised to $X_2(g)$ than $H_2O(l)$ gets oxidised to $O_2(g)$. Thus $X_2(g)$ (and not O_2 gas) is obtained on anode.

(*ii*) If the standard oxidation potential of $X^-(aq)$ ion is lower than that of $H_2O(l)$ [*i.e.* $E^0_{X^-/X_2} < E^0_{H_2O/O_2}$], $H_2O(l)$ gets oxidised to $O_2(g)$ more easily than $X^-(aq)$ ion gets oxidised to $X_2(g)$. Thus in this case $O_2(g)$ (not X_2 gas) is obtained on anode, *i.e.* the actual oxidation reaction taking place on anode is:

$$2H_2O(l) \longrightarrow O_2(g) + 2H^+(aq) + 2e^-$$

Example. Since $F^-(aq)$ ion ($F^-/F_2 = -2.87$ V) has lower value of E^0_{ox} than H_2O ($H_2O/O_2 = -1.23$ V), this ion is not oxidised to $F_2(g)$ in aqueous solution. Instead $H_2O(l)$ is oxidised to give $O_2(g)$.

Electrolysis of Some Electrolytes

1. Electrolysis of molten NaCl.

When NaCl(*s*) is melted, it gets dissociated into $Na^+(l)$ and $Cl^-(l)$ ions.

$$NaCl(s) \xrightarrow{\text{Melting}} Na^+(l) + Cl^-(l)$$

$Na^+(l)$ and $Cl^-(l)$ ions formed as above move towards cathode and anode respectively. $Na^+(l)$ ions get reduced to Na(*l*) on cathode and $Cl^-(l)$ ion get oxidised to $Cl_2(g)$ on onode

$$Na^+(l) + e^- \xrightarrow[\text{on cathode}]{\text{Reduction}} Na(l)$$

$$2Cl^-(l) \xrightarrow[\text{on anode}]{\text{Oxidation}} Cl_2(g) + 2e^-$$

Thus we see that the electrolysis of molten NaCl gives Na-metal on cathode and $Cl_2(g)$ on anode.

2. Electrolysis of concentrated solution of NaCl using Pt electrodes.

Aqueous soltion of NaCl dissociates to give $Na^+(aq)$ and $Cl^-(aq)$ ions.

$$NaCl(aq) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$Na^+(aq)$ and $Cl^-(aq)$ ions move towards cathode and anode respectively. $Na^+(aq)$ ions get reduced to Na(*s*) on cathode and $Cl^-(aq)$ ions get oxidised to $Cl_2(g)$ on anode. Thus the expected products obtained on cathode and anode should be Na(*s*) and $Cl_2(g)$ respectively. But, in fact, it has been observed that the electrolysis of aqueous solution of NaCl produces $H_2(g)$ [instead of Na(*s*)] on cathode and $Cl_2(g)$ on anode [$Cl_2(g)$ is the expected product].

Why Na metal in not formed on cathode can be explained as follows:

When the electrolysis of NaCl solution is carried out between Pt-electrodes, $H_2O(l)$ also undergoes reduction on cathode and oxidation on anode. Thus probable reactions taking place on electrodes are:

Probable reduction reactions on cathode. $Na^+(aq)$ and $H_2O(l)$ both undergo reduction and give Na(*s*) and $H_2(g)$ respectively.

$$\underset{(Na = +1)}{Na^+(aq)} + e^- \longrightarrow \underset{(Na = 0)}{Na(s)}, \quad E^0_{red} = E^0_{Na^+/Na} = -2.71 \text{ V}$$

$$\underset{(H = +1)}{2H_2O(l)} + 2e^- \longrightarrow \underset{(H = 0)}{H_2(g)} + 2OH^-(aq), \quad E^0_{red} = E^0_{H_2O/H_2} = -0.83 \text{ V}$$

Now since E^0_{red} of $H_2O(l)$ (= – 0.83 V) is higher than that of $Na^+(aq)$ ion (= – 2.71 V), reduction of $H_2O(l)$ to $H_2(g)$ takes place more easily than that of $Na^+(aq)$ ions to Na(*s*). Thus the actual reduction reaction taking place on cathode is:

$$2H_2O(l) + 2e^- \longrightarrow \boxed{H_2(g)} + 2OH^-(aq) \qquad ...(i)$$

This reduction reaction shows that on cathode $H_2(g)$ and not Na metal is obtained.

Probable oxidation reactions on anode. $Cl^-(aq)$ and $H_2O(l)$ both undergo oxidation and give $Cl_2(g)$ and $O_2(g)$ respectively.

$$\underset{(Cl\,=\,-1)}{2Cl^-(aq)} \longrightarrow \underset{(Cl\,=\,0)}{Cl_2(g)} + 2e^-, \quad E^0_{ox} = E^0_{Cl^-/Cl_2} = -1.36\text{ V}$$

$$\underset{(O\,=\,-2)}{2H_2O(l)} \longrightarrow \underset{(O\,=\,0)}{O_2(g)} + 2H^+(aq) + 2e^-, \quad E^0_{ox} = E^0_{H_2O/O_2} = -1.23\text{ V}$$

Since E^0_{ox} of $H_2O(l)$ is higher (= − 1.23V) than that of $Cl^-(aq)$ ions (= −1.36 V), oxidation of $H_2O(l)$ to $O_2(g)$ should take place more easily than the oxidation of $Cl^-(aq)$ ions to $Cl_2(g)$. Thus $O_2(g)$ and not $Cl_2(g)$ should be obtained on anode. As a matter of fact $Cl^-(aq)$ ions get oxidised in preference to $H_2O(l)$. This unexpected oxidation of $Cl^-(aq)$ ions in preference to that of $H_2O(l)$ is because of the fact that since oxygen voltage on Pt electrode is about 0.25 V, E^0_{ox} of $H_2O(l)$ on Pt electrode gets lowered by 0.25 V and hence E^0_{ox} of $H_2O(l)$ becomes equal to (− 1.23 − 0.25) V = − 1.48 V. Now since E^0_{ox} of $Cl^-(aq)$ ions (= − 1.36 V) becomes higher than E^0_{ox} of $H_2O(l)$ (= −1.48 V), oxidation of $Cl^-(aq)$ ions to $Cl_2(g)$ becomes easier. Thus the actual oxidation reaction taking place on anode is:

$$2Cl^-(aq) \longrightarrow \boxed{Cl_2(g)} + 2e^- \qquad ...(ii)$$

This reaction shows that on anode $Cl_2(g)$ and not $O_2(g)$ is obtained.

Above discussion shows that the actual products obtained by the electrolysis of concentrated solution of NaCl between Pt-electrodes are $Cl_2(g)$ on anode (expected product) and $H_2(g)$ on cathode (not Na-metal).

3. Electrolysis of aqueous solution of $CuCl_2$ or $CuBr_2$ using Pt-electrodes.

As an example let us consider the electrolysis of the aqueous solution of $CuBr_2$

$$CuBr_2(aq) \rightleftharpoons Cu^{2+}(aq) + 2Br^-(aq)$$

Probable reduction reactions on cathode. $Cu^{2+}(aq)$ and $H_2O(l)$ both undergo reduction on cathode to give $Cu(s)$ and $H_2(g)$ respectively.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s), \quad E^0_{red} = E^0_{Cu^{2+}/Cu} = +0.34\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq), \quad E^0_{red} = E^0_{H_2O/H_2} = -0.83\text{ V}$$

Now since $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) > $E^0_{H_2O/H_2}$ (= −0.83 V), the reduction of $Cu^{2+}(aq)$ ions to $Cu(s)$ takes place more easily than that of $H_2O(l)$ to $H_2(g)$. Thus the actual reduction reaction taking place on cathode is:

$$Cu^{2+}(aq) + 2e^- \longrightarrow \boxed{Cu(s)}$$

This reduction reaction shows that on cathode Cu-metal and not $H_2(g)$ is produced.

Probable oxidation reactions on anode. $Br^-(aq)$ and $H_2O(l)$ both undergo oxidation and give $Br_2(g)$ and $O_2(g)$ respectively.

$$Br^-(aq) \longrightarrow Br_2(g) + 2e^-, \quad E^0_{ox} = E^0_{Br^-/Br_2} = -1.08\text{ V}$$

$$2H_2O(l) \longrightarrow O_2(g) + 2H^+(aq) + 2e^-, \quad E^0_{ox} = E^0_{H_2O/O_2} = -1.23\text{ V}$$

Now since E^0_{ox} or $E^0_{Br^-/Br_2}$ ($= -1.08$ V) $> E^0_{ox}$ or $E^0_{H_2O/O_2}$ ($= -1.23$ V), $Br^-(aq)$ ions get oxidised to $Br_2(g)$ more easily than $H_2O(l)$ does to $O_2(g)$. Thus the actual oxidation reaction taking place on anode is:

$$2Br^-(aq) \longrightarrow \boxed{Br_2(g)} + 2e^-$$

This reaction shows that on anode $Br_2(g)$ is obtained.

Above discussion shows that the actual products obtained by the electrolysis of aqueous solution of $CuBr_2$ are Cu metal on cathode (expected product) and $Br_2(g)$ on anode (expected product). Similarly in case of $CuCl_2(aq)$ we get Cu-metal on cathode and $Cl_2(g)$ on anode.

In the above discussion, we have shown that $E^0_{H_2O/O_2}$ (standard oxidation potential) $= -1.23$ V. But when we consider the electrolysis of $CuCl_2(aq)$, the value of $E^0_{H_2O/O_2}$ decreases and becomes equal to $(-1.23 - 0.25)$ V $= -1.48$ V. The decrese in the value is due to oxygen voltage on Pt-electrode whch is equal to 0.25 V. Thus the value of $E^0_{H_2O/O_2}$ to be used in writting oxidation reactions taking place on anode during the electrolysis of $CuCl_2(aq)$ should be -1.48 V and not -1.23 V. Thus again since $E^0_{Cl^-/Cl_2}$ ($= -1.36$ V) $> E^0_{H_2O/O_2}$ ($= -1.48$ V), $Cl^-(aq)$ ions are oxidised to $Cl_2(g)$ more easily than $H_2O(l)$ to $O_2(g)$. Thus $Cl_2(g)$ gas is obtained on anode in the electrolysis of aqueous solution of $CuCl_2$.

4. Electrolysis of dil. aqueous solution of H_2SO_4.

Aqueous solution of H_2SO_4 dissociates to give $H^+(aq)$ and $SO_4^{2-}(aq)$ ions.

$$H_2SO_4(aq) \rightleftharpoons 2H^+(aq) + SO_4^{2-}(aq)$$

$H^+(aq)$ and $SO_4^{2-}(aq)$ ions move towards cathode and anode respectively. $H^+(aq)$ ions get reduced to $H_2(g)$ on cathode while $SO_4^{2-}(aq)$ ions get oxidised to $S_2O_8^{2-}(aq)$ ions on anode. Thus the expected products obtained on cathode and anode should be $H_2(g)$ and $S_2O_8^{2-}(aq)$ ions respectively. But in fact, it has been observed that the electrolysis of aqueous solution of H_2SO_4 produces $H_2(g)$ (expected product) on cathode and $O_2(g)$ [instead of $S_2O_8^{2-}(aq)$ ions] on anode. Why $S_2O_8^{2-}(aq)$ ions are not formed on anode can be explained as follows:

When electrolysis of aqueous solution of H_2SO_4 is carried out, $H_2O(l)$ also undergoes reduction on cathode and oxidation on anode. Thus the possible reactions taking place on electrodes are:

Probable reduction reactions on cathode: $2H^+(aq)$ and $H_2O(l)$ both undergo reduction on cathode to give $H_2(g)$. Thus on cathode $H_2(g)$ is produced

$$2H^+(aq) + 2e^- \longrightarrow \boxed{H_2(g),} \quad E^0_{red} = E^0_{H^+/H_2} = 0.00\ \text{V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq), \quad E^0_{red} = E^0_{H_2O/H_2} = -0.83\ \text{V}$$

Since E^0_{red} of $H^+(aq)$ is higher (= 0.0 V) than that of $H_2O(l)$ (= – 0.83 V), reduction of $H^+(aq)$ ions to $H_2(g)$ takes place more easily than that of $H_2O(l)$ to $H_2(g)$. Thus $H_2(g)$ produced on cathode is due to the reduction of $H^+(aq)$ ions and not due to the reduction of $H_2O(l)$.

Probable oxidation reactions on anode. $SO_4^{2-}(aq)$ and $H_2O(l)$ both undergo oxidation on anode and give $S_2O_8^{2-}(aq)$ and $O_2(g)$ respectively.

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-, \quad E^0_{ox} = E^0_{SO_4^{2-}/S_2O_8^{2-}} = -2.01\ \text{V}$$

$$2H_2O(l) \longrightarrow \boxed{O_2(g)} + 2H^+(aq) + 2e^-, \quad E^0_{ox} = E^0_{H_2O/O_2} = -1.23\ \text{V}$$

Now since E^0_{ox} of $H_2O(l)$ is higher than that of $SO_4^{2-}(aq)$ ions, $H_2O(l)$ gets oxidised to $O_2(g)$ more easily than $SO_4^{2-}(aq)$ get oxidised to give $S_2O_8^{2-}(aq)$. Thus the product formed on anode is $O_2(g)$ instead of $S_2O_8^{2-}(aq)$ ions.

Above discussion shows that main products obtained by the electrolysis of aqueous solution of H_2SO_4 are $O_2(g)$ on anode and $H_2(g)$ on cathode.

5. Electrolysis of aqueous solution of $CuSO_4$ using Pt-electrodes (inert electrodes).

$CuSO_4$ in solution ionises to give $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions

$$CuSO_4(aq) \rightleftharpoons Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Probable reduction reactions on cathode

$$Cu^{2+}(aq) + 2e^- \longrightarrow \boxed{Cu(s)}, \quad E^0_{red} = E^0_{Cu^{2+}/Cu} = +0.34\ \text{V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq), \quad E^0_{red} = E^0_{H_2O/H_2} = -0.83$$

Since $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) > $E^0_{H_2O/H_2}$ (= – 0.83 V), $Cu^{2+}(aq)$ ions get reduced to $Cu(s)$ more easily than $H_2O(l)$ to $H_2(g)$. Thus the product obtained on cathode is Cu-metal and not $H_2(g)$.

Probable oxidation reactions on anode

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-, \quad E^0_{ox} = E^0_{SO_4^{2-}/S_2O_8^{2-}} = -2.01\ \text{V}$$

$$2H_2O(l) \longrightarrow \boxed{O_2(g)} + 2H^+(aq) + 2e^-, \quad E^0_{ox} = E^0_{H_2O/O_2} = -1.23\ \text{V}$$

Since E^0_{ox} or $E^0_{H_2O/O_2}$ (= – 1.23 V) > E^0_{ox} or $E^0_{SO_4^{2-}/S_2O_8^{2-}}$ (= – 2.01 V), the oxidation of $H_2O(l)$ to $O_2(g)$ takes place more easily than that of $SO_4^{2-}(aq)$ to $S_2O_8^{2-}(aq)$. Thus the product obtained on anode is $O_2(g)$ and not $S_2O_8^{2-}(aq)$ ions.

Above discussion shows the electrolysis of aqueous solution of $CuSO_4$ gives Cu metal on cathode and $O_2(g)$ on anode.

6. Electrolysis of aqueous solution of $CuSO_4$ using Cu-electrodes (active electrodes).

Aqueous solution of $CuSO_4$ undergoes dissociation and gives $Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions. These ions move towards their respective electrodes

$$CuSO_4(aq) \rightleftharpoons Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Probable reduction reactions on cathode. $Cu^{2+}(aq)$ and $H_2O(l)$ both undergo reduction on cathode

$$Cu^{2+}(aq) + 2e^- \longrightarrow \boxed{Cu(s)},\ E^0_{Cu^{2+}/Cu} = +0.34\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq),\ E^0_{H_2O/H_2} = -0.83\text{ V},$$

Now since $E^0_{Cu^{2+}/Cu}$ (= + 0.34 V) > $E^0_{H_2O/H_2}$ (= − 0.83 V), $Cu^{2+}(aq)$ gets reduced to Cu(s) more easily than $H_2O(l)$ gets reduced to $H_2(g)$. Thus the product obtained on cathode is Cu-metal and not $H_2(g)$.

Probable oxidation reactions on anode. $SO_4^{2-}(aq)$ ions do not undergo oxidation. $H_2O(l)$ and Cu(s) (from anode) both undergo oxidation and give $O_2(g)$ and $Cu^{2+}(aq)$ respectively.

$$H_2O(l) \longrightarrow O_2(g) + 2H^+(aq) + 2e^-,\ E^0_{ox} = E^0_{H_2O/O_2} = -1.23\text{ V}$$

$$Cu(s)\text{ (from anode)} \longrightarrow Cu^{2+}(aq) + 2e^-,\ E^0_{ox} = E^0_{Cu/Cu^{2+}} = -0.34\text{ V}$$

Now since $E^0_{Cu/Cu^{2+}}$ (= −0.34 V) > $E^0_{H_2O/O_2}$ (= − 1.23 V), Cu from anode is more easily oxidised to $Cu^{2+}(aq)$ ions. Thus the actual oxidation reaction taking place on anode is:

$$Cu(s)\text{ (from anode)} \longrightarrow Cu^{2+}(aq) + 2e^- \quad ...(i)$$

$Cu^{2+}(aq)$ ions formed as above combine with the available $SO_4^{2-}(aq)$ ions and form $CuSO_4(s)$ around anode.

$$Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow CuSO_4(s)\text{ (around the anode)} \quad ...(ii)$$

On adding equations (*i*) and (*ii*) we get:

$$Cu(s)\text{ (from anode)} + SO_4^{2-}(aq) \longrightarrow \boxed{CuSO_4(s)\text{ (around anode)}} + 2e^-$$

Above equation shows that it is $CuSO_4$ which is formed on anode. This $CuSO_4$ gets dispersed in solution.

Above discussion shows that the electrolysis of aqueous solution of $CuSO_4$ with Cu-electrodes, produces Cu-metal on cathode and $CuSO_4$ around the anode.

7. Electrolysis of aqueous solution of $AgNO_3$ using inert electrodes.

$AgNO_3(aq)$, on being dissociated, gives $Ag^+(aq)$ and $NO_3^-(aq)$ ions. These ions move towards their respective electrodes.

$$AgNO_3(aq) \rightleftharpoons Ag^+(aq) + NO_3^-(aq)$$

Since $E^0_{Ag^+/Ag}$ (= + 0.80 V) > $E^0_{H_2O/H_2}$ (= − 0.83 V), $Ag^+(aq)$ ions get reduced to Ag(s) more easily than $H_2O(l)$ gets reduced to $H_2(g)$. Thus on cathode Ag metal is obtained.

$$Ag^+(aq) + e^- \longrightarrow \boxed{Ag(s)},\ E^0_{red} = E^0_{Ag^+/Ag} = 0.80\ V$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq),\ E^0_{red} = E^0_{H_2O/H_2} = -0.83\ V$$

Since the oxidation of $NO_3^-(aq)$ ions is not possible, $H_2O(l)$ gets oxidised to $O_2(g)$ on anode. Thus on anode $O_2(g)$ is produced.

$$2H_2O(l) \longrightarrow \boxed{O_2(g)} + 2H^+(aq) + 2e^-$$

Above discussion shows that the products obtained by the electrolysis of aqueous solution of $AgNO_3$ with inert electrodes are Ag metal on cathode and $O_2(g)$ on anode.

8. Electrolysis of aqueous solution of $AgNO_3$ with Ag electrodes (active electrodes).

Aqueous solution of $AgNO_3$ undergoes dissociation and gives $Ag^+(aq)$ and $NO_3^-(aq)$ ions. These ions move towards their respective electrodes.

$$AgNO_3(aq) \rightleftharpoons Ag^+(aq) + NO_3^-(aq)$$

Probable reduction reactions on cathode. $Ag^+(qq)$ and $H_2O(l)$ both undergo reduction on cathode

$$Ag^+(aq) + e^- \longrightarrow \boxed{Ag(s)},\ E^0_{Ag^+/Ag} = +0.80\ V$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq),\ E^0_{H_2O/H_2} = -0.83\ V,$$

Now since $E^0_{Ag^+/Ag}\ (= 0.80\ V) > E^0_{H_2O/H_2}\ (= -0.83\ V)$, the reduction of $Ag^+(aq)$ ions to $Ag(s)$ takes place more easily than that of $H_2O(l)$ to $H_2(g)$. Thus in the electrolysis of aqueous solution of $AgNO_3$ Ag metal is deposited on cathode.

Probable oxidation reactions on anode. $NO_3^-(aq)$ ions do not undergo oxidation. $H_2O(l)$ and $Ag(s)$ (from anode) both undergo oxidation and give $O_2(g)$ and $Ag^+(aq)$ respectively.

$$H_2O(l) \longrightarrow O_2(g) + 2H^+(aq) + 2e^-,\ E^0_{ox} = E^0_{H_2O/O_2} = -1.23\ V$$

$$Ag(s)\ (\text{from anode}) \longrightarrow Ag^+(aq) + e^-,\ E^0_{ox} = E^0_{Ag/Ag^+} = -0.80\ V$$

Now since $E^0_{Ag/Ag^+}\ (= -0.80\ V) > E^0_{H_2O/O_2}\ (= -1.23\ V)$, silver from anode is more easily oxidised to $Ag^+(aq)$ ions. Thus the actual oxidation reaction taking place on anode is:

$$Ag(s)\ (\text{from anode}) \longrightarrow Ag^+(aq) + e^- \quad ...(i)$$

$Ag^+(aq)$ ions formed as above combine with available $NO_3^-(aq)$ ions and form $AgNO_3(s)$ around anode.

$$Ag^+(aq) + NO_3^-(aq) \longrightarrow AgNO_3(s)\ (\text{around the anode}) \quad ...(ii)$$

On adding equations (*i*) and (*ii*) we get

$$Ag(s)\ (\text{from anode}) + NO_3^-(aq) \longrightarrow \boxed{AgNO_3(s)\ (\text{around anode}) + e^-}$$

Above equation shows that it is $AgNO_3$ which is formed on anode. This $AgNO_3$ gets dispersed in solution.

Above discussion shows that the electrolysis of aqueous solution of $AgNO_3$ with Ag electrodes produces Ag metal on cathode and $AgNO_3$ around the anode.

Summary

The electrolysis of the electrolytes has been summarised in Table 22.3.

Table 22.3.

Electrolytes	*Products obtained on cathode*	*Products obtained on anode*
1. NaCl(molten)	Na(l)	$Cl_2(g)$
2. NaCl(aq) (Pt-electrodes)	$H_2(g)$	$Cl_2(g)$
3. $CuCl_2(aq)$, $CuBr_2(aq)$ (Pt-electrodes)	Cu(s)	$Cl_2(g)$, $Br_2(g)$
4. $H_2SO_4(aq)$	$H_2(g)$	$O_2(g)$
5. $CuSO_4(aq)$ (Pt-electrodes)	Cu(s)	$O_2(g)$
6. $CuSO_4(aq)$ (Cu-electrodes)	Cu(s)	$CuSO_4$ (around anode)
7. $AgNO_3(aq)$ (Inert electrodes)	Ag(s)	$O_2(g)$
8. $AgNO_3(aq)$ (Ag-electrodes)	Ag(s)	$AgNO_3$ (around anode)

Some Commercial Cells/Batteries

A battery is an arrangement consisting of two or more galvanic cells connected with one another in series. The battery is used as a source of direct electric current at a constant voltage.

Characteristics of a battery.

(*i*) It should be light in weight and compact in size.

(*ii*) The voltage of the battery should not change much during its use.

(*iii*) It should provide power for a longer period.

(*iv*) It should be rechargeable.

Types of batteries.

Batteries/cells may be classified into three categories: (*A*) Primary cells (*B*) Secondary cells (*C*) Fuel cells.

Primary Cells

These are the cells in which the redox reaction is not reversible, *i.e.* redox reaction takes place only in one direction and hence cannot be reversed. As a result, after some time the cell reaction stops and the cell becomes dead. For this reason, primary cells cannot be recharged or reused. Some common examples of primary cells are *Daniell cell, dry cell* and *mercury cell*.

1. Daniell cell.

This cell consists of a Cu-vessel containing a concentrated solution of $CuSO_4$. A porous pot containing dil. H_2SO_4 is placed in the Cu-vessel which contains $CuSO_4$ solution. A Zn-rod is dipped into dil. H_2SO_4. Zn-rod acts as anode and Cu-vessel acts as cathode. Electrode reactions and cell reactions are:

Oxidation at anode: $Zn(s) \xrightarrow{\text{Oxidation}} Zn^{2+}(aq) + 2e^-,\ E^0_{Zn/Zn^{2+}} = +0.77\text{ V}$

Reduction on cathode: $Cu^{2+}(aq) + 2e^- \xrightarrow{\text{Reduction}} Cu(s),\ E^0_{Cu^{2+}/Cu} = +0.34\text{ V}$

Cell reaction : $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$

Daniell cell can be represented as:

$$\underset{\text{Anode}}{Zn(s) \mid Zn^{2+}(aq)} \parallel \underset{\text{Cathode}}{Cu^{2+}(aq) \mid Cu(s)}$$

e.m.f. of this cell = $E^0_{Zn/Zn^{2+}} + E^0_{Cu^{2+}/Cu} = 0.77\text{ V} + 0.34\text{ V} = \mathbf{1.11\ V}$

2. Dry cell.

Dry cell is a compact form of Leclanche cell which consists of a cylindrical Zn-container. This container acts as anode. A graphite rod is placed in the centre but does not touch the base. This graphite rod acts as cathode. The space between the anode and cathode is so packed that Zn-container is filled with the paste of NH_4Cl and $ZnCl_2$ and graphite rod is surrounded by MnO_2 powder and carbon. The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with pitch. Zn container is covered with cardboard so that the container may be protected from the atmosphere. Reactions taking placed in the cell are:

Oxidation of Zn(s) to $Zn^{2+}(aq)$ ions on anode.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad ...(i)$$

Reduction of $MnO_2(s)$ to $Mn_2O_3(s)$ on cathode. $MnO_2(s)$ (Mn = +4) is reduced to $Mn_2O_3(s)$ (Mn = +3)

$$\underset{(Mn = +4)}{2MnO_2(s)} + H_2O(l) + 2e^- \longrightarrow \underset{(Mn = +3)}{Mn_2O_3(s)} + 2OH^-(aq) \qquad ..(a)$$

$OH^-(aq)$ ions formed in reaction (*a*) combine with $NH_4^+(aq)$ ions derived from NH_4Cl to give $NH_3(g)$

$$2 \times [OH^-(aq) + NH_4^+(aq) \longrightarrow NH_3(g) + H_2O(l)] \qquad ...(b)$$

$NH_3(g)$ formed as above combines with $ZnCl_2(s)$ to form the complex salt, $[Zn(NH_3)_2Cl_2]$.

$$2NH_3(g) + ZnCl_2(s) \longrightarrow [Zn(NH_3)_2Cl_2] \qquad ...(c)$$

If $NH_3(g)$ is not consumed by forming $[Zn(NH_3)_2Cl_2]$, it will develop pressure which cracks the seal of the cell. Net reduction reaction occuring on cathode is obtained by adding reactions (*a*), (*b*) and (*c*). Thus net reduction reaction is:

$$\underset{(Mn = +4)}{2MnO_2} + 2NH_4^+(aq) + ZnCl_2(s) + 2e^- \longrightarrow \underset{(Mn = +3)}{Mn_2O_3(s)} + H_2O(l) + [Zn(NH_3)_2Cl_2] \qquad ...(ii)$$

The formation of $[Zn(NH_3)_2Cl_2]$ lowers the concentration of free $Zn^{2+}(aq)$ ions and hence the voltage of the cell is increased. A dry cell has a voltage of about 1.5 V.

Cell reaction is obtained by adding half-reaction (*i*) (oxidation half-reaction) and half-reacton (*ii*) (reduction half-reaction). Thus cell reaction is:

$$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) + ZnCl_2(s) \longrightarrow Mn_2O_3(s) + H_2O(l) + Zn^{2+}(aq) + [Zn(NH_3)Cl_2]$$

Dry cells are not really dry, since these contain wet paste of NH_4Cl and $ZnCl_2$. In fact, a dry cell works as long as the paste in it is moist. Dry cells cannot be recharged. These cells donot have an indefinite life, since NH_4Cl paste is acidic in nature and hence Zn-container dissolves in it slowly even when the cell is not being used.

3. Mercury cell.

It is a tiny cell. It is encased in a stainless steel case with amalgamated Zn (a solution of Zn in liq. NH_3) which acts as anode and a paste containing Hg and HgO which acts as cathode. A paste of KOH saturated with $Zn(OH)_2$ acts as electrolyte.

The reactions taking place on the two electrodes during discharge of the cell are:

$$\textit{At anode}: \underset{\text{(Amalgamated)}}{Zn(s)} + 2OH^-(aq) \xrightarrow{\text{Oxidation}} ZnO(s) + H_2O(l) + 2e^-$$

$$\textit{At cathode}: HgO(s) + H_2O(l) + 2e^- \xrightarrow{\text{Reduction}} Hg(l) + 2OH^-(aq)$$

$$\textit{Cell reaction}: \underset{\text{(Amalgamated)}}{Zn(s)} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The cell reaction shows that since there is no change in the concentration of the electrolyte *viz.* KOH and the substances involved in the cell reaction are solids, the voltage of mercury cell remains constant equal to 1.34 V for 95% of its life time. This cell gives excellent performance in heart pacemakers, hearning aids, light meters, digital watches etc.

Secondary Cells

These are the cells which can be recharged by passing electric current through them after every use. As a result, secondary cells can be used again and again for longer periods. In these cells, electrical energy is stored in the form of chemical energy. For this reason these cells are also called **storage cells** or **accumulators.** *Lead-acid storage battery* and *nickel-cadmium cell* are the examples of such cells.

1. Lead-acid storage battery.

This battery is frequently used in automobiles like cars, buses, trucks etc. A commercial form of a lead-acid storage battery consists of six or twelve lead-acid voltaic cells. Each cell gives an e.m.f. of 2 volts. Thus a lead-acid storage battery containing six cells will produce 2 × 6 = 12 V and having 12 cells will produce 2 × 12 = 24 V.

In each voltaic cell, a grid (plate) of lead coated with finely-divided spongy lead acts as anode (negative electrode) and a grid coated with red-brown PbO_2 acts as cathode (positive electrode). These electrodes are kept in alternate positions and are separated from each other by insulating material like thin wooden or fibre glass sheets. These are suspended in dil. H_2SO_4 which is 38% by mass or has density of 1.30 g. cm^{-3}. H_2SO_4 acts as electrolyte. The cell is represented as:

$$\underset{\substack{\text{Anode}\\\text{(Negative electrode)}}}{Pb(s), PbSO_4(s)} \mid H_2SO_4(38\%) \mid \underset{\substack{\text{Cathode}\\\text{(Positive electrode)}}}{PbO_2(s), Pb}$$

Lead shown at cathode is not involved in cell reaction but only serves the purpose of an electrical contact.

Reactions taking place on the two electrodes during discharge of the battery (*i.e.* when current is drawn from the battery) are:

Oxidation on Pb anode: Pb(s) (Pb = 0) is oxidised to $PbSO_4(s)$ (Pb = +2)

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

$$\underset{(Pb\,=\,0)}{Pb(s)} + SO_4^{2-}(aq) \xrightarrow{\text{Oxidation}} \underset{(Pb\,=\,+2)}{PbSO_4(s)} + 2e^-$$

Reduction on PbO_2 cathode: $PbO_2(s)$ (Pb = +4) is reduced to $PbSO_4(s)$ (Pb = +2)

$$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

$$\underset{(Pb\,=\,+4)}{PbO_2(s)} + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \xrightarrow{\text{Reduction}} \underset{(Pb\,=\,+2)}{PbSO_4(s)} + 2H_2O$$

Cell reaction is obtained by adding oxidation and reduction reactions (given above) taking place on anode and cathode respectively. Thus:

Cell reaction: $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$

or $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \xrightarrow[\text{of the battery}]{\text{During discharge}} 2PbSO_4(s) + 2H_2O$

Cell reaction shows that when lead storage battery is discharged, H_2SO_4 is consumed.

Recharging of the discharged battery/cell. Oxidation and reduction reactions taking place on anode and cathode respectively show that:

(*i*) Solid $PbSO_4$ (white) is formed on both the electrodes. This solid $PbSO_4$ gets deposited on both the electrodes.

(*ii*) Due to the formation of H_2O on cathode, the concentration of H_2SO_4 decreases and hence the acid becomes dilute. As a result, the density of the acid decreases to about 1.1 g.cm^{-3}.

When both the above things happen, the battery cannot produce electricity, *i.e.* the cell ceases to work. Under these conditions we say that the cell is dead or has discharged. Thus the cell needs recharging. In order to recharge the discharged storage cell, direct current (*dc*) is passed through the discharged storage cell by connecting it with a *dc* source. The positive electrode (*i.e.* anode) of the storage cell is connected with the positive terminal of *dc* source and negative electrode (*i.e.* cathode) of the storage cell is connected with the negative terminal of *dc* source. On passing the direct current through the discharged storage cell the following reactions take place on the two electrodes.

Oxidation on positive electrode (anode). $PbSO_4(s)$ (Pb = +2) is oxidised to $PbO_2(s)$ (Pb = +4).

$$\underset{(Pb\,=\,+2)}{PbSO_4(s)} + 2H_2O \xrightarrow{\text{Oxidation}} \underset{(Pb\,=\,+4)}{PbO_2(s)} + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$

Reduction on negative electrode (cathode). $PbSO_4(s)$ (Pb = +2) is reduced to Pb(s) (Pb = 0)

$$\underset{(Pb\,=\,+2)}{PbSO_4(s)} + 2e^- \xrightarrow{\text{Reduction}} \underset{(Pb\,=\,0)}{Pb(s)} + SO_4^{2-}(aq)$$

Cell reaction is obtained by adding the above two half-reactions. Thus:

Cell reaction: $2PbSO_4(s) + 2H_2O + \text{Energy} \xrightarrow[\text{of the acid discharged storage battery}]{\text{During recharging}} Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}$

or $2PbSO_4(s) + 2H_2O + \text{Energy} \xrightarrow[\text{of the discharged storage battery}]{\text{During recharging}} Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

Cell reaction shows that $PbSO_4(s)$ is converted back into $Pb(s)$ and $PbO_2(s)$. These materials again act as anode and cathode respectively.

It may be noted that during discharging process the concentration of H_2SO_4 decreases while in charging process the concentration of H_2SO_4 increases. It may also be noted that when the storage battery is used to start the engine of automobiles (*i.e.* when the battery is being discharged), it acts as a voltaic cell and hence produces electric energy. On the other hand when the discharged battery is recharged, the battery acts as an electrolytic cell. Thus this cell has the ability to work both ways, to receive electrical energy and also to supply it.

2. Nickel-cadmium (Nicad) cell.

This cell is also called nickel-cadmium accumulator. This cell is also rechargeable. It consists of Cd anode and metal grid containing NiO_2 as cathode. These electrodes are immersed in KOH solution which act as electrolyte. Reactions taking place on the electrodes are:

At anode: $Cd(s) + 2OH^-(aq) \xrightarrow{\text{Oxidation}} Cd(OH)_2(s) + 2e^-$

At cathode: $NiO_2(s) + 2H_2O(l) + 2e^- \xrightarrow{\text{Reduction}} Ni(OH)_2(s) + 2OH^-(aq)$

Cell reaction: $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

Since no gaseous products are formed during discharging and recharging, this cell can be sealed. This cell has vötage equal to 1.4 V. It has longer life than lead storage cell. The cell is expensive and hence is used in high cost equipments. The cell is becoming more and more popular these days and is being used in electronic watches and calculators.

Fuel Cells

The combustion of fuels like H_2, CO, CH_4 etc. is also a redox reaction. When this redox reaction (*i.e.* combustion of fuels) takes place, chemical energy is produced. The chemical energy produced in this manner can directly be converted into electrical energy in fuel cells. Thus fuel cells are the cells in which chemical energy produced by the combustion of fuels like H_2, CO, CH_4, C_3H_8 (propane), CH_3OH etc. is directly converted into electrical energy.

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Oxidation products} + \text{Electrical energy}$$

Characteristics (or advantages) of fuel cells.

(*i*) **Fuel cells donot cause pollution.** The reactions taking place in fuel cells donot produce harmful or objectionable products. Hence these cells donot cause pollution.

(*ii*) **Fuel cells have high efficiency.** The efficiency of fuel cells is approximately 70-75% which is much higher than that of conventional methods of converting chemical energy of a fuel into electrical energy. Conventional methods have efficiency approximately equal to 40%.

Thermodynamic efficiency (η) of H_2/O_2 cell is given by:

$$\eta = \frac{\text{Electrical free energy produced } (\Delta G)}{\text{Heat of combustion } (\Delta H)} = \frac{\Delta G}{\Delta H}$$

$$= \frac{-nFE}{\Delta H} = \frac{-229 \text{ kJ}}{-242 \text{ kJ}} = 0.95 = 95\%.$$

(*iii*) **Fuel cells are continuous source of energy.** Unlike conventional cells, energy can be obtained from the fuel cell continuously so long as the supply of fuel is maintained.

Examples of fuel cells:

These are given given below:

1. Hydrogen-oxygen (H_2/O_2) fuel cell. This cell consists of porous carbon electrodes which contain suitable catalysts (*e.g.* Pt, Pd etc.) incorported in them. Concentrated NaOH or KOH solution is placed between the electrodes. This solution acts as electrolyte. H_2 and O_2 gases are bubbled in KOH/NaOH solution through the porous carbon electrodes.

Electrode reactions are:

Oxidation of $H_2(g)$ to $H_2O(l)$ on anode:

$$\underset{(\text{H}=0)}{2H_2O(g)} + 4OH^-(aq) \xrightarrow{\text{Oxidation}} \underset{(\text{H}=+1)}{4H_2O(l)} + 4e^-, \ E^0_{\text{ox}} = 0.83 \text{ V}$$

Reduction of $O_2(g)$ to $OH^-(aq)$ on cathode:

$$\underset{(\text{O}=0)}{O_2(g)} + 2H_2O(l) + 4e^- \xrightarrow{\text{Reduction}} \underset{(\text{O}=-2)}{4OH^-(aq)}, \ E^0_{\text{red}} = 0.40 \text{ V}$$

Cell reaction: $\underset{(\text{H}=0)}{2H_2(g)} + \underset{(\text{O}=0)}{O_2(g)} \longrightarrow \underset{(\text{H}=+1,\, \text{O}=-2)}{2H_2O(l)},$

e.m.f. or $E^0_{\text{cell}} = 0.83 \text{ V} + 0.40 \text{ V} = 1.23 \text{ V}$

Although theoretical value of E^0_{cell} is equal to 1.23 V, the actual value is 0.8 to 1.0 V. The only product that is obtained in this cell is water. Usually a large number of hydrogen-oxygen fuel cells are connected together in series to make a battery which is called **fuel cell battery** or simply **fuel battery**.

Applications of (H_2/O_2) fuel cell: H_2/O_2 cell is used as auxiliary energy source in space vehicles (*e.g.* Apollo space craft), submarines or other military vehicles. The weight of fuel battery sufficient for 15 days in space is approximately 250 kg. This may be compared to several tones that have been required for an engine generator set. The product of combustion *viz.* H_2O was used for drinking by astronauts.

2. Propane-oxygen (C_3H_8/O_2) fuel cell: Half-reactions and cell reaction are:

Oxidation on anode: $C_3H_8(g) + 6H_2O(l) \longrightarrow 3CO_2(g) + 20H^+ + 20e^-$

Reduction on cathode: $5O_2(g) + 20H^+(aq) + 20e^- \longrightarrow 10H_2O(l)$

Cell reaction: $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

3. **Methyl alcohol-oxygen (CH_3OH/O_2) fuel cell:** Half-reactions and cell reaction are:

Oxidation on anode: $CH_3OH(l) + H_2O(l) \longrightarrow CO_2(g) + 6H^+(aq) + 6e^-$

Reduction on cathode: $\frac{3}{2}O_2(g) + 6H^+(aq) + 6e^- \longrightarrow 3H_2O(l)$

Cell reaction: $CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Important Questions

Question 1. *What is the role of $ZnCl_2$ in a dry cell?*

Answer. On cathode of the dry cell, $NH_3(g)$ is produced by the action of $OH^-(aq)$ ions on $NH_4^+(aq)$ ions.

$$OH^-(aq) + NH_4^+(aq) \longrightarrow NH_3(g) + H_2O(l)$$

$NH_3(g)$ produced in the above reaction combines with $ZnCl_2(s)$ to form $[Zn(NH_3)_2Cl_2]$.

$$NH_3(g) + ZnCl_2(s) \longrightarrow [Zn(NH_3)_2Cl_2]$$

If $NH_3(g)$ is not consumed by forming $[Zn(NH_3)_2Cl_2]$, this gas produces pressure which cracks the seal of the dry cell.

Question 2. *Which type of cells are rechargeable?*

Answer. Those cells are rechargeable in which the product formed during discharge (*i.e.* when the cell is being used) get deposited on the electrodes. When electrical energy is supplied to the cell, the deposited materials get decomposed to give the original substances.

Question 3. *What is the electrolyte used in dry cell?*

Answer. Electrolyte used in a dry cell is a paste containign NH_4Cl, $ZnCl_2$, MnO_2 and carbon.

Question 4. *What is the reason that a lead storage battery can be recharged?*

Answer. During discharging operation of the lead storage battery, $PbSO_4(s)$ is deposited on both the electrodes. Now when direct electric current is passed through the discharged battery, the electrode reactions are reversed and hence the deposited $PbSO_4(s)$ on both the electrodes is converted into $Pb(s)$ and $PbO_2(s)$.

Question 5. *Why a dry cell becomes dead after a long time even if it has not been used?*

Answer. A dry cell becomes dead, even if it has not been used. This is because of the fact that NH_4Cl paste is acidic in nature and hence Zn-container dissolves in it slowly and slowly.

Question 6. *Why a mercury cell gives a constant voltage throughout its life?*

Answer. Since the overall redox reaction taking place in the mercury cell does not involve any ion whose concentration may change, this cell gives a constant value of its voltage throughout its life time.

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