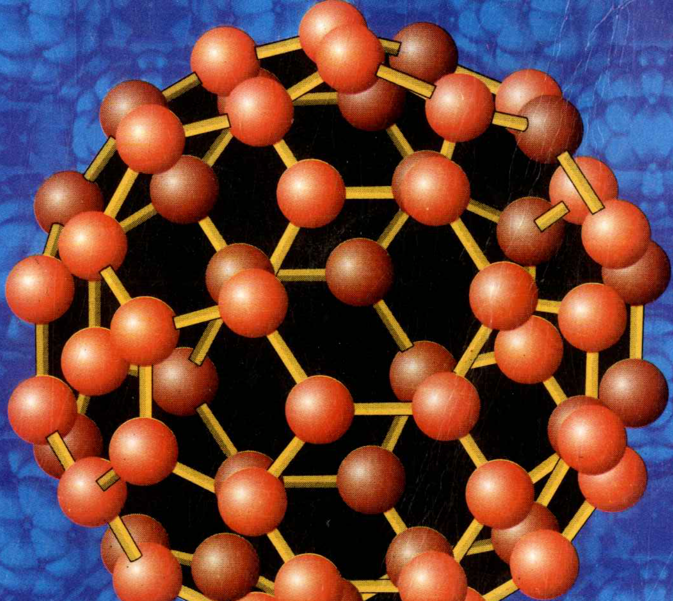
Revised & Enlarged Edition

Text Book of
INORGANIC CHEMISTRY

For B.Sc. Students



Muhammad Zafar Iqbal

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OF
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By

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Revised and Enlarged Edition

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Preface

This textbook is written in accordance with the new syllabus prescribed for B.Sc. Students of the Universities of Pakistan. In presenting this book, care has been taken to fill a gap that often develops in teaching the students of chemistry in colleges. The objective of this book is to provide maximum information in a systematic manner regarding the elementary principles of atomic and molecular structures, which are useful in describing, interpreting and correlating the structure, reactivity and energetics of chemical systems. These structural principles are supported by extensive applications and examples.

Various topics have been discussed with due consideration to the limitations set by the syllabi and courses of reading for undergraduates. However, certain topics get confused if they are not discussed at length. Thus efforts have been made to discuss such topics in detail e.g., theories of chemical bonding, acids and bases, shapes of molecules, etc. Care has been taken to deal with these topics to such an extent that further reading does not remain a necessity. Some additional topics have been discussed in this edition e.g., Modern Materials, Silicones, Silicon for Solar Energy, Fullerenes, Analytical Techniques, Solvent Extraction, Chromatography, Spectroscopy etc.

In the beginning of this book the general principles of chemistry and physical aspects of Inorganic Chemistry have been discussed. The chemistry of both non-transition and transition elements is discussed subsequently along with some industrial topics in the syllabus. The reaction chemistry is described in elaborated, extended and strengthened form by using recent interpretations wherever required. The structural aspects that determine the state of a substance are fully explored. The figures, tables, examples and graphs have been given liberally in order to clarify various points. The references have not been provided due largely to the fact that students taking a course on the level for which this book is intended have not much inclination to such references and often have limited access to adequate library facilities. The chapters on Periodic Table, Periodicity of Properties, Acids and Bases, Nuclear Chemistry as well as Chemical Industries have been revised keeping in view the recent developments in Chemistry. Objective type and short questions have liberally been added at the end of each chapter.

It is hoped that factual errors are not present in the book. The author will appreciate having errors, if any, called to his attention and would welcome all types of suggestions for improvement of this text. Thanks are due to Dr. Hafiz Muhammad Farooq, Dr. Amjad Nasim, Dr. Farhana Mazhar & Dr. Nargis Naz for useful suggestions and to all those who helped in proof reading during the printing of this book.

Lahore

June, 2005

AUTHOR

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1

CLASSIFICATION OF ELEMENTS

One of the important scientific activities is the search for an organised way of presenting the facts. If a large number of observations can be categorised according to some common features, it becomes easier to describe them. As more and more of chemical elements were discovered, need was felt to systematise them.

Muslim scientists were the first to categorise the then known elements and compounds. One of the first attempts to arrange elements and compounds on the basis of their origin was made by Al-Razi. In 1789, Lavoisier also arranged elements into four groups. The first type included gases such as oxygen and nitrogen. The second type contained elements such as sulphur and phosphorus which form acidic oxides. The third type included metals such as copper, zinc, tin, lead, etc. The fourth type contained simple earthy salt-forming substances such as oxides of calcium, barium, magnesium and silicon.

DOBEREINER'S TRIADS:

The German chemist Johann Dobereiner in 1829 made a serious attempt to classify elements. He observed that some groups of three elements (triads) showed similar physical and chemical properties *i.e.*, chlorine, bromine and iodine. The properties and atomic weights of these elements were found to be such that the middle element had average of the properties and atomic weights of the other two. Thus the average of the atomic weights of chlorine (35.45) and iodine (126.9) is 80.75 a.m.u., which is close to the atomic weight of bromine, 79.9 a.m.u. The elements of a triad also have similar chemical properties. The acids of halogens, HCl, HBr and HI are all compounds of similar nature. A list of Dobereiner's triads is given in Table 1.1.

Dobereiner's concept of triads in spite of its limitations has provided the background to seek further information for the classification of elements.

TABLE 1.1
Dobereiner's Triads

Element	Atomic weight	Average Atomic weight	Density (g/ml)	M.P. (°C)
Lithium Sodium Potassium	7.0 23.0 39.0	23.0	0.53 0.57 0.86	180.5 97.9 63.7
Chlorine Bromine Iodine	35.45 79.90 126.90	80.75	1.6 3.1 4.9	– 101.0 – 7.0 113.5
Sulphur Selenium Tellurium	32.10 79.00 127.60	79.6	2.1 4.8 6.2	95.5 217.0 452.0
Calcium Strontium Barium	40.10 87.60 137.30	88.3	1.6 2.6 3.5	845.0 770.0 725.0

SPIRAL ARRANGEMENT:

Elements were arranged subsequently in order of their relative atomic masses in a spiral around a cylinder divided into vertical strips. Elements with similar physical and chemical properties fall on the same vertical (Figure 1.1).

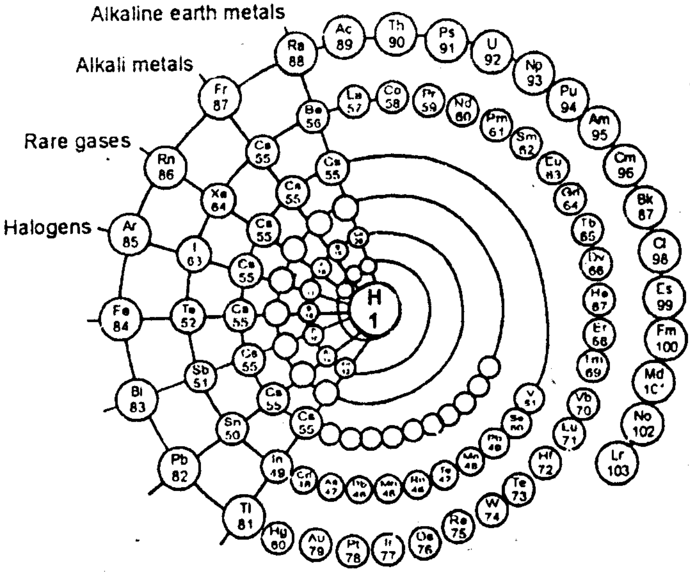


Fig. 1.1. A spiral arrangement of the Periodic Table.

NEWLAND'S OCTAVES:

In 1866, an English chemist John Newland examined the then known elements and arranged them in the increasing order of their atomic weights. He observed that chemically similar elements reoccur at regular intervals and the properties of elements are repeated after every eighth element. Newland noted that similarity of periodic reoccurrence of the properties of elements resembles the musical octaves and postulated the law of octaves (Table 1.2).

"Chemically similar elements reoccur in octaves when arranged in order of increasing atomic weights."

There were valid objections to the Newland's arrangements of elements in octaves. Several elements were arranged out of place. For example, iron could not be with oxygen and sulphur due to its quite different physical and chemical properties. In spite of objections and drawbacks of Newland's arrangement of elements in octaves, more extensive ordering of elements was visualized.

TABLE 1.2

Newland's Arrangement of Elements in Octaves

H^{1}	Li^{7}	Be^{9}	B^{11}	C^{12}	N^{13}	O^{16}
F^{19}	Na^{23}	Mg^{24}	Al^{27}	Si^{28}	P^{31}	S^{32}
Cl^{35}	K^{39}	Ca^{40}	Ti^{48}	Cr^{52}	Mn^{55}	Fe^{56}

MEYER'S ATOMIC VOLUME CURVE:

In 1870, Lothar Meyer produced a table showing periodic arrangement of the elements by plotting the atomic volume (relative atomic mass density) of elements against their relative atomic masses (Figure 1.2).

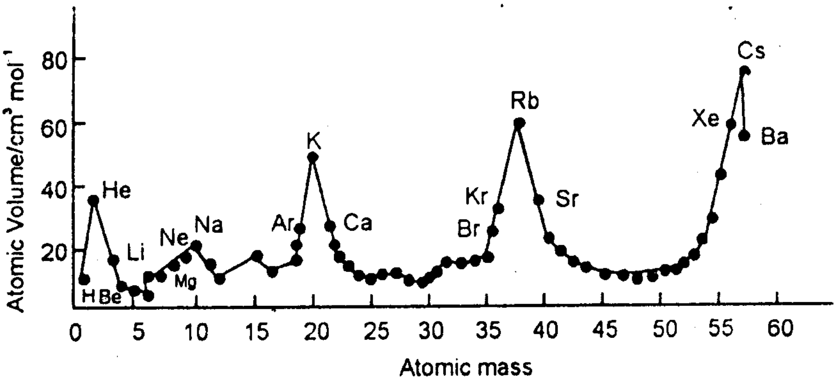


Fig. 1.2. Variation of atomic volume with atomic mass.

MENDELEEV'S PERIODIC TABLE:

About the same time that Meyer (1871) produced his arrangement based on his atomic volume curve, the Russian chemist Dmitri Mendeleev produced a form of the Periodic Table (Table 1.3) by arranging atomic weights of elements in increasing order from which the modern Periodic Table has been developed. Mendeleev arranged the elements into horizontal rows called periods and eight columns called groups. The elements in the same group were found to possess similar properties and formed similar compounds.

TABLE 1.3

Mendeleev's early periodic table, published in 1872. Note the gaps left for missing elements with atomic masses 44, 68, 72 and 100 and the other gaps for elements with unpredicted masses.

Periods	Gruppe I — R^2O	Gruppe II — RO	Gruppe III — R^2O^3	Gruppe IV RH^4 RO^2	Gruppe V RH^3 R^2O^5	Gruppe VI RH^2 RO^3	Gruppe VII RH R^2O^7	Gruppe VIII — RO^4
1.	H = R							
2	Li = 7	Be = 9, 4	B = 11	C = 12	N = 14	O = 16	F = 19	
3.	NO = 33	Mg = 24	Al = 27,3	SI = 28	P = 31	S = 32	Cl = 35, 5	
4.	K = 39	Ca = 40	– = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Ce = 59,
5	(Cu = 63)	Zn = 65	– = 68	– = 72	As = 75	Se = 78	Br = 80	Ni = 59, Cu = 63,
6	Rb = 85	Sr = 87	?Vt = 88	Zr = 90	Nb = 94	Mo = 98	– = 100	
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	Ru = 104, Rh = 104,
8	Cs = 133	Sa = 137	?Di = 138	?Ce = 140	–	–	–	Pd = 106, Ag = 108
9	(–)	–	–	–	–	–	–	
10	–	–	?E = 176	?Lo = 180	To = 182	W = 184	–	Os = 195, Tr = 197,
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	–	–	Pt = 195, Au = 199
12	–	–	–	Th = 231	–	U = 240	–	

As is obvious from the table, Mendeleev placed some elements in a separate group that did not fit into the arrangement. He also left gaps if none of the known elements could fit in. However, he predicted properties of unknown elements which fitted remarkably well to those predicted. For example, he noted that elements of Group III form halides and oxides of the type, MCl_3 ($AlCl_3$) and M_2O_3 (Al_2O_3), but titanium forms compounds such as $TiCl_4$ and TiO_2, similar to those of Group IV elements. Accordingly Mendeleev placed titanium in Group IV and a space was left for the undiscovered element, which was later found to be scandium, Sc.

PERIODIC LAW:

Mendeleev interpreted this relation between elements on the basis of Periodic Law which he stated as:

"The properties of elements are periodic functions of their atomic weights."

However, certain discrepancies were noted while arranging the elements on the basis of atomic weights. For example, beryllium was out of place in the table as its atomic mass was 13.5 which should fit in between carbon and nitrogen. Similarly, inert gases had no proper place in the Periodic Table.

These problems were not fully resolved until 1914 when Moseley showed that elements could be arranged in a periodic pattern on the basis of their atomic numbers. The Periodic Law now states as:

"The properties of elements are periodic functions of their atomic numbers."

By taking atomic numbers as the basis of the periodic classification of elements, various anomalies and misfits have been removed. For example, proper positions to cobalt and nickel, potassium and argon, etc., have been given.

The classification of elements was an interesting arrangement and attracted considerable attention. Several gaps in the table suggested discovery of new elements. Chemical and physical properties of unknown elements could be predicted which helped in the search of new elements. Mendeleev suggested that elements similar to aluminium and silicon should exist. Gallium, Ga (similar to aluminium) was discovered in 1875 and Germanium, Ge in 1886. Mendeleev solved the problem of odd elements (which could not be adjusted properly in a group) by dividing groups into subgroups 'A' and 'B'. For example, among metals of the first group, sodium and potassium were placed in Group IA and copper and silver in Group IB because of the difference in properties. Noble gases were discovered in the last decade of the nineteenth century and were placed in zero group because of their inertness.

The main features of Mendeleev's Periodic Table were the arrangement of elements in vertical columns or groups and the horizontal rows or periods. He left spaces for the unknown elements and predicted properties of the Germanium which was not discovered until 1886. He called it eka-Silicon as it fell below Silicon.

LIMITATIONS OF MENDELEEV'S PERIODIC TABLE:

Mendeleev's Periodic Table in spite of its advantages suffers from the following drawbacks and has thus limitations in its application.

(1) Position of hydrogen is not clear because it resembles with both alkali metals and halogens. It gives the positive H^+ ions like alkali metals and gives the hydride ions like halides.

(2) Certain chemically similar elements, *e.g.*, copper, gold, platinum are placed in different groups while some dissimilar elements are grouped together.

(3) Certain elements of higher atomic weight precede others with lower atomic weight

Argon (At. Wt. = 40) Precedes Potassium (At. Wt. = 39)
Cobalt (At. Wt. = 59) Precedes Nickel (At. Wt. = 58.6)

(4) No position is assigned to isotopes in different groups.

(5) Maximum valence state is depicted by an element in a particular group. The elements of group VIII usually do not depict 8 maximum oxidation state except ruthenium and osmium.

(6) No explanation is available for the inert pair effect and stability of valence states differing by units of two.

(7) The anomalous behaviour of the first member of a group and for the diagonal relationship cannot be explained.

(8) The lanthanides or rare earths and actinides do not find any appropriate places in the Periodic Table.

PERIODIC TABLES:

The standard form of Periodic Table is shown in Table 1.4. This is not the only form of Periodic Table possible. Different types of Periodic Tables such as rectangular, triangular, circular and even three-dimensioned tables have been presented. Each table has its advantages and disadvantages. All tables depict interrelationship between the elements.

TABLE 1.4

Transition elements

	1 I-A	2 II-A	3 III-B	4 IV-B	5 V-B	6 VI-B	7 VII-B	8	9 VIII-B	10	11 I-B	12 II-B	13 III-A	14 IV-A	15 V-A	16 VI-A	17 VII-A	18 0 or VIIIA
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0063	8 O 15.9994	9 F 18.9981	10 Ne 20.180
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 [illegible] 30.[illegible]	16 S 32.066	17 Cl 35.4522	18 Ar 39.948
4	19 K 39.0938	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.59	3[illegible] A[illegible] 74.[illegible]6	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.80	53 I 126.905	54 Xe 131.29
6	55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.59	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.02	89 +Ac 227.02	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)									

* Lanthanide series	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
** Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (244)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

ATOMIC NUMBER AND THE MODERN PERIODIC LAW:

After arranging the elements in the Periodic Table, it was natural to give each element a number indicating only its position on the series based on increasing atomic weight. No real physical significance was associated with the concept of atomic number when it first came into use, but after Rutherford proposed the atomic model with a nucleus in the centre it was estimated that the charge on the nucleus was very close to one-half the atomic weight:

$$\text{Nuclear charge} \simeq Z = \frac{1}{2}\ \text{(atomic weight)} = \text{atomic number}$$

For many elements one-half of atomic weight is equal to atomic number *e.g.*, helium with an atomic weight of 4 is second in the table, carbon with an atomic weight of 12 is sixth in the table; oxygen, 16, is eighth, and sulphur, 32, is sixteenth. In the second and third periods this rule holds good

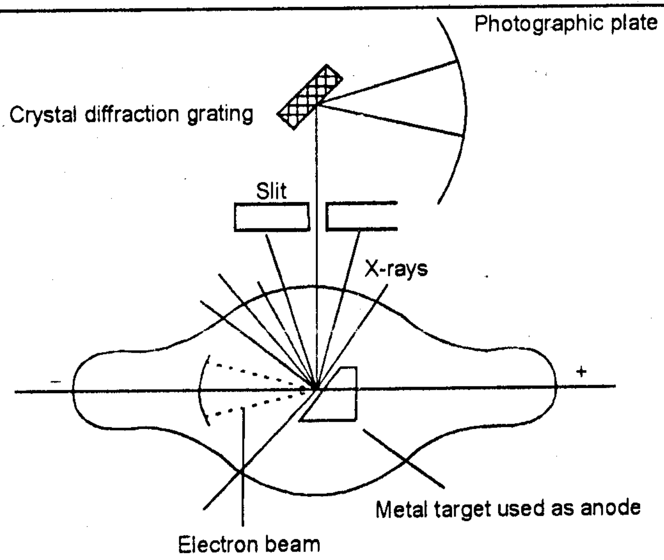
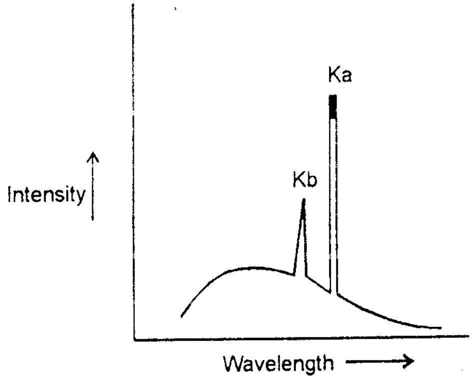


Fig. 1.3. Moseley's apparatus.

The verification of this hypothesis came from the work of Moseley. He analysed X-rays produced when cathode rays strike metal target. When metallic elements are used as targets for cathode rays (electron beams) they emit an X-ray spectrum. Figure 1.3 shows a diagram of the apparatus used by Moseley, and Fig. 1.4 shows a typical X-ray spectrum produced by a metal target.



A typical X-ray spectrum

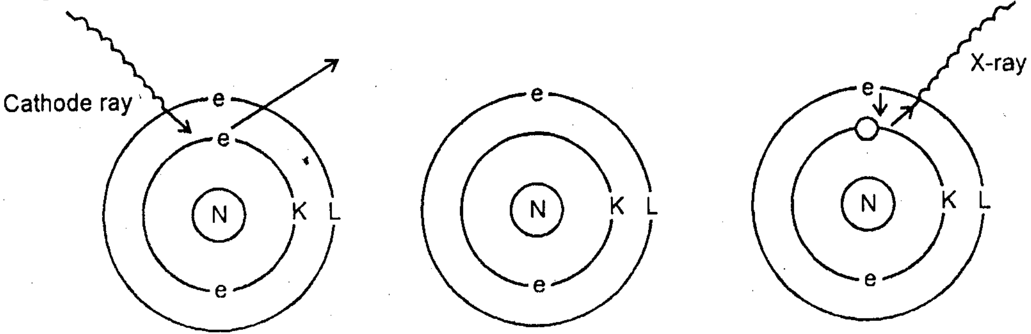
Fig. 1.4.

The X-rays are generated when the cathode ray collides with an electron in the K shell knocking the electron out of the atom. The vacancy in the K shell is filled when electrons in higher energy levels fall into the K shell. This causes the emission of X-radiation (Fig. 1.5).

$$\sqrt{\nu} \propto Z \qquad \sqrt{\nu} = a(Z-b)$$

a & b are constants ν = Frequency Z = atomic number

The energy of an electron in an atom depends on the nuclear charge Z (the atomic number). As the nuclear charge increases, the force holding the electron also increases. Hence, the energy and frequency of the X-rays emitted by metal targets must depend on the atomic number of the target element. Moseley found that the frequency and hence the energy at the bright lines of the X-ray spectrum increases in a regular way as the atomic number increases. A plot of the atomic numbers versus the square roots of the frequencies of either line is linear for 38 metallic elements investigated by Moseley. Following the publication of Moseley's work in 1913, it became obvious that ***the properties of the elements are periodic functions of their atomic numbers.***



(a) An electron in the K shell is ejected by a cathode ray

(b) Ejection leaves a vacancy in the K shell

(c) An X-ray is emitted when an electron from a higher orbit falls into the K shell

Fig. 1.5. Production of X-rays.

The order of the elements according to atomic number is almost identical with the order according to atomic weight but there are a few important differences. The atomic weight guide would put potassium before argon, nickel before cobalt, and iodine before tellurium.

K(39.10), Ar (39.95) ……… Ni (58.69), Co(58.93)

I(126.90), Te(127.60).

The atomic numbers for these elements are in the reverse order. Argon should appear in the Periodic Table as it does because atomic number of Ar is 18 and that of K, 19. Similarly, Co(27) is put before Ni(28) and Te(52) before I(53).

In order to have similar elements in the same group Mendeleev found it necessary to transpose certain pairs of elements arbitrarily in his Periodic Table based on atomic weights. When the elements are placed in order of atomic number, no transpositions are necessary. The modern Periodic Law states that ***the properties of the elements are periodic functions of their atomic numbers.***

THE QUANTUM MECHANICAL PICTURE OF ATOMS:

The Bohr theory describes the electron shell K, L, M and N. Close examination of atomic spectra indicates that they correspond to the quantized energy levels which may in fact split into finer lines. The electron shells are split further into sub-shells each with its own quantized energy level. These sub-shells have been labelled keeping in view the types of spectral lines in the atomic spectra to which they correspond *i.e.*, *s* for sharp, *p* for principal, *d* for diffused and *f* for fundamental. An *s* sub-shell consists of one *s* orbital, a *p* sub-shell consists of three *p* orbitals, a *d* sub-shell has five *d* orbitals and an *f* sub-shell has seven *f* orbitals.

The spectral lines correspond to transitions between the sub-shells. The sub-shells are further split when atoms of elements are subjected to a magnetic field. This is called the Zeeman effect. It has been shown that only *p*, *d* and *f* sub-shells can be split into further energy levels. A magnetic field has no effect on an *s* sub-shell because *s* orbitals are spherical.

The atomic spectra of elements can also be split due to the spin of an electron which may be either clockwise or anticlockwise.

The work of de Broglie, Davisson and Germer, and others, has indicated that electrons in atoms can be treated as waves although they are compact particles continuously travelling in orbits. Very small particles such as electrons, atoms and molecules do not obey the laws of classical Newtonian mechanics which are applicable to larger objects such as hockey ball. Quantum mechanics describes the behaviour of very small particles more precisely and is based on quantization of energy.

One of the underlying principles of quantum mechanics is that we cannot determine precisely the paths that electrons follow In 1927, Werner Heisenberg gave a theoretical statement that is consistent with experimental observations called Heisenberg uncertainty principle. It states that it is impossible to determine accurately both the momentum and the position of an electron simultaneously Since according to Heisenberg's uncertainty principle it is not possible to determine both the position and the velocity of an electron, we can talk in terms of probability of finding an electron within specified regions in space

According to one of the postulates of quantum mechanics the allowed energy states of atoms and molecules can be described by the sets of numbers called quantum numbers. In 1926, Erwin Schrödinger deduced an equation by imposing wavelength restrictions suggested by de Broglie's experiments. This equation allowed him to calculate the energy levels in hydrogen atom. The quantum mechanical treatment of atoms and molecules is highly mathematical. The solution of Schrödinger wave equation gives rise to the concept of quantum numbers which are in accord with the experimental observations. Solutions of Schrödinger equation also provide information about the shapes and orientations of the probability distribution of electrons. The atomic orbitals, deducted from Schrödinger equation are directly related to quantum numbers.

QUANTUM NUMBERS:

There are four quantum numbers which describe the electron in an atom. They are denoted by the letters n, l, m and s, called the ***principal quantum number, azimuthal quantum number, magnetic quantum number and spin quantum number***, respectively.

1. Principal Quantum Number (n):

This quantum number describes the motion of an electron in an orbit and stands for the number of shell or orbit. In other words, it is a rough measure of the size of the orbit. The larger the value of n, the greater is the volume of the bulk of the electronic density, n may have any integral value *i.e.*, 1, 2, 3, 4, 5, ······ It may take the values up to 7 corresponding roughly to seven horizontal rows of the Periodic Table. The value of n describes the binding force and distance between the nucleus and the orbit in which an electron moves. The lower value of n corresponds to lower energy, while the higher value of n corresponds to the higher energy. The energy levels K, L, M, N, O, P and Q correspond to $n = 1, 2, 3, 4, 5, 6$ and 7, respectively.

The value of n also determines the number of breaks and discontinuities in the electron cloud. These breaks are also called **nodes.** The number of breaks is given by $n - 1$ and is denoted by l called azimuthal quantum number.

2. Azimuthal Quantum Number (l):

This quantum number describes the shape of an orbit. Its value corresponds to the value of n and is given by $n - 1$. It is also called secondary quantum number. The value of 'l' tells whether the orbit is spherical, is like a dumb bell, sausage shaped or even more complicated. It means that 'l' is associated with a certain value of an angular momentum. The larger the value of l, the more complicated will be the shape of the electronic cloud. The angular momentum is given by

$$mvr = \frac{h}{2\pi}\sqrt{l\,(l+1)}$$

This quantum number explains the fine structure of the spectral lines in the hydrogen spectrum, thus lending support to the Sommerfeld's assumption that the orbits are somewhat elliptical rather than being circular. The values of l and the number of orbitals are given in Table 1.5.

The resolution of single line into two or more than two lines indicates that there are various sublevels in an energy level, in which an electron revolves. The energy is also quantized in various sublevels. The main energy shell thus can be considered as being made up of one or more energy sublevels. According to Sommerfeld modification the electrons in any particular energy level could either have a circular orbit or a number of elliptical orbits about the nucleus. The number of sublevels is always equal to the value of n. For example, when $n = 1$, $l = 0$, this means that the main energy level and sublevel coincide with each other. When $n = 2$, $l = 0$ or 1, which means that there are two sublevels in the second energy level, one having elliptical shape and the other circular shape. Similarly, when $n = 3$, $l = 0, 1, 2$. This means that there are three sublevels, one having circular shape and the two other with elliptical shapes.

When $n = 4$, l can have four values (0, 1, 2, 3) corresponding to 4 sublevels, one with circular and three with elliptical shapes. Thus it is seen that the number of sublevels for a given principal quantum number is equal to the value of that quantum number. So if $l = 0, 1, 2$ or 3, the electrons are said to be in the *s*, *p*, *d* or *f* sublevels after the spectral names called sharp, principal, diffused or fundamental, respectively.

3. The Magnetic Quantum Number (m):

This quantum number explains the magnetic properties of an electron. The motion of an electron around a nucleus produces a magnetic field, which can be presented as a vector in the direction of an external applied field. This vector is zero for an *s* orbital because of its spherical symmetry. When there are more than one orbital of a given type (l value), these cannot possibly all line up equally with an external magnetic field. This difference in orientation is represented by magnetic quantum number m, which may have values from zero to ± l as shown in Figure 1.6.

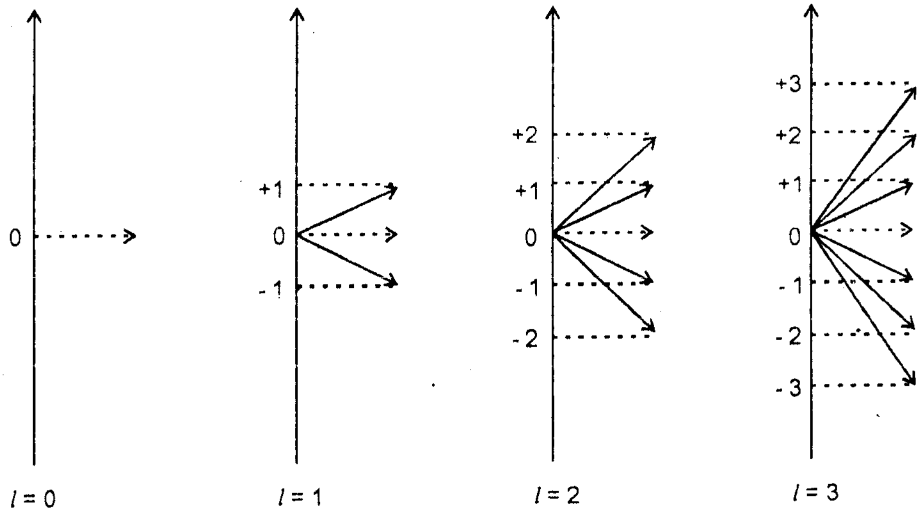


Fig. 1.6. Representation of Allowed Orientations of Orbital Magnetic Moment in Magnetic Field.

In the above figure the splitting of the spectral lines are shown for $l = 1$ (*p*-orbitals), $l = 2$ (*d*-orbitals) and $l = 3$ (*f*-orbitals) with the value of 3, 5 and 7 with different orientations in space. The arrows indicate an appropriate quantum number *i.e.*, the value of m. The angular momentum in the direction of the applied field is given by

$$\text{Angular momentum} = \frac{mlh}{2\pi}$$

The values of m are given in Table 1.5. It is clear from the table that when $n = 1$, $l = 0$, $m = 0$. Hence the number of orbital is one which is circular and is called s orbital.

When $n = 2$, $l = 1$, $m = +1, 0, -1$, the number of orbitals is 3 corresponding to three p orbitals with their orientations parallel to three co-ordinate axes x, y, and z and called p_x, p_y and p_z, respectively. Similarly, for $l = 2$ and $l = 3$, the number of orbitals will be 5 and 7 orbitals, respectively corresponding to 5 type of d orbitals and 7 type of f orbitals. Each of these orbitals can accommodate two electrons at the most. Thus s, p, d and f orbitals accommodate 2, 6, 10 and 14 electrons, respectively as shown in Table 1.5.

4. The Spin Quantum Number (s):

This quantum number is associated with the spin of an electron in the atom. All the electrons spin either in clockwise direction or in anticlockwise direction of the motion. The direction of the motion can be found out by the application of an external magnetic field. Since the probability of motion in each case is 50 % clockwise, therefore the motion is described by the spin quantum number having a value of + 1/2. Similarly, the motion in anticlockwise direction has a value of 1/2. This quantum number is denoted by the letter 's'. It is also a measure of the number of units of magnetic moment associated with a given electron due to its interaction with a magnetic field externally applied. The value of the spin momentum is given by

$$\text{Spin momentum} = +\frac{1}{2}\left(\frac{h}{2\pi}\right)$$

$$\text{and} = -\frac{1}{2}\left(\frac{h}{2\pi}\right).$$

The angular momentum is then given by

$$\text{Angular momentum} = mvr = \frac{h}{2\pi}\sqrt{s(s+1)}$$

The positive value has a lower energy and the negative one has a higher energy.

TABLE 1.5
Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom.

n	l	Orbital Designation	m_l	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	−1, 0, +1	3
3	0	3s	0	1
	1	3p	−1, 0, +1	3
	2	3d	−2, −1, 0, +1, +2	5
4	0	4s	0	1
	1	4p	−1, 0, +1	3
	2	4d	−2, −1, 0, +1, +2	5
	3	4f	−3, −2, −1, 0, +1, +2, +3	7

ATOMIC STRUCTURE:

The fundamental concept of atomic theory describes that matter is made up of ultimate units called atoms. An atom is a smallest object which has a shape, size and mass. It consists of a central part or nucleus which contains protons and neutrons and is the seat of energy and mass. Extranuclear portion of the atom consists of electrons which revolve around the nucleus in circular paths called orbits, shells or energy levels. The discovery of these and other fundamental particles is based on various experimental observations such as production of cathode rays and canal rays (positive ions) in a discharge tube, attraction of cathode rays towards the positive pole of the electric field, Millikan's oil drop experiment, scattering of alpha and beta rays etc. Alpha particles are emitted from radioactive elements with great velocities, on an average about 180,000 miles per second.

All the elements depict the physical and chemical properties which can be correlated with the structure of their atoms. The chemistry of the elements can be better understood on the basis of knowledge of atomic structure. The chemical characteristics of elements and their compounds are essentially functions of electronic configuration of the atoms of elements.

Rutherford, in 1911, projected a beam of alpha particles from a radioactive source upon a thin gold foil. He found that most of the particles passed through the solid gold foil without deflection, and only a few of them suffered abrupt back deflection as if the alpha particles in that area have met with some obstacles in their onward journey. From this, Rutherford assumed that the mass of an atom is concentrated in a central body called the nucleus which is exceedingly small as compared to the total size of the atom and it carries the entire positive charge of the atom. The electrons carry equal negative charge and constitute the extranuclear part of the atom. Rutherford also measured the nuclear charges of a large number of atoms and proved that the number of positive charges on the nucleus is, in many cases, approximately one-half the atomic weights of the elements and also equal to the number of free electrons in the atom which keeps the atoms electrically neutral.

In 1914, Moseley worked out a method for determining the number of positive charges on the nucleus of an atom. The method is based on measurement of the wavelengths of X-rays produced by bombarding various targets of elements with cathode rays. Moseley arranged the X-ray spectra of elements in the increasing order of their atomic weights and found that the wavelengths of X-rays produced varied with atomic weights of elements. It was observed that heavier the atomic weight shorter would be the wavelength. However, the frequencies of X-rays produced by the elements were directly proportional to their atomic weights. This could be correlated to the number of positive charges in the nucleus. Thus all the elements can be arranged in the increasing order of the positive charge on the nuclei of their atoms. The number of positive charges in the atoms were designated as atomic numbers (Fig. 1.7)

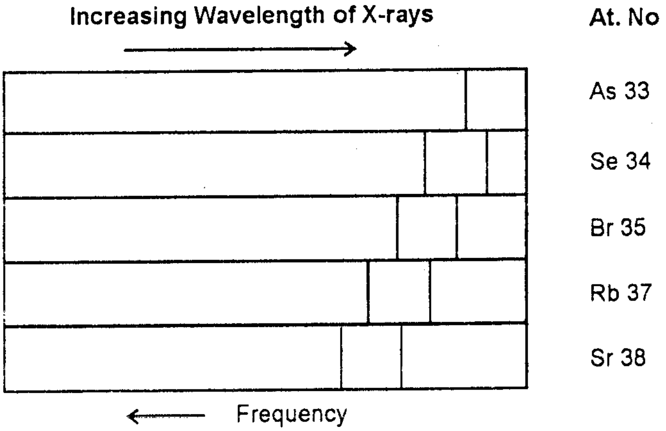


Fig. 1.7. X-rays Spectra of Moseley.

FUNDAMENTAL PARTICLES OF ATOM:

An atom is the smallest object which has definite shape, size and mass. It also possesses its own chemical identity and properties. Various experiments indicate that atoms can be sub-divided into smaller sub-atomic particles known as fundamental particles. A large number of particles (about 35), have so far been identified but mass of them are short-lived and unstable. For the study of chemistry, three fundamental particles namely, electron, proton and neutron are important.

Electron:

An electron is the smallest of the sub-atomic particles. It has the unit negative charge. Its mass is about 1/1840 times less than that of a hydrogen atom or proton. The charge of electron is 1.602 m × 10^{-19} coulombs and mass is 9.110×10^{-28} g. The charge to mass ratio, 1.76×10^{8} coulombs per gram e/m of an electron has been experimentally determined and found to be constant irrespective of the source and the method of production. Electrons are emitted from the surface of a substance exposed to the action of X-rays, ultraviolet rays and even on exposure to ordinary light. Electrons appear to constitute the outer structures of atoms, since they are easily dislodged under the influence of electric field. The chemical properties of elements and their compounds depend upon the electronic arrangement of electrons in their atoms. Electrons are present in the extranuclear part of atoms.

Proton:

A proton carries a unit positive charge, which is equal but opposite to the charge of an electron. A proton is 1840 times heavier than electron. It has a unit positive charge of 1.602×10^{-19} a.m.u but is about 1840 times heavier than an electron. The mass of proton is 1.673×10^{-24} g. If hydrogen is present in the discharge tube, the positive rays formed consist of protons. The protons are present in the nucleus of an atom. The number of protons is always equal to the number of electrons and therefore atom is electrically neutral.

Neutron:

In 1932, Chadwick discovered neutron as a fundamental particle of atom. He observed that when α-particles are bombarded on thin sheets of beryllium metal, uncharged particles are emitted. The uncharged particles are called neutrons. They have a mass equal to 1.0087 on the atomic weight scale. It was later discovered that a neutron may disintegrate to form a proton and an electron. It has a mass of 1.675×10^{-24} g. The sum of protons and neutrons in the nucleus is known as Atomic Mass.

The Nucleus:

The nucleus of an atom contains protons and neutrons except hydrogen which consists of a single proton. If occupies only about 10^{-13} of the volume of an atom, each proton and neutron has a mass of approximately 1 a.m.u. on the basis of atomic weight of carbon, C = 12 a.m.u. The atomic weight of an element is approximately equal to the sum of the weights of the total number of protons and the total number of neutrons in the nucleus by neglecting the negligibly small weight of the electrons present.

The protons and neutrons are held together in the nucleus by a force known as nuclear force. According to Heisenberg, a neutron in the nucleus sometimes is transformed into an electron and a proton. The electron might escape in the form of beta rays.

In 1935, Yukawa proposed that a fundamental particle known as meson is absorbed by the neutron when a proton and a neutron interact. The two type of mesons are pi-mesons and mu-mesons. These may be positive, negative or neutral. In the exchange of positive pi-mesons, the proton becomes a neutron and the neutron becomes a proton.

$$P \rightleftharpoons \pi^{+} + n$$

$$n \rightleftharpoons \pi^{-} + p$$

The present day knowledge of the structure of the nucleus has progressed so far as to present a very complicated picture. However, only the proton-neutron concept of the nuclear structure will be sufficient to understand the elementary aspects of the subject

EXTRANUCLEAR STRUCTURE OF ATOM:

Extranuclear structure of an atom consists of electrons in various energy levels. Bohr's model atom describes the motion of an electron in a circular path in an orbit of definite energy state. When an electron jumps from one energy state to another, it involves change in energy state. In this manner, origin of special lines can be visualised.

Since there is an uncertainty in the position and momentum (or energy) of an electron, therefore one can speak of the probability that an electron is in a certain region or space. The greater the probability of finding an electron in a certain region of space about a nucleus, the greater is the density of electronic charge, *i.e.*, the quantity of the negative charge per unit volume. The theory that predicts such probability for different electrons is called *quantum mechanics*. The probability of finding an electron is denoted by $|\psi^2|$ where Ψ (Psi) is the wave function.

Electron density can be depicted in two ways. One is with the help of probability curves and the second by plotting the contour maps of the probability of finding an electron shown in Fig. 1.8. The concentric shells are obtained which describe 90 % of Ψ^2, *i.e.*, the probability of finding the electrons within the boundary surface of the shell. Such shells are spherically symmetrical and represent the ground state of the hydrogen atom and are called 'atomic orbitals' or 'sub-levels'. Spherically symmetrical orbital is called '*s*' orbital. The boundary surfaces of '*s*', '*p*' and '*d*' and '*f*' orbitals are given in Fig. 1.9.

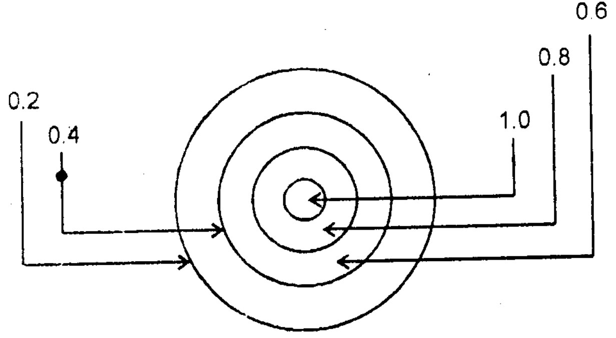


Fig. 1.8. Contours of Ψ^2 relative to Ψ^2 at the origin.

All atoms have energy levels (orbits) and sublevels (orbitals). The electrons reside in various energy levels, lower energy levels are occupied first. Each energy level can accommodate $2n^2$ as maximum number of electrons, where 'n' is the principal quantum number for that level. For example, when $n = 1$, 2 (2×1^2) electrons can be accommodated in the first level. Similarly, for $n = 2$, 3 and 4; 8, 18 and 32 electrons will be accommodated at the most in all these levels, respectively.

Each energy level is subdivided into sublevels. The number of sublevels is equal to the value of n. Hence the first level will have one subshell called 's' orbital which can accommodate only two electrons at the most. Similarly, the second, the third and the fourth levels will have 2 (s, p), 3 (s, p, d) and 4 (s, p, d, f) sublevels. The s, p, d, f, sublevels or orbitals can accommodate at the most 2, 6. 10 and 14 electrons, respectively.

The order of filling of various orbitals is based on increasing energy or $n + l$ value (n = principal quantum number or number of the orbit *i.e.*, K = 1, L = 2, M = 3 etc., l = azimuthal quantum number which describes the shape of the orbital and its value for 's' orbital is = 0, for 'p' orbital is = 1, for 'd' orbital is = 2 and for 'f' orbital is = 3). Thus 1s orbital has lower energy state ($n + l$ for 1s is $1 + 0 = 1$) than 2s because $n + 1$ for 2s is $= 2 + 0 = 2$ and lower than 2p etc. (for 2p is $2 + 1 = 3$).

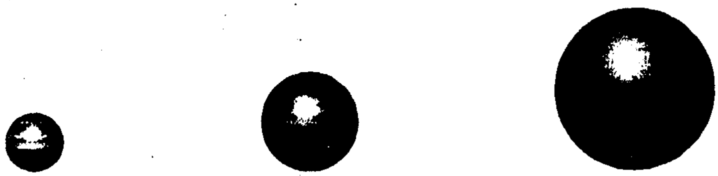
The order of electron filling of the orbitals for Ca (At. no. = 20) will be $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2$ because the energy levels have energy in the order:

$$1s < 2s < 2p < 3s < 3p < 4s$$

If two levels have the same value of $n + l$, then the electron will prefer the level which has lower value of n. For example, in the case of scandium, Sc (At. no. = 21) the arrangement of electrons should be $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^1\, 4p$. After 4$s$ ($n + l$, $4 + 0 = 4$) the next incoming electron goes to 3d orbital because applying $n + l$ rule, 3d ($n = 3$, $l = 2$, $n + l = 5$) and 4p ($n = 4$, $l = 1$, $n + l = 5$) both have $n + l$ values 5 but 3d orbital belongs to lower level ($n = 3$) than 4p ($n = 4$).

The overall order of filling the orbitals is:

$$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^2\, 3d^{10}\, 4p^6\, 5s^2\, 4d^{10}\, 5p^6\, 6s^2\, 4f^{14}\, 5d^{10}\, 6p^6$$



1s 2s 3s

Boundary surface representations of the 1s, 2s and 3s orbitals. These representations show the boundaries of the orbitals that contain 95 % of the electron density of the orbital. For example, there is a 95 % probability that an electron in the 1st orbital will be within the volume shown for the 1s orbital.

Fig. 1.9. (a) Boundary surface of s orbitals.

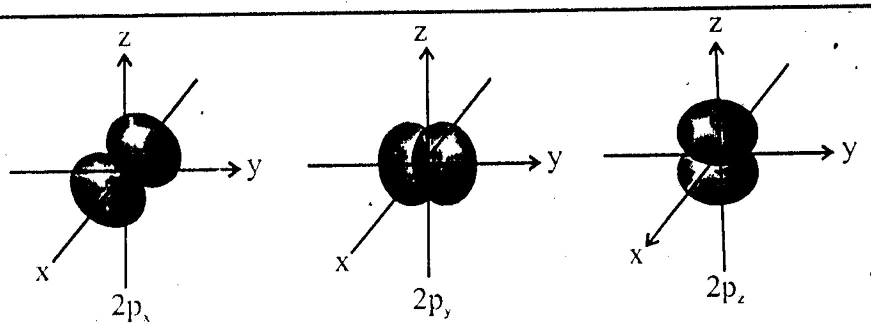


Fig. 1.9.(b): Boundary surfaces of 'p' orbitals.

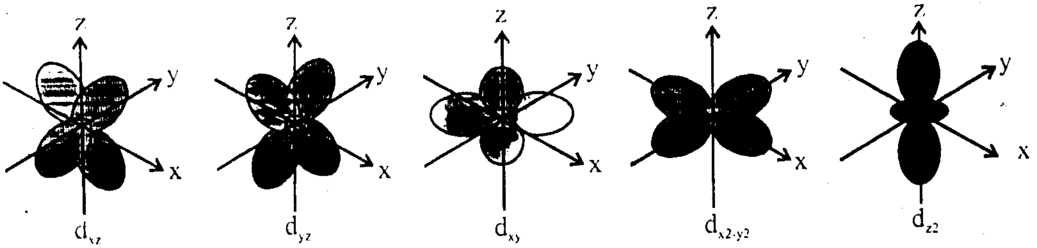


Fig. 1.9.(c): Boundary surfaces of 'd' orbitals.

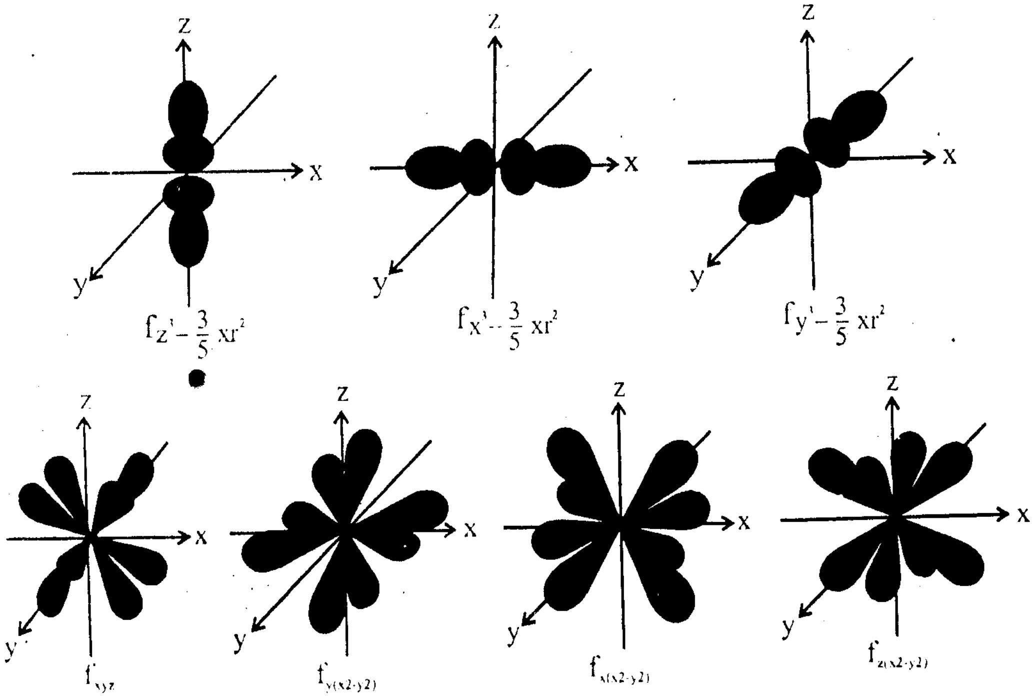


Fig. 1.9.(d): Boundary surfaces of 'f' orbitals. The + and – signs show the orientation of orbitals above (+) and (–) the planes and not the charge.

The electronic configuration of the atoms in their ground states is given in Table 1.6.

HUND'S RULE OF MAXIMUM MULTIPLICITY:

Magnetic measurements have helped to determine the electronic configurations of many elements and thereby establish a hypothetical order in which the orbitals may be assumed to fill. The electronic configurations of orbitals of the first five elements is simple as shown below:

	1s	2s	2p		
^{1}H =	↑				
^{2}He =	↑↓				
^{3}Li =	↑↓	↑			
^{4}Be =	↑↓	↑↓			
^{5}B =	↑↓	↑↓	↑		

A question arises concerning the electronic distribution of the sixth element, carbon, since there are three $2p$ orbitals. Does the next incoming electron belong to the $2p$ orbital already holding one electron or does it belong to another $2p$ orbital? This has been explained by the **Hund's rule**, which states that *electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons.* Therefore, each of the two $2p$ electrons of carbon must assume its own orbital instead of pairing with the other electrons in a single orbital. Similarly, the arrangement of electrons in Nitrogen, Oxygen, Fluorine and Neon is:

	1s	2s	2p		
^{6}C =	↑↓	↑↓	↑	↑	
^{7}N =	↑↓	↑↓	↑	↑	↑
^{8}O =	↑↓	↑↓	↑↓	↑	↑
^{9}F =	↑↓	↑↓	↑↓	↑↓	↑
^{10}Ne =	↑↓	↑↓	↑↓	↑↓	↑↓

Electrons are negatively charged and repel each other. Hence they spread out and occupy the $2p$ orbitals singly before they begin to pair. After each of the $2p$ orbitals holds one electron, pairing occurs because less energy is required to overcome the interelectronic repulsion and to add an electron to an orbital already holding an electron. This general order of orbital filling is observed for all subshells.

The spectroscopic notations for electronic configuration can be written with superscripts indicating the number of electrons in each subshell. Thus the electronic configuration of oxygen may be indicated $1s^2\ 2s^2\ 2p^4$ or $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$.

ORDER OF FILLING ORBITALS:

The electronic structure of an element is correctly deduced by successive addition of electrons into orbitals arranged in order of increasing energy until the proper number of electrons for that element has been accommodated.

It is assumed that each electron enters the lowest energy level available to it, and since all of the orbitals of a given sublevel have equivalent energies, this amounts to an arrangement of sublevels. It is possible for a simple orbital of one level (*e.g.*, 4*s*) to have a lower energy than a more complicated orbital of an inner level (*e.g.*, 3*d*) and hence the 4*s* sublevel fills before the 3*d*, the order of filling is then not by increasing value of *n*, but may be derived from the order of occupancy atomic orbitals. (Fig. 1.10)

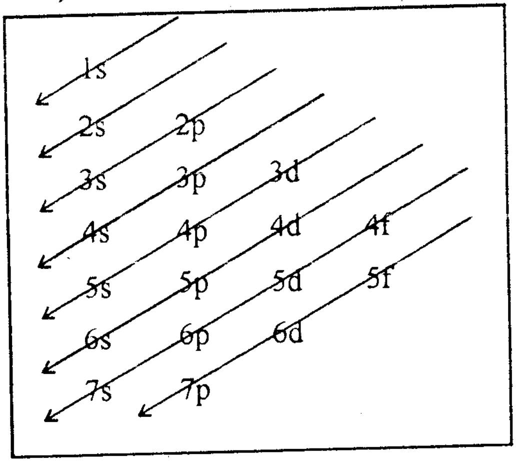


Fig. 1.10. Order of occupancy of atomic orbitals. The orbitals fill in order, starting with the 1s orbital, in the direction of each arrow, going down the arrows from top to bottom.

In the use of this diagram, the orbitals are being filled starting at the bottom of the chart and proceeding upward. Aufbau way of filling sublevels is shown in Fig. 1.11.

Subshell Electron Capacity

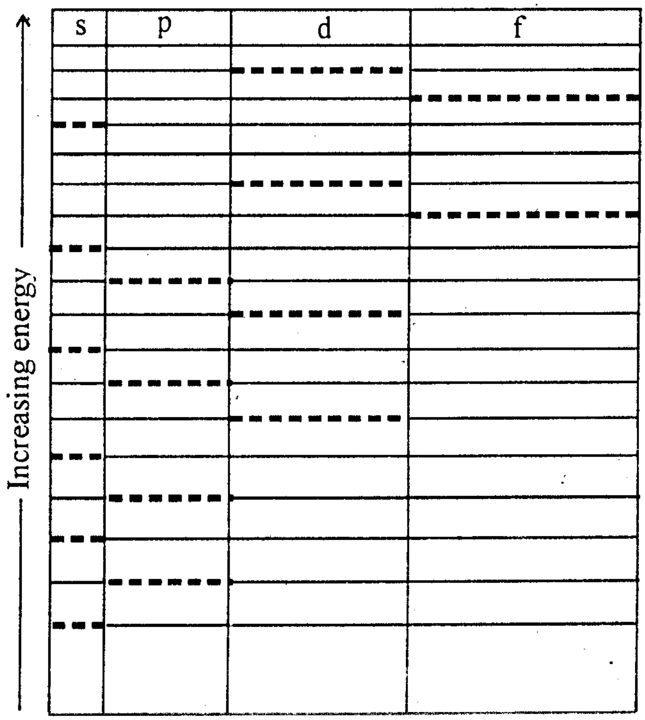


Fig. 1.11. Generalised energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

To determine the electronic configuration of any element, one starts with hydrogen and on the basis of the Periodic Table accounts for every electron added until the desired element is reached. Thus for tungsten (Z = 74) the first period gives $1s^2$, the second period, $2s^2\ 2p^6$, the third $3s^2\ 3p^6$; the fourth, $4s^2\ 3d^{10}\ 4p^6$; and the fifth, $5s^2\ 4d^{10}\ 5p^6$. The sixth period in which tungsten is found — starts with $6s^1$ for caesium and $6s^2$ barium, adds $4f^{14}$ for the inner transition elements and the final term is $5d^4$, since tungsten is the 4th element in the $5d$ transition series. Rearranging these terms in sequence we get its electronic configuration:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^4\ 6s^2$$

The electronic configurations predicted by the aufbau procedure are confirmed by spectral and magnetic studies for most of the elements.

ATOMIC STRUCTURE AND PERIODIC TABLE:

The elements arranged in horizontal rows in the table are called periods. The vertical columns are called groups in which elements of similar physical and chemical properties are present. In the Periodic Table, the elements are arranged in seven periods and eight groups. The symbols of elements are written in boxes along with their atomic numbers and atomic weights. Sometimes additional information is provided in the box.

The horizontal rows or periods indicate the gradual filling of energy levels with electrons. The first element, hydrogen (H) having one electron in '*s*' orbital is represented as $1s^1$. The next element helium (He) having two electrons has electronic configuration $1s^2$. The number on the left of '*s*' orbital indicates the number of orbital and on the right upper corner gives the number of electrons. The first period starts with H and ends with He and has only two elements because only '*s*' orbital becomes available and orbital gets completed with two electrons.

The second period starts with lithium $_3$Li (atomic number = 3) having electronic configuration $1s^2\ 2s^1$. The next element is beryllium $_4$Be with electronic configuration $1s^2\ 2s^2$. Here the '*s*' orbitals are completely filled ('*s*' orbitals can have at the most 2 electrons). The next electron goes to $2p$ orbital of boron, $_5$B with electronic configuration $1s^2\ 2s^2\ 2p^1$. Five more electrons are regularly added to $2p$ orbitals to get elements $_6$C, $_7$N, $_8$O, $_9$F and $_{10}$Ne (an inert gas with $2p^6$ configuration) (Table 1.6). As $2p$ orbitals can have at the most 6 electrons, the next incoming electron enters the next available $3s$ orbital to give sodium, $_{11}$Na($1s^2\ 2s^2\ 2p^6\ 3s^1$). The process of addition of electrons continues in the third period as the second one is completed with argon $_{18}$Ar configuration. Consequently, second and third periods have eight elements each on the basis of complete filling of orbitals of '*s*' with 2 electrons and *p* with 6 electrons.

In fourth period starting with $_{19}$K, one electron is added in fourth energy level $4s^1$ orbital. The next element calcium, Ca has electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. After that the filling of the $3d$ orbitals starts as they are the next available orbitals. As the complete filling of $3d$ orbitals requires 10 electrons, the next ten elements after calcium *i.e.*, scandium ($_{21}$Sc) to zinc ($_{30}$Zn) are members of '*d*' block or transition elements which have properties different from the main group elements due to '*d*' orbital filling. Transition elements were assigned '*B*' subgroup in the Periodic Table. After zinc, $_{30}$Zn (electronic configuration $_{18}$[Ar] $3d^{10}\ 4s^2$) six more electrons are added to $4p$ orbitals to get $_{36}$Kr (inert gas) configuration ([Ar] $3d^{10}\ 4s^2\ 4p^6$). The fifth period is filled in the same manner as the fourth period and has also 18 elements.

The interruptions take place in the sixth period. After the $6s$ orbital is filled (in barium) and one electron is added to $5d$ orbital (in lanthanum), the $4f$ orbitals are filled (Table 1.6). The '*f*' orbitals require 14 electrons to be filled. Therefore, 14 elements after lanthanum ($_{57}$La) belong to *f* block elements (cerium, $_{58}$Ce to lutetium $_{71}$Lu). These elements are called inner transition elements and written at the bottom of the Periodic Table. All of them have the same chemical properties. When $4f$ orbitals have been completed, $5d$ orbitals become available for filling. So 10 members of 6th period (from atomic number 71 to 80) belong to *d*-block elements. After $5d$ orbital filling $6p$ orbitals are filled and six elements after mercury, $_{80}$Hg (thallium, $_{81}$Tl to radon, $_{88}$Rn) appear. The sixth period has, therefore, 2 + 14 + 10 + 6 (due to $7s^2$, $4f^{14}$, $5d^{10}$, $6p^6$) or 32 elements. Similarly, seventh period is filled in this manner.

PERIODS:

There are seven periods of elements in the Periodic Table (1.4). These are horizontal rows which are across the table. The first period contains two elements H and He. Second and third periods have eight elements each and are all main group elements. Fourth and fifth periods contain eighteen elements (two of '*s*' block, ten of '*d*' block and six of '*p*' block). Sixth period has thirty-two elements (two of '*s*' block, ten of '*d*' block, fourteen of '*f*' block and six of '*p*' block). Similarly, seventh period should have the same number of elements as are present in the sixth period but is still incomplete. Members of lanthanides are present in sixth period and actinides in the seventh period. Both are presented at the bottom of the Periodic Table because they possess identical chemical characteristics and cannot be adjusted in the normal manner.

GROUPS:

The vertical columns in the Periodic Table are called groups or families. Each group is labelled with a number and a letter 'A' or 'B'. There are eight groups in the Periodic Table (IUPAC has recently resolved to recommend 18 groups to avoid 'A' and 'B' classification). Inert gas elements are shown as group 8A or 0 because of their zero valent state and inactivity towards chemical reactions.

The elements in a group have similar physical and chemical properties. Elements in the same group show similar chemical properties because of similar electronic configuration in the outermost energy levels.

The elements present in Group I-A (except hydrogen) are called alkali metals. They react with water to form strong alkalies. They have one electron in the outermost '*s*' energy level, ($1s^1$). The members of alkali metals are Li, Na, K, Rb, Cs and Fr. They are soft metals and quickly tarnish in air. They react readily with water to form corresponding hydroxides. They are mostly used as heat exchanger in certain type of nuclear reactors. The bright yellowish street lights are sodium vapour lamps. Group I-B includes Cu, Ag and Au.

Group II-A elements are called the alkaline earth metals. Each one of them has outermost '*s*' orbital filled with two electrons. The elements in this group are Be, Mg, Ca, Sr, Ba, Ra. Magnesium and calcium are the most abundant among them. Magnesium is a light metal and is used to build aircraft parts. Beryllium is hard and has high melting point. For this reason it is used to prepare window-panes of aircraft. Group II-B includes Zn, Cd and Hg.

Group III-A elements include B, Al, Ga, In and Tl. They have electronic configuration in the outermost energy level, $ns^2\ np^1$. Aluminium is abundantly found in earth's crust and is very useful. It is used in construction and to prepare foils and wires. Gallium is a liquid (m.p. 30°C) at room temperature in summer.

Group IV-A contains elements, carbon (a non-metal), silicon and germanium (semi-metals or metalloids) tin and lead (metals). They all have $ns^2\ np^2$ configuration and are tetravalent. Carbon is extremely important for life processes. It is the building block of organic compounds. It exists in different forms. Diamond and graphite are allotropic forms of carbon. Different forms of an element which have the same chemical properties but different physical characteristics are called allotropic forms or allotropes and phenomenon is known allotropy. Silicon is the most abundant element on the earth's crust. Silicon is a semi-conductor and silicon technology is gaining significance because of its use as semi-conductor. Tin cans are useful in storing food. Lead is used in chemical industry and storage batteries. It is poisonous and damages the nervous system.

Group V-A contains N, P, As, Sb and Bi. They have electronic configuration $ns^2\ np^3$ in outermost orbitals. Nitrogen gas is present to the extent of about 78 % in air. It is converted by nitrogen fixing bacteria to its compounds which are useful for fertility of soil. Nitrogen is also converted into artificial fertilizers such as urea, etc. Liquid nitrogen is used as coolant. Phosphorus exists in allotropic forms — yellow and red. Red phosphorus is used in safety metals.

Group VI-A consists of O, S, Se, Te and Po. The electronic configuration of outermost orbitals is $ns^2\ np^4$. Oxygen and sulphur are the most abundant elements among these. Oxygen is present to about 20 % in the air. It is essential for life processes. Ozone is an allotrope of oxygen found in the upper atmosphere. It helps in preventing the ultraviolet light to reach the surface of earth. Sulphur is mainly used in chemical industry and vulcanization of rubber. Selenium is a component of photoelectric cell and is used to convert energy of sunlight into electric energy.

Group VII-A constitutes the halogen family. The members of this family are F, Cl, Br, I and At. They are typical non-metals and have electronic configuration $ns^2\ np^5$. Fluorine is the most reactive element. Its compounds are useful for healthy teeth. Chlorine is used commercially for the purification of water and its compounds are commercially useful. Tincture of iodine contains iodine in alcohol and is used as disinfectant.

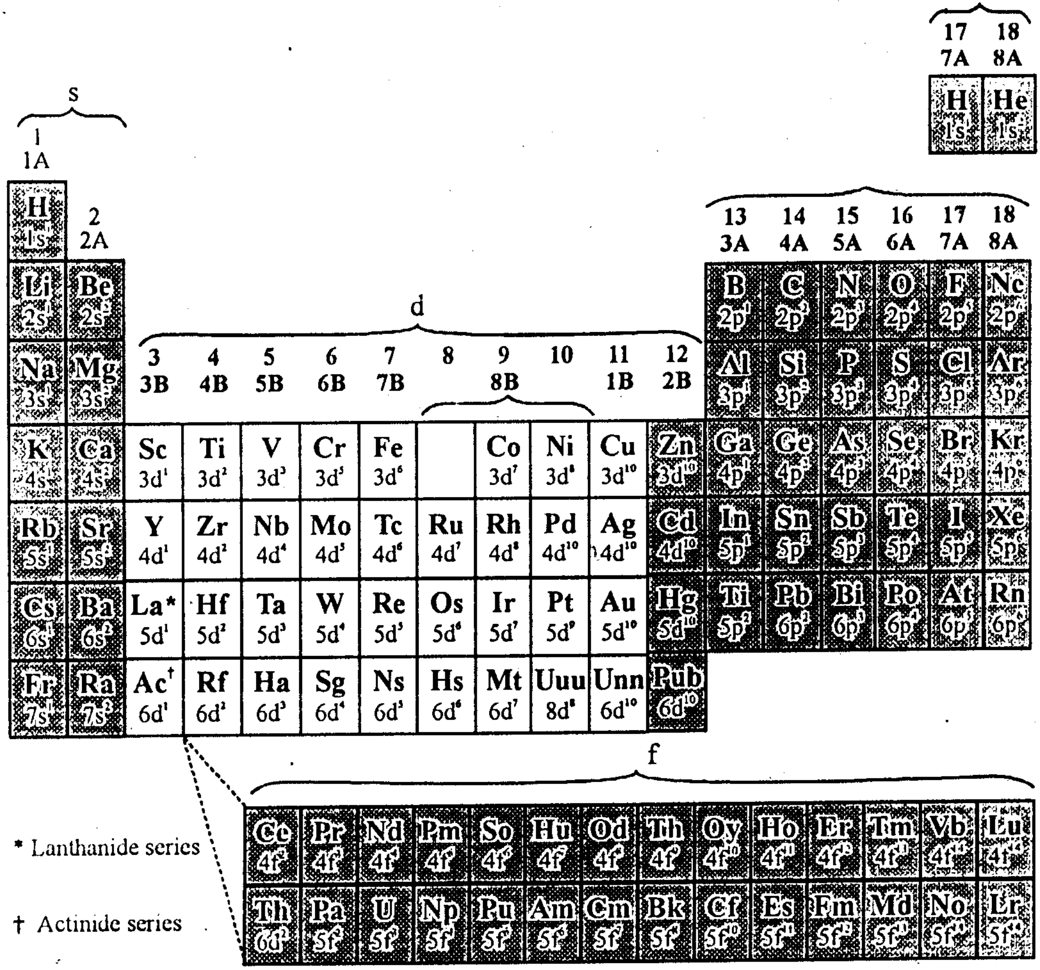
Inert gases comprise of Group zero (0) of the Periodic Table. The members include He, Ne, Ar, Kr, Xe and Rn and have electronic configuration $ns^2\ np^6$. As p orbitals are completely filled they show chemical inertness. They make up about 1 % of the atmosphere by volume. Neon gas produces orange-red glow of neon signs. Argon is used in incandescent light bulbs. Krypton is used in incandescent lamps along with mercury. Xenon is used in flash bulbs.

Groups III-B to VIII-B consist of transition elements. They have different characteristics from main group elements. The most prominent characteristic properties of transition metals include their high melting points, variable valencies, coloured ions and formation of complex compounds.

TABLE 1.6

Electron Configurations of the Elements

Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	[Kr] $5s^2$	78	Pt	[Xe] $6s^1\ 4f^{14}\ 5d^9$
2	He	$1s^2$	39	Y	[Kr] $5s^2\ 4d^1$	79	Au	[Xe] $6s^1\ 4f^{14}\ 5d^{10}$
			40	Zr	[Kr] $5s^2\ 4d^2$	80	Hg	[Xe] $6s^2\ 4f^{14}\ 5d^{10}$
3	Li	$1s^22s^1$ = [He]$2s^1$	41	Nb	[Kr] $5s^1\ 4d^4$	81	Tl	[Xe] $6s\ 4f^{14}\ 5d^{10}\ 6p^1$
4	Be	[He] $2s^2$	42	Mo	[Kr] $5s^1\ 4d^5$	82	Pb	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$
5	B	[He] $2s^22p^1$	43	Tc	[Kr] $5s^1\ 4d^6$	83	Bi	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$
6	C	[He] $2s^22p^2$	44	Ru	[Kr] $5s^1\ 4d^7$	84	Po	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^4$
7	N	[He] $2s^22p^3$	45	Rh	[Kr] $5s^1\ 4d^8$	85	At	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^5$
8	O	[He] $2s^22p^4$	46	Pd	[Kr] $4d^{10}$	86	Rn	[Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$
9	F	[He] $2s^22p^5$	47	Ag	[Kr] $5s^1\ 4d^{10}$			
10	Ne	[He] $2s^22p^6$	48	Cd	[Kr] $5s^2\ 4d^{10}$	87	Fr	[Rn] $7s^1$
			49	In	[Kr] $5s^2\ 4d^{10}\ 5p^1$	88	Ra	[Rn] $7s^2$
11	Na	[Ne] $3s^1$	50	Sn	[Kr] $5s^2\ 4d^{10}\ 5p^2$	89	Ac	[Rn] $7s^2\ 6d^1$
12	Mg	[Ne] $3s^2$	51	Sb	[Kr] $5s^2\ 4d^{10}\ 5p^3$	90	Th	[Rn] $7s^2\ 6d^2$
13	Al	[Ne] $3s^23p^1$	52	Te	[Kr] $5s^2\ 4d^{10}\ 5p^4$	91	Pa	[Rn] $7s^2\ 5f^2\ 6d^1$
14	Si	[Ne] $3s^23p^2$	53	I	[Kr] $5s^2\ 4d^{10}\ 5p^5$	92	U	[Rn] $7s^2\ 5f^3\ 6d^1$
15	P	[Ne] $3s^23p^3$	54	Xe	[Kr] $5s^2\ 4d^{10}\ 5p^6$	93	Np	[Rn] $7s^2\ 5f^4\ 6d^1$
16	S	[Ne] $3s^23p^4$				94	Pu	[Rn] $7s^2\ 5f^6$
17	Cl	[Ne] $3s^23p^5$	55	Cs	[Xe] $6s^1$	95	Am	[Rn] $7s^2\ 5f^7$
18	Ar	[Ne] $3s^23p^6$	56	Ba	[Xe] $6s^2$	96	Cm	[Rn] $7s^2\ 5f^7\ 6d^1$
			57	La	[Xe] $6s^2\ 5d^1$	97	Bk	[Rn] $7s^2\ 5f^8\ 6d^1$
19	K	[Ar] $4s^1$	58	Ce	[Xe] $6s^2\ 5f^2$	98	Cf	[Rn] $7s^2\ 5f^{10}$
20	Ca	[Ar] $4s^2$	59	Pr	[Xe] $6s^2\ 5f^3$	99	Es	[Rn] $7s^2\ 5f^{11}$
21	Sc	[Ar] $4s^24d^1$	60	Nd	[Xe] $6s^2\ 5f^4$	100	Fm	[Rn] $7s^2\ 5f^{12}$
22	Ti	[Ar] $4s^24d^2$	61	Pm	[Xe] $6s^2\ 5f^5$	101	Md	[Rn] $7s^2\ 5f^{13}$
23	V	[Ar] $4s^24d^3$	62	Sm	[Xe] $6s^2\ 5f^6$	102	No	[Rn] $7s^2\ 5f^{14}$
24	Cr	[Ar] $4s^14d^5$	63	Eu	[Xe] $6s^2\ 5f^7$	103	Lr	[Rn] $7s^2\ 5f^{14}\ 6d^1$
25	Mn	[Ar] $4s^24d^5$	64	Gd	[Xe] $6s^2\ 4f^7\ 5d^1$	104	Rf	[Rn] $7s^2\ 5f^{14}\ 6d^2$
26	Fe	[Ar] $4s^24d^6$	65	Tb	[Xe] $6s^2\ 4f^9$	105	Haf	[Rn] $7s^2\ 5f^{14}\ 6d^3$
27	Co	[Ar] $4s^24d^7$	66	Dy	[Xe] $6s^2\ 4f^{10}$	106	Sg	[Rn] $7s^2\ 5f^{14}\ 6d^4$
28	Ni	[Ar] $4s^24d^8$	67	Ho	[Xe] $6s^2\ 4f^{11}$	107	Ns	[Rn] $7s^2\ 5f^{14}\ 6d^5$
29	Cu	[Ar] $4s^14d^{10}$	68	Er	[Xe] $6s^2\ 4f^{12}$	108	Hs	[Rn] $7s^2\ 5f^{14}\ 6d^6$
30	Zn	[Ar] $4s^14d^{10}$	69	Tm	[Xe] $6s^2\ 4f^{13}$	109	Mt	[Rn] $7s^2\ 5f^{14}\ 6d^7$
31	Ga	[Ar] $4s^2\ 3d^{10}\ 4p^1$	70	Yb	[Xe] $6s^2\ 4f^{14}$	110	Um	[Rn] $7s^2\ 5f^{14}\ 6d^8$
32	Ge	[Ar] $4s^2\ 3d^{10}\ 4p^2$	71	Lu	[Xe] $6s^2\ 4f^{14}\ 5d^1$	111	Uuu	[Rn] $7s^2\ 5f^{14}\ 6d^9$
33	As	[Ar] $4s^2\ 3d^{10}\ 4p^3$	72	Hf	[Xe] $6s^2\ 4f^{14}\ 5d^2$	112	Uub	[Rn] $7s^2\ 5f^{14}\ 6d^{10}$
34	Se	[Ar] $4s^2\ 3d^{10}\ 4p^4$	73	Ta	[Xe] $6s^2\ 4f^{14}\ 5d^3$			
35	Br	[Ar] $4s^2\ 3d^{10}\ 4p^5$	74	W	[Xe] $6s^2\ 4f^{14}\ 5d^4$			
36	Kr	[Ar] $4s^2\ 3d^{10}\ 4p^6$	75	Re	[Xe] $6s^2\ 4f^{14}\ 5d^5$			
			76	Os	[Xe] $6s^2\ 4f^{14}\ 5d^6$			
37	Rb	[Kr] $5s^1$	77	Ir	[Xe] $6s^2\ 4f^{14}\ 5d^7$			



The order of occupancy of Atomic Orbitals in the Periodic Table.

Placement of Elements Based on Electronic Configuration in Periodic Table:

An important feature of the long form of the Periodic Table is that it can be divided into *s*, *p*, *d* and *f* blocks. The division is based upon the type of atomic orbital which receives the last electron in its atom.

***s*-Block elements** belong to the class of representative or non-transition elements. The incoming electrons enter the outermost *s*-orbitals in the atoms of these elements. They have the configuration ns^1 and ns^2. The *s*-block elements with ns^1 configuration are alkali metals and belong to Group IA. These elements with ns^2 configuration are called alkaline earth metals and are members of Group IIA.

***p*-Block elements** are also representative elements having the outermost orbital electronic configuration ns^2, np^{1-6}. These elements belong to Groups IIIA (13), IVA (14), VA (15), VIA (16), VIIA (17) and VIIIA (18) and consist of a set of six elements, *e.g.*, B, C, N, O, F and Ne.

***d*-Block elements** have the orbital electronic configuration $(n-1)\,d^{1-10}\,ns^2$ or $(n-1)\,d^{1-10}\,ns^1$. The last electron enters the $(n-1)$ *d*-orbital. The elements are called transition elements (a set of ten) and lie between *s*- and *p*-blocks *e.g.*, members of first transition series Cu, Zn, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and belong to groups (IB to VIIIB).

***f*-Block elements** have the general orbital electronic configuration $(n-2)\,f^{1-14}\,ns^2$ or $(n-2)\,f^{1-14}\,(n-1)\,d^1\,ns^2$. These elements are also called inner transition elements. They are assigned special place at the bottom of the Periodic Table as members of first or Lanthanide series in which 4 *f*-orbitals are being filled to get a set of 14 elements and the members of second or Actanide series in which 5 *f*-orbitals are in the process of completion.

According to recommendations of IUPAC (International Union of Pure and Applied Chemistry) adopted in 1984, the groups are numbered 1 to 8 as shown in Table 1.4. Thus, the alkali metal Group IA becomes 1, while alkaline earth metals Group IIA becomes 2 and so on. The *d*-block or transition elements are labelled from group 3(Sc—) to 12 (Zn, Cd, Hg). The noble or inert gases are placed in group 18.

Elements of groups IA (1), IIA (2), IIIA (13), IVA (14), VA (15), VIA (16), VIIA (17) have the outermost shells incompletes. These are called normal or representative or non-transition elements.

Elements or groups IIIB (3), IVB (4), VB (5), VIB (6), VIIB (7), VIIIB (8, 9 and 10), IB (11), IIB (12) are known as transition elements. These have their *d*-orbitals incompletely filled. Elements of zero (18) group are called inert or noble gases and have the shells completely filled.

Anomalies:

Elements of second period at the top of Group I to VII are sometimes called head elements. They are interesting because some of the properties of these elements and their compounds are slightly different from those of the other elements in their respective groups. These instinctive properties can be attributed to the smaller size of their atoms, their higher electronegativities and ionisation energies. For example, hydroxides of lithium and beryllium show more covalent character than the corresponding hydroxides of other metals of Group I and II. Lithium hydroxide is thermally more stable than other alkali metal hydroxides.

Oxidation States of Lanthanides:

The lanthanides or lanthanons are the fourteen elements that follow lanthanum (At. no. 57) in the Periodic Table. Electrons are successfully added to the lanthanum configuration (------- $5d^1\ 6s^2$) in $4f$ orbitals for these elements. (Table 1.7)

TABLE 1.7

Atomic Number	Name of Elements	Symbol	Electronic Configuration
57	Lanthanum	La	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 5d^1\ 6s^2$
58	Cerium	Ce	- - - $4f^1\ 5d^1\ 6s^2$
59	Praseodymium	Pr	- - - $4f^3\ 6s^2$
60	Neodymium	Nd.	- - - $4f^4\ 6s^2$
61	Promethium	Pm	- - - $4f^5\ 6s^2$
62	Samarium	Sm	- - - $4f^6\ 6s^2$
63	Europium	Eu	- - - $4f^7\ 6s^2$
64	Gadolinium	Gd	- - - $4f^7 5d^1\ 6s^2$
65	Terbium	Tb	- - - $4f^9\ 6s^2$
66	Dysprosium	Dy	- - - $4f^{10}\ 6s^2$
67	Holmium	Ho	- - - $4f^{11}\ 6s^2$
68	Erbium	Er	- - - $4f^{12}\ 6s^2$
69	Thulium	Tm	- - - $4f^{13}\ 6s^2$
70	Ytterbium	Yb	- - - $4f^{14}\ 6s^2$
71	Lutetium	Lu	- - - $4f^{14} 5d^1\ 6s^2$

The chemistry of these elements is predominantly ionic and is determined by the size of M^{3+} ion. They are highly electropositive and their compounds have ionic character.

The oxidation states of lanthanides can be correlated to their ionization potential values. Ytterbium and Lanthanum form only M^{3+} ions since removal of three electrons give stable inert gas configuration. Lutetium and Gadolinium also form M^{3+} ions due to attainment of stable $4f^{14}$ and $4f^7$ configurations after removal of three electrons from $5d$ and $6s$ orbitals. Ce^{4+} and Yb^{2+} ions are stable due to f^0 and f^{14} configurations after removal of four electrons from Ce and two electrons from Yb atoms. (Table 1.9)

Eu^{2+} attains f^7 configuration after the removal of two electrons from its atoms, since half-filled orbitals have the tendency to gain stability. Similarly, thermodynamic and kinetic factors impart stabilities to $Nd^{2+,4+}$, $Pr^{2+,4+}$ and Ce^{2+}.

Artificial (Man-Made) Elements:

Elements beyond uranium (92) are not found in nature. They are artificially prepared. Man-made elements were named after the person or place of discovery. For example, element 98 is named 'Californium' because it was first produced in California. Element 99 was named 'Einsteinium' after Albert Einstein.

In recent years conflicts have arisen between scientists on the nomenclature of the artificially prepared elements. To avoid such controversies, a systematic approach for naming elements beyond 103 has been adopted. It is based on naming the element according to its atomic number. The following terms have been adopted while naming these elements:

0 nil (*n*)	5 pent (*p*)
1 un (*u*)	6 hex (*h*)
2 bi (*b*)	7 sept (*s*)
3 tri (*t*)	8 oct (*o*)
4 quad (*q*)	9 en (*e*)

Names are given on the basis of above terms to represent atomic numbers and they end in '—ium'. For example, element 105 would be called 'unnilpentium' as follows:

un	nil	pent	ium
1	0	5	ending

The symbol for unnilpentium is Unp. Similarly, the names of the elements with atomic numbers higher than 105 are given below:

Atomic Number	Nomenclature	Symbol
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilenium	Une

Oxidation States of Actinides:

Actinium (Atomic no. 89) and the elements following it are called actinides. (Table 1.8). These include both naturally occurring (up to Uranium) and artificially prepared elements.

TABLE 1.8

Atomic Number	Name of Elements	Symbol	Electronic Configuration
89	Actinium	Ac	- - - $6d\ 7s^2$
90	Thorium	Th	- - - $6d^2\ 7s^2$
91	Proactinium	Pa	- - - $5f^2\ 6d\ 7s^2$
92	Uranium	U	- - - $5f^3\ 6d\ 7s^2$
93	Neptunium	Np	- - - $5f^5\ 7s^2$
94	Plutonium	Pu	- - - $5f^6\ 7s^2$
95	Americium	Am	- - - $5f^7\ 7s^2$
96	Curium	Cm	- - - $5f^7\ 6s\ 7s^2$
97	Berkelium	Bk	- - - $5f^9\ 7s^2$
98	Californium	Cf	- - - $5f^{10}\ 7s^2$
99	Einsteinium	Es	- - - $5f^{11}\ 7s^2$
100	Fermium	Fm	- - - $5f^{12}\ 7s^2$
101	Mendelevium	Md	- - - $5f^{13}\ 7s^2$
102	Nobelium	No	- - - $5f^{14}\ 7s^2$
103	Lawrencium	Lr	- - - $5f^{14}\ 6d\ 7s^2$

The known oxidation states of actinides are :

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
3^+	3^+	3^+	3^+	3^+	3^+	2^+			2^+	2^+	2^+	2^+	2^+
	4^+	4^+	4^+	4^+	4^+	3^+	3^+	3^+	3^+	3^+	3^+	3^+	3^+
		5^+	5^+	5^+	5^+	4^+	4^+	4^+	4^+				
			6^+	6^+	6^+	5^+							
				7^+	7^+	6^+							

The actinides form complexes with high coordination numbers.

Questions

1. What was the basis of classification of elements early in chemical history?
2. How Dobereiner proceeded to classify elements into triads? What were the characteristics of triads?
3. What is meant by Newland's octaves? Discuss discrepancies in this arrangement.
4. Who presented the first Periodic Table of elements? What was the basis of his presentation?
5 Discuss Mendeleev's Periodic Table of elements. Why did he leave gaps and what discrepancies were noticed in the first Periodic Table?
6. What is Periodic Law? Discuss the various aspects of this law.
7. Discuss classification of elements on the basis of electronic configuration.
8. What are atomic numbers? How is Periodic Law correlated to atomic numbers?
9. Discuss various groups and periods on the basis of atomic structure.
10. Justify the position of groups and periods on the basis of electronic configuration.
11. Discuss the periodicity of properties in the modern form of Periodic Table.
12. What are the anomalies found in the Periodic Table?
13. How are the elements with atomic number more than 103 named? Discuss with examples.
14. Discuss merits and demerits of various forms of Periodic Table.
15. Write notes on the following:
    (a) Periods (b) Groups
    (c) Periodic Law (d) Periodic Tables
16. Discuss the quantum mechanical picture of atoms.
17. What are the common oxidation states of lanthanides. Give reasons with specific examples.
18. What are actinides? Give the common oxidation states of actinides.

19. **Write short answers to the following questions:**

(i) State Periodic Law.

(ii) What are the limitations of Mendeleev's Periodic Table?

(iii) What is the correlation in Atomic Numbers and Modern Periodic Law?

(iv) How are elements placed in Periodic Table based on electronic configuration?

(v) What is the significance of the principal and the azimuthal quantum numbers?

(vi) Describe the significance of the magnetic and the spin quantum numbers.

(vii) What are the fundamental particles of atom?

(viii) What is extranuclear structure of atom based on?

(ix) Describe Hund's rule of maximum multiplicity giving suitable examples.

(x) Discuss Aufbau order of filling orbitals. Give electronic configuration of element with atomic number 26.

(xi) Draw correlation between Atomic Structure and Periodic Table.

(xii) What are Periods? Give their significance in the Periodic Table.

(xiii) What do you understand by groups? What is the basis of forming these groups in the Periodic Table?

(xiv) What are man-made elements? How are they named?

20. **Give the correct answer:**

(i) Electrons are distributed among the orbitals in such a way as to give the maximum multiplicity *i.e.*, maximum number of unpaired electrons, which is according to:

(a) Pauli Exclusion principle (b) Hund's rule

(c) Aufbau's Principle (d) none of these

(**Ans**: a)

(ii) Which of the following has the same number of electrons as an alpha particle?

(a) H (b) H^+

(c) H_2 (d) He^{2+}

(**Ans**: d)

(iii) The atoms A and B have the electronic configurations given below:

A: $1s^2 2s^2 2p^6 3s^2$ B: $1s^2 2s^2 2p^4$

Which of the following compounds are they likely to form?

(a) AB (b) AB_2

(c) A_2B (d) A_2B_4

(**Ans**: a)

(iv) Which of the following represents the configuration of the three electrons of highest energy for the ground state of an element in Group III?

(a) $1s^2 2s^1$ (b) $1s^2 2s^1 2p^1$

(c) $3p^3$ (d) $4s^2 4p^1$

(**Ans**: d)

(v) Which of the following electronic configurations represents an element that forms a simple ion with a charge of −3?

(a) $1s^2 2s^2 2p^6 3s^2 3p^1$ (b) $1s^2 2s^2 2p^6 3s^2 3p^3$

(c) $1s^2 2s^2 2p^1$ (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

(**Ans**: b)

(vi) What is the atomic number of an element that has four unpaired electrons in its ground state?

(a) 6 (b) 14

(c) 22 (d) 26

(**Ans**: d)

(vii) Which of the following ions has more electrons than protons?

(a) He^+ (b) H_3O^+

(c) H^+ (d) OH^-

(**Ans**: d)

(viii) Which of the following ions contains an unpaired electron?

(a) Ca^{2+} (b) Cu^{2+}

(c) K^+ (d) Zn^{2+}

(**Ans**: b)

(ix) Which of the following would, on losing an electron, have the half-filled set of *p*-orbitals?

(a) N (b) Li

(c) O (d) F

(Ans: c)

(x) What is the electronic configuration of the atom of the element which is isoelectronic with H_2S?

(a) $1s^2\ 2s^2\ 2p^6$ (b) $1s^2\ 2s^2\ 2p^6\ 3s^2$

(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ (d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(**Ans**: d, because S^{2-} in H_2S has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$)

(xi) For which element does its ground state atom has no paired *p* electrons?

(a) C (b) O

(c) Mg (d) S

(Ans: a)

(xii) What kind of orbital must an electron with a principal quantum number $n = 2$ may occupy?

(a) an *s*-orbital (b) *s* or *p*-orbital

(c) *p*-orbital (d) *d*-orbital

(Ans: b)

(xiii) Which particles are the same for the two nuclides $^{40}_{18}Ar$ and $^{40}_{19}K$?

(a) the number of electrons

(b) the number of neutrons

(c) the number of nucleons (protons & neutrons)

(d) the number of protons

(Ans: c)

(xiv) Which of the following ions contain five unpaired *d*-electrons?

(a) Cr^{3+} (b) Fe^{3+}

(c) Cu^{2+} (d) Ni^{2+}

(Ans: b)

(xv) Which statement is correct about the composition of an atom of the gallium isotope $^{68}_{31}Ga$ used to detect tumours?

(a) it has 37 neutrons (b) it has 32 protons

(c) it has 32 electrons

(d) it has 4 electrons in outer shell

(Ans: a)

(xvi) An ion contains 42 protons. What is the electronic configuration of the ion?

(a) $[Ar]\,3d^{10}\,4s^2\,4p^6\,4d^4$ (b) $[Ar]\,3d^{10}\,4s^2\,4p^6\,4d^2$

(c) $[Ar]\,3d^{10}\,4s^2\,4p^6\,4d^6$ (d) $[Ar]\,3d^{10}\,4s^2\,4p^6\,4d^8$

(Ans: c; with 42 electrons)

(xvii). Carbon-14 is radioactive and is used by archaeologists in carbon dating. Which of the following species has both the same number of neutrons and the same number of electrons as an atom of C-14?

(a) $^{14}N^+$ (b) $^{16}O^{2+}$

(c) $^{17}F^+$ (d) ^{28}Si

(Ans: b; 6 electrons & 8 neutrons)

(xviii) Which of the following statements about the *s*, *p* and *d* orbitals of principal quantum numbers are true?

(a) each *s* orbital can have a maximum of two electrons.

(b) a transition metal arises from the filling of *d* orbitals.

(c) a *p* orbital has higher energy than the *s* orbital of the same principal quantum number.

(d) a *d* orbital has lower energy than *p* orbital.

(Ans: a)

(xix) Which of the following statements about the two isotopes $^{32}_{15}P$ and $^{32}_{16}S$ are correct?

(a) P has more neutrons than S.

(b) on adding a neutron to P, sulphur is produced.

(c) both P and S contain 32 electrons.

(d) both P and S contain 32 protons.

(Ans: a)

(xx) Which of the statement is correct?

(a) the nucleon number of an element is the number of neutrons in an atom.

(b) the proton number is always equal to number of neutrons.

(c) the electron number is always equal to number of neutrons.

(d) the charge of an electron is equal to that of proton.

(Ans: d)

(xxi) Which of the following is the strongest reducing agent?

(a) Cl^- (b) Ar

(c) K^+ (d) Ca^{2+}

(Ans: a)

(xxii) Which of the following elements would be expected to form the largest ion with a noble gas electronic configuration?

(a) Al (b) Cl

(c) P (d) K

(Ans: c)

(xxiii) The chloride of one of the following elements does not react with water or dissolve in it. Which of the following element it could be?

(a) aluminium (b) phosphorus

(c) carbon (d) silicon

(Ans: c)

(xxiv) When either chlorine or hydrogen chloride is passed over a heated metal, M, the chloride is produced. An aqueous solution of this chloride is acidic. Which is the following metal, M?

(a) aluminium (b) copper

(c) iron (d) calcium

(Ans: a)

(xxv) Which of the following set of elements have giant metallic structures?

(a) Na Mg Al (b) Mg Al Si

(c) C Si Sn (d) Si P S

(Ans: d)

(xxvi) Fruit juices are often packed in aluminium cans. Why aluminium is considered to be the most suitable?

(a) aluminium can be recycled.

(b) aluminium has a very low density.

(c) aluminium is a cheap metal.

(d) aluminium is resistant to corrosion.

(Ans: d)

(xxvii) The element has a low atomic number. It forms an amphoteric oxide and its chloride when anhydrous is readily hydrolysed in water. To which group the element belongs?

(a) Group II (b) Group III

(c) Group IV (d) Group V

(Ans: b)

(xviii) Which property of the first six elements of Period 3 (sodium, calcium, aluminium, silicon, phosphorus, sulphur) continuously increases numerically?

(a) atomic radius

(b) first ionization energy

(c) maximum oxidation number in oxide

(d) melting point

(Ans: c)

21. **Fill in the blanks:**

(i) One of the first attempts to arrange elements and compounds on the basis of their origin was made by _____________.

(ii) The concept of groups of three elements or triads was developed by _____________.

(iii) Chemically similar elements reoccur in _____________ when arranged in order of increasing atomic weights.

(iv) Meyer produced a table showing periodic arrangement of the elements by plotting ______________ of elements against their relative ______________.

(v) Mendeleev arranged the elements into ______________ rows called periods and eight ______________ called groups.

(vi) The properties of elements are ______________ of their atomic weights.

(vii) X-rays are produced when cathode rays strike ______________.

(viii) The principal quantum number describes the motion of an electron in ______________.

(ix) The Azimuthal quantum number describes the ______________ of an orbit.

(x) ______________ measured the nuclear charges on the nucleus.

(xi) Fundamental particles of atom are:

(a) (b) (c)

(xii) ______________ proposed a fundamental particle known as meson.

(xiii) Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of ______________ electrons.

(xiv) Elements beyond ______________ are not found in nature.

❀ ❀ 1 ❀ ❀

2

GROUP TRENDS AND PERIODIC PROPERTIES

We have studied the Periodic Table and noticed that the arrangement of elements in the Periodic Table is based on atomic number and the outer electronic configuration. It results in two patterns emerging in the properties of the elements and their compounds:

(a) Elements with similar chemical properties are all in the same groups. For example, alkali metals are members of Group IA and halogens are in Group VIIA.

(b) The most electropositive elements and thus the most reactive metals are in the bottom left-hand corner of the table. In general, the electropositivity of elements increases down a group on the left of the Periodic Table and decreases from left to right in a period on crossing the periods. Consequently, the *s*-block metals tend to form cations readily and thus form ionic compounds. The *p*-block elements in the centre of the table tend to form covalent compounds only. The more electronegative *p*-block elements on the right side of the table can form either covalent or ionic compounds depending upon the atoms with which they react. The inert or noble gases, of course, with their stable electronic configuration (where outermost *p* orbitals are completely filled with 6 electrons) form relatively few compounds (Table 2.1).

TABLE 2.1

Trends in Compound Formation

Electropositive nature decreases (Electronegativity increases) →

Electropositive Nature Increases ↓

Electronegativity Increases ↑

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
Form cations and thus ionic compounds.		Form covalent compounds			Form either covalent or form ionic compounds.	

The maximum attainable oxidation states of elements also exhibit a periodic variation. They tend to increase on crossing a period until maximum is reached in Group VII.

The *d*-block elements tend to be ionic with a high degree of covalent character. They tend to form complex ions. The *d*-block elements exhibit variation in oxidation states. The maximum oxidation states usually occur in the middle of the series.

The variation and periodicity can well be described in terms of physical properties such as sizes of the atoms, ionization potentials, electron affinities, electronegativities, etc. Therefore, these properties will first be described.

SIZE OF ATOMS AND IONS:

If we look at the Periodic Table, we find a gradual decrease in the atomic size with increasing atomic number in a period. As we proceed across the Periodic Table, a progressive addition of electrons takes place in the orbitals having very nearly the same energy. The result is that the increased nuclear charge will pull the entire electron cloud to an increasingly greater extent. It has been found that the decrease in size is more pronounced in *s* orbitals and the relative decrease in size becomes progressively smaller for electrons in *p*, *d* and *f* orbitals. When we move to the next period, electronic addition takes place and the size increases. Thus, the size of the atom will be more for the first member of each period and will decrease as we go across the Periodic Table from left to right as shown in Table 2.2.

TABLE 2.2

Sizes of the atoms and their ions (pm)

Atomic	Na	Mg	Al	Si	C	N	O	F
Size	151	136	125	117	77	70	66	64
Ionic	Na^+	Mg^{+2}	Al^{3+}	Si^{4+}	C^{4-}	N^{3-}	O^{2-}	F^-
Size	95	65	50	41	260	171	140	136

It is seen in the above table that for the iso-electronic series C^{4-}, N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+} and Si^{4+}, the contraction in size of ions is more as compared to the trend in parent atoms. This is due to increasing nuclear charge on the ions.

A decrease in size of the atom in a period is due to a shrinkage caused by the increased nuclear charge resulting in an increased attraction for all the electrons in quantum shell. Similarly, the increase in size of the atoms in a group is due to the introduction or addition of new shells of electrons which outweigh the effect of increased nuclear charge. In Table 2.2, a decrease in size is observed in passing from a neutral atom to a positive ion. This is attributed to the reduction in the number of shells of electrons with the loss of electrons from the outermost shells and the greater attraction of the remaining ones by the nucleus. A positive ion thus has a smaller size than the corresponding neutral atom. More the electrons are removed, smaller will be the size. On the other hand, a negative ion is bigger due to the decreased attraction of the outer electrons to the nucleus because of the greater number of negative charges, reduced effect of nuclear charge and the expansion of the electronic cloud.

The sizes of atoms are expressed in terms of atomic radii, ionic radii, covalent radii and Van der Waal's radii.

The size of an atom is measured by the most probable distance from the nucleus to the outermost shell. This distance is called the atomic radius of an atom. Various factors effect the atomic radii

ATOMIC RADII:

Owing to the wave nature of the electron, an atom does not have strictly defined boundaries. So that it is impossible to determine its absolute dimensions. In practice, we are forced to deal with the radii of atoms linked together by some type of chemical bond. The atomic radius of an atom is defined as half of bond length or the distance between two identical atoms in a chemical bond.

TABLE 2.3

Molecule	Bond Length (pm)	Atomic Radius (pm)
H – H	110	55
F – F	144	72
Cl – Cl	202	101
Br – Br	266	133

The relationship between atomic radii of elements and bond length are given in Table 2.3. Within a period the radii of the atoms decrease as the charge on the nucleus increases. The greatest decrease is observed in the elements of the short periods, since their outer shells are filled. In longer periods we observe a smoother reduction of radii within the families of *d* and *f* elements (This is generally known as *d* or *f* or lanthanide contraction).

The atomic radii of many of the regular elements in the Periodic Table are given in Table 2.3. The atomic radii are found to decrease across a period and increase down a group. The decrease in atomic radius across a period is due to the fact that the valence electrons in atoms experience a greater and greater attractive force as the nuclear charge increases resulting in the contraction of atoms and reduction of radius. For example, all atoms of the third period have a neon core, $1s^2\ 2s^2\ 2p^6$. Thus Na can be represented as [Ne] $3s^1$, Mg as [Ne] $3s^2\ 3p^1$ and so on. Experimental evidence strongly indicates that the neon core of the third period elements is not very much disturbed by the addition of electrons to the $3s$ and $3p$

orbitals. As the atomic number increases in a period, the nuclear charge on the core increases and the more attractive forces between nuclear and electronic charge (in the same orbit) result in contraction of atom and therefore, reduction in atomic radii from left to right in the period.

The increase in atomic radii down the group is due to increase in nuclear charge and simultaneous increase in the number of energy shells. This results in the increase of atomic radii down a group.

The radii of atoms in general increase with the increase of atomic number; but to a large extent in the *s* and *p* sub-groups than in the *d* subgroups, as shown in Table 2.4.

TABLE 2.4

Element	At. No.	At. radius (pm)	Element	At. No.	At. radius (pm)
As	33	148	V	23	134
Sb	51	161	Nb	41	145
Bi	83	182	Ta	73	146

As is seen in Table 2.4, the atomic radius increases in the arsenic sub-group by 21 pm from Sb to Bi, while in the vanadium sub-group it increases only by 1 pm between Nb and Ta.

This should be known that radii of atoms and ions of *d* elements in the fifth and sixth periods of a given sub-group are approximately equal. This is explained by the fact that the increase in radii due to the increase in number of electron shells in passing from the fifth to the sixth period is compensated by the 4*f* contraction (lanthanide contraction) due to the filling of the 4*f* sub-shell of elements of the sixth period. Because of the similar structure of their valency electron shells and the approximately equal radii of their atoms and ions, the properties of the *d* block elements are particularly close to one another.

(a) Variation of Atomic Radii Within a Group of the Periodic Table:

The distance of an electron from the nucleus of an atom depends primarily on the principal quantum number, (n = 1, 2, 3, ······ which represents the number of orbit or shell). Higher the value of n, the larger the atom. In other words, more electronic shell in an atom, the larger is the atomic radius. Thus the atomic radii increase down a group with increasing size of the atoms of elements in the same group.

(b) Variation of Atomic Radii Within a Period in the Periodic Table:

With increasing atomic number from left to right in a period, the effect of the effective nuclear change on the incoming electron in the same shell increases resulting in decrease of atomic radius. The result is that the atomic radius decreases from left to right across a period in the Periodic Table.

(c) Variation of Atomic Radii Within a Transition Series:

In transition elements, additional electrons go into inner *d* orbitals, which participate effectively in screening the outer-shell electrons. There is initial decrease in atomic radii for the first two or three members but following that atomic radii change little in a transition series.

The unit that has long been used to describe atomic dimensions is the angstrom unit, A°. In SI units, the either nanometer (nm) or picometer (pm) is used.

$$1A^\circ = 1 \times 10^{-10}\,m = 0.10\,nm = 100\,pm.$$

For bonded atoms, we customarily speak of atomic radii, covalent radii, ionic radii and metallic radii (in case of metals). For atoms that are not bonded together, the radius is described by Van der Waals' radii.

COVALENT RADII:

The covalent bonds are formed from the overlap of the orbitals in the region between the centres of two atoms. As a result of it the nuclei of bonded atoms approach each other more closely than do the nuclei of non-bonded atoms. ***The covalent radius of an atom is taken as one half the distance between the nuclei of two identical atoms forming a single covalent bond.***

Thus we can say that the bond distance between the two atoms A — B should be the arithmetic mean of the bond lengths A — A and B — B. Take the case of covalent radius of carbon which is one half the experimentally determined distance between C — C single bond. This gives the value of 77 pm. Similarly, for the Si — Si linkage the covalent radius comes to be 117 pm. Now if we consider the bond distance between carbon and silicon, we should expect a bond length of 194 pm. This is in very good agreement with the experimentally determined C — Si distance of 193 pm in carborundum (silicon carbide). Covalent radius of C — Si bond is half of the bond length.

The covalent radii decrease with increase in bond order because there is corresponding decrease in internuclear distance. Thus in carbon, the internuclear distance and atomic radii decrease with increase in bond.

Bond Order	Inter Nuclear Distance (pm)	Atomic Radius (pm)
C – C	154	77
C = C	134	67
C ≡ C	120	60

Although the above rule works in many simple diatomic molecule, but this is not generally the case. Very often there is a considerable deviation from the expected result. This deviation can be attributed to many factors like multiple bonds, ionic character and various possible hybridized orbitals that determine the geometry of covalently bonded molecules. The covalent radii can be named in terms of their geometry. For instance, covalent radii for the tetrahedral structure are called tetrahedral radii. Similarly, for octahedral structures, these are known as octahedral radii.

The covalent radii are usually classified as either normal radii, tetrahedral radii, octahedral radii, square radii or metallic radii as the case may be. The metallic radius is invariably larger than the single bond covalent radius for the same atom. Atomic radii and single bond covalent radii of some metals and non-metals are given in Table 2.5.

TABLE 2.5

Comparison of Atomic Radii and Single Bond Covalent Radii for Some Metals and Non-Metals (pm)

Metals	Atomic radius	Single bond covalent radius	Non-Metal	Atomic radius	Single bond covalent radius
K	231	202	C	77	77
Ba	217	198	P	110	110
La	188	169	S	104	104
Zr	157	145	Br	115	114
Pd	138	128			
In	162	150			

In the above table, the discrepancies in the values of radii are due to difference in the electronegativities between the bonded atoms. In order to compensate for this ionic difference, many empirical formulae have been suggested by different workers like Schomaker and Stevenson. According to their equation, the covalent energy distance r°_{AB} which is related to the actual bond length r_{AB} and the bond energy E_{AB} is given by

$$r^{\circ}_{AB} = r_{AB} + \frac{1}{2} \log_{10} E_{AB}$$

Except for hydrogen, it is in agreement with the experimental results.

IONIC RADII:

When neutral atoms gain or lose electrons completely, ions are obtained. Positive ions will be smaller than their parent atoms and negative ions will be larger. This is readily understood in terms of the number of electrons, the nuclear charge holds. For a positive ion, the nuclear charge is exerting influence on a few electrons and hence pulls them all closer together, whereas in the case of a negative ion the nuclear charge must act upon more electrons so that each is held less tightly and the electron cloud expands. As shown in Table 2.6, the radius of the ion decreases with an increase in the number of electrons lost and size of ion.

TABLE 2.6

Ionic Radii (pm)

	H^-	Li^+	Be^{2+}	B^{3+}	C^{4+}			
	154	60	31	20	15			
O^{-1}	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
140	136	95	65	50	41	34	29	26
S^{-2}	Cl^-	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
184	181	133	99	81	68	59	52	46
Se^{-2}	Br^-	Rb^+	Sr^{2+}	Y^{3+}	Zi^{4+}	Nb^{5+}	Mo^{6+}	Tc^{7+}
198	195	148	113	93	80	70	62	—
Te^{-2}	I^-	Cs^+	Ba^{2+}	La^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+}
221	216	169	135	115	79	71	65	50

It is not simple to calculate ionic radii as in the case of covalent radii since like atoms do not form ionic bonds with each other. The measured distance between the nuclei held by ionic bonds cannot be halved to give the desired ionic radii. The only way radii can be assigned is to determine how closely the centres of the two atoms or ions actually approach each other in solid substances and then to assume that such a distance is equal or closely related to the sum of the radii of the two atoms or ions. Even this procedure is ambiguous and many assumptions are made to get the desired set of radii. Pauling calculated the radii of the four salts NaF, KCl, RbBr and CsI, in each of which the cation and anion are isoelectronic and the radius ratio ($r$cation / $r$anion = r^+ / r^-) should be similar in all four cases. Two assumptions were made:

(a) The cation and anion were assumed to be in contact so that the internuclear distance was equal to the sum of the radii.

(b) For a given noble gas electronic configuration, the radius is assumed to be inversely proportional to the effective nuclear charge felt by the outer electrons.

The application of these rules can be illustrated by taking the case of NaF in which the internuclear distance is 231 pm. Hence

$$r\text{Na}^+ + r\text{F}^- = 231 \text{ pm}$$

Now using the rule developed by Slater to estimate how much the various electrons in the $1s^2\ 2p^2\ 2p^6$ configuration shield the outer electrons from the nuclear charge, we obtain the value 4.15 for the shielding parameter. The effective nuclear charges Z, felt by the outer electrons for Na^+ with $Z = 11$ will be

$$11 - 4.15 = 6.85$$

and for F^- ion with $Z = 9$

$$9 - 4.15 = 4.85.$$

According to the rule (b), the radius ratio rNa^+ / rF^- must be inversely proportional these numbers. Thus

$$rNa^+ \phi\, rF^- = \frac{4.85}{6.85} = 0.71.$$

Solving this and the previous equation for the sum of the radii simultaneously, we get

$$rNa^+ = 95 \text{ pm}$$

$$rF^- = 136 \text{ pm}$$

The radii for a number of important ions given by this procedure are given in Table 2.6.

Among the five species Na, Mg, Ne, Na^+ and Mg^{2+} the Na atom is larger than Mg. The ionic radii are smaller than atomic radii because of the removal of electrons and resulting in the reduction of size of the ion. Na^+, Mg^{2+} and Ne are said to be ***iso-electronic*** because they have the same number of electrons (10) with identical configuration ($1s^2\ 2s^2\ 2p^3$). Ne has a nuclear charge of + 10, Na^+ has a nuclear charge of + 11. So Na^+ has a smaller ionic radius due to the attraction between + 11 nuclear charge on to the same number of electrons (10) as compared to that of Ne. Similarly, Mg^{2+} is still smaller because it has a nuclear charge of + 12.

When a non-metal atom gains one or more electrons to form a negative ion (anion) there is an increase in size. The addition of electrons to an atom causes an increase in repulsion among the electrons. The electrons spread out more, and the size of the ion increases. The covalent, ionic and metallic radii are compared in Figure 2.1.

PROBLEM:

The following species are iso-electronic with the noble gas argon. Without reference to figures or tables in the text, arrange in order of increasing size:

$$Ar, Ca^{2+}, K^+, Cl^-, S^{2-}$$

The forces of attraction or pull on energy level of electrons and thus smaller in size. Thus order is:

$$Ca^{2+} < K^{+} < Ar < Cl^{-} < S^{2-}$$

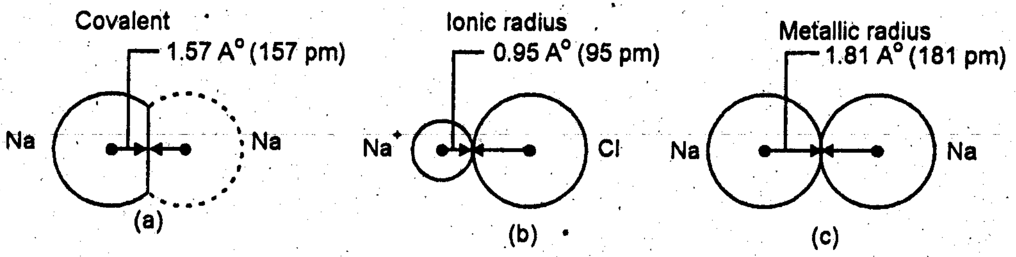


Fig. 2.1. *(a)* ***The covalent radius is one half the distance between the centres of two Na atoms in the gaseous molecule.***

(b) ***The ionic radius is based on the distance between centres of ions in an ionic compound, such as NaCl.***

(c) ***The metallic radius is taken as one half the distance between the centres of adjacent atoms in solid metallic sodium.***

VARIATION OF IONIC RADII IN THE PERIODIC TABLE:

Two general periodic trends are found for ionic radii, (a) Size decrease along a period, (b) Size increase down a group in long form of the Periodic Table as shown in Fig 2.2.

On moving from left to right across a period in the Periodic Table, there is a regular decrease in ionic radii. This is because as the nuclear charge increases and electrons are added to the same energy levels, the increase in nuclear charge draws the electron cloud closer and closer to the nucleus. The rate of decrease in size becomes smaller as the atoms become heavier. A relatively small decrease in ionic radii is observed in transition elements. The rate of decrease in size along the lanthanide series is even less than in the transition series because of addition of electrons in inner '*f*' orbitals which screen out the effect of effective nuclear charge on outer electrons. This small decrease of size along the lanthanides is referred to as the lanthanide contraction.

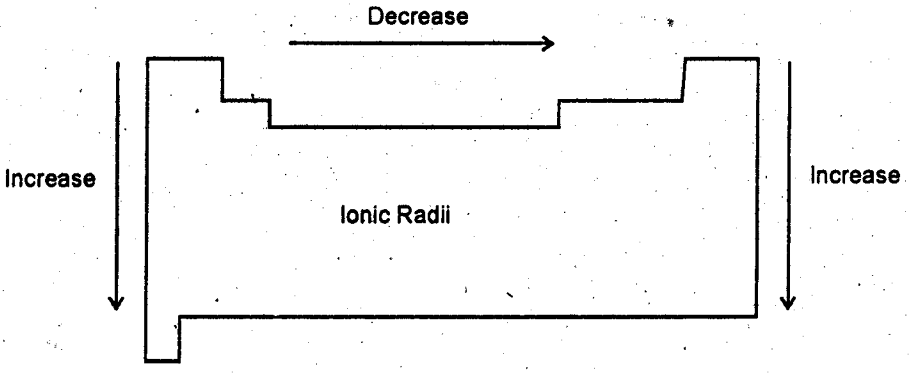


Fig. 2.2. General trend in ionic radii in the periodic table.

VAN DER WAALS' RADII:

In addition to ionic and covalently bonded atoms, there are certain atoms in solids and liquids, which are not bonded to one another either ionically or covalently. For example, noble gases can be liquefied and solidified, hence it is assumed that there are some forces of attraction between these atoms; and since extremely low temperature is required to condense them, this proves that these forces are very weak. Such forces are usually called Van der Waals' forces or London forces. One half of the distance between the atoms of the noble gases such as Krypton (Kr – Kr) is called Van der Waals' radius of Krypton. The Van der Waals' radii are much larger than covalent radii *e.g.*, ionic radius of Br^- ion is 1.25 A°, the covalent radius of Br is 1.15 A° and the Van der Waals' radius of Br is 2.00 A°.

Van der Waals' radii for all elements may be estimated if the distance of closest approach of their atoms to other atoms (when no chemical bond exists between them) and are known from structural studies. For example, in solid bromine, the distance between the non-bonded bromine atoms is 3.90 A°, giving a Van der Waals' radius of 1.95 A°. In case of the molecules with permanent dipole moments, the dipole-dipole attraction will also contribute to the stability of the crystals, but even the closest approach of the two non-bonded atoms can be taken as the sum of their Van der Waals' radii. Some of the van der Waals' radii of non-metallic atoms are given in Table 2.7.

TABLE 2.7

Van der Waals' radii of some non-metallic atoms (pm)

H	110					He	179
N	150	O	140	F	135	Ne	160
P	190	S	185	Cl	180	Ar	192
As	200	Se	200	Br	195	Kr	—
Sb	220	Te	220	I	215	Xe	200

IONIZATION POTENTIAL OR IONIZATION ENERGY, I:

Ionization potential is one of the few fundamental properties which can be measured directly. Atoms can lose electrons. They must absorb energy to bound. The energy that the gaseous atom must absorb in order to separate most loosely held electron from the atom is called ionization energy or ionization potential. ***The ionization potential of an element is defined as the minimum energy required to remove an electron from its isolated atom (in the gaseous state) when at ground level,*** to form a cation *e.g.*,

$$\frac{1}{2} H_2 \longrightarrow H^+ + e^- \Delta H$$

The ionization potential is expressed in electron volts/atom or in kilocalories per mole or kJ/mole. The symbol I_1 stands for first ionization potential.

If second electron is ejected from the singly positive ion, it is known as second ionization potential, I_2 *e.g.*,

$$Mg(g) \longrightarrow Mg^+(g) + e^-, \qquad I_1 = (738 \text{ kJ/mole})$$
$$Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-, \qquad I_2 = (1451 \text{ kJ/mole})$$

Similarly, the third ionization potential relates to a process in which one electron is removed from +2 ion.

The ionization potential depends upon the following factors:

1. The magnitude of the nuclear charge.
2. The distance of the outermost electron from the nucleus *i.e.*, atomic radius.
3. The shielding effect of the underlying shells of electrons.
4. The extent to which the outer electron penetrates the charge cloud set up by the low-lying electrons.

It has been found that the degree of penetration of electrons in a given principal quantum level decreases in the order $s > p > d > f$. This corresponds to the extent of binding of the various electrons. An *ns* electron is more tightly bound than any *np* electron, which in turn, is more tightly bound than an *nd* electron etc.

The periodicity of the ionization potential can be seen in the plot between the first ionization potential and atomic number as shown in Figure 2.3.

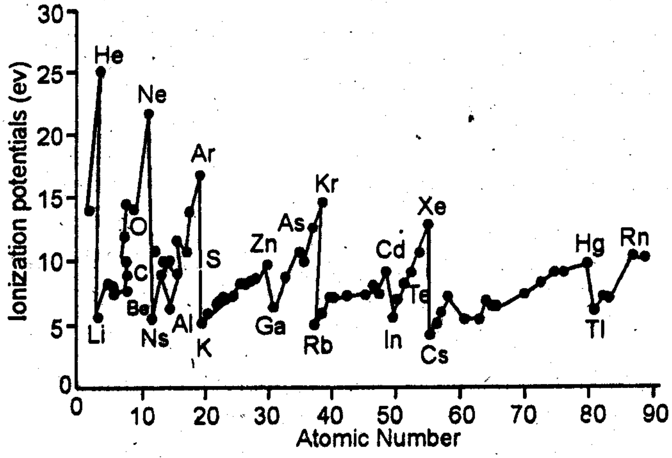


Fig. 2.3.

In this plot the minima occupied by the IA elements on the curve *i.e.*, alkali metals, are consistent with the lone pair valence electron being at a relatively large distance from the nucleus in addition to being well-shielded from it by the underlying inert gas configuration. Gradual increase occurs as we proceed across the given period in the Periodic Table until maxima are reached at the inert gases on the extreme right corresponding to the peaks in the curve. The minor irregularities which appear in the general trend are associated with the stability of filled, half-filled or empty orbitals.

Very little change in the ionization potential is noticed across a given transition series. This may be attributed due to the increased nuclear charge which is offset by increased screening by the additional electrons entering low-lying *d* orbitals.

The peaks which occur at zinc, cadmium and mercury and the minima which occur at gallium, indium and thallium are most likely the result of filled *s* sublevel stability and the very effective screening of the *s* electron pair.

Ionization energies decrease as the sizes of atoms increase. Ionization potential values of alkali metals are given in Table 2.8.

In the Periodic Table, the ionization potential decreases in the groups, and this decrease is rapid up to 4th period, less up to sixth and slight from 6th to seventh. Effect from first to 4th period is due to the effect of additional shells which outweighs the attraction due to the increased positive charge on the nucleus. From 4th to sixth period in each step, 18 protons are added up and attractive influence is increased. The lower the ionization potential values, the more metallic is the element.

TABLE 2.8

Ionization Potential Values

	ev/atom	kJ/mole
Li ($2s^1$)	5.39	520
Na ($3s^1$)	5.14	495
K ($4s^1$)	4.34	418
Rb ($5s^1$)	4.17	403
Cs ($6s^1$)	3.89	375

The ionization potential increases from left to right when we move along a period. The number of protons in the nucleus and the nuclear charge goes on increasing with an increase in the atomic number. The attractive influence of the nucleus on the shells increases and the electrons become more tightly bound and difficult to remove. Thus energy required to eject an electron increases and there is an increase in the ionization potential from left to right. This is shown in the Table 2.9.

TABLE 2.9
First Ionization Potential (KJ/mole)

H							He
1312							2373
Li	Be	B	C	N	O	F	Ne
520	897	800	1090	1398	1312	1678	2083
Na	Mg	Al	Si	P	S	Cl	Ar
492	733	578	781	1061	1003	1254	1524
K	Ca	Ga	Ge	As	Se	Br	Kr
418	589	578	760	946	940	1142	1349
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	452	557	707	833	869	1007	1170
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
376	493	588	714	703	813	—	1036
Fr	Ra	Ac					
—	508	—					

ELECTRON AFFINITIES:

Electron affinity is defined as the minimum energy released when an electron is absorbed in the lowest energy state of an isolated atom to form an anion. Electron affinities similar to ionization potentials are expressed in electron volts or kJ/mole, *e.g.*,

$$A_{(g)} + e^-_{(g)} \longrightarrow A^-_{(g)} \qquad Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} + 384\ KJ$$

$$A^-_{(g)} + e^-_{(g)} \longrightarrow A^{2-}_{(g)} \qquad O_{(g)} + e^- \longrightarrow O^-_{(g)} - 142\ KJ$$

$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} + 780\ KJ$$

When a second electron is absorbed to a uni-negative ion, the incoming electron is repelled by the –ve ion and energy is absorbed in this process, *i.e.*, it is an endothermic process. For example, E.A. for O^{-1} is 1.48 e.v. and for O^{2-} is – 7.3 e.v. as shown in Table 2.10.

TABLE 2.10
Electron Affinities Data For Some Elements (KJ/mole)

H							
74							
Li	Be	B	C	N	O	F	Ne
52	– 57	19	120	9	141	332	0
Na	Mg	Al	Si	P	S	Cl	Ar
71	– 28	28	100	57	199	348	0
For 2 electrons						Br	Kr
O		S		Se		324	0
– 704		– 328		– 405		I	Xe
						295	0

There are only a few cases which have the positive values of E.A. These are mainly lighter and non-metallic elements. Larger positive values are shown only by those elements which have one or two vacancies in a valence shell close to the nucleus. Electron affinity increases with the increase in atomic number within a period and decreases with increasing atomic number within a group of the periodic table.

As shown in the table, Be and Mg have low values of E.A. It is because Be and Mg atoms have completely filled '*s*' sub-shells and thus an electron added will occupy a sublevel of higher energy which is not so easy and hence these atoms have low E.A. If both the *s* and *p* orbitals are filled up, the incoming electrons will enter into still higher energy levels and the E.A. will be zero as is shown by inert gases. In case of nitrogen and phosphorus the orbitals are half-filled and extra-stable. The E.A. for them would be less than that expected otherwise.

It is also observed that E.A. decreases from lighter to heavier elements in a given group of the Periodic Table. This is quite clear in Cl, Br and I. The representative member of each period *i.e.*, Li, Be, B, C, N, O and F have lower electron affinity than the next heavier members. It is because the incoming electrons are repelled by the electrons already present in the atom. This effect is unusually high for the smaller atoms in the 2nd period. Second and higher order E.A. are all negative in sign because of the repulsion between the electrons being added and the negatively charged ions already present.

The elements of group VIIA(17), halogens have relatively small size and the nucleus has rather strong attraction for electrons. Addition of electrons also produces the stable noble gas configuration.

It is difficult to determine the electron affinity as compared to ionization potential. Electron affinities can be obtained by using Born-Haber cycle (See Chapter 3).

CHARGE DENSITY OF IONS:

(Polarization and Polarizability). ***The ratio of the size of an ion to its charge is called Charge Density.*** Generally positive ions have high charge density and smaller size and negative ions have larger size but low charge density (except F^{-1} and O^{2-} ions).

When two ions A^+ and B^- (perfect spheres with equal charge) are brought close to each other, the positive ion attracts the electrons on the negative ion but repels its nucleus; thus distorting its shape. The negative ion is said to be **polarized** as shown in Figure 2.4.

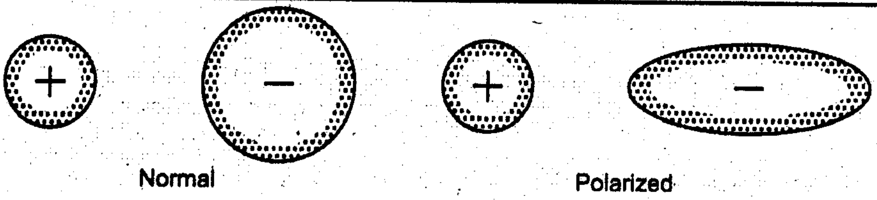


Fig. 2.4.

If the polarization is quite small, the bond is ionic; if the degree of polarization is large, electrons are drawn to the positive ion and an appreciable covalent character results. The extent of distortion depends on both polarizing power of a positive ion and ***the susceptibility of polarization of the other ion i.e., its polarizability.*** Generally the polarizing power increases as ions become smaller and more highly charged.

The polarizability of a negative ion is greater than that of a positive ion, since the electrons in the former case are weakly held due to the weaker effective nuclear charge. Large negative ions with low charge density are more polarizable than the smaller ones. The trends of the polarizability are given by **Fajan's Rule** which states that the covalent bonding is favoured by:

(a) Small positive ions *e.g.*, Li^{1+}, Be^{2+}, Al^{3+}.

(b) Large negative ions *e.g.*, I^-, Br^-, Cl^-.

(c) Large charges on either ions *e.g.*, Al^{3+}, Mg^{2+}.

$AlCl_3$ is more covalent than $MgCl_2$. The former sublimes whereas, the latter melts at 112°C.

(d) The positive ions (if they do not have a noble gas electronic configuration).

Examples:

1. The large iodide and bromide ions are relatively distorted by the small positive ions. For example, Mg^{2+}, Fe^{3+} and Al^{3+} are more effective polarizing agents.

2. More covalent character is shown by compounds made up of small positive and large negative ions.

   e.g., $AlCl_3$, $FeCl_3$, $SnCl_4$ are the compounds which show relatively more covalent character.

3. A gradual change from covalent to ionic bond character is shown by the hydrogen halides from HI to HF.

		HI	HBr	HCl	HF
Ionic Character	=	5 %	11 %	17 %	43.6 %

4. The ions with charge greater than 3+ do not exist as discrete free particles. For example, C^{4+}, P^{5+}, S^{6+} and Cl^{7+} do not exist, because such ions are easily attracted to the negative ions to form covalent molecules. However, their oxidation states 4^+, 5^+, 6^+ and 7^+ are exhibited in the corresponding covalent compounds such as CCl_4 . CO_2, PCl_5, SF_6, SO_3 and Cl_2O_7.

Similarly, when $MgSO_4$ is dissolved in water, Mg^{2+} and $SO^{2-}{}_4$ ions will be produced. The S^{6+} and O^{2-} ions do not exist because these have smaller size and high charge. Even if they are generated, they will not exist in contact with water molecules as shown in the following reaction

$$O^{2-} + H_2O \longrightarrow 2OH^{1-}$$

ELECTRONEGATIVITY:

Electronegativity is defined as the relative tendency of an atom in a molecule to attract a shared pair of electrons. Electronegativity depends upon the atomic structure and the number and nature of atoms tending to combine together. Generally small atoms are more electronegative. The atoms with nearly filled shells of electrons have higher electronegativity than those with less than half-filled or scarsely filled. For example, alkali metals are the elements with scarsely filled shells and are least electronegative. Halogens, on the other hand, are the elements with nearly filled shells and hence they are the most electronegative.

It must be made clear that electronegativity is not the same as electron affinity. Electronegativity is a relative property of atoms in their molecules whereas electron affinity is a property of isolated atoms.

In the Periodic Table, electronegativity decreases when we descented from top to bottom in a periodic group with a few minor exceptions in the transition elements. Electronegativity decreases due to the successive appearance of electronic shells in each step forward. The addition of extra shells in larger atoms screen the shared pair from the nucleus and the pair is attracted less by the element in the combined state. Electronegativity values increase from left to right in the periods.

Electronegativity is not a directly measurable because it is not a precise quantity. The electronegativity of an element is taken relative to the value of other elements. Electronegativity of an element refers to its most common oxidation state. Higher the oxidation of an element, more strongly will it attract the electron.

ELECTRONEGATIVITY SCALES:

Several methods for the estimation of relative electronegativity have been used.

THE PAULING'S SCALE:

Pauling was the first to introduce the concept of electronegativity. He defined electronegativity difference for two atoms A and B in a molecule A — B, in terms of deviation (Δ) of the A — B bond energy from the geometric mean of A — A and B — B bond energies.

If two atoms A and B have the same electronegativity, the bond energy of the A — B bond would be equal to the geometric mean of A — A and B — B bond energies. This would be so since the electrons in the bond would be equally shared in purely covalent bonds in all three cases. Thus, the A — B bond energy could be expressed as

$$E_{A-B} = [E_{A-A} \times E_{B-B}]^{1/2}$$

Pauling, however, observed that for the majority of A — B bonds the energy exceeds the geometric average because generally the atoms A and B have different electronegativities and there is an ionic contribution to the bond in addition to the covalent one.

Let the difference between A — B bond energy and the geometric mean of A — A and B — B be Δ.

$$\Delta = E_{A-B} - [E_{A-A} \times E_{B-B}]^{1/2}$$

In H — F, molecule, H — H and F — F bond energies are 436 KJ mol^{-1} and 158 KJ mol^{-1} respectively. Their geometric mean E_{A-B} is

$$= (158 \times 436)^{1/2}$$

$$= 244 \text{ KJ mol}^{-1}$$

The experimentally determined bond energy is 566 KJ mol^{-1}. The difference is 322 KJ mol^{-1}. This excess energy is known as the ionic resonance energy. This energy can be used as an empirical basis to determine the electronegativity differences. If X_A and X_B represent the electronegativities of A and B, respectively. The difference $X_A - X_B$ could be related to Δ as:

$$X_A - X_B = \frac{\Delta}{(96.5 \text{ KJ mol}^{-1})^{1/2}}$$

The factor 96.5 KJ mol^{-1} converts Δ from KJ mol^{-1} (SI units) to electron volts (ev) per molecule.

Examples: The bond energies of H_2, Cl_2 and HCl are,

$$E_{H-H} = 436 \text{ KJ mol}^{-1}$$

$$E_{Cl-Cl} = 243 \text{ KJ mol}^{-1}$$

$$E_{H-Cl} = 431 \text{ KJ mol}^{-1}$$

What is electronegativity difference $X_H \times X_{Cl}$-.

Solution:

$$\Delta HCl = E_{H-Cl} - [E_{H-H} \times E_{Cl-Cl}]^{1/2}$$
$$= 431 - [436 \times 243]^{1/2}$$
$$= 106 \text{ KJ mol}^{-1}$$
$$X_H - X_{Cl} = \left[\frac{\Delta HCl}{96.5 \text{ KJ mol}^{-1}}\right]^{1/2}$$
$$= \left[\frac{106}{96.5}\right]^{1/2} = 1.05$$

The value devised by L. Pauling are given in Table 2.11.

From Table 2.11 it appears that the electronegativity values gradually increase as we pass from one element to the other element in a horizontal period. Similarly, in a group going from lighter to the heavier elements, the trend is generally a slow decrease in the electronegativity. However, a few exceptions are seen particularly in the case of transition elements.

TABLE 2.11

Electronegativities of the Elements (Pauling's Values)

Li	Be											B	C	N	O	F
1.0	1.5											2.0	2.5	3.0	3.5	4.0
Na	Mg											Al	Si	P	S	Cl
0.9	1.2											1.5	1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Th	Pb	Bi	Po	At
0.7	0.9	1.1–1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2

MULLIKEN'S SCALE:

According to Mulliken, electronegativity is determined, partly by the tendency of an atom to bind an additional electron and partly by its tendency to hold on to those it already has. On this scale, the electronegativity is taken as the mean value of the first ionization energy and the first electron affinity. Both the quantities are given a positive value if loss of electron involves absorption of energy and gain of electron involves release of energy. Thus,

$$X_M = \frac{IE + EA}{2}$$ [IE = Ionization Energy,
EA = Electron Affinity]

The commonly accepted values in terms of Pauling Scale may be obtained from the relation.

$$\text{E.N.} = \frac{\text{Ionization energy} + \text{Electron affinity (in KJ mol}^{-1}\text{)}}{544}$$

A complete electronegativity scale cannot be constructed based on Mulliken's concept since electron affinities (EA) are known for only a few atoms.

ORBITAL ELECTRONEGATIVITY:

Electronegativity is believed to depend on the nature of orbitals involved in bonding. For example, *s*-orbital penetrates nearer to the nucleus than a *p*-orbital and the former contributes more electronegative character. The orbital electronegativities, therefore, depend on the percentage of *s* and *p* character in sp^3, sp^2 and *sp* hybridization. Thus for carbon atom, the electronegativities (on Pauling's Scale) are 2.48, 2.75 and 3.29 in sp^3, sp^2 and *sp* hybridization, respectively. The commonly used value of 2.5 for carbon is based on sp^3 (tetrahedral) hybridization.

GROUP ELECTRONEGATIVITY:

The electronegativity of an atom adjusted for the presence of substituents is known as the group electronegativity. The group electronegativity of CH_3 or CF_3 will be the electronegativity of carbon adjusted in presence of three H or F atoms. Several methods making use of kinetic data, atomic electronegativities and other physical measurements, have been developed to calculate the group electronegativities. Electronegativities of some common groups are given in Table.2.12.

TABLE 2.12

Electronegativities of Some Groups

Group	Electronegativity
CH_3	2.3
CF_3	3.35
CCl_3	3.0
CN	3.3
COOH	2.85
C_6H_5	3.0

ELECTROPOSITIVITY (THE METALLIC CHARACTER):

Electropositivity is the converse of electronegativity. It is related to the tendency of conveniently losing an electron. The stronger the tendency to lose electrons, the more electropositive will be the element. The larger the size of an atom, the valency electrons in the outermost orbit will be placed farther from the nucleus and hence will be easily removed making that atom electropositive.

Greater the electropositivity of an element, more will be its metallic nature. When two atoms have the same size, the one with greater atomic number will be more metallic in nature. Metallic character decreases from left to right across the Periodic Table because of the decrease in the atomic size and an increase in the ionization potential. For example, sodium and magnesium are more metallic than silicon and germanium. The most electropositive elements are found in the lower left of the Periodic Table and the most non-metallic are found on the top right.

The electropositive elements are also more basic in nature. Basic properties increase as we go down the group since the elements become more electropositive. This does not hold good in the case of transition elements *e.g.*, Cr, Mn, Fe, Co, Ni where the basicity decreases as we go down a group. Electropositive elements have the following properties:

(a) They react with water to form basic oxides and hydroxides.

(b) Strongly electropositive metals have a greater tendency to attract the opposite charges. Thus, they are not readily hydrated.

(c) They have little tendency to hydrolyse and form oxy-salts.

(d) They have little tendency to form complexes.

REDOX POTENTIAL:

Oxidation process involves loss of electrons and reduction involves gain of electrons. In oxidation process there is the gain or increase of positive charge and in reduction loss or decrease of positive charge.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{(Oxidation)}$$

$$Cl + e^- \longrightarrow Cl^- \quad \text{(Reduction)}$$

Oxidizing agents cause oxidation and are themselves reduced *i.e.*, $KMnO_4$, $K_2Cr_2O_7$, HNO_3 etc. Reducing agents cause reduction and are themselves oxidised *i.e.*, Na.

Redox potential is a measure of the tendency of an element or ion to gain or lose electrons. It is a combined term involving oxidation potential and the reduction potential.

Oxidation potential of an electrode is its standard electrode potential in volts as compared with that of standard hydrogen electrode arbitrarily fixed as zero at 25 °C when it is in contact with 1 M solution of its cations. Standard hydrogen electrode is an inert platinum electrode with a coating of platinum black at one end. It is dipped in 1.0 M solution of an acid at 25°C and hydrogen at one atmosphere pressure is bubbled over it. Oxidation potential of zinc, for example, is 0.76 volts and that of copper is – 0.34 volts.

Reduction potential of an electrode is the oxidation potential with the changed sign and that is the measure of the tendency to gain electrons. Thus reduction potential of zinc is – 0.76 and that of copper is + 0.34 volts.

The potential of an electrode under changed conditions is given by Nernst equation. The generalized form of Nerst equation is expressed as:

$$E = E^0 + \frac{RT}{nF}\, ln\, (ion)$$

E = Electrode potential
E_0 = Standard electrode potential at unit activity
R = Gas constant
T = Temperature in Kelvin's scale
n = Number of electrons transferred in the half reaction
F = Faraday
(ion) = activity of the ion which can be replaced by concentration under certain conditions.

The Nerst equation can be expressed in terms of activities as:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{aRed}{a\,Ox}$$

[Rex] is concentration of oxidization agent or reduction species.

[OX] in the concentration of reduction agent or oxidized species.

From the knowledge of oxidation and reduction potentials we can determine the feasibility of a chemical reaction. A cell can be constructed by utilizing an oxidation-reduction reaction. If the voltage of the cell is positive then the reaction is possible, and if negative, the reaction is not possible. The voltage can be calculated from the knowledge of the single electrode potentials of the two half reactions. Let us take the case of the reaction in the Daniel cell.

$$Zn_{(s)} + Cu^{++} \longrightarrow Zn^{++} + Cu_{(s)}$$

The reaction proceeds in two steps:

$Zn_{(s)} \longrightarrow Zn^{++} + 2e$ (+ 0.76 Anodic oxidation)
$Cu^{++} + 2e \longrightarrow Cu_{(s)}$ (+ 0.34 Cathodic reduction)
$Zn_{(s)} + Cu^{++} \longrightarrow Zn^{++} + Cu_{(s)}$ (+ 1.10 Volts)

As the voltage is positive the reaction proceeds in the forward direction and not in the backward direction. So the reaction is feasible.

Let us take another example as to what reaction is possible if I_2 and Br_2 are added to a solution containing I^- and Br^-. Let us suppose that the concentration of each species is 1 M.

The two possible reactions are:

$2I^- + Br_2 \longrightarrow I_2 + 2Br^-$ ...... (i)
$2Br^- + I_2 \longrightarrow Br_2 + 2I^-$ ...... (ii)

Voltage of reaction (i) from the table of the electrochemical series is calculated as given below:

$2I^- \longrightarrow I_2 + 2e^-$ − 0.535 volts.
$Br_2 + 2e^- \longrightarrow 2Br^-$ + 1.065 volts.
$2I^- + Br_2 \longrightarrow 2Br^- + I_2$ + 0.530 volts.

The voltage is positive, hence the reaction is possible.

Voltage for reaction (ii) is:

$2Br^- \longrightarrow Br_2 + 2e^-$ – 1.065 volts.

$I_2 + 2e^- \longrightarrow 2I^-$ + 0.535 volts.

$2Br^- + I_2 \longrightarrow Br_2 + 2I^-$ – 0.530 volts.

Voltage is negative, hence this reaction is not possible.

ELECTROCHEMICAL SERIES:

Electrochemical series of elements is the arrangement of elements in the order of increasing or decreasing electrode potentials. In the series Li has got highest potential and fluoride ion has got the lowest as shown in Table 2.13.

TABLE 2.13

Electrochemical Series of Elements

		Redn. Potential in volts
Li^{1+}	Li	– 3.05
K^{1+}	K	– 2.92
Ca^{2+}	Ca	– 2.84
Al^{3+}	Al	– 1.66
Mn^{2+}	Mn	– 1.08
Zn^{2+}	Zn	– 0.76
Fe^{2+}	Fe	– 0.44
Cd^{2+}	Cd	– 0.40
Co^{2+}	Co	– 0.27
Ni^{2+}	Ni	– 0.23
Sn^{2+}	Sn	– 0.15
Pb^{2+}	Pb	– 0.13
H^+	H	0.00
Cu^{2+}	Cu	+ 0.34
Ag^+	Ag	+ 0.80
Au^{3+}	Au	+ 1.38
O_2	OH^{1-}	+ 0.40
I_2	I^{1-}	+ 0.57
Br_2	Br^{1-}	+ 1.07
Cl_2	Cl^{1-}	+ 1.36
F_2	F^{1-}	+ 2.87

All the other elements occupy their positions above or below zero of hydrogen in the series.

Electrochemical series have got the following applications:

1. From the position of an element in the series we can know the strength of an oxidising agent or that of a reducing agent. In the series given above we can say that lithium is the strongest reducing agent as it has greatest tendency to lose electrons and fluoride ion is the weakest reducing agent. On the other hand, F_2 is the strongest oxidising agent as it has got the greatest tendency to accept electrons and lithium is the weakest oxidising agent.
2. From the series we can determine whether a metal will be displaced by another metal or not. In the series a metal will displace the positive ion of another metal provided the latter metal is below the first one in the electrochemical series. For example, zinc precedes copper in the electrochemical series. That is why zinc can displace copper.

   $$Zn_{(s)} + Cu^{++} \longrightarrow Zn^{++} + Cu_{(s)}$$
3. From the positions of the reactants in the electrochemical series, we can see whether a reaction is feasible or not. We sum up the voltages of two half reactions by constructing a cell. If voltage of the cell is positive, the reaction is possible and if negative, the reaction is not possible. Let us consider the following reactions:

   $$Zn_{(s)} + Cu^{++} \longrightarrow Zn^{++} + Cu_{(s)}$$

   From the table of electrochemical series, we have

   $$\begin{array}{ll} Zn_{(s)} \longrightarrow Zn^{++} + 2e & +0.76 \text{ volts.} \\ Cu^{++} + 2e \longrightarrow Cu_{(s)} & +0.34 \text{ volts.} \\ \hline Zn_{(s)} + Cu^{++} \longrightarrow Zn^{++} + Cu_{(s)} & +1.10 \text{ volts} \end{array}$$

   The voltage of the cell is positive. The reaction is possible and the electron current in this cell flows from zinc to copper as the former has got a greater tendency to donate electrons than that of copper.
4. From the electrochemical series of elements, we can calculate the voltage of any cell which can be constructed by using any two elements as electrodes or by combining any two oxidation-reduction reactions. An example of such an arrangement is the Daniel cell and its calculated voltage is + 1.10 volts.

PERIODICITY IN REDOX PROPERTIES:

The redox properties of the elements also exhibit periodicity. In general, elements on the left of the Periodic Table (*s*-block elements) are strongly reducing. On crossing a period from left to right the elements become weakly *reducing or weakly oxidising*. Group VI elements are strongly oxidising. The general trends summarised as:

The *s*-Block Elements are Strongly Reducing:

The characteristic features of *s*-block metals (Na, K, Mg, Ca, etc.) are:

(a) low ionization energies.
(b) low electron affinities
(c) low electronegativity values
(d) high electropositivity values
(e) negative standard redox potentials

Examples:

1. Alkali and alkaline earth metals react with air or oxygen:

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

2. They react with chlorine to form chlorides:

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

3. They react with dilute acids to liberate H_2:

$$Mg_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

These are all examples of reducing action of *s*-block metals as each metal readily gives up electrons and themselves are easily oxidised:

$$Na \longrightarrow Na^+ + e^-$$
$$Mg \longrightarrow Mg^{2+} + 2e^-$$

The Group VII Elements are Strongly Oxidising:

Their characteristic features are:

(a) high ionization potential values (b) high electron affinities
(c) high electronegative values (d) positive standard redox potentials

Examples:

Chlorine is strongly oxidising. It reacts violently with hydrogen in sunlight to produce HCl. It does not react with other oxidising agents such as oxygen and acids.

The Group V and VI Elements:

The *p*-block elements in the middle of period tend to be weakly reducing or weakly oxidising. For example, in Group IV, silicon reacts slowly with oxygen to form silicon dioxide:

$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$$

In Group V, nitrogen can act either as a weak reducing agent or as weak oxidising agent:

$$N_{2(g)}\ O_{2(g)} \longrightarrow 2NO_{(g)} \quad (N_2 \text{ as weak reducing agent})$$
$$N_{2(g)}\ 3H_{2(g)} \longrightarrow 2NH_{3(g)} \quad (N_2 \text{ as weak oxidizing agent})$$

The *d*-block elements mostly act as weak reducing agents. For example, iron reacts in hot with steam to liberate H_2 from water:

$$Fe + H_2O \longrightarrow FeO + H_{2(g)} \text{ (steam)}$$

Questions

1. What do you understand by ionization potential? How is it related to the tendency of the elements to form positive ions?

2. What is meant by electron affinity? Explain why the electron affinities of the atoms increase from left to right along a row in the Periodic Table?

3. (a) How do the ionization potentials vary in the Periodic Table?

   (b) Where are the elements with the greatest electron affinity found?

4. Explain the term electronegativity of the element. How does the electronegativity change within a periodic group?

5. Explain what is meant by redox potential? How this can be applied for determining the feasibility of a chemical reaction?

6. What is meant by electrochemical series of elements? What are the applications of this series?

7. Briefly explain the following statement:

   (i) Cl^{1-} is larger than Cl°, but K^{1+} is smaller than K.

   (ii) The first ionization potential of the elements with At. no. 17, 18, 19, are in the order $18 < 17 < 19$.

   (iii) The first ionization potential of Mg is larger than that of Na.

   (iv) The sizes of the following atoms and ions are not in order:

   $$Na^{1+}, Na, Fe^{2+}, Mg^{2+}$$

   (v) As has a larger ionization potential than Cs.

8. (a) What trends in the atomic size are to be expected in a given family like the alkali metals? Support your answer on the basis of electronic structure of the atoms.

   (b) Write brief notes on:

   (i) Atomic radii. (ii) Ionic radii. (iii) Covalent radii.

   (iv) Van der Waals' radii.

9. **Write short answers to the following:**

   (i) Why elements with similar chemical properties are in the same group?

   (ii) Why most electropositive elements and the most reactive metals are in the bottom left-hand corner of the Periodic Table?

   (iii) Why most electronegative *p*-block elements are on the right side of the Periodic Table?

(iv) Why atomic radii and ionic radii of *d*-block elements in the fifth and sixth periods of a given subgroup are approximately equal?

(v) What is the variation trend of atomic radii within a group, within a period and within a transition series?

(vi) Why covalent radii decrease with increase in bond order?

(vii) How did Pauling calculate the ionic radii of salts?

(viii) What is the trend of variation of ionic radii in the Periodic Table? Give suitable reason for this trend.

(ix) What is the correlation of ionization potential and atomic number? Draw a graph to explain the situation.

(x) What is the trend of variation of ionization potential in periods and groups in the Periodic Table?

(xi) What is electronegativity? Give salient features of Pauling's scale of electronegativity.

(xii) What is redox potential? How can you determine the feasibility of a chemical reaction based on redox potential?

10. **Give the correct answer:**

(i) Which of the following elements has the largest second ionization potential?

(a) O (b) F (c) Mg (d) Na **(Ans**: d)

(ii) The second ionization potential or energy of calcium is 1150 KJ mol^{-1}. Which of the following correctly represents this statement?

(a) $Ca_{(g)} \longrightarrow Ca^{2+}_{(g)} + 2e^-$ $\Delta H = +1150 \text{ KJ mol}^{-1}$

(b) $Ca^+_{(g)} \longrightarrow Ca^{2+}_{(g)} + e^-$ $\Delta H = +1150 \text{ KJ mol}^{-1}$

(c) $Ca^+_{(g)} \longrightarrow Ca^{2+}_{(g)} + e^-$ $\Delta H = -1150 \text{ KJ mol}^{-1}$

(d) $Ca_{(s)} \longrightarrow Ca^{2+}_{(aq)} + 2e^-$ $\Delta H = +1150 \text{ KJ mol}^{-1}$

(Ans: b)

(iii) The ionization energies, in KJ mol^{-1}, of a series of elements of increasing atomic number are given below:

548 620 660 660 680

Where in the Periodic Table is this sequence of elements likely to be located?

(a) group I (b) group II (c) group VII (d) from Sr to Mo

(Ans: d

(iv) Which of the following elements with electronic configuration has the highest first ionization potential values?

(a) $1s^2\, 2s^2\, 2p^3$ (b) $1s^2\, 2s^2\, 2p^4$

(c) $1s^2\, 2s^2\, 2p^6\, 3s^1$ (d) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$

(Ans: a)

(v) Which equation relates to the first ionization energy of bromine?

(a) $Br_{(g)} \longrightarrow Br^-_{(g)} - e^-$ (b) $Br_{(g)} \longrightarrow Br^+_{(g)} + e^-$

(c) $\frac{1}{2} Br_{2(g)} \longrightarrow Br^-_{(g)} - e^-$ (d) $\frac{1}{2} Br_{2(g)} \longrightarrow Br^+_{(g)} + e^-$

(Ans: b)

(vi) Which equation is used to define the first ionization of bromine?

(a) $Br_{(g)} \longrightarrow Br^-_{(g)} - e^-$ (b) $Br_{(g)} \longrightarrow Br^+_{(g)} + e^-$

(c) $\frac{1}{2} Br_{2(g)} \longrightarrow Br^-_{(g)} - e^-$ (d) $\frac{1}{2} Br_{2(g)} \longrightarrow Br^+_{(g)} + e^-$

(Ans: b)

(vii) Which property of the first six elements of period 3 (sodium to sulphur) continuously increases numerically?

(a) atomic radius (b) first ionization energy

(c) maximum oxidation number in oxide (d) melting point

(Ans: c)

❀ ❀ 2 ❀ ❀

CHEMICAL BONDING

3

CHEMICAL BONDING

You are already aware of the fact that forces of attraction exist between atoms. These forces are either relatively weak which exist between the atoms of inert gases or they may be quite strong which bind the metal atoms into a metallic solid.

The force which hold two atoms together in the molecule are described by the word bond. Before the consideration of the electronic structure of atoms, the nature of forces binding atoms together to form molecules were considered to be due to their combining capacity called valencies. Thus the valeny was considered as ***the number of valence bonds formed by an atom of one element with other atoms.*** This classical concept of chemical bond formation has now been replaced by modern and more useful theories of bonding discussed in next chapter.

A stable molecule is a group of atoms held together by valence forces. The distances of separation of atoms in the molecules are of the order of atomic diameter taken in Angstrom units (1 Angstrom = 10^{-8} cm = 10^{-1} nm). The forces which are responsible for chemical bonding depend upon the structure of atoms. It is due to this reason that progress in the understanding of chemical bonding has gone hand in hand with progress in the elucidation of atomic structure.

Thomson suggested that electrostatic forces of attraction between oppositely charged ions were responsible for chemical bonding. According to Kossel (1916), the atoms of more electropositive elements immediately following inert gases lose one or more electrons to produce positively charged ions with inert gas configuration. In the same way, atoms of strongly electronegative elements which precede the inert gases would gain one or more electrons to produce negatively charged ions having inert gas configuration. The electrostatic forces of attraction between the oppositely charged ions are responsible for the formation of chemical bond. This type of bond is referred to *ionic* or *polar bond.* Lewis (1916) suggested that the atoms of some elements would form bonds by sharing of electrons. Such type of bonds are called *covalent* or *non-polar bonds.* It needs to be mentioned over here that these are not the only forces responsible for all chemical bonds, but the ion-dipole forces or dipole-dipole forces, interactions arising out of the polarization of atomic systems, and the forces operative in solids also play an important role. Following discussion will deal with the simple concepts of electron transfer and electron sharing and a brief treatment of other types of bonds.

When atoms combine to form molecules, they come close together and interact in such a way that the energy of system is lowered. During the bond formation the energy of the molecular systems falls due to the attractive forces. It continues to fall until the two atoms come so close together that the nuclear repulsions of the system go through a minimum and show a rise afterwards (Fig. 3.1). The energy is minimum at an equilibrium internuclear distance R_e (curve A) where the two atoms are held together very firmly with the maximum possible decrease in energy. As this energy is much lower than that present in atoms, the stability of the molecule is gained and a chemical bond is formed. Depending upon the nature of the atoms it is sometimes possible that with the decrease in interatomic distance R, the energy increases. In this situation atoms do not combine to form molecules (curve B in Figure 3.1). At R_e the repulsive and attractive forces are equal so that the net force is zero.

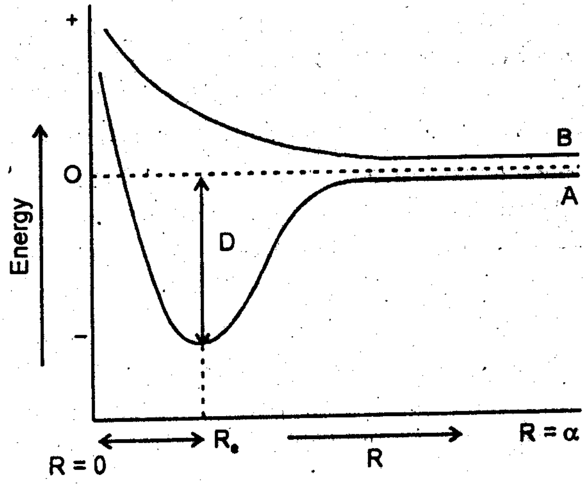


Fig. 3.1. Potential energy diagram for the formation of a chemical bond between two atoms. R = Internuclear distance, R_e = internuclear distance at equilibrium on bond formation. D = bond dissociation energy.

Nature and Types of Chemical Bond:

We shall now consider the following types of bonds:

(1) Ionic or electrovalent bond.
(2) Covalent or electron pair bond.
(3) Coordinate-covalent pair bond (a type of covalent bond).
(4) Metallic and non-localised bond.
(5) Van der Waals' and long-range bond.
(6) Hydrogen bonding
(7) Electron Deficient Molecules.

(1) IONIC OR ELECTROVALENT BOND:

This type of bond is exhibited by atoms which can either lose electrons to form positively charged ions (cations) or gain electrons to form negatively charged ions (anions). The atom which can lose electrons is said to be *electropositive* or basic and the atom capable of gaining one or more electrons is referred as *electronegative.* The more electropositive atom has always low value of ionization potential and is thus capable of losing electrons with greater ease. The electrons lost by electropositive atoms are completely transferred to other atoms which show greater electronegativities. ***The bond formed by complete transfer of electrons from electropositive atom to more electronegative atom is called ionic or electrovalent bond.*** The electropositive elements in energy terms should have higher energy states than those of electronegative elements. This energy difference will be responsible for the flow of electrons from higher energy states to lower energy states. The two atoms are held together by electrostatic forces of attraction acting between such atoms.

$$M^{\circ} + X^{\circ} \longrightarrow M^{+} : X^{-} \qquad \cdots\cdots \quad (3.1)$$

The energy required to completely separate the ions from a diatomic molecule is given by the following expression:

Potential energy = Electrostatic energy + Van der Waals' energy.

$$\text{The electrostatic energy} = \frac{q_1 q_2 e^2}{R}$$

where q_1 and q_2 are charges on atoms M and X and R is the internuclear separation.

The general tendency of various atoms to form molecules is to attain inert gas configuration, being the most stable. The atoms of the inert gases have outermost *p* orbitals completely filled. Such a configuration will not easily lose or gain any electron because very high ionization potentials (or electronegativities) will be required to remove an electron or gain any additional electron. Let us consider potassium and chlorine atoms which would combine to form potassium chloride molecule. Potassium atom (Atomic number of K = 19) has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. Chlorine (Atomic number of Cl = 17) has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. None of these has an inert gas structure. But they possess an incomplete shell of electrons and orbitals. The nearest inert gas to both is argon having electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Thus the loss of one electron from potassium and gain of this lost electron by chlorine would leave both the atoms with argon configuration. ***During this process, K^+ and Cl^- would be produced and the electrostatic attraction between these oppositely charged ions should be responsible for a stable ionic bond.***

Let us take some more examples to elaborate the ionic bonding situation.

(i) Formation of Sodium Chloride Molecule:

$$\underset{(1s^2 2s^2 2p^6 3s^1)}{Na^\circ - 1e^-} \longrightarrow \underset{(1s^2 2s^2 2p^6)}{Na^+}$$

Neon configuration

$$\underset{(1s^2 2s^2 2p^6 3s^2 3p^5)}{Cl^\circ + 1e^-} \longrightarrow \underset{(1s^2 2s^2 2p^6 3s^2 3p^6)}{Cl^-}$$

Argon configuration

Another way of representing the bonding situation is:

$$\overset{\curvearrowright}{Na + \cdot}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow \overset{+}{Na}\ :\ddot{\underset{\cdot\cdot}{Cl}}:^- \longrightarrow Na - Cl$$

(ii) Formation of Magnesium Chloride Molecule:

$$\underset{(1s^2 2s^2 2p^6 3s^2)}{Mg^\circ - 2e^-} \longrightarrow \underset{(1s^2 2s^2 2p^6)}{Mg^{2+}}$$

Neon configuration

$$\underset{(1s^2 2s^2 2p^6 3s^2 3p^5)}{2Cl^\circ + 2e^-} \longrightarrow \underset{(1s^2 2s^2 2p^6 3s^2 3p^6)}{2Cl^-}$$

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot \overset{\curvearrowleft}{+ Mg\cdot} \overset{\curvearrowright}{+ \cdot}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:^-\ Mg^{2+} :\ddot{\underset{\cdot\cdot}{Cl}}:^- \longrightarrow Cl - Mg - Cl$$

(iii) Formation of Aluminium Fluoride:

$$Al^\circ - 3e^- \longrightarrow Al^{3+}$$

$$3F^\circ + 3e^- \longrightarrow 3F^-$$

$$Al^{3+} + 3F^- \longrightarrow AlF_3$$

The ions O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+} with outer configuration $2s^2 2p^6$ belong to neon configuration and S^{2-}, Cl^-, K^+, Ca^{2+} belong to argon configuration.

Various positive ions do not attain inert gas configurations after the ionic bond formation. Thus transition metal ions show such behaviour. For example,

$$\underset{(1s^1 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2)}{Zn - 2e^-} \longrightarrow \underset{(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10})}{Zn^{2+}}$$

Other ions belonging to this category are:

Cu^+ $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10})$

Fe^{2+} $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^6)$

Fe^{3+} $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^5)$

Co^{2+} $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^7)$

Co^{3+} $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^6)$

Ni^{2+} $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^8)$

Transition metal ions which do not resort to inert gas configuration attain their stability through the formation of complex ions. The ions with odd number of *s* or *p* electrons are not known, but an odd number of *d* electrons is found in transition metal ions.

It should be noted that ***important forces between atoms or groups of atoms are electrostatic in nature.***

Crystal Structure of Ionic Compounds:

Many solid substances consist of an ordered array of ions. Since the solid as a whole is electrically neutral, the total number of positively charged ions (cations) must be equal to the total number of negatively charged ions anions. Crystalline sodium chloride, for example, consists of equal number of sodium ions, Na^+ and chloride ions, Cl^- arranged in a face-centred cubic arrangement.

(a) Sodium Chloride Structure:

The ion pair of sodium chloride can be represented as shown in Figure 3.2. Two ion pairs will join to form electrically neutral structure (see Figure 3.2). In the $[Na^+ - Cl^-]_2$ configuration there is an additional attractive force of each Na^+ ion for the Cl^- ion of the other ion pair. As a result of this the energy of the system would decrease. The coulomb attraction energy $= 2\left[\dfrac{q^+q^-}{(r^+ + r^-)}\right]$.

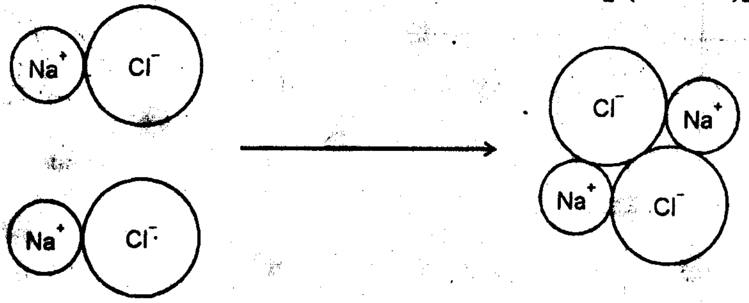


Fig. 3.2. Ion-pairs of sodium chloride.

If more than two 'ion pairs' join to form the crystal shape, a three dimensional ionic lattice is set up. In case only four 'ion pairs' come together, a cubic arrangement is formed (Figure 3.3). It constitutes the unit cell for sodium chloride structure. ***A structural unit of definite shape which is repeated over and over again during the formation of the crystal is called a 'unit cell'.*** The unit cells are distinguished by the lengths of edges and angles between them. The common unit cells are: cubic, hexagonal tetragonal and monoclinic.

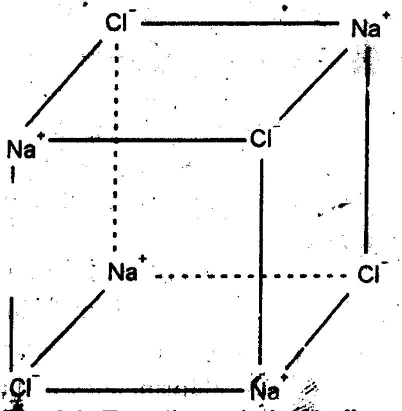
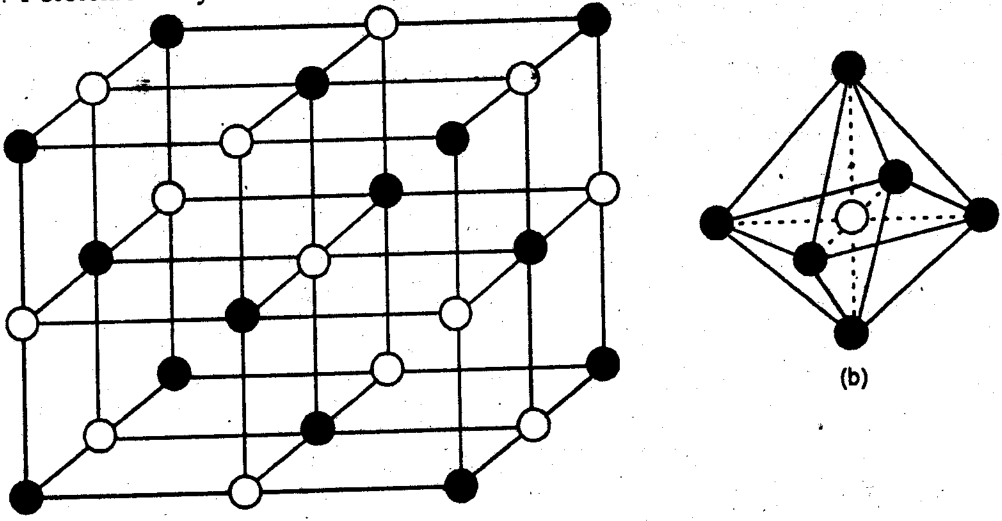


Fig. 3.3. Four 'ion pairs' of sodium chloride.

The unit of sodium chloride structure is a cube. Let us designate the chlorine atoms by ○ and sodium atoms by ●. (The term ion should be used instead of the term atom, but the term atom is used because the true nature of the bond has not been considered over here). The arrangement of the chlorine and sodium atoms is found to be face-centred cubic. They would be closely packed only if the atoms are in contact.

Consider the chlorine atom marked 'A' in the Figure 3.4. It is surrounded by six atoms of sodium arranged around the corners of a regular ***octahedron.*** This holds good for all the chlorine atoms. Thus chlorine atoms occupy the octahedral sites in a cubic closely packed type of crystal structure. Similarly, sodium atoms can be shown to be surrounded by chlorine atoms along octahedral sites. In order to occupy an octahedral site there is maximum limiting ratio of the radii of both atoms.

In case of sodium chloride $r\text{Na}^+ / r\text{Cl}^-$ is 0.414 which would be required by an octahedral site to form. All the octahedral sites are occupied and each octahedral site is available for sodium and chlorine atoms. This corresponds to a 1 : 1 stoichiometry as is found in sodium chloride molecules.



(a)

(b)

Fig. 3.4. (a) The sodium chloride structure.
(b) Octahedral coordination in NaCl.

There are three different ways of describing the structure of sodium chloride:

(i) A cubic closely packed type of arrangement of chlorine atoms with sodium atoms filling all the octahedral sites.

(ii) A cubic closely packed type of arrangement of sodium atoms, with chlorine atoms filling all the octahedral sites.

(iii) Two interpenetrating closely packed cubic type of crystal lattices, one of chlorine atoms and the other of sodium atoms.

The first description is more close to the true crystal shape because it is very convenient to consider the larger atoms as being closely packed and the smaller atoms present in the interstitial sites. It should be noted that all the three descriptions given above are true for describing the sodium chloride structure. However, the structure should be better described to be built up of ions rather than of atoms, because of the ionic nature of the compound. Since each ion is surrounded by six ions of opposite charge, the sodium chloride structure has coordination No. 6 (6 : 6). On counting the total number of sodium and chlorine atoms it is found that four atoms of each kind (or four molecules) are present in the unit cube. This corresponds to stoichiometry of 1 : 1 keeping with the formula NaCl.

The face-centred cubic structure is quite common and is present in alkali metal halides and most of the oxides, sulphides, selenides etc., of alkaline earth metals. Silver fluoride, chloride and bromide have the sodium chloride structure; but iodide does not show this structure due to the bigger ionic radius of iodine.

(b) Caesium Chloride Structure:

The structure of caesium chloride is cubic. Chlorine atoms are again represented by O and caesium atoms by ●. The caesium atoms are present in the body-centre of the cube with eight chlorine atoms present as nearest neighbours as shown in Figure 3.5. On extending the structure further it would become clear that each chlorine is also surrounded by eight caesium atoms. Thus both type of atoms have equivalent positions in this structure and the coordination number is 8. It is not reasonable to refer this structure as body-centred cube because this term implies that the body-centre is occupied by the same kind of atom as that at the corners of the cube, but it is customary to refer it to a body-centred structure.

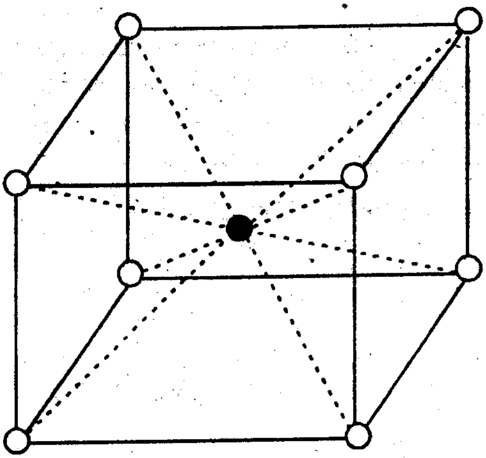


Fig. 3.5. The caesium chloride lattice and its unit cell.

RADIUS RATIO:

The structures of solids are determined by the relative numbers of different ions (depending upon the formula type) and their sizes. The effect of the sizes of different ions is discussed in terms of the *radius ratio. **The radius ratio is the ratio of the radii of the cations and the anion,*** rM^+/rX^-.

Let us consider a compound of the type MX in which the coordination number is six. The arrangement of X^- ions around M^+ ions will be octahedral (but a square planar arrangement of four X^- ions about M^+ at the centre of the square plane is also possible) as shown in Figure 3.6. X^- ion one above and one below M^+ are not shown.

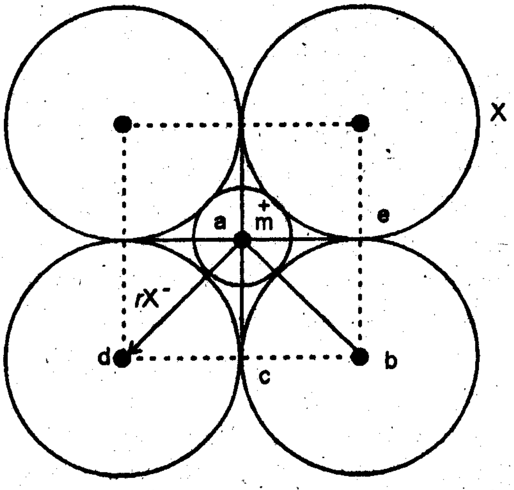


Fig. 3.6. A cross-section through an octahedral site.

$$\text{Radius ratio} = \frac{rM^+}{rM^-} = \frac{\text{radius of cation}}{\text{radius of anion}}$$

Radius ratio can be calculated from the geometry of the molecule. Let us calculate the radius ratio for sodium chloride type structure having octahedral sites. Consider Figure 3.6 for this purpose. There are two ways to calculate the value of the radius ratio.

1st Method: In the triangle *a b c*

$$bc = ab \cos 45^\circ$$

$$\text{or} \quad rX^- = (rM^+ + rX^-)/\sqrt{2}$$

$$\left(bc = rX^-; ab = rM^+ + rX^-; \cos 45^\circ = \frac{1}{\sqrt{2}}\right)$$

$$\frac{rX^-}{rM^+ + rX^-} = \frac{1}{\sqrt{2}}$$

on inverting we get,

$$\frac{rM^+ + rX^-}{rX^-} = \sqrt{2}$$

$$\frac{rM^+}{rX^-} + 1 = \sqrt{2}$$

$$\frac{rM^+}{rX^-} = \sqrt{2} - 1$$

$$= 1.414 - 1 = 0.414$$

2nd Method: In the right angle triangle *a b c*

$$\begin{aligned}(ab)^2 &= (bc)^2 + (ac)^2 \qquad (\because ac = bc = rX^-)\\ (rM^+ + rX^-)^2 &= (rX^-)^2 + (rX^-)^2\\ &= 2(rX^-)^2\\ rM^+ + rX^- &= \sqrt{2}\, rX^-\\ rM^+ &= \sqrt{2}\, rX^- - rX^-\\ rM^+ &\doteq 1.414\, rX^- - rX^-\\ rM^+ &= 1.414\, rX^-\\ \frac{rM^+}{rX^-} &= 0.414\end{aligned}$$

Thus

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = 0.414 \text{ (for octahedral site)}$$

Limiting radius ratio is the maximum ratio of the radius of the cation to the radius of anion up to which the crystal structure is retained. Above this radius ratio the particular crystal structure will not be retained. Values for the radius ratio of various crystal structures are shown in Table 3.1.

TABLE 3.1

Values for the Radius Ratio

No.	Structure Type	Coordination Number	Limiting radius ratio, rM^+/rX^-
1.	Closely Packed Hexagonal	12	1
2.	Cubic	8	0.732 to 1
3.	Octahedral	6	0.414 to 0.732
4.	Square Planar	4	0.414 to 0.73
5.	Tetrahedral	4	0.225 to 0.414
6.	Triangular	3	0.155 to 0.225
7.	Linear	2	0.155

It is obvious that the knowledge of ionic radii can give us a clue to the possible crystal structures. But the limiting radius ratio condition should not be applied very strictly, since other factors such as repulsive forces between ions of similar sign will also decide about the possible structure among the two at limiting radius ratio.

The coordination number of the positive ion is not always equal to the coordination number of the negative ion. But it remains the same in structures of general formula AB. In such cases electrical neutrality principle would be observed and there must be equal number of A^+ and B^- ions in the structure. The essential features of a number of simple inorganic substances are summarized in Table 3.2.

TABLE 3.2

Ionic Structure

Structure Type	Examples	Radius Ratio	Coordination number of positive ions	Coordination number of negative ions
1. Caesium chloride	CsCl, CsBr, CsI	0.732 or more $(\sqrt{3}-1)$	8 (Cubic) 6	8(Cubic)
2. Sodium chloride	NaCl, NaBr, NaI, MgO, CaO, MnO	0.414 – 0.732	6(Octahedral)	6(Octahedral)
3. Fluorite	CaF_2, SrF_2, ThO_2	0.732 or more	8(Cubic)	4(Tetrahedral)
4. Rutile	TiO_2, SnO_2, PbO_2	0.414 or more	6(Octahedral)	3(Trigonal)

It should be noted that the relative sizes of the combining ions play the key rôle in deciding the crystal structures of various compounds. The degree of ionic or covalent character of the compound has also a strong influence on its nature and behaviour. The fluorite and rutile type lattices are shown in Figures 3.7 and 3.8.

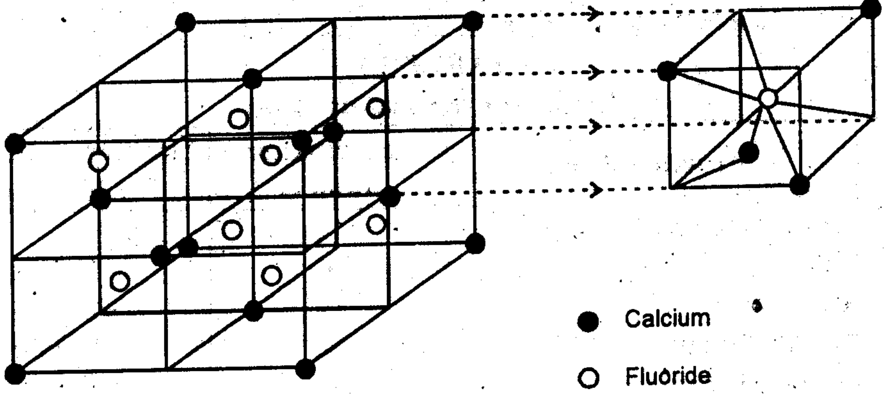


Fig. 3.7. Fluorite lattice.

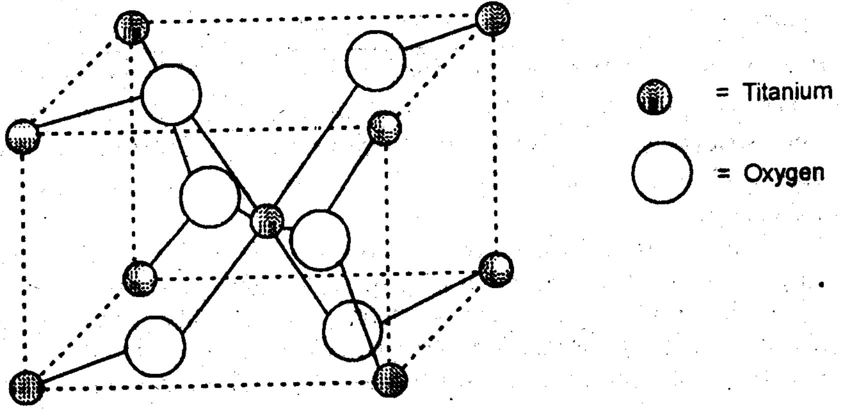


Fig. 3.8. Rutile lattice.

LATTICE ENERGY:

Lattice energy is the amount of energy given out when gaseous ions of opposite charges are brought together from infinity into a solid lattice to form 1 gram mole of a compound. It is also called the crystal energy of the compound. The lattice energy depends upon (a) the sum of the coulomb attractions and repulsions between all ions in the lattice and (b) the Born repulsion between ions in contact. A theoretical value of the lattice energy can be obtained from the equation 3.2.

$$U = \frac{e^2 Z^2 N_A}{r}\left(1 - \frac{1}{n}\right) \qquad \ldots\ldots (3.2)$$

where U = is the lattice energy.

e = is the charge on an electron.

Z = is the common factor of the charges on two ions.

N = is the Avogadro number.

A = is the Madelung constant (depends upon the geometry of the crystal lattice and is independent of the charges of ions).

(A = 1.76267 for CsCl lattice; A = 1.74756 for NaCl lattice; A = 12.51937 for fluorite lattice; and A = 2.408 for rutile lattice),

r = is the distance of nuclei of the two unlike ions.

n = is an integer which is almost equal to 10.

Since large values of the lattice energy will increase the energy of formation, it is obvious that large charges on both ions would enhance the stability of ionic compounds. This is because in polyvalent ions the term Z^2 will be more and consequently the value for the lattice energy would correspondingly increase.

THE BORN-HABER CYCLE:

It is based on the principle that sum of the energy changes in the initial and final states of various processes occurring in a closed cycle is zero. This principle is based on the law of conservation of energy in accordance with the first law of thermodynamics.

The standard heat of formation, H_f of sodium chloride is the heat given out when one gram molecule is formed from solid sodium and gaseous chlorine. The experimental value of it is 98.2 kcals. It is possible to proceed from the starting materials to the same product by a series of steps where the energy of each step is known. In accordance with Hess's law the total energy changes involved in various routes by which the final product is formed can be equated to each other.

Let us consider the step-wise route for the formation of solid sodium chloride from solid sodium and gaseous chlorine. The first step is the conversion of sodium from the solid to the gaseous state in which it exists as sodium atoms. The energy required during this step is the ***Energy of Sublimation, S.*** In the second step, an electron is removed from the gaseous sodium atom to form gaseous sodium ion, the energy required to remove an electron will be the ***Ionization Potential, I.*** The third step involves the dissociation of chlorine molecules to give gaseous chlorine atoms which requires the ***Dissociation Energy, D*** for this purpose. Since only one gram molecule of sodium chloride is taken into consideration, only one gram atom of chlorine would be required. As the dissociation energy, D would produce two gram atoms of chlorine from one gram molecule of NaCl, the amount of dissociation energy, required to produce one gram atom of chlorine would be D/2. The fourth step would require the addition of one electron to gaseous chlorine atom with the formation of gaseous chlorine ions. This depends upon the ***Electron Affinity, E*** of the chlorine atom and energy is given out in this process. The final step is the formation of solid sodium chloride from gaseous ions, and again the energy is given out known as the ***Lattice Energy, U.***

$$Na_{(s)} + S \longrightarrow Na_{(g)} \quad \ldots\ldots \quad \text{1st step}$$

$$Na_{(g)} + I \longrightarrow Na^{+}_{(g)} \quad \ldots\ldots \quad \text{2nd step}$$

$$\frac{1}{2}Cl_{2(g)} + \frac{1}{2}D \longrightarrow Cl_{(g)} \quad \ldots\ldots \quad \text{3rd step}$$

$$Cl_{(g)} - E \longrightarrow Cl^{-}_{(g)} \quad \ldots\ldots \quad \text{4th step}$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)} - U \longrightarrow NaCl_{(s)} \quad \ldots\ldots \quad \text{5th step}$$

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} + \left(S + I + \frac{1}{2}D - E - U\right) \quad \ldots\ldots \quad NaCl_{(s)}$$

All these processes can be shown diagramatically as a cycle (The Born-Haber cycle) with energies involved and expressed in kcals (See Figure 3.9).

A cycle of this type can be constructed for other compounds also. A compound having large value of the energy of formation and being exothermic

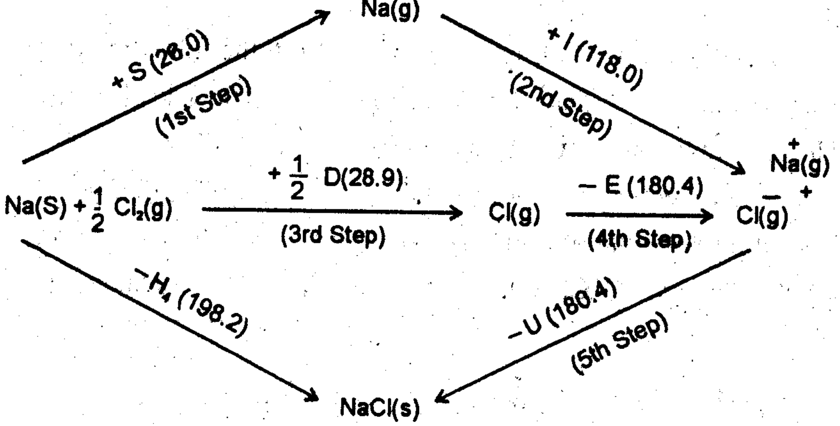


Fig. 3.9. The Born-Haber cycle (By convention (+) sign denotes that energy is supplied to the system and (–) sign to energy given out).

would be more stable. Magnitude of the values of various energy changes indicate that the most important terms in the above cycle are (i) the ionization potential, (ii) the electron affinity, and (iii) the lattice energy. Thus an ionic compound is formed if the ionization potential of one atom is relatively low, the electron affinity of the other atom A and the lattice energy of the compound as high as possible. Such values of these energy terms would produce a large heat of formation and thus give stability to the molecule.

Using Born-Haber cycle, the lattice energy can be calculated knowing other values which can be experimentally determined. This can be done by using the following equation based upon Born-Haber cycle given above.

$$H_f = S + I + \frac{1}{2}D - E - U$$

Example:

Calculate the lattice energy of CsCl. The other values are S = 18.8, I = 89.7, D = 58.0, E = − 87.1 and H_f = − 103.5.

$$-H_f = S + I + \frac{1}{2}D - E - U$$

Putting the values given in this equation,

$$-103.5 = 18.8 + 89.7 + \frac{1}{2}(58) - 87.1 - U$$

$$-103.5 = 50.4 - U$$

$$-103.5 - 50.4 = -U$$

$$U = 153.9 \text{ Kcals / mole (644 KJ/mole)}$$

Example:

Calculate the electron affinity of chlorine from the following data:

Standard heat of formation of KCl (H_f) = -105.0 kcal mole^{-1}
Heat of sublimation of potassium (S) = $+21.7$ kcal g-atm^{-1}
Dissociation energy of chlorine (D) = $+57.8$ kcal mole^{-1}
Ionization potential of potassium (I) = $+99.6$ kcal g-atom^{-1}
Lattice energy of KCl (U) = -163.2 kcal mole^{-1}

Since

$$-H_f = S + I + \frac{1}{2}D - E - U \quad \text{(Hess's Law)}$$

Putting the values in this equation derived from Born-Haber cycle, we get:

$$-105.0 = 21.7 + 99.6 + \frac{1}{2}(57.8) - E - 163.2$$

$$E = 255.2 - 163.2 = 92.0$$

Thus the electron affinity of chlorine is 92.0 kcals g-atom^{-1} (385 KJ/mole)

Similarly, other energy values of various compounds can be calculated based upon the Born-Haber cycle. Thus, electron affinities of atoms are usually calculated from Born-Haber cycle because it is difficult to determine electron affinities directly.

Factors Responsible for the Stability of Ionic Compounds:

The energy data required in Born-Haber cycle are useful in determining the stability of various ionic compounds. We shall discuss the correlations between energy terms and the stability of compounds.

1. **Heat of Sublimation, S:** ***The lower the heat of sublimation of the metal the more stable will be the ionic solid.*** Thus the heat of sublimation may be considered to be the measure of the attractive forces between the atoms in the solid. High melting and high boiling solids and liquids have strong attractive forces.

2. **Heat of Dissociation, D:** ***The greater the heat of dissociation of the diatomic gas, the less stable the compound.*** Most of the compounds have relatively small values of dissociation energy. But some ionic compounds are instable due to large dissociation energy.

3. **Ionization Potential, I:** ***The smaller the value of the ionization potential of the metal the more stable the ionic solid would be.*** The elements of lowest ionization potential are found among alkali and alkaline earth metals indicating more stability of their compounds.

4. **The Electron Affinity, E:** ***The greater the electron affinity of the element forming the onion, more stable the ionic compound.*** The halogens have the largest electron affinities and therefore form the most stable ionic compounds.

5. **Lattice Energy, U:** ***The greater the lattice energy more stable the ionic solid.*** A decrease in the size of the cations and anions would result in a large lattice energy.

CHARACTERISTIC FEATURES OF IONIC COMPOUNDS:

The strong coulomb forces existing between ions in such compounds render special properties to them. These properties are:

1. **High Melting and Boiling Points:** Ionic solids would be expected to have high melting and boiling points because of the strong attractive forces. These forces are not localized between two molecules but distributed among all the ions of the solid.

Since molecules with large dipoles would have stronger mutual attractions, a considerable amount of work will be needed to separate them from one another. Therefore, ionic compounds are expected to show high melting and boiling points ($NaCl$ boils at 1470°C but a covalent compound CCl_4 boils at 77°C only). On heating, due to the increase in kinetic energy of the molecules, the molecular vibrations will be enhanced. As a result, the forces holding the particles together will be overcome and atoms would move apart.

2. **Electrical Conductivity:** The molten salts of ionic compounds are good conductors of electricity because cations and anions are free to move under the influence of electric field. However, ionic crystals are very poor conductors of electricity as they are not free to move around. The crystal lattice may be broken down by melting or dissolving the ionic solids in polar solvents, whereby the ions freely move and would migrate in the presence of electric field and conduct electricity.

3. **Solubility in Polar Solvents:** A polar solvent consists of molecules which, even though electrically neutral as a whole, have centres of negative and positive charges. Non-polar solvents are both locally and totally neutral. Ionic solids tend to be insoluble in polar solvents only because dissolution involves rupture of the crystals lattice and separation of ions which is enhanced by polar solvents only. Non-polar solvents do not affect the ionic solids and would not be able to dissolve them.

Ionic compounds are quite soluble in water, which consists of polar molecules (dipole moment = 1.8 D) and also a high value of dielectric constant (~78). The water molecules gather around the lattice ions and the electrostatic forces of attraction between water molecules and lattice ions are strong enough to make the ions leave the crystal lattice as shown in Figure 3.10. The ions leaving the lattice would be solvated by water molecules and hydrated ions thus formed are also shown in Figure 3.10.

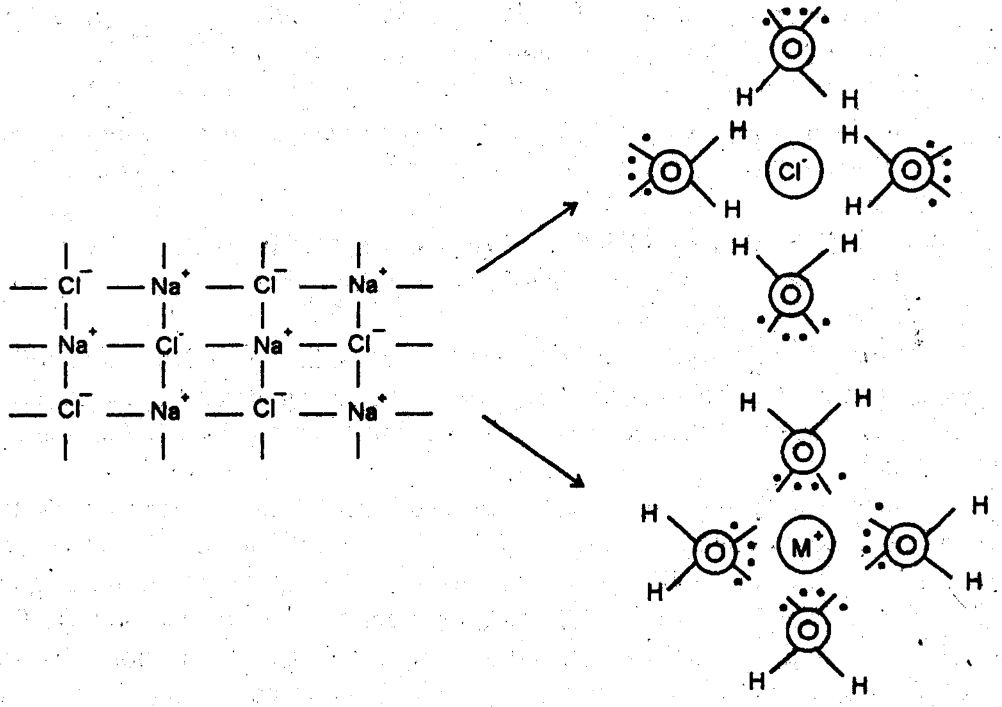


Fig. 3.10.

In addition to water, the ionic compounds are soluble in other polar solvents and the solubility of ionic solids depends upon the polarity of the bonds of both the solute and the solvent. Ionic solids would dissolve easily in those solvents which have fairly high values of dielectric constants. Liquid ammonia, liquid sulphur dioxide, liquid hydrofluoric acid etc., are mostly used as solvents for ionic compounds.

4. **Reactions in Solution:** The reactions of ionic compounds in solution are due to the constituent ions. Thus all ionic chlorides would give reactions of chloride ions and the respective cations. The ionic reactions are instantaneous. For example, on adding a solution of silver nitrate to a solution of some chloride, an immediate white precipitate of AgCl is obtained.

$$Ag^+ + Cl^- \longrightarrow \underset{\text{(white precipitate)}}{AgCl\downarrow}$$

5. **Crystalline State:** Ionic compounds are composed of cluster of ions in the crystal lattice and form definite structure or crystal shapes. For instance, sodium chloride has a crystal structure consisting of one sodium atom surrounded by six chlorine atoms and each chlorine atom surrounded by six sodium atoms. This fact is proved by the X-ray diffraction produced by the crystals of sodium chloride and other ionic crystals.

6. **Isomorphism:** Ionic crystals having the same crystalline structures are found to have identical electronic arrangements. For example, NaF is isomorphous with MgO. Both possess similar crystalline forms and similar electronic arrangements.

Na^+	$1s^2 2s^2 2p^6$	F^-	$1s^2 2s^2 2p^6$
Mg^{2+}	$1s^2 2s^2 2p^6$	O^{2-}	$1s^2 2s^2 2p^6$

7. **Dielectric constant:** The ionic compounds show high values of dielectric constants. Since a polar or a dipolar molecule when placed in an electric field would adjust the ends of the dipole in such a way that its negative pole will be directed towards the positive pole of the electric field and vice versa. The oriented dipole will oppose the field and would cause the reduced intensity of the electric field. This reducing tendency is measured in terms of what is called ***dielectric constant***.

8. **Non-Directional Bonds:** The ionic bonds are held together by electrostatic force of attraction between oppositely charged ions. These coulomb forces are non-directional.

9. **Low Coefficient of Expansion:** The ionic compounds are stable and the electrostatic forces holding the oppositely charged ions render low values of coefficient of expansion.

10. **Optical properties:** Absorption of compounds is same as that of individual ions.

VARIABLE VALENCY:

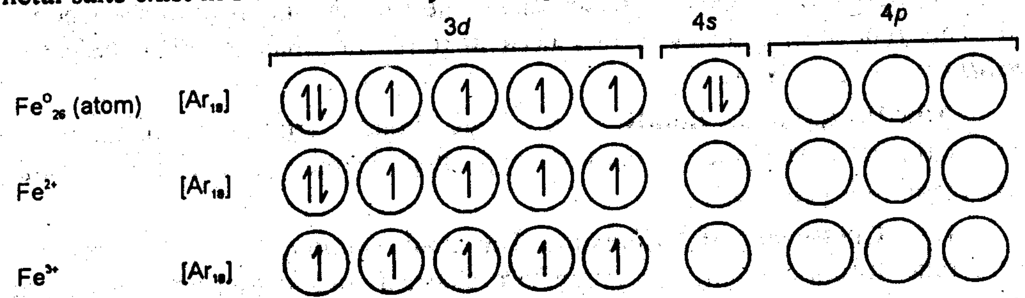
Certain elements exist in more than one oxidation state and thus show variable valency. For example, transition metals show wide range of valence states, *e.g.*, Fe^{2+}, Fe^{3+}; Cr^{2+}, Cr^{3+} ; Co^{2+}, Co^{3+}, (more common), Co^{4+} and Co^{5+} (less common) etc. Similarly, normal metals, *e.g.*, Pb^{2+} and Pb^{4+} ; Sn^{2+} and Sn^{4+} also show variable valencies. Certain non-metals are also found to show more than one valence states *e.g.*, P^{3+} and P^{5+}.

Variable valency may be due to different reasons and would be discussed over here accordingly.

(i) In transition elements (elements in which *d* orbitals are in the process of completion) the variable valency is due to the partially filled '*d*' orbitals, state of hybridization and type of reactants (usually called ligands). Such elements can involve different number of electrons in compound formation and would show variable valencies. The stability of the particular valence state would also depend upon the nature of the reacting species and the number of *d* electrons present.

Iron (Fe) shows normally Fe^{2+} and Fe^{3+} valence states. Atomic number of Fe is 26 and its electronic configuration would be: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$.

Loss of two electrons from 4*s* orbitals would not leave behind an inert gas configuration. Therefore, more chances of electrons to be pulled out exist. Since '*d*' orbitals would be more stable when half-filled (with d^5 configuration), so loss of one electron from 3*d* orbital along with two electrons from 4*s* orbitals would give a more stable state of the ion. Therefore, iron in Fe^{3+} state would be more stable. Let us show the valence shell having 3*d* orbitals and arrange the electrons in accordance with valence bond theory (See Chapter 4). In order to get next inert gas configuration more electrons would be required which are supplied by reacting species (Lewis bases or ligands) and the ions are thus stabilized. Mostly water will be acting as Lewis base and due to this reason most of the transition metal salts exist in stable state as hydrated species.



Elements of lanthanides and actinides show variable valencies due to the involvement of '*f*' orbitals.

(ii) Some of the '*p*' block elements show variable valency due to the involvement of an 'inert pair' of electrons. The 'inert pair' of electrons are present in the '*s*' orbitals and do not take part in chemical reactions under the prevailing conditions. Under such conditions only '*p*' orbitals would take part in bond formation. However, if the 'inert pair' of electrons present in '*s*' orbitals is actuated to take part in bond formation, an increase in valence state by two units will be observed. It is due to the 'inert pair' of electrons that the difference in valence states of such elements is always by two units. Following are given some of the examples of such type of ions:

$$\mathrm{Pb(II)} \longrightarrow \mathrm{Pb(IV)} \qquad \mathrm{In(I)} \longrightarrow \mathrm{In(III)}$$
$$\mathrm{Sn(II)} \longrightarrow \mathrm{Sn(IV)} \qquad \mathrm{Bi(III)} \longrightarrow \mathrm{Bi(V)}$$
$$\mathrm{Tl(I)} \longrightarrow \mathrm{Tl(III)} \qquad \mathrm{Sb(III)} \longrightarrow \mathrm{Sb(V)}$$

The stability of the 'inert pair' increases as the quantum shell containing them is further removed from the nucleus. In case of lead the bivalent state is far more stable than the tetravalent state. Thus, Pb(IV) compounds are oxidizing agents, being readily reduced to bivalent lead compounds.

$$\mathrm{Pb(IV)} + 2e^- \longrightarrow \mathrm{Pb(II)}$$

Although the inert pair effect is quite marked for bivalent tin compounds but tetravalent tin is more stable of the two. Hence, bivalent tin is readily converted to tetravalent state, and thus the former ion is a reducing agent.

$$\mathrm{Sn(II)} - 2e^- \longrightarrow \mathrm{Sn(IV)}$$

(iii) The '*p*' block elements which have vacant '*d*' orbitals available in their electronic configuration also show variable valency by utilizing these '*d*' orbitals in addition to the corresponding '*s*' and '*p*' orbitals. Thus the involvement of vacant '*d*' orbitals would be responsible for the variation in valence state of such elements. Let us consider the first two members of Vth group namely, nitrogen and phosphorus. There is no chance for the presence and involvement of '*d*' orbitals in nitrogen as indicated by its electronic configuration ($1s^2\ 2s^2\ 2p^3$) *i.e.*, no '*d*' orbital is available in the 2nd shell. Therefore, nitrogen would show a covalency of three only due to the involvement of $2p$ orbitals. It is for this reason that halides of nitrogen are always of type NX_3, (X = F, Cl, Br, I). However, phosphorus can form trivalent and pentavalent halides *e.g.*, PCl_3 and PCl_5, due to the involvement of $3d$ orbitals in addition to $3p$ orbitals (P_{15} has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3\ 3d^0$).

(2) COVALENT OR ELECTRON PAIR BOND:

There are many compounds which have low melting points, poor electrical conductivities in the liquid state and are freely soluble in non-polar solvents. These properties are not within the domain of ionic bonding and the class of compounds bearing such properties concerns mostly with the homonuclear diatomic molecules *e.g.*, H_2, Cl_2 etc. In such cases one cannot believe that an atom may be losing an electron which may be gained by the other atom during bond formation because both the atoms are expected to show identical behaviour. The compounds which show non-ionic behaviour are said to be covalently bonded.

The formation of a covalent bond involves the mutual sharing of a pair of electrons between two atoms, each atom contributing one electron to the pair. ***The sharing of electrons establishes the bond in covalent compounds.*** The mutually shared pair is considered to be possessed by both the atoms in common, which would contribute to the electronic configuration of each atom in the molecule. For example, each of the two chlorine atoms present in its molecule have seven electrons in their valence shell ($Ne_{10}\ 3s^2\ 3p^5$). Each chlorine atom would contribute one electron to the electron pair which is shared between two atoms in the molecule. In this way both the chlorine atoms would attain eight electrons (octet) in their valence shells (six electrons are possessed completely by each atom and the other two are mutually shared). Thus each chlorine atom acquires the stable electronic configuration of the next inert gas, argon ($Ne_{10}\ 3s^2\ 3p^6$). The process of mutual sharing may be represented diagrammatically as shown in Figure 3.11.

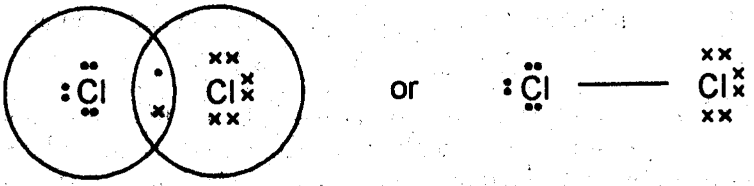


Fig. 3.11.

It is very convenient to show a single covalent bond by a single line joining the atoms of the elements together.

Water is a heteronuclear molecule containing oxygen and hydrogen atoms. In this compound the oxygen atom has electron configuration $1s^2\ 2s^2\ 2p^4$ and attains the next inert gas configuration by sharing an electron from each of the two hydrogen atoms. In this process, hydrogen atoms having electronic configuration $1s^1$ would attain the helium configuration ($1s^2$) upon sharing an electron of oxygen atom (Figure 3.12).

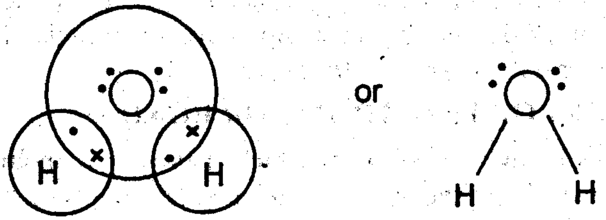


Fig. 3.12.

It is found that two or even three pairs of electrons also share mutually between atoms to produce double or triple bonds, respectively. Ethylene, for example, contains double bond and acetylene a triple bond between the carbon atoms.

In the original Lewis theory, it was suggested that elements forming covalent bonds have tendency to attain the electronic configuration of inert gases. However, many covalent compounds are also known in which the inert gas configuration is not reached. For example, boron ($1s^2\ 2s^2\ 2p^1$) forms only three covalent bonds in boron trifluoride, BF_3. This would give the outer electron shell of boron only six electrons, two electrons short of the next inert gas (neon) configuration ($1s^2\ 2s^2\ 2p^6$).

We can explain the formation of a covalent bond based upon the involvement of the concerned orbitals. Thus during the formation of a covalent bond in two fluorine atoms to form fluorine molecule, the unpaired electron in one of the orbitals (conventionally assumed to be 2*pz* orbital) pairs up with the unpaired electron in 2*pz* orbital of another F atom to form the bond pair of F_2 molecule. We can represent the chemical union of two fluorine atoms to form a fluorine molecule as shown in Figure 3.13.

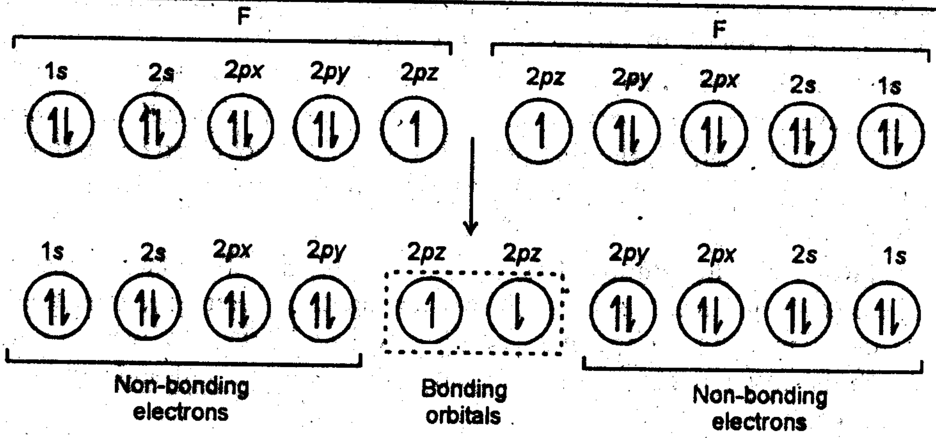
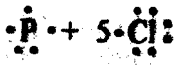


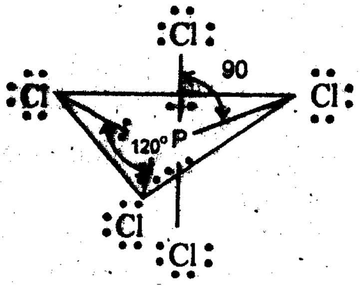
Fig. 3.13.

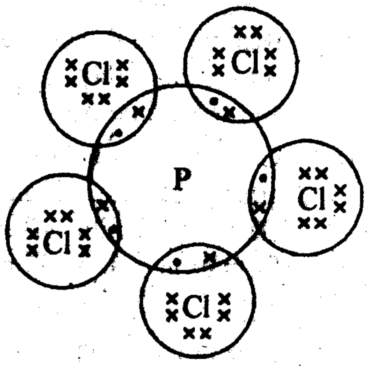
The above picture can be simplified as:

In phosphorus pentachloride, PCl_5, the phosphorus atom (Ne_{10} $3s^2$ $3p^3$) forms five covalent bonds. That is, the phosphorus atom would share its five electrons with five electrons of five chlorine atoms and thus increases the electron content in other shell from five to ten, two more than the next inert gas, argon (Ne_{10} $3s^2$ $3p^6$).

The formation of PCl_5 molecule with five covalent bonds have directional effect and can be represented as:







Similarly, sulphur hexafluoride, SF_6, attains six covalent bonds, thus attaining twelve electrons in its outer shell which is more than the electronic configuration of the next inert gas. In iodine heptafluoride, IF_7, the iodine (Kr_{36} $4d^{10}$ $6s^2$ $5p^5$) increases the number of electrons in its outer shell to fourteen by forming seven covalent bonds. Thus it may be seen that the attainment of an electron octet in the outer shell is not necessarily the only factor which determines the stability of covalent compounds.

Characteristic Features of Covalent Compounds:

During the formation of a covalent bond no ions are produced and thus very little mutual attraction exists between molecules. As a result the molecules are easily separated from one another. Therefore, the covalent compounds are gases or volatile liquids under normal conditions of temperature and pressure. Most common features of covalent compounds are:

(i) **Nature of the Bond:** The bonds are obtained by mutual sharing of electrons and may be intramolecular or intermolecular. The intermolecular forces in solid compounds having covalent bonds are weak (Van der Waals' forces). Therefore, the solid compounds are soft and can be easily broken.

(ii) **Melting and Boiling Points:** The melting and boiling points are relatively low due to weak intermolecular forces. If intermolecular forces are larger, the crystals will be somewhat harder and have higher melting points *e.g.*, Diamond, SiC etc.

(iii) **Conductance:** Since covalent compounds do not contain ions they will not be able to conduct heat and electricity *i.e.*, they are non-electrolytes.

(iv) **Solubility:** They are soluble in non-polar solvents such as benzene, ether etc., but insoluble in polar solvents such as water unless some interaction occurs with the solvent molecules. For example, the solubility of sugar (a covalently bonded organic compound) in water (a polar solvent) is attributed to the hydrogen bonding between the –OH groups in this organic molecule and water.

(v) **Reactivity:** Reactions between covalent compounds are generally much slower than those of ionic compounds because they involve the breaking and reforming of bonds.

(vi) **Conditions of Formation:** The covalent molecules are obtained from atoms of the elements having very similar ionization potential and electron affinity values. Under such conditions the possibility for the formation of ionic bond is ruled out.

(vii) **Directional Character of the Bond:** Whereas the ionic bonds are non-directional, the covalent bonds are directional in character. Hence individual covalent compounds possess definite shapes of their molecules. This factor may also be responsible for slow rate of reaction and may even determine the nature of the reaction in some cases.

(viii) **Dielectric Constant:** The dielectric constant ($\in$, the ratio of the coulombs for a substance compared to that of a vacuum) values of covalent molecules are low (benzene = 2.3). The molecules of compounds having dielectric constant of unity must have a dipole moment zero.

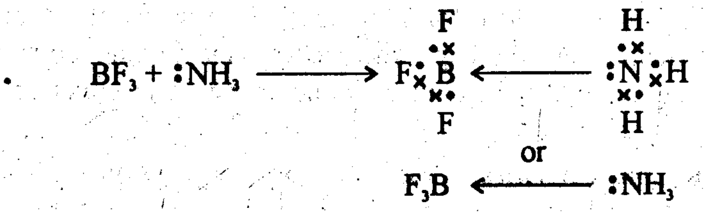
(ix) **Resonance:** More than one conceivable structure may be achieved while considering the possible distribution of electrons between atoms within a molecule. Out of all the possible electronic structures obtained by rapid interchange (resonance), the one which actually exists (resonance hybrid) will possess the minimum energy of the system. The minimum energy is the criteria of maximum stability. Resonance is very common phenomenon occurring in organic compounds.

(x) **Covalency Maximum:** Sidgwick pointed out in 1933 that the maximum number of covalent bonds formed by an element would be related to its position in the Periodic Table. Thus carbon, a member of the IVth group will be able to form four covalent bonds. Similarly, phosphorus (a member of the Vth group) would be able to form at the most 5 covalent bonds and sulphur (a member of the VIth group) would form 6 covalent bonds. The maximum number of covalent bonds formed by an atom will depend upon the number of paired and unpaired electrons present as well as upon the number of vacant orbitals available in the atom of that element.

(3) COORDINATE-COVALENT BOND:

A covalent bond in which the shared electron pair is donated by one atom only is called ***coordinate-covalent bond***. This type of bond is obtained between atoms which are either ***electron-pair donors or electron-pair acceptors***. The electron-pair donor atoms are usually called Lewis bases and electron pair acceptors as Lewis acids. Lewis acid-base reactions would result in the formation of coordinate-covalent bonds. The process of such bond formation is called **coordination**. The bond is usually shown by an arrow which runs from the donor atom and goes towards the acceptor.

The Lewis bases or electron pair donors are atoms, molecules or compounds which possess lone-pair of electrons as yet not utilized by any bond. Lewis acids are usually electron deficient atoms, molecules or compounds which would resort to inert gas or stable configuration by taking up one or more lone-pair of electrons. The lone-pair donated by Lewis base would now be commonly shared between the donor and the acceptor atoms and hence the idea of a coordinate-covalent bond. Let us take an example of an electron deficient molecule BF_3. It reacts readily with NH_3 to form an adduct.



$$BF_3 + :NH_3 \longrightarrow \begin{array}{c} F \\ \bullet\times \\ F{\overset{\bullet}{\underset{\times}{}}}B \\ \times\bullet \\ F \end{array} \longleftarrow \begin{array}{c} H \\ \bullet\times \\ :N{\overset{\bullet}{\underset{\times}{}}}H \\ \times\bullet \\ H \end{array}$$

or

$$F_3B \longleftarrow :NH_3$$

(coordinate-covalent bond)

Similarly, transition elements (such elements which have partially filled *d* or *f* orbitals) would form compounds with electron-pair donors (ligands), called coordination compounds. Here transition elements would act as Lewis acids because they are short of electrons due to the presence of unfilled *d* or *f* orbitals.

For example, silver chloride dissolves in ammonia to form the coordination compound, $[Ag(NH_3)_2]$ Cl or its ion $[Ag(NH_3)_2]^+$ (soluble in water). The reaction may be written as:

$$Ag^+Cl^- + 2 : NH_3 \longrightarrow [H_3N \longrightarrow Ag \longleftarrow NH_3]^+ Cl^- \text{ or } [Ag(NH_3)_2]Cl$$

Thus any atom which possesses a lone pair of electrons in its valence shell can act as a donor to a suitable acceptor. On the other hand, any atom which does not possess the electron pairs in its valence shell can act as an acceptor of lone-pair of electrons.

The most common donors are the halogen atoms in the form of halides, $:\underset{\cdot\cdot}{\ddot{X}}:^{-}$; the oxide ion, $:\underset{\cdot\cdot}{\ddot{O}}:^{-2}$; the hydroxide, $:\underset{\cdot\cdot}{\ddot{O}}\cdot H^{-}$; the water molecule, $H_2\underset{\cdot\cdot}{\ddot{O}}:$; the nitrogen atom of ammonia, $:NH_3$, and the phosphorus and arsenic atom in phosphorus and arsenic compounds such as $:PF_3$ and $:AsCl_3$, respectively.

The most common acceptors are electron deficient molecules (usually 3rd group elements, *i.e.*, BCl_3, AlF_3, $GaCl_3$ etc.) or transition elements having partially or incompletely filled *d* orbitals. A typical electron pair acceptor is H^+. As hydrogen ion, H^+ is simply a proton with no electron cloud around it, Its tendency to accept an electron pair is extremely large.

CHARACTERISTIC FEATURES OF COORDINATION COMPOUNDS:

The coordination compounds contain coordinate-covalent bonds and are characterised by properties close to covalent compounds. The physical properties of coordination compounds depend upon the nature of the donor atoms or molecules (ligands) as well as the oxidation state of the transition metals (electron-pair acceptors).

Following points will give us the broad spectrum view of the physical and chemical characteristics of coordination compounds. However, these features should not be taken very rigorously:

1. **Melting and Boiling Points:** The coordination compounds possess fairly high melting and boiling points which are more than those of the covalent compounds but less than the true ionic compounds. Usually these compounds decompose while melting and boiling. The melting and boiling point range for such compounds indicates that coordinate bond is not true covalent bond but possesses a partial polar character.

2. **Electrical Conductivities:** Some of the coordination compounds are fairly good conductors of electricity but this is due to the presence of complex

ions which have been stabilized by oppositely charged ions linked through ionic bonds. The neutral complexes which carry no charge on the complex ions are non-conductors.

3. **Solubility:** The solubility of coordination compounds varies. Some of these compounds are soluble in water but may be decomposed in this solvent or when brought into contact with it due to the replacement of other weak donors by water molecules (H_2O molecule has lone-pair of electrons and possesses donating power to establish new coordinate bonds). The neutral complexes mostly carrying organic reagents as donor molecules (ligands) are soluble in organic solvents.

4. **Stability:** Some of the coordination compounds are very stable but others are easily decomposed. A deep blue coordination compound, copper phthalocyanine is very resistant to attack by air, water, sunlight, acid, heat, etc. and is used as a pigment in automobile paints. The tetrammine copper (II) sulphate, $[Cu(NH_3)_4]\ SO_4$ is not very stable and decomposes upon heating in aqueous solution to liberate ammonia. (The factors affecting the stability of coordination compounds will be discussed in detail in chapter 18).

5. **Reactivity:** There are two types of coordination compounds, *labile* and *inert*. The labile complexes undergo rapid reactions but inert complexes show very slow reactivities with other substituents. An example of a labile complex is a water complex with Ag^+ which undergoes rapid *substitution reaction* with ammonia molecules:

$$[Ag(H_2O)_2]^+ + 2NH_3 \xrightleftharpoons{\text{Water}} [Ag(NH_3)_2]^+ + 2H_2O$$

6. **Colour:** Almost all the coordination compounds of transition metals are coloured. The colour of these compounds is the result of electronic transitions.

7. **Paramagnetism:** Many of the coordination compounds of transition metals are paramagnetic (show magnetic behaviour), which indicates the presence of unpaired electronic spins. We shall see in the next chapter that the number of unpaired electrons give information about the insight into the nature of bonding in coordination compounds. $\mu = \sqrt{n(n+2)}$

μ = magnetic moment in Bohr magneton.

8. **Isomerism:** The coordination compounds show a variety of isomerism, because coordinate bonds are directional and arrange along definite directions in space around the central metal ions (mostly transition metals).

(4) METALLIC AND NON-LOCALISED BOND:

A metal may be defined as a substance which possesses a bright appearance called *metallic luster* and is a good conductor of heat and electricity. In addition to that a metal shows high tensile strength, malleability and ductility. In spite of the extensive use of many common metals as well as the extensive studies on their physical and chemical characteristics, the nature of the bonding between the atoms in a metal has been until recently very unsatisfactory. In order to understand the nature of the metallic bond and the structures of the metals, we shall review the general characteristics of metals.

CHARACTERISTIC PROPERTIES OF METALS:

Metal structures have some common characteristic properties such as:

1. **Metallic Luster:** Metal surface have a bright shiny appearance because they are good reflector of visible light incident upon them. Most of the metals reflect all wavelengths of white light and thus have silvery white appearance. However, copper and gold are coloured because they absorb fairly good amount of blue light and reflect the rest.

2. **Malleability or Ductility:** Metals can be drawn into foils and beaten into thin sheets instead of breaking up on striking as ionic crystals would do. The malleability and ductility of metals vary from one metal to another. Thus gold is highly malleable but tungsten is worked with extreme difficulty. The malleability varies in various allotropic forms of the same metal. For example, white tin is highly malleable and soft and possesses metallic luster, but the grey tin is brittle and crumbles to dull grey powder.

3. **Electrical and Thermal Conductivity:** Metals are good conductors of electricity *i.e.*, when potential difference is maintained between two ends of the metal bar or wire, electric current rapidly flows through it. Similarly, if two ends of the metal are maintained at different temperatures, heat energy is rapidly transmitted from hot source to cold sink. Metals usually conduct heat 10 to 1,000 times more than other substances, but differences in electrical conductivities are even greater.

4. **Thermionic Emission:** When a metal is heated it emits electrons by thermionic emission collected at the anode *i.e.*, diode. Thus a heated metal may be considered to boil off or sublime electrons.

5. **Photoelectric Effect:** On irradiating the clean surface of a metal with light of *suitable wavelength* electrons are emitted, called photoelectrons. The rate of emission of photoelectrons depends upon the *intensity of radiation* but the kinetic energy of emitted electrons is a function of wavelength of the light radiation.

6. **Magnetic Behaviour:** When a metal is placed in a non-uniform magnetic field it may either be attracted or repelled from regions of higher field. The substances attracted by the magnetic field are called *paramagnetic* and those repelled, *diamagnetic*.

Such and other properties of metals would help in understanding their structure, and the nature of the metallic bond as given in the following discussion.

STRUCTURE OF METALS:

The structures of metals have very high coordination number (eight or twelve) and possess very high electrical and thermal conductivities. The metal atoms are packed closely to build up the crystal structure or lattice. Thus a metal may be regarded as an assembly of positive ions, usually considered as spheres of identical radius which are packed together to fill space as completely as possible.

In order to understand the close packing of atoms in metal structures, let us consider an analogy. If a number of solid spheres or metallic balls are packed in a box as shown in Figure 3.14(a) and box is well shaken, the balls will rearrange in the manner shown in Figure 3.14(b). The arrangement of spheres in Figure 3.14(b) is more stable and more closely packed. Same is the type of arrangement of atoms present in metal structures.

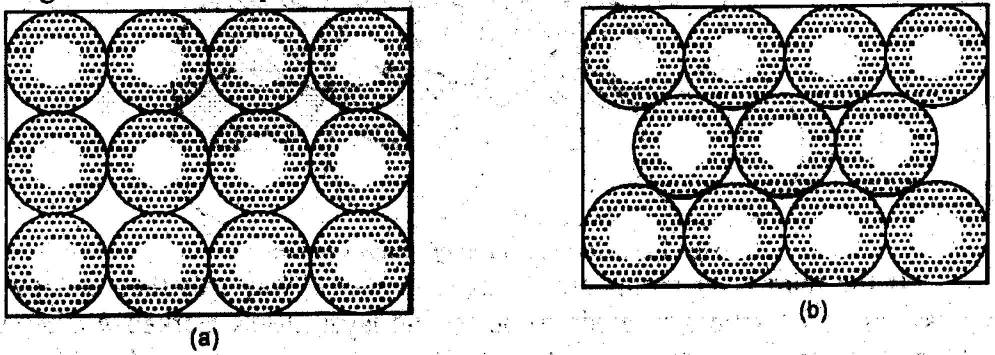


Fig. 3.14. Packing of spheres in a box (two dimensional views).

The majority of metals possess one of the three major types of crystal structures *i.e.*, face-centred cubic, body-centred cubic, and closely packed hexagonal structures.

Let us see how various unit cells of the crystal lattices are developed from various type of arrangements of atoms in metal structures. If three atoms join together in one plane and in the first layer and then a fourth atom is inserted in the space created by the other three as second layer atom, a tetrahedral structure is obtained (see Figure 3.15). Similarly, other crystal lattices are developed.

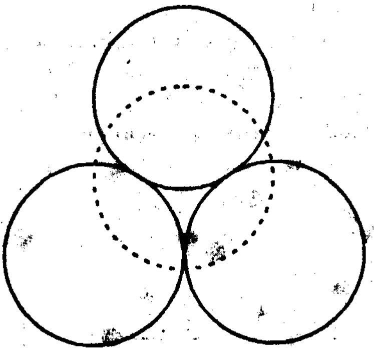


Fig. 3.15. The formation of a tetrahedral site.

Now consider 11 atoms arranged in the first layer (See Figure 3.16). The second layer atoms (shaded) would fit into the depressions (crevices or interstices) creating some new interstices (marked A) or allowing the interstices (marked B) created by the first layer atoms to continue as shown in Figure 3.16.

Now the third layer atoms may fit into the interstices A or B. If the third layer atoms fit into the interstices marked B those interstices will be blocked by them and atoms will not lie directly above those of the first layer atoms. This layer pattern will be of 1 2 3 or A B C type which represents *face-centred cubic arrangement*. This arrangement is generally represented as ABC ABC ABC or 1 2 3 1 2 3 1 2 3 ……,

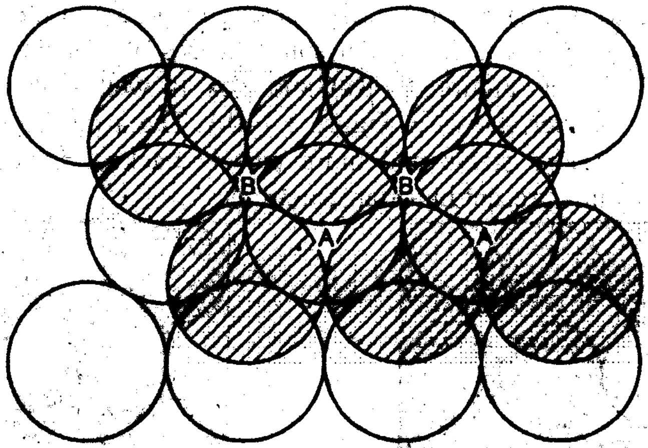


Fig. 3.16. Close packing of spheres (atoms).

If the third layer atoms are arranged in such a way that they occupy the depressions or interstices created by the second layer atoms marked A, they will be directly above the first layer atoms. This pattern represents *closely packed hexagonal* arrangement and is usually written 121 or ABA arrangement. The body centred cubic structure has also a layer pattern of the type 121 or ABA, but the spheres (atoms) are not so closely packed as in the close-packed hexagonal structure.

The closely packed hexagonal and face-centred cubic structures have 12-fold coordination, *i.e.*, each metal atom is surrounded by twelve nearest neighbours. In body centred cube each atom is surrounded by eight other atoms, *i.e.*, 8-fold coordination (Figure 3.17).

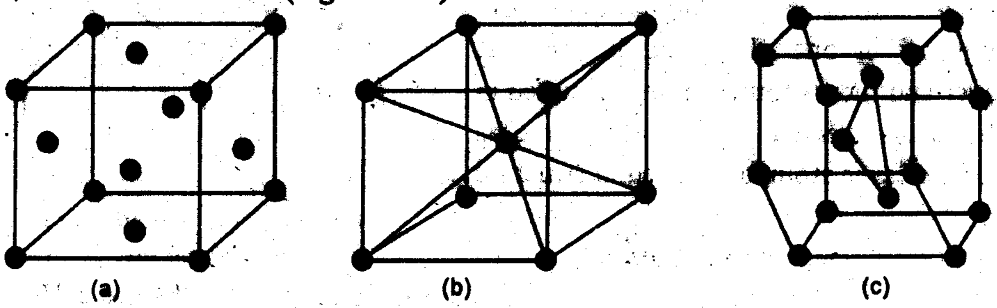


Fig. 3.17.

(a) Face-centred cubic structure.

(b) Body-centred cubic structure.

(c) Closely-packed hexagonal structure.

THEORIES OF METALLIC BOND:

The high coordination numbers and presence of relatively poor electrons available for bonding in the atoms of metals do not favour the possibility of the existence of ordinary covalent bonds between metallic atoms. At the same time the physical properties of metals are not like those of ionic compounds which indicate the absence of electrostatic forces operating between atoms within a metal. Moreover, the metallic structures possess considerable strength which indicates the presence of forces greater than those of the Van der Waals' type. It becomes interesting to study the nature of the metallic bond. Following theorics have been put forward to explain the metallic bonds:

(a) Electron gas theory. (b) Bloch-Sommerfeld theory.
(c) Pauling theory. (d) Band theory. (MOT)

(a) Electron Gas Theory: The properties of the metals suggest that the valence electrons are relatively free to move through the metallic structure. Figure 3.18 suggests a model about the metallic structure in which electrons form a sea of negative charges around the positive ions which are held together tightly. Since metals have high melting points and high densities. It should be pointed out that *'electron sea'* or *'electron gas'* must strongly bind the positive ions in the crystal.

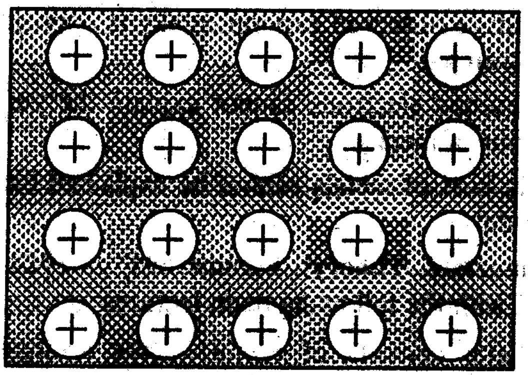


Fig. 3.18. Cross-section of structure of a metal with an 'electron sea' or 'electron gas'.

Electron gas theory is based upon three assumptions:

1. The metal atoms are arranged in a closely packed crystal lattice. Each atom loses one or more electrons resulting in the formation of charged metal ions called atomic cores.
2. The electrons move freely within the boundaries of the metal structure like ideal gas molecules within a container.
3. The electrons hold the metallic ions or atomic cores by coulomb attractive forces like an 'electronic glue'.

The electron gas model easily accounts for the high electrical conductivity of metals because of the tremendous speed of very light electrons (the speed of an electron is 1.2×10^{15} A°/sec and the distance between atomic cores in metals is usually less than 5 A°. As a result, an electron can move from one electron core to another in less than 4×10^{-15} seconds) which rapidly transfers electrical charge from one end to another. Thermal energy is transferred by the translational motion of electrons and vibrational motion of the atomic core or metal ions.

Since there is no preferred direction of bonding, it should be quite easy to distort the metal lattice. This would explain the malleability of metals because it would be easy to slide one plane of atoms over another which can be easily packed.

The metals have shiny surfaces because of their high reflectance. Electromagnetic radiation of visible light (wavelength 4000 – 8000 A° and frequencies of about 5×10^{14} cycles/second) causes the surface electrons to oscillate back and forth with the same frequency as that of incident light. Thus radiation of the same frequency as that of incident radiation is emitted as a reflection of the incident beam.

In spite of its merits in explaining some characteristics of metals, the electron gas theory meets with many failures. Some of its *drawbacks* are :

1. The decrease in electrical and thermal conductivity with increasing temperature observed experimentally is opposite to the behaviour of an electron gas.
2. Free gaseous electrons cannot explain the very small paramagnetic behaviour of metals.
3. Specific heat of metals cannot be explained based upon the electron gas model.

(b) Bloch-Sommerfeld Theory: Sommerfeld in 1928 and later on Bloch proposed this theory with the following main features:

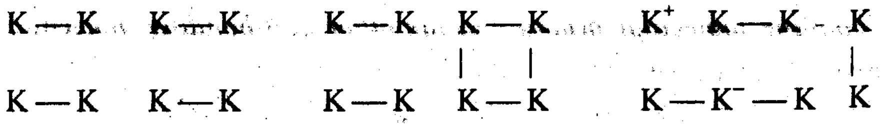
1. The metal consists of atomic cores arranged in closely packed structures. The electrons are removed from the neutral metal atoms which would be loosely bound and are referred to as valence electrons.
2. The positive cores have a region of negative potential within the volume occupied by the metal. The potential is assumed to be zero within the metal and very high outside the metal.
3. The electrons are confined to the interior of the metal due to high potential outside obeying all requirements of quantum mechanics.

The first and the second postulates are very similar to electron gas model. According to the third postulate, quantum mechanical treatment would offer wave character to electrons and restrict the electron energies to certain 'permitted' bands called *Brillouin Zones*. There would be empty bands of forbidden energies and to cross these empty bands a large amount of energy would be required.

The Brillouin zone or energy band corresponds to one quantum state and the breadth of zone depends on the overlapping of the electron clouds. The electrons present in the overlapping zones may be considered mobile. ***It is these mobile electrons which produce metallic bonds.***

Although Bloch-Sommerfeld concept explains most of the characteristic properties of metals and need not be modified but it is subject to criticism. Firstly, some of the properties of metals are only imperfectly explained by this theory. Secondly, the idea of uniform potential everywhere in the metal is unrealistic and very crude. Thirdly, if variation in potential is allowed in the concept about metallic bond, properties of metals can more reasonably be explained.

(c) **Pauling Theory (Valence Bond Concept):** According to Pauling, the structures of metals may be considered in terms of covalent bonds which resonate among interatomic positions in the metals. Resonance permits the formation of covalent bonds more than expected. For example, we can write down a large number of resonating structures of metals, and the overall stable character of the metallic structure is due to the resonance hybrid of all these different forms. In structure III, two covalent bonds are formed by making use of *sp* hybrid orbitals. The resonating structures can best be considered if unoccupied orbitals of suitable energy are available for hybridization.

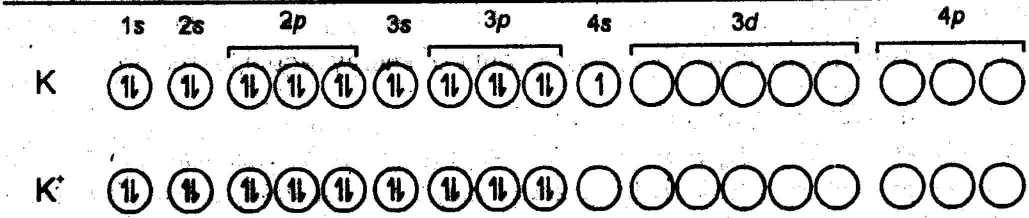


$$\begin{array}{cccccccc} K—K & K—K & K—K & K—K & K^+ & K—K & & K \\ & & & | \quad\ | & & & & | \\ K—K & K—K & K—K & K—K & K—K^- & —K & & K \end{array}$$

I II III

The characteristic properties of metals can be explained based upon this valence bond resonance concept. Thus, the electrical conductivity of metals can be explained in presence of an electric field due to the rearrangement of positive charges towards cathode and negative charges moving towards the anode.

Let us now consider the electronic configuration of potassium (K_{19}) *i.e.*, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. In such an arrangement, it is obvious that $3d$ and $4p$ orbitals are unfilled and by loss of one electron from $4s$ it is also rendered vacant. These extra-orbitals which are not occupied partially or fully by electrons are called 'metallic orbitals'. These orbitals will be responsible for the formation of metallic bonds and would characterise the elements bearing them as metals. Carbon will not be a metal because it does not contain any vacant orbitals after sp^3 hybridization.



The strength of the metallic bonds would also depend upon the valency electrons that each atom can attribute. In going from left to right in the Periodic Table; K, Ca, Sc, Ti, V and Cr the valence electrons shown are 1, 2, 3, 4, 5, and 6, respectively. Thus, the strength of metallic bond would increase from K to Cr which is observed by increase in melting points, hardness and other metallic characteristics.

(d) Molecular Orbital Theory (Band Theory) : The details of molecular orbital theory will be discussed in Chapter 4 but the important points concerning its applications to the nature of metallic bonds are discussed over here.

When identical atoms in their ground states are infinitely separated, the waves functions (and thus their energies) of their electrons are identical. On bringing the two electrons closer together their electron clouds overlap more and more resulting in more and more interaction. When two atoms come close together a mutual perturbation of orbitals takes place and two new molecular orbitals are formed with different energies. One of these molecular orbitals is called ***bonding molecular orbital and the other anti-bonding molecular orbital*** as shown in Figure 3.19.

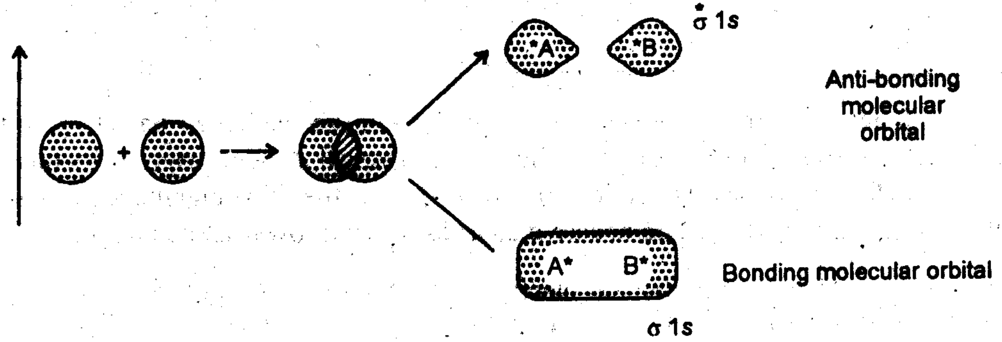


Fig. 3.19. Overlapping of atomic orbitals results in the formation of a low energy bonding M.O. and high energy anti-bonding M.O.

Let us now consider four identical atoms A, B, C and D. On bringing them close together it would be seen that each atomic orbital pair gives rise to one bonding (σ) and one anti-bonding (σ*) molecular orbitals as shown in Figure 3.20.

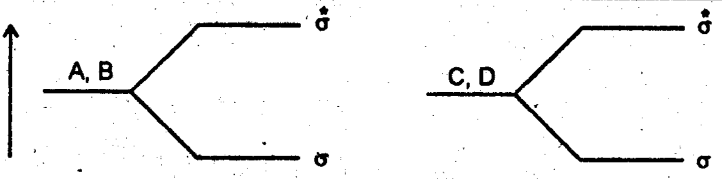


Fig. 3.20.

If we combine the overlap criterion of A, B, C and D, we get the diagram shown in Figure 3.21.

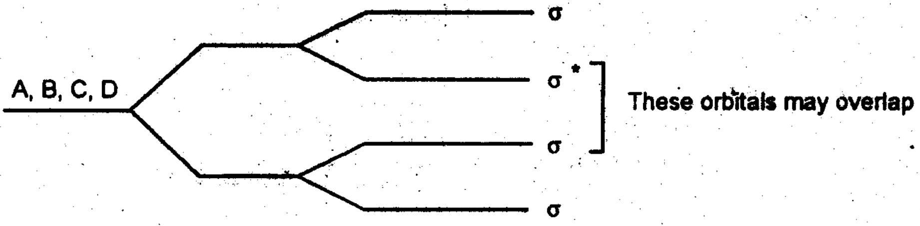


Fig. 3.21.

Thus four atomic orbitals would give rise to a total of four molecular orbitals — two are of bonding and two of anti-bonding type. Similarly, eight atomic orbitals would form a total of eight molecular orbitals. Thus N identical atoms (say of metals) would form N molecular orbitals. If N is very large number, the difference in energy between various molecular orbitals would be very small *i.e.*, in 1 cm^3 of metal about 10^{22} atoms would give rise to 10^{22} molecular orbitals with 10^{-20} kcal./mole as the average energy separation. Each of the closely spaced groups of molecular orbitals would look like a band (Figure 3.22).

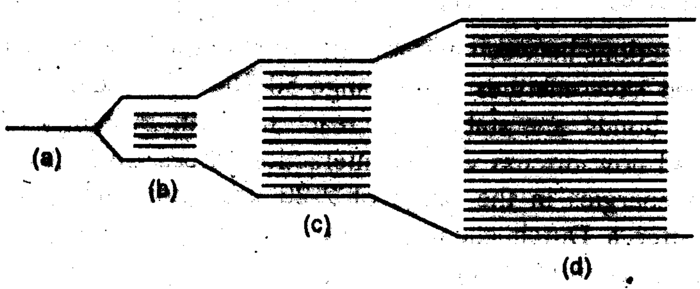


Fig. 3.22. Molecular orbital energy states of a system with 'N' atoms.

(a) An atomic orbital of infinitely separated atoms, (b) N molecular orbitals of internuclear distance r_b; (c) N molecular orbitals at internuclear distance $r_e < r_b$; (d) N orbitals at internuclear distance $r_d < r_e$ (equilibrium distance).

Let us apply these band model concepts to the formation of crystal lattice for sodium. Take N atoms of sodium and place them in a body centred cubic lattice. The electrons of $n = 1$ and 2 are closer to the nucleus and will not be affected much. In other words, lower orbitals will be completely filled up to $2p$ orbitals. In going to $3s$, N orbitals will overlap frequently to form a conduction band as shown in Figure 3.23. Since this conduction band is half-filled, vacant orbitals would be created by overlap criterion as discussed above. These vacant orbitals will get electrons which are excited from lower orbitals and would explain the properties of metallic sodium.

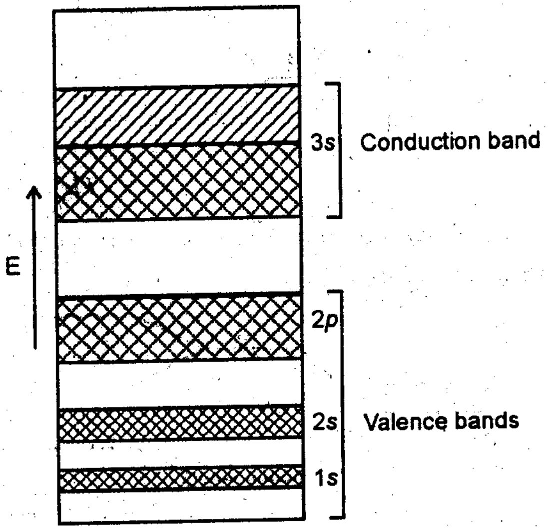


***Fig. 3.23.* Filling of energy bands of sodium. The filled orbitals are indicated by vertical cross-hatching.**

The electrical conductance depends upon the movement of electrons under the influence of an applied field. The electrons accept energy and move to higher unoccupied levels. Thus in metal structures unoccupied orbitals become available which are mainly responsible for the movement of electrons and hence the electrical conductivities.

(5) VAN DER WAALS' FORCES AND BONDS:

The interactions between atoms considered uptill now are quite strong and the bonds formed have energies in the range 50-300 kcal./mole. The compounds possessing such bonds are stable and react to form products of even more stability. We shall now discuss weaker interaction forces which give rise to small values of bond energies in the range of 2-20 kcal./mole. The Van der Waals' forces named after a Dutch chemist, were originally postulated to explain the deviation of real gases from the ideal gases.

There are two principal Van der Waals' forces. The important force at short range is the repulsion between electrons in the filled orbitals. The second force is the attraction due to dipole-dipole interaction as shown in Figure 3.24. Permanent dipole-dipole interactions are slightly stronger than dipole-induced dipole attraction. The forces of attraction between fluctuating dipoles are weaker and are called London forces.

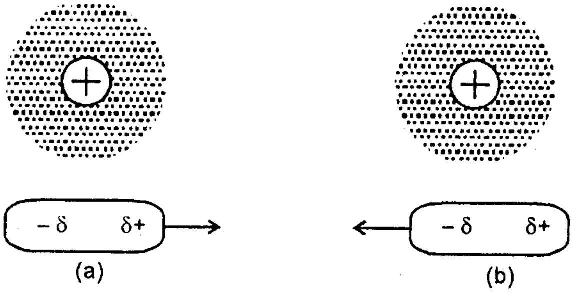


Fig. 3.24. The dipole-dipole interaction resulting in attractive forces.

The Van der Waals' forces operate effectively when the distance between molecules is about 5 A°. The strength of the Van der Waals' forces depends upon the size and molecular weight of molecules. Also, the attraction between molecules increases with an increase in size and molecular weight. This attraction also affects the boiling points of non-polar molecules, since boiling point of a substance is a measure of the amount of energy required to disrupt Van der Waals' forces present in bonds. For example, the strength of the Van der Waals' bonds increases in inert gases with the increase in atomic number. Similarly, boiling points of inert gases also increase with increasing molecular weight as shown in Table 3.3.

TABLE 3.3

A Comparison of Size, Molecular Weight and Boiling Points of Inert Gases

Inert Gas	Radius of Molecule (pm)	Molecular Mass	Boiling Point, °C
Helium	93	2	– 269
Neon	112	10	– 246
Argon	154	18	– 186
Krypton	169	36	– 152
Xenon	190	54	–108
Radon	22	86	– 62

Similarly, straight chain alkanes, with general formula C_nH_{2n+2}, show increasing boiling points with increasing value of *n* because of the increase in molecular size. Increase in melting and boiling points with increase in molecular weight and size may be due to greater energy needed to move a heavy molecule. The larger surface area with increasing molecular weight is also an important factor in determining the stability of molecules.

Van der Waals' forces are important in P_4 and S_8 molecules. The size affect is also considerable. Thus solid O_2 melts −219°C whereas sulphur having greater molecular weight and size has sold S_8 which melts at 119°C. Similarly, intermolecular Van der Waals' bonding is much stronger in solid P_4 (m.p. 45.1°C) than in solid N_2 (m.p. − 210°C).

Evidence of Van der Waals' Forces:

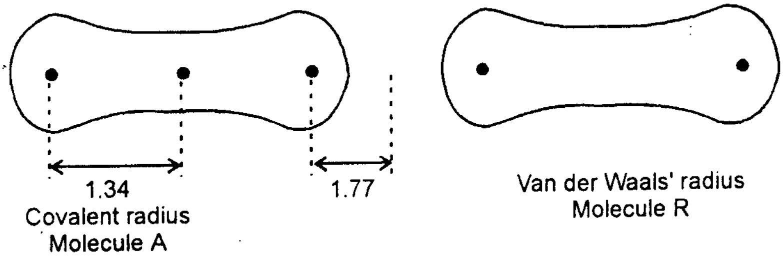
Abundant evidence is available in favour of Van der Waals' forces operating between uncharged atoms and molecules in the solid, liquid or gaseous states. The evidences in favour of the presence of Van der Waals' forces are :

(a) **The inert gases:** The atoms of these gases are incapable of forming normal valence bonds but can be condensed to liquid and solid phases with the evolution of energy. This behaviour indicates the presence of cohesive forces operating between the inert gas structures.

(b) **The Joule-Thomson effect:** Cooling effect of gases, when allowed to expand suddenly, is called Joule-Thomson effect. Cooling on expansion must be taking place due to the fact that attractive forces (Van der Waals' forces) are to be overcome in the course of expansion resulting in the absorption of energy and thus the cooling effect.

(c) **The non-ideality of real gases:** Van der Waals (1873) while dealing with the behaviour of gaseous phase introduced a mathematical term $\frac{a}{V^2}$ and proved the existence of attractive forces acting between atoms.

Let us now compare the values of Van der Waals' and covalent radii. Van der Waals' radii are always larger than the corresponding covalent radii which indicates that the Van der Waals' forces are much weaker.



(6) HYDROGEN BONDING:

Polar molecules are stabilized in a molecular solid by the interaction of oppositely charged ends of the dipole resulting in mutual attraction, called *dipole-dipole interaction* as shown in Figure 3.25. An important type of polar interaction

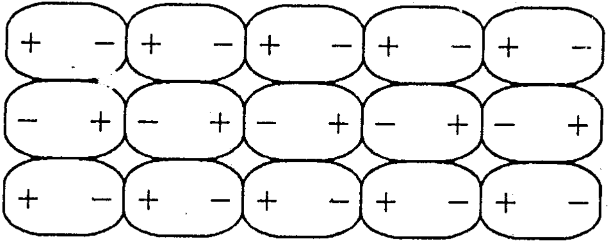
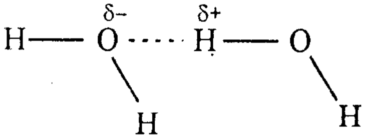


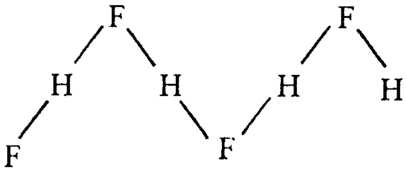
Fig. 3.25. Packing of polar molecules arising out of polar interaction.

is called hydrogen bond. This is primarily an electrostatic bond present between positively charged hydrogen atoms and a small, electronegative atom *i.e.*, F, N, O. The hydrogen bond arises out of imprisonment of a proton between two electronegative atoms. Hydrogen bonding is very weak with bond energies in the range of 2-10 kcal./mole. A hydrogen bond between two atoms A and B can be written A--H ······ B where A--H bond indicates a covalent bond and H ······ B, the hydrogen bonding. The extra attraction due to hydrogen bonding is stronger than Van der Waals' forces but smaller than ordinary covalent or ionic bonds. Thus hydrogen bond is moderately strong. In general, whenever polar molecules come near to one another, the positive end (δ^+) of one molecule interacts with the negative end (δ^-) of another because of the electrostatic attraction between them. For example, the partially charged hydrogen atom, $H^{\delta+}$ of one water molecule interacts with partially charged negative oxygen, $O^{\delta-2}$ of another water molecule.

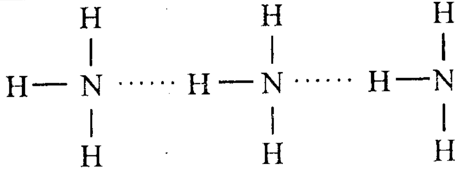


Ice is an example of a cluster of water molecules having extensive hydrogen bonding. The structure of ice bears tetrahedral symmetry in which relatively large open spaces are found. Upon melting ice, some of the hydrogen bonds are ruptured. As a result of this the water molecules may rotate slightly and move into open spaces which decrease the molar volume. Since the bond rupturing process takes place by increasing temperature which decreases the volume whereby increasing the density at about 4°C.

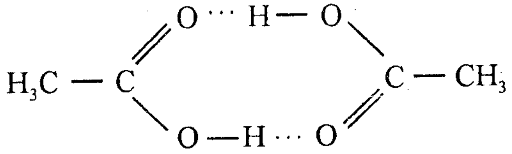
Other examples of hydrogen bonded molecules are:



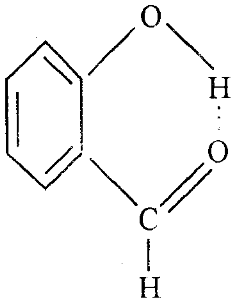
Hydrofluoric acid



Ammonia



Acetic acid dimer (note two hydrogen bonds)



Salicylaldehyde-hydrogen bond

NATURE OF HYDROGEN BONDING:

A hydrogen atom has electronic configuration $1s^1$ and can form either one covalent or ionic bond. Since $2s$ and $2p$ orbitals are too high to be involved in the formation of bonds so the following theories are adopted to explain the nature of hydrogen bonding.

(i) **Electrostatic approach:** Since hydrogen bonding occurs between hydrogen and a very electronegative element so electrostatic forces must be responsible for such type of bond.

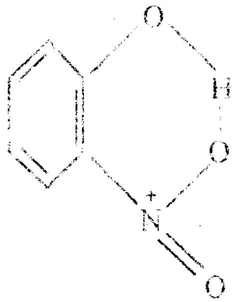
(ii) **Valence-bond treatment:** In this treatment the covalent contribution to hydrogen bond is emphasized. For example, the following structures are contributing towards hydrogen bonding.

$A—H \cdots\cdots B$	Covalent A — H bond
$A^{\delta-}—H^{\delta+} \cdots\cdots B$	Ionic $A^{\delta-}—H^{\delta+}$ bond
$A^{\delta-}—H^{\delta+}—B$	Covalent H — B bond

(iii) **Molecular orbital treatment:** Pimentel has considered hydrogen bond based upon molecular orbital theory. Thus linear combination of s atomic orbitals of hydrogen and p orbitals of electronegative element would form hydrogen bonds. Bonding, non-bonding and anti-bonding orbitals are produced.

THE IMPORTANCE OF HYDROGEN BONDING:

1. Hydrogen bonding is quite important in explaining the properties of certain liquids such as dielectric constants, high boiling points and low vapour pressures of solvents (water and alcohol etc., bearing hydrogen bonds) Water is a liquid at room temperature (b.p. 100°C) but H_2S is a gas because of presence of hydrogen bonding in water and absence of hydrogen bonding in H_2S. *m* and *p*-nitrophenols because of hydrogen bonding in the ortho isomer. The *m*- and *p*-isomers show inter-molecular association which causes increase in boiling points. Since O-nitrophenol has hydrogen bond in its molecule, it cannot show intermolecular association and can readily be separated from one another having low boiling points



2. Hydrogen bond energies are relatively small and chemical reactions which involve breaking of weak bonds take place readily. Thus biochemical systems undergo smooth and rapid chemical reactions. Hydrogen bonding in proteins is very important in biochemical functions, *e.g.*, oxygen transport and storage (haemoglobin), regulation of metabolism, control of hereditary transmission and various enzyme reactions.
3. The structure of nucleic acid has hydrogen bonds which plays major role in its behaviour in biochemical processes.
4. Special characteristics of water are due to hydrogen bonding in its molecules. Thus water has unusually high heat of vaporization and specific heat. Therefore, water acts as a large thermostat and confines the temperature of the earth within moderate limits. Water is also used to transfer heat from one place to another. That is why it is used in automobile radiators, heating systems and solar-energy collectors.

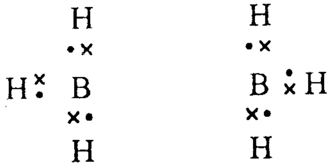
   Other simple hydrides of strongly electronegative elements associated through hydrogen bonds also show high melting and boiling points etc
5. Hydrogen bonding is responsible for unexpected high solubilities of compounds containing oxygen and nitrogen in solvents having one or more hydrogen atoms on a fairly electronegative atom. For example, organic acid halides are generally soluble in $CHCl_3$ rather than CCl_4.

   The high solubility of ammonia in water is due in part to the formation of fairly strong hydrogen bonding between them.

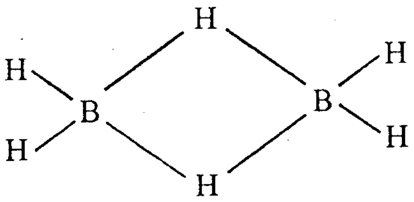
6. Many ionic compounds having oxygen in them are soluble in water due to hydration of anions through the formation of hydrogen bonds.
7. Hydrogen bonds are important in determining the crystal structures of some compounds. Thus, hydrogen bonds in crystalline oxalic acid may produce either two-dimensional layer lattices (the α form) or one dimensional chains (β-form).
8. Due to hydrogen bonding water shows maximum density at 4°C and on further cooling to 0°C density decreases with expansion in volume of ice. Water pipes burst if temperature falls below 0°C. Ice floats on the surface of water. This has a great advantage as marine animals and fish etc., remain unaffected by ice formation on the surface of water.

(7) ELECTRON DEFICIENT MOLECULES:

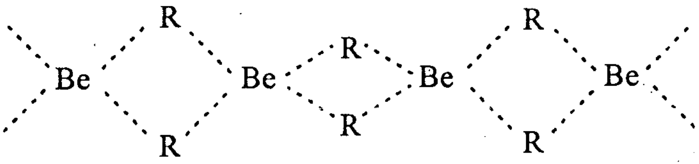
The class of compounds which have strong tendency to accept electrons because they have too few electrons to provide a total count of electrons required for next inert gas configuration are called electron deficient molecules. Elements of Group II and III (beryllium, boron and aluminium etc.) have strong tendency to accept electrons and require tetrahedral configuration. The molecules possessing 'lone pair' of electrons and readily combine with the electron deficient molecules to remove their electron deficiency. Thus boron has electronic configuration $1s^2\ 2s^2\ 2p^1$ which indicates the shortage of electrons. In order to get the due share of electrons the orbitals overlap with some atoms which form bridge structures. Diborane is a typical example of compounds having bridge hydrogen atoms. Let us consider the structure of diborane. Diborane is made up of two BH_3 units. Each BH_3 unit is short of two electrons than required to complete the octet for stability.



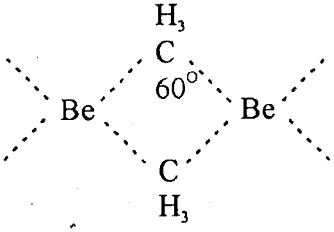
As both the BH_3 groups are short of electrons, it is difficult to visualize the formation of a direct link between boron atoms. The only possibility is the formation of a dimeric structure through hydrogen bridges. The bridge structure is elaborated by the overlap of sp^3 hybrid orbitals of boron with $1s$ orbitals of hydrogen as shown in chapter 8.



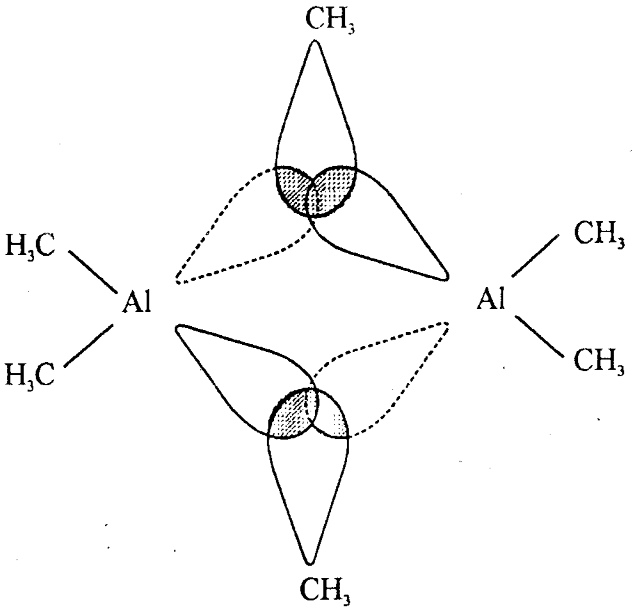
Beryllium alkyls are also electron deficient compounds and polymerize through carbon of the alkyl group to remove the electron deficiency. The $\mathrm{Be}\overset{\mathrm{C}}{\wedge}\mathrm{Be}$ angle is 66 and each Be atom is surrounded by four alkyl groups tetrahedrally arranged.



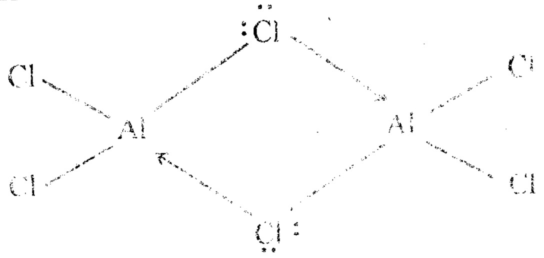
If R = CH_3



Similarly, aluminium trimethyl is found to be dimeric in solution and vapour state which results out of electron deficiency of the molecules.



Aluminium chloride exists as Al_2Cl_6 and this dimeric structure is held through chlorine bridges. Chlorine atoms donate a pair of electrons to electron deficient aluminium atoms.



Sometimes adducts are formed by the interaction of electron deficient compounds with electron pair donors.

$H_3B \longleftarrow :CO:$

$F_3B \longleftarrow :\ddot{O}Et_2$

$Cl_3Al \longleftarrow :NH_3$

Transition elements, which have *d* or *f* orbitals incompletely filled, may also be considered to be electron deficient atoms. That is why, they preferably combine with electron pair donors (ligands) to form stable compounds commonly known as coordination compounds. The addition of electrons usually takes place to the unfilled *d* orbitals and the atoms have strong tendency to acquire next inert gas configuration. Thus the important consequence of electron deficiency in molecules is to behave as electron pair acceptors (Lewis acids) which would react with electron pair donors (Lewis bases).

BOND LENGTHS AND BOND STRENGTH

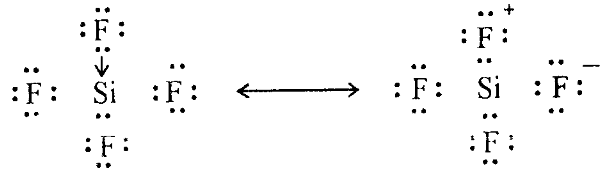
The distance between the nuclei of two atoms forming a covalent bond is called the ***bond length.*** The bond lengths are generally determined either by electron diffraction, X-ray diffraction, spectral studies, or by a combination of these methods. The bond lengths will be given to the nearest 0.01 A° unit (1A° = 10^{-8} cm) or 0.1 nm.

The covalent bond length between two atoms is often (not always) independent of the nature of the moleeule or lattice containing such a bond. Thus in most of the aliphatic hydrocarbons, the C — C single bond length is very close to 1.54 A°; the same length as the C — C bonds in diamond.

The covalent radii of various elements are very nearly additive in nature. The single-bond ***covalent radius*** of carbon is 0.77 A° which is one half of the C — C bond lengths (1.54 A°). Similarly, the covalent radii of chlorine and iodine are 0.99 A° and 1.33 A°, respectively, one half of the bond lengths between Cl_2 and I_2 molecules.

As the difference in electronegativities of two bonded atoms increases, the bond is shortened, *i.e.*, departures from additivity of bond lengths take place. For example, the covalent radii of silicon and fluorine add up to give bond length 1.81

A° whereas the Si — F bond length is 1.54 — 1.59 A°. Similar contraction in bond lengths are observed in Si — Cl, Si — O, P — F etc. The contraction in bond lengths may be due to double bond character shown by the molecule as suggested by Pauling. Thus SiF_4 molecule becomes a resonance 'hybrid' of two resonating forms (A and B).



(A) (B)

Some selected bond lengths are given in Table 3.4 and covalent radii in Table 3.5. Comparison of experimentally measured bond lengths with those calculated by making use of covalent bond radii shows that calculated values are almost always high which indicates the effect of difference in electronegativities or resonance as indicated above especially in electronuclear molecules.

TABLE 3.4

Selected Bond Lengths

Bond	**Bond Length (pm)**	**Compound**	**Hybridization**
B – F	130	BF_3	sp^2
B – Cl	175	BCl_3	sp^2
B – Br	187	BBr_3	sp^2
Si – H	148	SiH_4	sp^3
Si – F	155	SiF_4	sp^3
Si – Cl	201	$SiCl_4$	sp^3
Si – Br	215	$SiBr_4$	sp^3
Sn – Cl	230	$SnCl_4$	sp^3
Sn – Br	244	$SnBr_4$	sp^3
S – F	158	SF_6	$d^2 sp^3$
S – Cl	199	(SCl_2)	sp^3
C – C	154	C_2H_6	sp^3
C = C	133	C_2H_4	sp^2
C ≡ C	120	C_2H_2	sp
C = O	122	$(CH_3)_3\ C = O$	(sp^2)

A corrected bond length can be calculated in these cases by using the equation proposed by Schomaker:

$$r\,A-B = r\,A + r\,B - 0.09\,\Delta,$$

where r A – B is the bond length, r A and r B are covalent radii for atoms A and B, respectively and Δ is the difference in electronegativities of A and B.

TABLE 3.5

Covalent Radii (pm)

(a)	***Single Bonds***						
	H						
	37						
	Li	Be	B	C	N	O	F
	123	89	80	77	74	74	72
			Al	Si	P	S	Cl
			125	117	110	104	99
				Ge	As	Se	Br
				122	121	117	114

(b)	***Multiple Bonds***			
		C	N	O
	Double bonds	67	60	55
	Triple bonds	60	55	50

The bond lengths go on increasing from top to bottom in the groups. Thus the bond length between Si – Si is more than C – C bond length. Similarly, P – P bond length is relatively much more than N – N bond length. The bond length of C – C bonds is much more than N – N bonds as shown in Figure 3.26. Two factors are important in determining the bond lengths (a) increase in nuclear charge will pull the electrons with greater force and would decrease the bond length and (b) radius of the shell increases by the square of n, the principal quantum number. The shortening of bond lengths from left to right in a period (C – C to N – N) can be attributed to the pull by the increase in nuclear charge with the same value of n. As the atomic radii increase from top to bottom in a group (N to P or C to Si) the effect of the effective nuclear charge on the electrons decreases and with the addition of more and more electrons greater forces of repulsion would be set up. Consequently, bond lengths would increase.

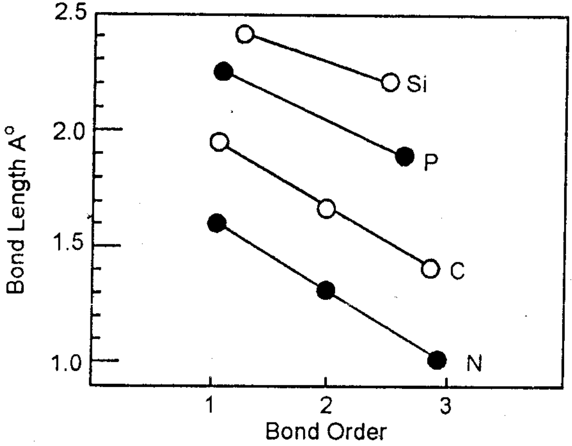


Fig. 3.26. Change in bond length with bond orders 1, 2 and 3 for C — C, N — N and 1 and 2 for Si– Si and 1 and 3 for P– P.

Bond strength refers to the average electron density around atoms compared to a hypothetical charge density in case of an inert gas. Thus stable molecules are formed when there is an excess of bonding electrons. Relationship between excess of bonding electrons to bond strength of simple diatomic molecules is given in Table 3.6. The excess of bonding over anti-bonding electron pairs is called 'bond order'. There is definite correlation between bond lengths and bond orders. Usually, with increasing bond order the values of bond lengths go on decreasing.

TABLE 3.6

Molecule	Pairs of bonding electrons	Pairs of anti-bonding electrons (Bond order)	Excess bonding pairs or bond order	Valency	Heat of Dissociation (KJ/mole)
H_2	1	0	1	1	432
He_2^+	$\frac{1}{2}$	0	$\frac{1}{2}$	—	255
N_2	4	1	3	3	712
O_2	4	2	2	2	490
CO	4	1	3	3	881

Questions

1. What do you understand by the term chemical bond? What are its various types? Discuss the formation of ionic and covalent bonds.

2. Discuss the formation of ionic bond quoting suitable examples. What are the general characteristics of ionic bonds?

3. Distinguish between ionic and covalent bonds. Discuss their characteristic features. What are the various factors responsible for the stability of ionic compounds?

4. Discuss various types of crystal structures commonly found in ionic compounds. Give in detail the various aspects of sodium chloride lattice.

5. (a) What is radius ratio? How are the values of limiting radius ratios able to predict the structure types?

   (b) Predict the coordination number and structure type for the following compounds based upon the data on ionic radii given below:

   NaCl, KI, LiCl, LiF, NaBr, CsCl, RbCl

   The ionic radii of alkali metals are:

Li^+	68 pm
Na^+	95 pm
K^+	133 pm
Rb^+	148 pm
Cs^+	169 pm

   The ionic radii of halides are:

F^-	136 pm
Cl^-	181 pm
Br^-	195 pm
I^-	216 pm

6. (a) Define lattice energy. What does it depend upon?

   (b) Calculate the lattice energy of AgCl using Born-Haber cycle.

   Thermodynamic values of AgCl are:

   Heat of sublimation (H_s) = 68.0 kcal/g. atom.

   Standard heat of formation (H_f) = – 30.4 kcal/mole.

   Ionization potential (I) = 174.7 kcal/g. atom.

   Dissociation energy of Cl_2 (D) = 58.0 kcal/mole.

   Electron affinity (E_a) = – 85.1 kcal/g. atom.

7. What do you mean by variable valency? Why do some of the elements show variable valencies?

8. What type of elements would form covalent bonds? Explain the general characteristics of covalent compounds.

9. Differentiate between covalent and coordinate-covalent bonds. What are the characteristic features of coordinate-covalent bonds?

10. What are general features of the metallic bond? Discuss the common structures of metals. Describe the general theories put forward to explain the nature of the metallic bond.

11. What do you understand by Van der Waals' forces? How do they differ from other types of forces? Discuss their importance in chemical compound formation.

12. (a) Explain hydrogen bond formation in various compounds. What may be the nature of hydrogen bonding? Discuss the importance of hydrogen bonding in various fields.

    (b) Arrange the following compounds with increasing possibility of hydrogen bonding:

    H_2O, HF, NH_3, CH_3COOH

13. What type of elements would show electron deficiency? Illustrate your answer with suitable examples.

14. Establish the relationship between covalent radii and bond lengths. Why are the bond lengths between atoms of larger atomic weight more than the others?

15. Given the covalent radius of potassium at 1.96 A° and of chlorine 0.99 A°, calculate the bond length of K-Cl bond.

16. Write Lewis formula for the following:

    (a) N_2 (b) N_2O_4 (c) H_2SO_4

    (d) Br_2 (e) CO (f) HCHO

17. Describe the bonding in water molecules. Explain why water is a polar molecule?

18. What is hydrogen bonding? How does the strength of a hydrogen bond compare with that of a covalent bond?

19. **Write short answers to the following questions:**

    (i) What is chemical bond?

    (ii) How a chemical bond is formed?

    (iii) Describe nature and types of chemical bond

(iv) Describe the crystal structure of sodium chloride.

(v) What is radius ratio?

(vi) Describe the usefulness of radius ratio.

(vii) What do you understand by lattice energy?

(viii) Describe the Born-Haber cycle. What is this principle based on?

(ix) What are the factors responsible for the stability of ionic compounds?

(x) Describe the characteristic features of ionic compounds.

(xi) What is variable valency of elements due to?

(xii) Describe the characteristic features of covalent compounds.

(xiii) What are the characteristic features of coordination compounds?

(xiv) What are the characteristic properties of metals?

(xv) Describe the structure pattern of metals.

(xvi) Discuss the electronic gas theory of metals.

(xvii) Describe Bloch-Sommerfeld theory of metals.

(xviii) Discuss Pauling theory of metals based on valence bond concept.

(xix) Discuss molecular orbital theory or band theory of metals.

(xx) What do you understand by Van der Waals' forces and bonds?

(xxi) What is the evidence of Van der Waals' forces?

(xxii) What is meant by hydrogen bonding?

(xxiii) What is the importance of hydrogen bonding?

(xxiv) Describe the features of electron deficient molecules.

(xxv) What is the correlation between bond lengths and bond strengths?

20. **Give the suitable answer:**

(i) In which of the following does ionic bonding occur?

(a) aluminium and chlorine (b) boron and chlorine

(c) hydrogen and chlorine (d) hydrogen and sodium

(**Ans**: d)

(ii) Which of the following molecules has no dipole moment?

(a) C_2Cl_4 (b) CF_2Cl_2

(c) C_2H_5Cl (d) $CHCl_3$

(**Ans**: a)

(iii) Which of the following solids consist of atoms or molecules held together only by Van der Waals' forces?

(a) CO_2 (b) H_2O

(c) MgO (d) SiO_2

(**Ans**: a)

(iv) Which of the following statements explains why copper conducts electricity when a potential difference is applied?

(a) copper (II) ions move to the cathode

(b) crystal lattice breaks down

(c) the atoms of copper become ionized

(d) bonding electrons in the crystal lattice move

(**Ans**: d)

(v) Which of the following molecules contains six bonding electrons?

(a) CO_2 (b) H_2S

(c) NCl_3 (d) SF_6

(**Ans**: c)

(vi) Graphite can be used as a lubricant; diamond is not. This is because graphite has:

(a) mobile ions. (b) delocalised electrons.

(c) hexagonal arrangement of atoms in the layers.

(d) Van der Waals' forces between the layers of atoms.

(**Ans**: d)

(vii) In which of the following pairs do the molecules have similar shapes?

(a) $AlCl_3$ and BCl_3 (b) $AlCl_3$ and PCl_3

(c) BF_3 and NH_3 (d) CO_2 and SO_2

(**Ans**: a)

(viii) Which type of bond is responsible for intermolecular forces in liquid CCl_4?

(a) covalent bonding (b) hydrogen bonding

(c) induced dipole-induced dipole attractions

(d) permanent dipole-permanent dipole attractions

(**Ans**: c)

(ix) Which of the following are features of the structure of metallic copper?

(a) ionic bonds (b) delocalised electrons

(c) lattice of ions

(Ans: c)

(x) Which of the following statement is about lattice structure of diamond and graphite are correct?

(a) the shortest carbon-carbon bond occurs in diamond

(b) the C – C – C bond angle is smaller in diamond than in graphite.

(c) all bonds in diamond are of the same strength but those in graphite are not.

(Ans: c)

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4

MODERN THEORIES OF CHEMICAL BONDING (NATURE OF THE CHEMICAL BOND)

In the previous chapter, we have discussed the bond types but it still remains to be ascertained as to why these bonds are formed and what are the energy changes which favour their formation, *e.g.*, ***the nature of the chemical bond?*** Various theories in this regard have been put forward which reasonably explain the bond types and their chemical behaviour. We shall discuss in this chapter only two concepts, namely: (i) Valence Bond Theory, and (ii) Molecular Orbital Theory.

The application of quantum mechanics to bonding and structures of chemical compounds is most popular and challenging field in bringing agreement between the experimental facts and theory. In order to understand the nature of bonding, the valence bond and molecular orbital treatments of molecules are more useful and would be discussed at length.

VALENCE BOND THEORY (VBT):

This theory was first proposed by Heitler and London (1927) and later on developed by Pauling. This concept is based on wave-mechanical treatment of molecules and has been successful in explaining the bond energies, bond lengths and shapes of covalent molecules. The valence bond method is often capable of greater accuracy but the treatment is so intricate that it has only been applied to a limited number of molecules. There is a good agreement between theory and experiment in case of H_2 molecule.

Let us see how valence bond theory explains the formation of H_2 molecule starting from hydrogen atoms. We shall begin by imagining two hydrogen atoms far apart so that no interaction occurs. Let us label the electrons and nuclei of both the interacting hydrogen atoms, H_A and H_B as.

$$H_A\,(a) \text{ and } H_B\,(b)$$

The electron of the hydrogen atom H_A is represented as (*a*) and that of hydrogen atom H_B as (*b*). The wave functions for separate atoms would be given by $\psi_A(a)$ and $\psi_B(b)$. In accordance with the theorem of quantum mechanics the total wave function for the atoms still wide apart may be written as simple product:

$$\phi = \psi_A(a) \, . \, \psi_B(b) \qquad \cdots\cdots \quad (1)$$

However, on bringing the atoms close together, there is little doubt that wave functions would be modified by interaction. The energy variation taking place during the interaction of the two atoms is given by the energy curve shown in Figure 4.1.

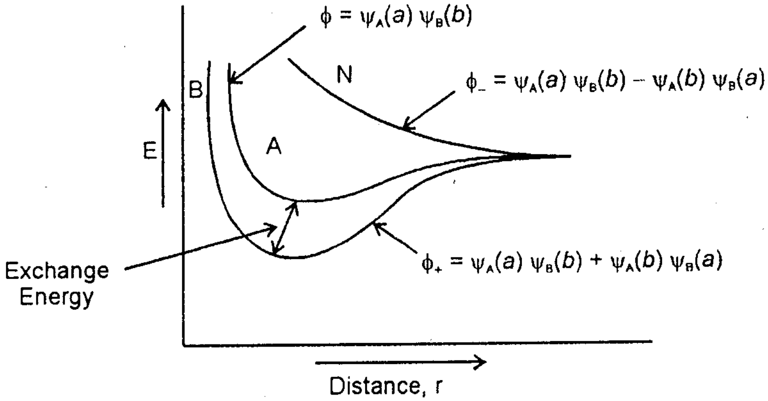


Fig. 4.1. Curves showing valence bond potential energy for the H_2 molecule.

Variation method generally gives an energy value of much greater accuracy. Because due consideration is given to the presence of electron (*b*) with nucleus of hydrogen atom H_A and that of electron (*a*) with the nucleus of hydrogen atom H_B. As the electrons (*a*) and (*b*) are indistinguishable, it is difficult to tell which electron is associated with which nucleus of hydrogen atoms. This means to say that the following two wave functions are equally acceptable for a covalent bond between hydrogen atoms.

$$\psi_A(a) \, . \, \psi_B(b) \ \text{and} \ \psi_A(b) \, . \, \psi_B(a) \qquad \cdots\cdots \quad (2)$$

The true wave function should be the combination of the wave functions given in equation (2). As the atoms come close together, their standing waves would interact, and a new wave motion is attained. London and Heitler suggested that the wave functions could be described as ***a linear combination of the two wave functions given in equation (2) and would represent a covalent bond formation.*** We may try

$$\phi = C_1 \times \psi_A(a) \, . \, \psi_B(b) + C_2 \times \psi_A(b) \, . \, \psi_B(a) \qquad \cdots\cdots \quad (3)$$

The parameters C_1 and C_2 impart general form to equation (3). But in case of H_2 molecule, because of symmetry, the wave function would contribute equally well. The contribution is favourable to the square of the coefficients. So,

$$C_1^2 = C_2^2 \text{ and } C_1 = \pm C_2$$

and there are two possible wave functions,

$$\phi_+ = \psi_A(a)\,\psi_B(b) + \psi_A(b)\,\psi_B(a) \qquad \cdots\cdots \quad (4)$$

and

$$\phi_- = \psi_A(a)\,\psi_B(b) - \psi_A(b)\,\psi_B(a) \qquad \cdots\cdots \quad (5)$$

On calculating the energies of the system, it is revealed that ϕ_- represents the non-bonding state or the repulsive interaction as shown by curve N in Figure 4.1. This repulsive effect is also indicated by 'Pauli's principle' due to the two electrons possessing the same spin in two atoms.

The energy curve B (Figure 4.1) is shown to have acquired a minimum energy state for *bonding* at an internuclear distance of 0.80A and represents the wave function ϕ_+. The wave function ϕ_+ represented in equation (4) gives the bond energy for H_2 molecule to be 72.4 Kcal, which is in agreement with the experimental value as compared to that calculated from equation (1).

Let us assign wave function ψI to $\psi_A(a)\,\psi_B(b)$ and ψII to $\psi_A(b)\,\psi_B(a)$. Applying these alternative expressions in equations (4) and (5), we get equations (6) and (7), respectively.

$$\phi_+ = \psi I + \psi II \qquad \cdots\cdots \quad (6)$$

$$\phi_- = \psi I - \psi II \qquad \cdots\cdots \quad (7)$$

In order to get a very close agreement between the experimental bond dissociation energy of H_2 molecule (103.2 Kcal), the screening effects of electrons and polarization of atomic orbitals (AO's) should also be taken into consideration.

Valence bond method is also capable of explaining the nature of the ionic bond. Accordingly, there is a possibility that both the electrons are simultaneously present near one of the two nuclei. In such cases the ionic wave functions would be:

$\psi_A(a)\,\psi_A(b)$ ··· for both electrons near the nucleus of hydrogen atom A.

$\psi_B(a)\,\psi_B(b)$ ··· for both electrons near the nucleus of hydrogen atom B.

The wave function due to ionic character of the bond would be represented by ϕ ionic and is given by

$$\phi \text{ ionic} = \psi_A(a)\,\psi_A(b) + \psi_B(a)\,\psi_B(b) \qquad \cdots\cdots \quad (8)$$

Since ϕ covalent (the wave function for covalent bond formation) and ϕ ionic would make up to form total wave function for the hydrogen molecule and would be represented as ϕ.

$$\phi = \phi \text{ cov} + \phi \text{ ionic} \quad \cdots\cdots (9)$$

Getting value of ϕ cov from equation (4) and that of ϕ ionic from equation (8), we get:

$$\phi = \psi_A(a)\,\psi_B(b) + \psi_A(b)\,\psi_B(a) + [\psi_A(a)\,\psi_A(b) + \psi_B(a)\,\psi_B(b)] \quad \ldots (10)$$

Usually a λ' factor is necessary to be introduced and the equation (9) is written as,

$$\phi = \phi \text{ cov} + \lambda' \phi \text{ ionic} \quad \cdots\cdots (11)$$

The constant λ' is a measure of the degree to which the ionic structure is able to contribute to the bonding as well as the overall structure. For H, λ' is 0.17 and, therefore, the ionic contribution to the total binding energy is only 23 kJ/mol $\left(\text{about } \frac{1}{20}\text{th of the total}\right)$.

The ionic term in the wave equation is introduced based upon the resonance concept. We can represent the mathematical terms given in above equations by structures based upon resonance. Thus, we represent a covalent bond between hydrogen atoms as H – H and ionic structures are represented as $H_A^+ - H_B^-$ or $H_A^- - H_B^+$ in terms of resonance. However, it is wrong to think these structures as actually existing because resonance phenomenon would mean to indicate that the overall character of H_2 molecule is contributed by covalent and ionic bonds represented by these structures.

The following assumptions are taken during the formation of H_2 molecule:

(i) Each hydrogen atom has a partially filled 1*s* atomic orbital, having only one electron.

(ii) The molecular wave function ϕ is obtained by the linear combination of the wave functions of atomic orbitals using the concept of resonance.

(iii) The indistinguishability of the electrons is based upon ***exchange*** phenomenon introduced by Heitler and London.

(iv) The pairing of electrons in the molecule should satisfy the Pauli's exclusion principle and the two electrons would have different values of spin quantum numbers.

(v) The electron pair may be localized between the two nuclei.

(vi) Electron pairing is responsible for attractive force between the atoms (bond energy)

(vii) The overlapping orbitals have similar symmetry and energy. The extent of overlap determines the bond strength. ***Greater the overlap stronger will be the bond formed (shorter bond length).***

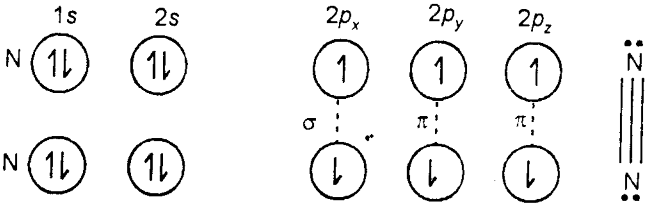
ELECTRON EXCHANGE INTERACTION:

The formation of covalent bond between hydrogen atoms is considered to arise from the exchange forces between a pair of electrons with opposite spin. The concept of electron exchange phenomenon is similar to resonance and is very useful in valence bond treatment. An additional binding energy arises out of the electron exchange interaction and is called ***exchange energy***. Let us see this effect in He atom (the dotted arrow is used to distinguish between two electrons). Electron exchange interaction is most effective when the electron spins are parallel In the (state I) the electron represented by dotted lines is in 2*s* orbital but in He (state II) the same electron is present in 1*s* orbital due to exchange interaction.

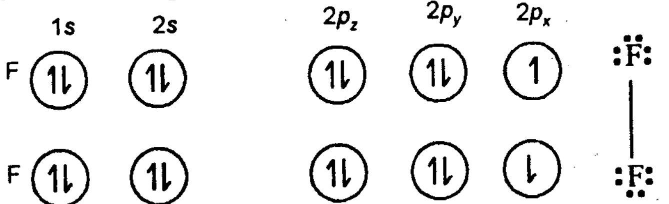
APPLICATIONS OF VALENCE BOND THEORY:

The valence bond approach describes bonds in terms of the pairing of electrons and may be considered an extension of the Lewis concept of covalent bond formation. The valence bond theory pictures the bond as forming from the coupling or pairing of electrons having anti-parallel spin (from each of the combining atoms). Thus, it is necessary that atoms involved in bond formation should have unpaired electrons in them. The number of unpaired electrons would give rise to equal number of bonds which may be formed by any given atom. The isolated number of paired electrons are considered to be the lone pairs in this approach

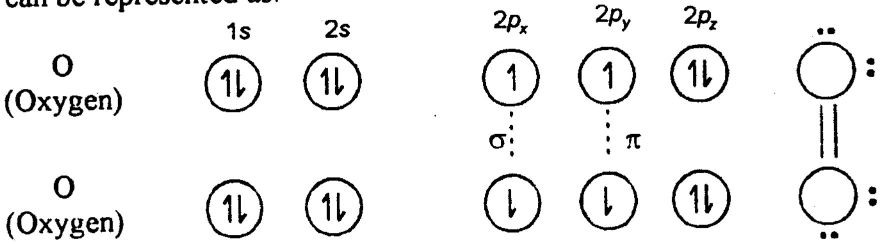
There are three unpaired electrons in nitrogen atom with electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. A N_2 molecule is formed by the interaction of these three unpaired electrons from each nitrogen atom to form electron pairs resulting in the formation of three bonds (one of them is termed σ bond and the other two, π bonds).



Fluorine molecule is formed from two fluorine atoms, each containing one unpaired electron. The electronic configuration of each F atom is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^2\ 2p_z^2$. The formation of F_2 molecule can be diagrammatically represented as:



Oxygen molecule is obtained by the combination of two oxygen atoms. Each atom has electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^2$ and the formation of O_2 molecule would involve two unpaired electrons resulting in the formation of a double bond. On the basis of the maximum overlap criterion, one of the bonds should be a σ bond formed by pairing of the $2p_x$ electrons. However, the other bond is referred to be a π bond resulting from the coupling of unpaired electrons in $2p_y$ or $2p_z$ orbitals. The formation of O_2 molecule based upon valence bond theory can be represented as:



One of the major drawbacks of valence bond concept is that it cannot explain the paramagnetic behaviour of oxygen molecule. The number of unpaired electrons present in a molecule are responsible for its paramagnetic behaviour. But valence bond method explains the bond formation by the pairing up of electrons leaving no unpaired electrons in O_2 molecules. As a result, no paramagnetic behaviour should be expected from this molecule which is against the experimental findings. No solution to this dilemma has been proposed by the valence bond theory. However, molecular orbital theory (to be discussed later) is able to offer a solution to this problem.

An example of heteronuclear diatomic molecule is hydrochloric acid, which may be considered to have been formed from a hydrogen atom and a chlorine atom or of a proton H^+, with a chloride ion $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^-$, as represented by the equations:

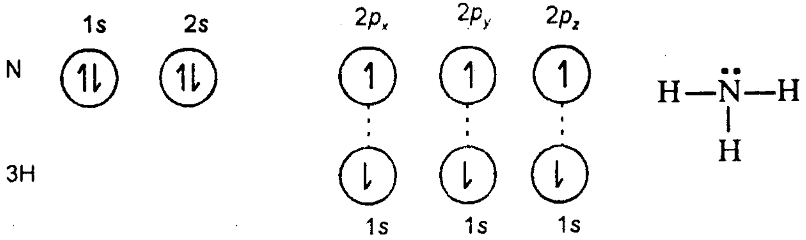
$$\mathrm{H}\,\overset{\cdot}{\times} + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{H}\overset{\times}{\cdot}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

$$\mathrm{H}^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^- \longrightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

The formation of HCl may be represented as:

$$\underset{\text{H}}{1s^1} + \underset{\text{Cl}}{3p_z^1\ 3p_y^2\ 3p_x^2\ 3s^2\ 2p^6\ 2s^2\ 1s^2} \rightarrow \underset{\substack{\text{(Electron pair}\\ \text{of HCl)}\\ \text{H} - \text{Cl}}}{\boxed{1s^1\ 3p_z^1}}\ \underbrace{3p_y^2\ 3p_x^2\ 3s^2\ 2p^6\ 2s^2\ 1s^2}_{\substack{\text{(non-bonding}\\ \text{electrons of Cl)}}}$$

A reasonably simple molecule that illustrates the details of valence bond theory is the ammonia molecule. NH_3 molecule consists of a nitrogen atom which is bonded to three hydrogen atoms. Nitrogen atom has electronic configuration $1s^2$ $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^1$ whereas hydrogen atoms have $1s^1$ configuration. The essence of valence bond theory is that an unpaired electron in nitrogen atom undergoes exchange interaction with an unpaired electron present in $1s$ orbital of hydrogen atom. In other words, the exchanged electrons would occupy the same region in space with opposite spins. Thus two electrons having opposite spins are regarded in valence bond theory as being responsible for bond formation between two atoms forming a molecule and this corresponds to the shared pair of electrons.



The model for ammonia molecule leads to three valence bonds at right angles to each other which correspond to p_x, p_y and p_z orbitals. But NH_3 molecule, in fact, has H — N — H bond angles of 107.3°. Although proton-proton repulsion would be expected to open the bond angle from 90° but this effect is not sufficient to give the observed angle. A more refined valence bond approximation leads to more closeness with the experimental facts and is based on the concept of ***orbital hybridization***.

We shall now consider this concept to gather more information and refinement.

HYBRIDIZATION OF ORBITALS:

The valence bond description of molecules given above is not able to explain the true character of the bonds and geometry of the molecules. Thus, beryllium with electronic configuration $1s^2$ $2s^2$ could be considered to behave as an inert gas and forms no bond at all. In fact, beryllium is a member of Group II and undergoes reactions to form compounds showing its bivalency. The electronic configurations for boron and carbon are:

B $1s^2\ 2s^2\ 2p_x^1$

C $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$

Based upon the electronic configurations shown above, boron should behave as a monovalent element and carbon should be able to form compounds with only two bonds at the most. This does not explain the experimental facts about the behaviour and nature of compound formation with these elements. Boron is trivalent and carbon invariably behaves as a tetravalent element. If valence bond theory described above is to withstand the test of experimental facts, it should be able to explain the well-known behaviour of these elements.

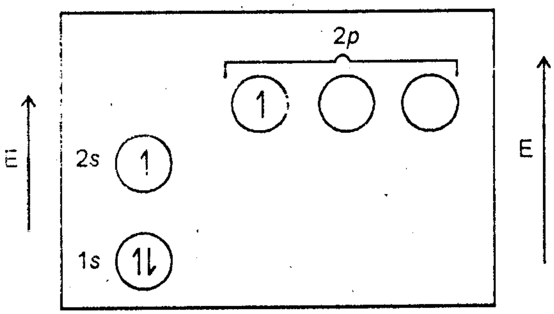


Fig. 4.2. Electronic structure of beryllium in the excited state.

The bivalent nature of beryllium can be explained based upon its electronic configuration in the excited state (higher energy state). Beryllium will undergo chemical reactions if enough energy is available to promote one of the electrons in 2*s* orbitals to one of the 2*p* orbitals when an excited state (Be*) is obtained as shown in Figure 4.2. The two unpaired electrons (present one each) in 2*s* and 2*p* orbitals would give rise to two bonds in beryllium. Now if one bond is formed by 2*s* electron of beryllium and the other by the 2*p* electron the two bonds should differ in strength. ***The formation of two Be — Cl bonds from dissimilar beryllium orbitals (2s and 2p) describes a structure with ill-defined bond angles and bonds of unequal strength.*** However, it is well established that both bonds in compounds of bivalent beryllium are equal and collinear. It is obvious that beryllium atom does not use simple 2*s* and 2*p* orbitals individually but a combination of both. We describe the electronic states of the beryllium atom by solving the appropriate wave equation and producing suitable solutions. Each of these solutions represents orbital or energy state capable of accommodating two electrons with opposed spins. If two solutions, $\psi 2s$ and $\psi 2p$, have equal significance, we get two new equivalent functions corresponding to state of lowest energy, which describes two linearly-directed orbitals:

$$\psi sp\,(\mathrm{I}) = \frac{1}{\sqrt{2}}\,(\psi 2s + \psi 2p) \qquad \cdots\cdots \quad (12)$$

$$\psi sp\,(\mathrm{II}) = \frac{1}{\sqrt{2}}\,(\psi 2s + \psi 2p) \qquad \cdots\cdots \quad (13)$$

In wave-mechanical language, we say that two *sp* hybrid orbitals have been formed from one *s* and one *p* orbital. These new hybrid (or equivalent) orbitals have directional characteristics. Orbitals of the same atom which lie close to one another in energy have an unusual ability of combining with ***one another in additive manner to form hybrid orbitals. The hypothetical process of forming these orbitals is termed hybridization.*** By taking *n* atomic orbitals of approximately equal energy, *n* hybrid orbitals are obtained. We shall now describe in detail how atomic orbitals combine to obtain some of the most important hybrid orbitals.

***sp* Hybrid Orbitals:** One *s* orbital can combine with one *p* orbital on the same atom to form two new and completely equivalent orbitals called *sp* hybrid orbitals. We know that *s* orbitals are spherically symmetrical and have positive probability amplitude everywhere. A *p* orbital has two lobes, one of positive and other of negative probability amplitude and the combination of wave functions (equation 12 and 13) would give two *sp* hybrid orbitals (using *s* and p_x orbitals). The formation of *sp* hybrid orbitals obtained by the combination of *s* and p_x atomic orbitals is shown in Figure 4.3. The hybrid orbitals have directional characteristics of *p* orbitals and are called diagonal or *sp* hybrids because one *s* orbital and one *p* orbital is sacrificed to make them. Both the *sp* hybrid orbitals of beryllium altogether are shown in Figure 4.4.

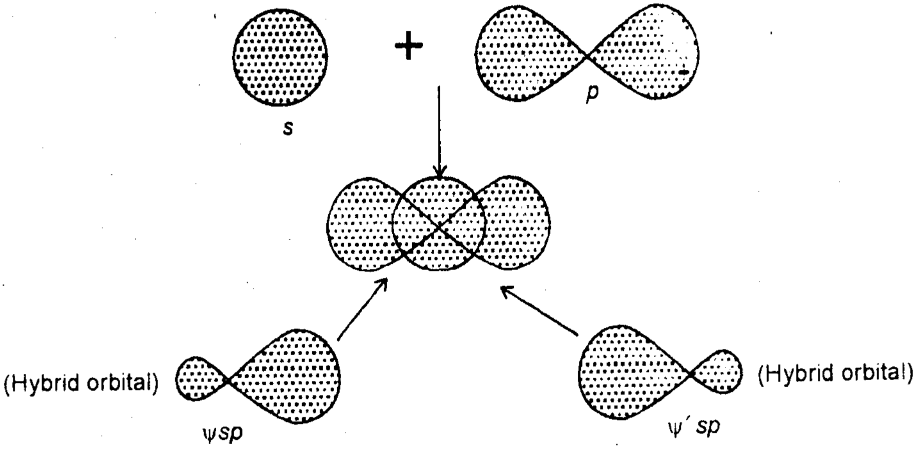


Fig. 4.3. Formation of sp hybrid orbitals.

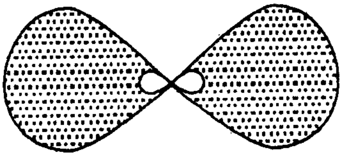


Fig. 4.4. sp Hybrid orbitals of beryllium.

The formation of $BeCl_2$ can be visualized as the overlap of $3p_x$ orbitals of chlorine atoms (containing unpaired electrons) with the *sp* hybrid orbitals of beryllium atom. The two Cl — Be — Cl bonds must be equivalent and collinear (Figure 4.5).

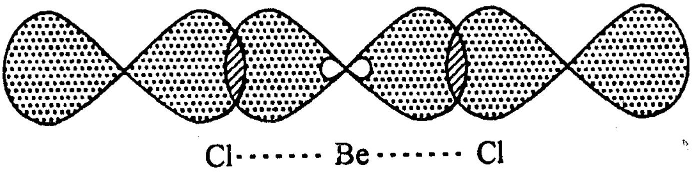


Fig. 4.5.

***sp*^{2} Hybrid Orbitals:** These are a set of three hybrid orbitals which arise from the appropriate combination of one *s* and two *p* orbitals. Let us consider these sp^2 hybrids to have been formed from *s*, p_y and p_x orbitals. The hybrid orbitals have the following wave functions (leaving the numerical factors).

$$\psi sp^2 = \psi s - \psi p_x - \psi p_y \qquad \cdots\cdots \quad (14)$$

$$\psi' sp^2 = \psi s + \psi p_x - \psi p_y \qquad \cdots\cdots \quad (15)$$

$$\psi'' sp^2 = \psi s + \psi p_x + \psi p_y \qquad \cdots\cdots \quad (16)$$

The shapes of the hybrid orbitals are obtained by simple pictorial additions (Figure 4.6).

The sp^2 hybrid orbitals are all identical in shape, all lie in one plane and point at angles of 120° from each other. The sp^2 hybrids have ***trigonal planar symmetry***.

Boron trifluoride is a typical example of the sp^2 hybridization. Boron utilizes its 2*s*, $2p_x$ and $2p_y$ orbitals for the formation of hybrid orbitals. These three hybrid orbitals overlap with three *p* orbitals from three different fluorine atoms to form three B — F bonds at an angle of 120° from each other.

***sp*^{3} Hybrid Orbitals.** On combining one *s* and all the three *p* orbitals, a set of four hybrid orbitals denoted by sp^3 hybrids pointing at the corners of a tetrahedron with an angle of 109° 28′ to each other are obtained. Thus all the four sp^3 hybrid orbitals have *tetrahedral symmetry* as shown in Figure 4.7.

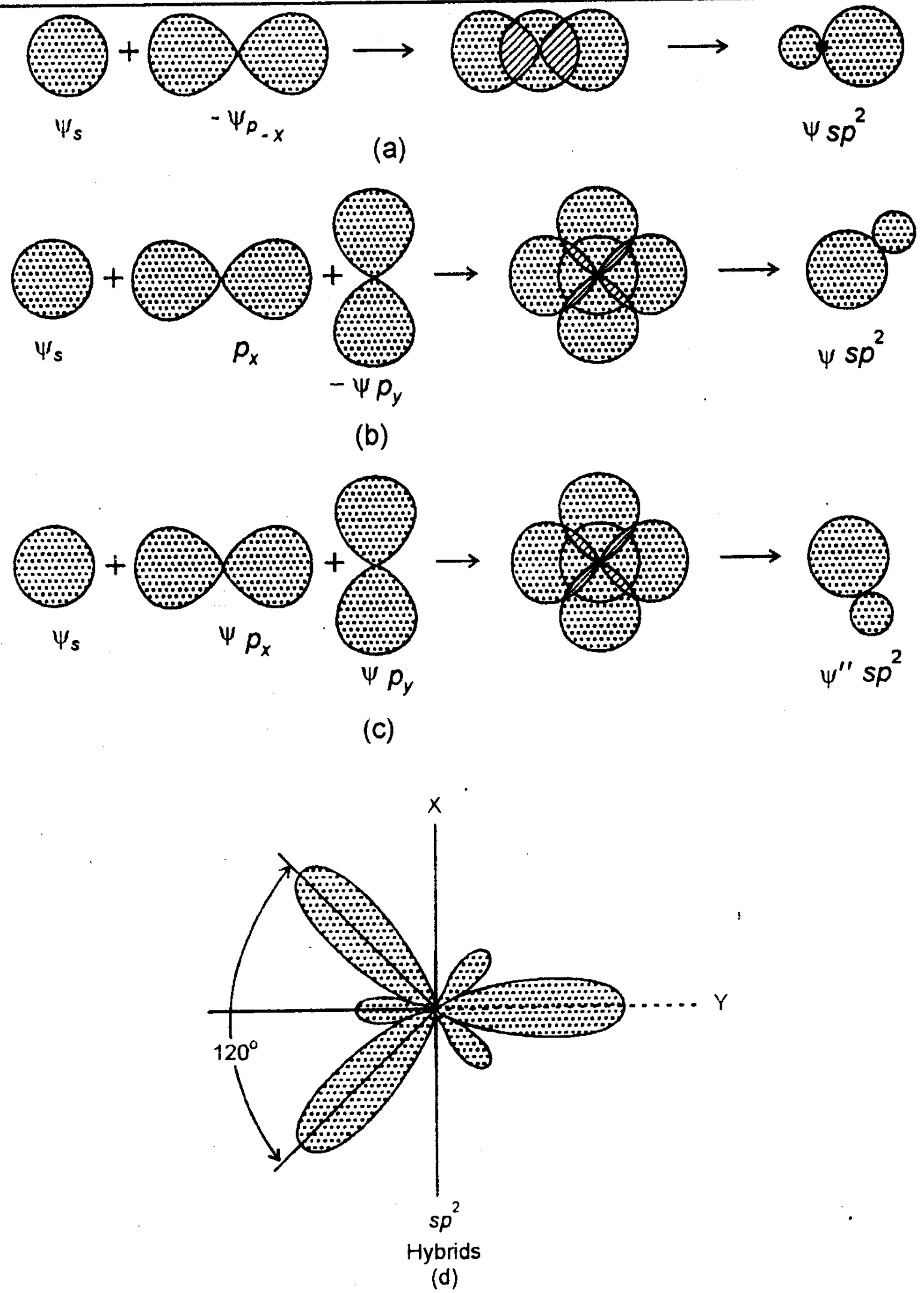
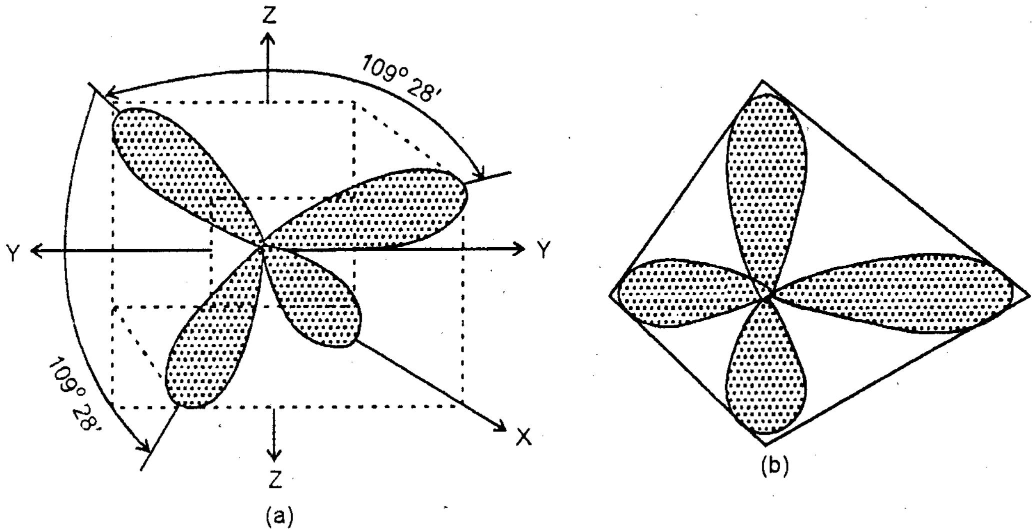


Fig. 4.6. ***(a) Formation of one of the sp² hybrids according to equation 14.***
(b) Formation of one of the sp² hybrids according to equation 15.
(c) Formation of one of the sp² hybrids according to equation 16.
(d) Three sp² hybrid orbitals at an angle of 120°.



(a)

(b)

Fig. 4.7. Tetrahedral sp^3 hybrid orbitals.

Methane, CH_4, is an example of a molecule obtained by the hybridization of a 2*s* and three 2*p* orbitals of carbon to get a set of four equivalent sp^3 hybrid orbitals. Each sp^3 hybrid orbital has one-fourth *s* and three-fourth *p* character. As the four sp^3 orbitals are directed towards the corners of a regular tetrahedron, the structure of CH_4 is considered tetrahedral (Figure 4.8).

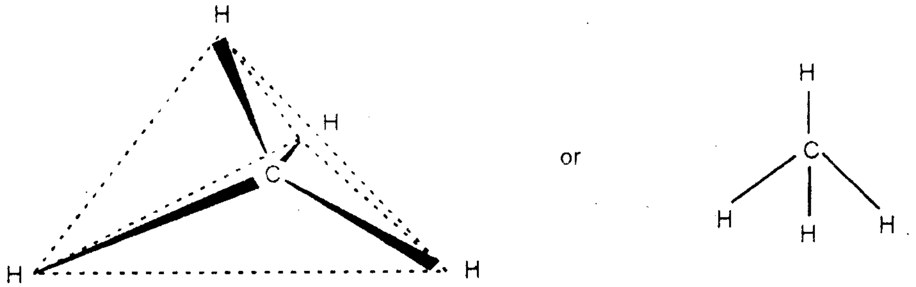
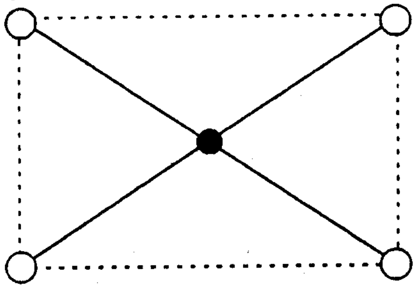


Fig. 4.8. Structure of CH_4.

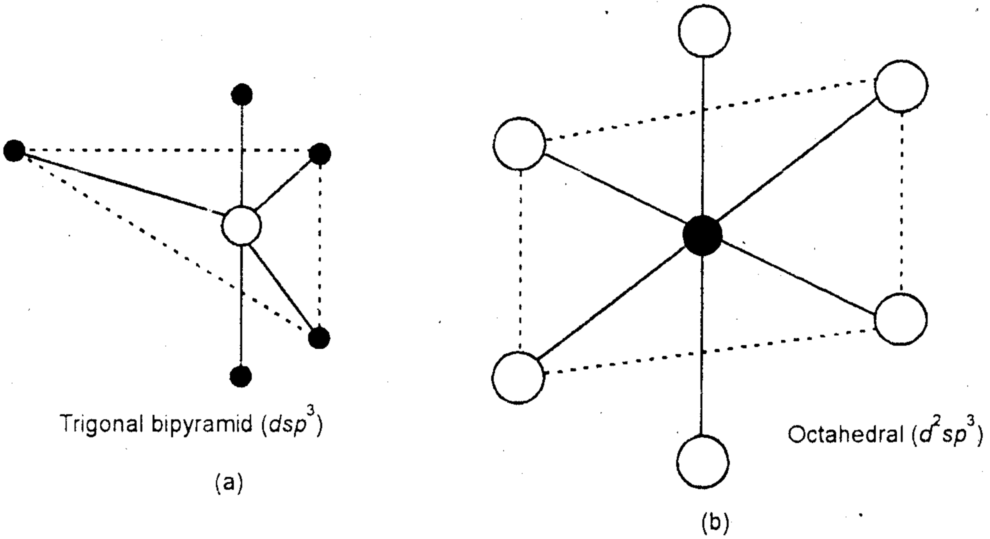
In addition to the involvement of *s* and *p* orbitals in the process of hybridization, *d* orbitals may also be involved. Thus, dsp^2 hybridization would arise by the involvement of one *d* orbital, one *s* orbital and two *p* orbitals of similar energy states. A dsp^2 hybridized structure would be square planar as shown in Figure 4.9.



Square Planar Arrangement

Fig. 4.9. dsp^2 hybridization to give square planar structure.

Similarly, dsp^3 hybridization will result in the formation of 5-bonds arranged in trigonal bipyramidal manner (Figure 4.10 a). A more common type of hybridization commonly met with transition metal compounds is d^2sp^3 hybridization which gives rise to ***octahedral structures*** (Figure 4.10 b).



Trigonal bipyramid (dsp^3)

(a)

Octahedral (d^2sp^3)

(b)

Fig. 4.10. dsp^3 *and* d^2sp^3 *bonding configurations.*

SUMMARY OF HYBRIDIZATION RULES:

The basic principles involved during hybridization of orbitals are summarised below:

1. Hybridization is a process of mixing orbitals on a single atom (or ion).
2. Only orbitals of similar energies can be mixed to form hybrid orbitals. Thus orbitals must belong to the same 'energy group'.
3. The number of orbitals mixed is always equal to the number of hybrid orbitals obtained.
4. In hybridization, a certain number of orbitals and not the electrons are mixed.
5. Once an orbital has been used to form hybrid orbitals it is no longer available to hold electrons as such.
6. Due to non-directional character of *s* orbitals, they do not add to the direction of the hybrids.
7. Most hybrids are similar but do not have necessarily identical shapes.

8. The orientation in space of the hybrids is determined by,
   - (i) the number of orbitals mixed and thus the number of hybrid orbitals obtained.
   - (ii) the preference of orbitals in pure state along x, y and z directions.
   - (iii) the assumption that electrons occupying the hybrid orbitals try to avoid one another as far as possible.
9. The particular type of hybrid orbitals chosen for discussing a structure are based upon the experimental observations regarding the geometry of the molecules. Thus, bond angles of 120° should point to sp^2 hybrids and 109° 28′ bond angles to sp^3 hybrid orbitals.

Relationship between hybrid orbitals and structures of the molecules formed are shown in Table 4.1.

TABLE 4.1

Hybrid Orbitals and Structure

No. of bonds formed	**Orbitals used**	**Symmetry**	**Examples**
2	sp	Linear	N_2O, $BeCl_2$, C_2H_2
	p^2	Angular	NO_2^-, $H_3C-O-CH_3$
3	sp^2	Triangular planar	BF_3, CO_3^{2-}, NO_3^-
	p^3	Trigonal pyramidal	NH_3, PCl_3
4	sp^3	Tetrahedral	CCl_4, CH_4, SiF_4
	dsp^2	Square planar	$I\,Cl_4^-$, $[Pt\,Cl_4]^{2-}$
6	d^2sp^3	Octahedral	SF_6, $W(CO)_6$, $[MoF_6]^-$

Sigma (σ) and Pi (π) bonds: You are now well aware of the fact that a bond is formed by the combination or linear overlap of atomic orbitals. Thus a single bond is formed by the overlap of two s orbitals or an s and a p orbital or two p orbitals. These orbitals have a linear overlap along the same axis to form bonds. If one of these atoms is related with respect to the other along the bond axis, the internuclear electron distribution remains the same. In other words, bonds of this type possess axial symmetry and are called *sigma* (σ) *bonds*. All single bonds are, in fact, (σ) bonds and are formed by head-on overlap of the atomic orbitals as shown in Figure 4.11. ***A bond in which the electron distribution is concentrated along the internuclear axis and possesses axial symmetry is called σ (sigma) bond.***

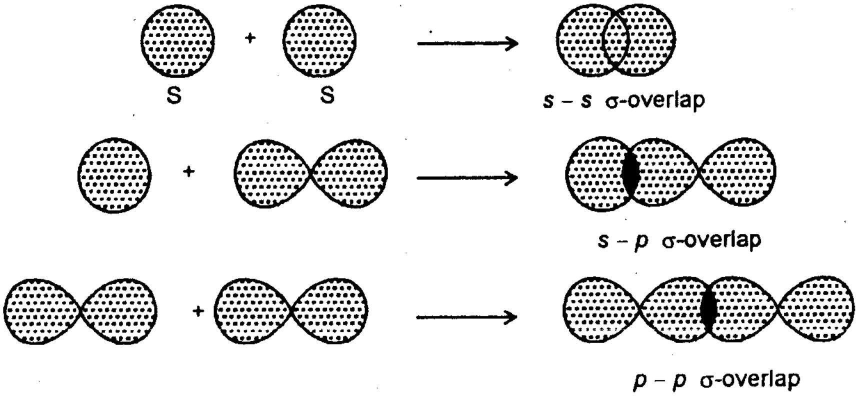


Fig. 4.11. Formation of σ-bonds.

An example of σ-bond formation is between ammonia and boron trifluoride. One of the p orbitals (say p_x) has a lone pair of electrons and would be able to form linear overlap with the vacant $2p_x$ orbital on the same axis (Figure 4.12).

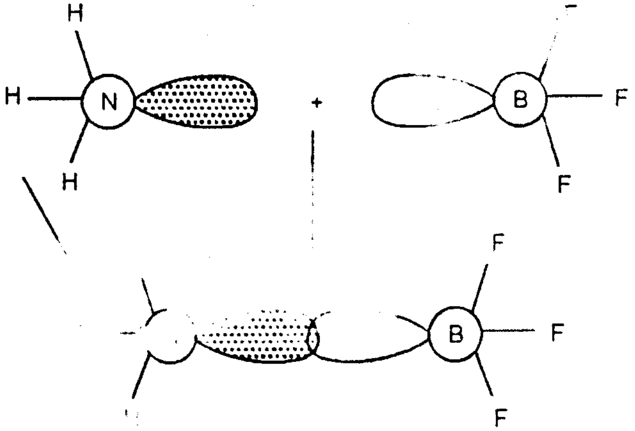
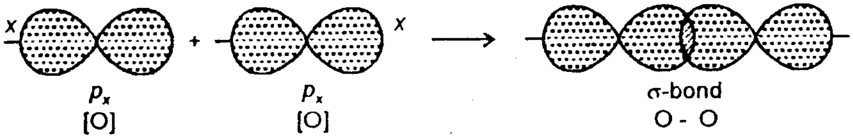
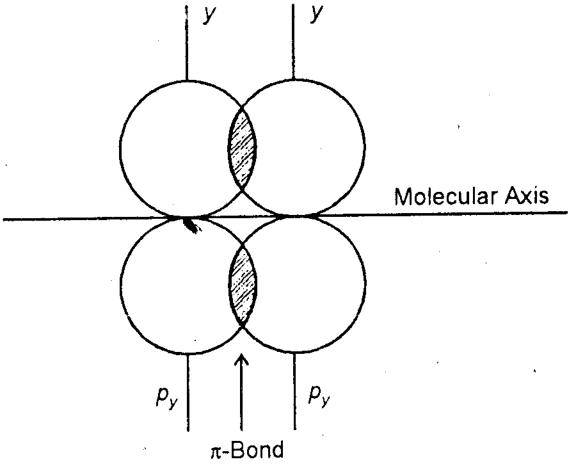


Fig. 4.12. Formation of a σ-bond between NH_3 and BF_3.

Let us see the situation in double and triple bonds. We ought to know whether these bonds are all of σ-type or some other type of bond may be associated in them. Let us consider oxygen molecule as a representative of compounds containing double bonds. The oxygen atom has the electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^2$. Based upon the valence bond concept, two bonds are expected between two oxygen atoms due to the presence of two unpaired electrons. In O_2 molecule, p_x orbitals of two oxygen atoms undergo direct or head-on overlap and form a σ-bond.





The other bond formed in O_2 molecule is obtained by ***parallel, lateral or sideways overlap*** of two p_y orbitals of two oxygen atoms. ***Such bonds are known as pi (π) bonds and in these bonds orbital's overlap produces an electron cloud lying above and below the molecular axis.*** It should be mentioned that both the *p*-orbitals have parallel axis and should be coplanar (in one plane). The overlap criterion of p_y orbitals to form π-bond is:

In order to explain the formation of σ-bond, let us take the example of O_2 molecule. Each oxygen atom which combines with the other oxygen atom has electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^2$. The valence bond theory predicts the formation of two bonds between two oxygen atoms. One of them is formed by the axial or head-on overlap of say, p_x orbitals and would form a σ-bond. The p_y orbitals have the only possibility of overlapping through parallel or lateral overlap. This would result in the formation of a π-bond, as described before. The diagrammatic representation of σ and π-bonds is shown in Figure 4.13 (For the sake of simplicity only p_x and p_y orbitals are shown).

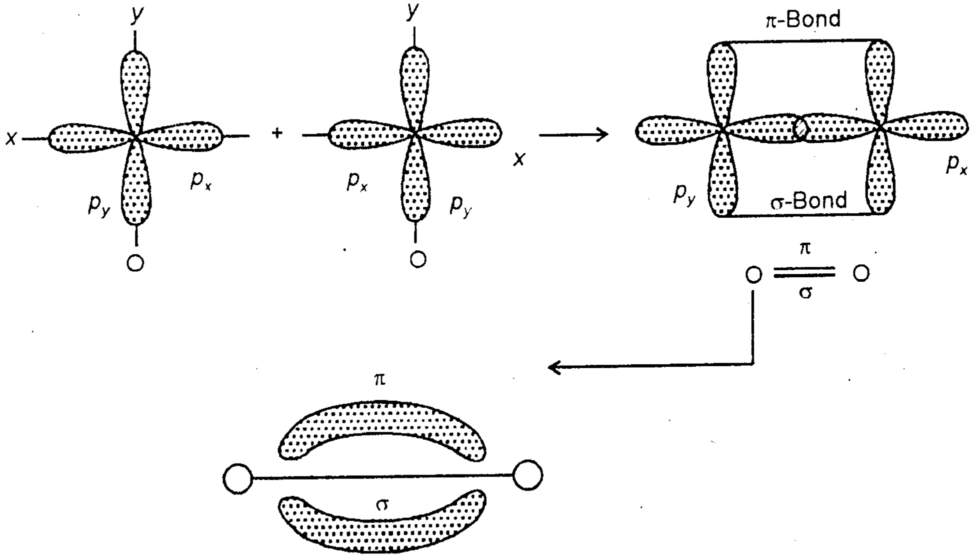
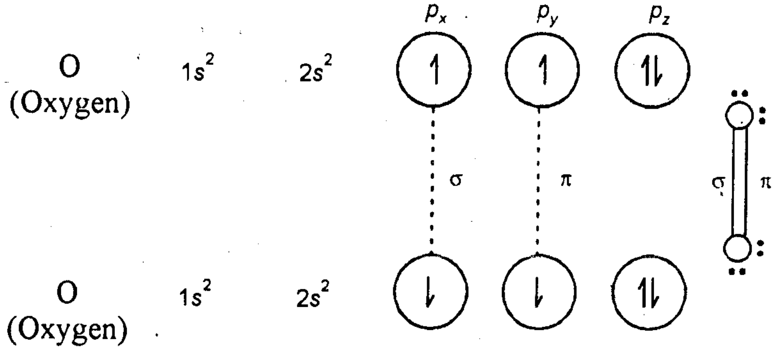


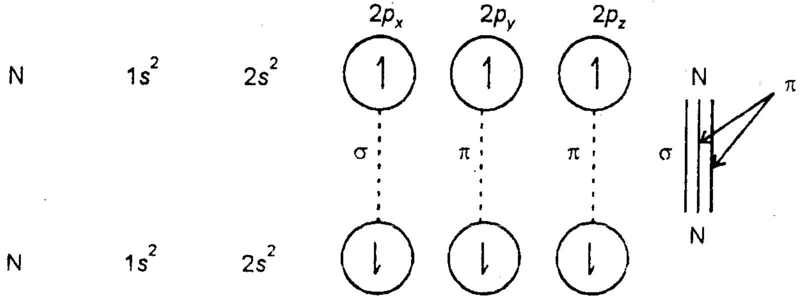
Fig. 4.13. σ and π-bond formation in O_2 molecule.

The electronic arrangement in O_2 molecule showing the σ and π bonds is represented as:



According to valence bond theory, O_2 molecule should have a double bond leaving no unpaired electron. But the paramagnetic nature and magnetic moment value of oxygen molecule indicates the presence of two unpaired electrons which cannot be shown by the valence bond theory. This is an example of the failure of this theory to explain the true structure and electronic structure of the molecules.

Let us now consider the formation of a triple bond in N ≡ N molecule. The electronic structure of nitrogen atom is, $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. The number of unpaired electrons indicate the formation of three bonds, one σ and two π-bonds.



The overlap of two $2p_x$ orbitals of two nitrogen atoms is axial or head-on and would give rise to one σ-bond. However, the overlap or combination of $2p_y$ and $2p_z$ orbitals would be parallel or lateral and two π-bonds would be formed (one by $2p_y$ – $2p_y$ overlap and other by $2p_z$ – $2p_z$ overlap) as shown in Figure 4.14.

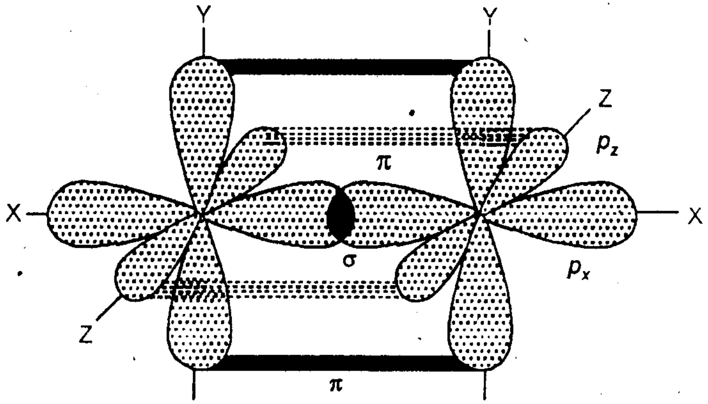
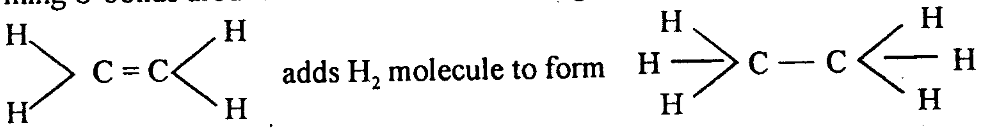


Fig. 4.14. Formation of one σ and two π-bonds in N_2 molecule.

It may be concluded that in general a compound formed by a single bond possesses one σ-bond only; a compound having a double bond possesses one σ-bond and one π-bond; and a compound having a triple bond possesses one σ-bond and two π-bonds. Thus, ethane possesses a σ-bond between C – C atoms; ethylene has one σ-bond and one π-bond between C = C skeleton and acetylene possesses one σ-bond and two π-bonds between C ≡ C skeleton. The presence of a π-bond in ethylene molecule explains its restricted 'free rotation'. The bond strength of a π-bond is less than that of a σ-bond. It explains the ease with which the double bond undergoes addition reaction, thereby breaking π-bonds and forming σ-bonds around the concerned atoms *e.g.*,



The π-bond is rarely the only link between two atoms. It is almost always accompanied by a σ-bond.

MOLECULAR ORBITAL THEORY (MOT):

The molecular orbital theory describes the valence electrons as associated with all the nuclei concerned. The nuclei are in equilibrium positions in the stable molecule and electrons associated with all the nuclei can be described by wave functions. The energy states of electrons can be described in the combined states or molecular orbitals. ***The molecular orbitals are multicentred or delocalised***. They are filled with the required number of electrons (each molecular orbital is usually filled with two electrons). Molecular orbitals may be obtained by the linear combination of atomic orbitals (LCAO method).

The molecular orbitals are assumed to possess the following characteristics:

(i) Each electron in the molecule is described by a wave function ϕ. The value of ϕ is such that the value of ϕ^2 at any point represents the probability of finding the electrons in unit volume around that point. The wave functions are called ***molecular orbitals***. These molecular orbitals are polycentric so that the electron moves in the field of all the nuclei.

(ii) Each molecular orbital has its own energy.

(iii) Each electron has a definite spin $\left(+\frac{1}{2} \text{ or } -\frac{1}{2}\right)$ and Pauli's exclusion principle is observed.

(iv) The appropriate form of the wave equation is quite complicated and cannot be used for exact solution except for hydrogen. Thus approximations are necessary. One of the approximations is that when an electron comes in the vicinity of one nucleus, the force arising on it is due to the nucleus and its other electrons. Both the wave equation and its solutions resemble those for the isolated atom, and the molecular orbital consists of a series of superposed self-consistent orbitals. ***This procedure is known as the linear combination of atomic orbitals (LCAO)***.

(v) The greater the overlap of atomic orbitals a~~mong themse~~lves, more stable molecular orbitals (with least energy states) are obtained.

(vi) The energy of a molecular orbital is least when the combining atomic orbitals have equal or almost equal energy states. Atomic orbitals of low energy will not be able to overlap with other atomic orbitals and electrons carried by them will be ***non-bonding.***

(vii) Each molecular wave function corresponds to a definite energy value. The sum of the individual energies of the molecular orbitals, after correction, represents the total energy of the molecule.

Let us now apply these factors to a simple homonuclear diatomic molecule such as hydrogen in which two identical atoms are linked by an electron pair bond.

Although the atoms are identical but it will be convenient to distinguish the two atoms by writing H_A and H_B. Each hydrogen atom has a single electron in $1s$ atomic orbital. Let ψ_A be the wave function of atomic orbital of hydrogen atom H_A, and ψ_B the atomic wave function of hydrogen atom H_B. The effective overlap of the wave functions ψ_A and ψ_B will take place only if (i) the orbitals have similar energy state, (ii) the orbitals overlap to a considerable extent, and (iii) orbitals have the same symmetry. All these conditions are fulfilled by atomic orbitals of both the hydrogen atoms. Now the molecular wave function ϕ will be obtained by the linear combination of the atomic orbital wave functions *e.g.*, ψ_A and ψ_B.

$$\phi = \psi_A(1s) + c\,\psi_B(1s) \qquad \cdots\cdots \quad (17)$$

Here c is a coefficient which represents the relative proportions of $\psi_A(1s)$ and $\psi_B(1s)$ in the molecular orbital ϕ in the ratio of $1^2 : c^2$. But both H_A and H_B are identical, so $\psi_A(1s)$ and $\psi_B(1s)$ must make equal contributions to the molecular orbitals. In such case, $c^2 = 1$, *i.e.*, $c = \pm 1$. Thus, there are two possible ways of representing the molecular orbitals which are obtained by substituting c in equation (17).

$$\phi_B = \psi_A(1s) + \psi_B(1s) \qquad \cdots\cdots \quad (18)$$

$$\phi_A = \psi_A(1s) - \psi_B(1s) \qquad \cdots\cdots \quad (19)$$

The molecular orbital wave-function ϕ_B described in equation (18) indicates that the two atomic orbitals reinforce between the two nuclei. This wave function corresponds to the molecular orbital of low energy which is called ***'bonding' molecular orbital***. The bonding molecular orbital can have a pair of electrons with opposite spins. ϕ_B represents here a bonding molecular orbital of σ-symmetry formed by linear combination of 1*s* atomic orbitals. It is designated as σ 1*s*.

The molecular orbital ϕ_A, described in equation (19), is obtained by superposing ψ_A (1*s*) and ψ_B (1*s*) atomic wave functions after the sign of the latter has been changed. The resulting wave function corresponds to what is called ***'anti-bonding' molecular orbital*** of high energy. This corresponds to a configuration where both the electrons will have the same spin and would not be able to form a bond. ϕ_A represents a molecular wave function corresponding to anti-bonding molecular orbitals. In the case of linear combination of 1*s* atomic orbitals, it is represented as σ* 1*s*.

Thus, the linear combination of two ***atomic orbitals*** would result in the formation of ***two molecular orbitals***, one is called "bonding" molecular orbital and the other, 'anti-bonding' molecular orbital. The formation of bonding and anti-bonding orbitals by the linear combination of 1*s* atomic orbitals of two hydrogen atoms, H_A and H_B, is shown in Figure 4.15.

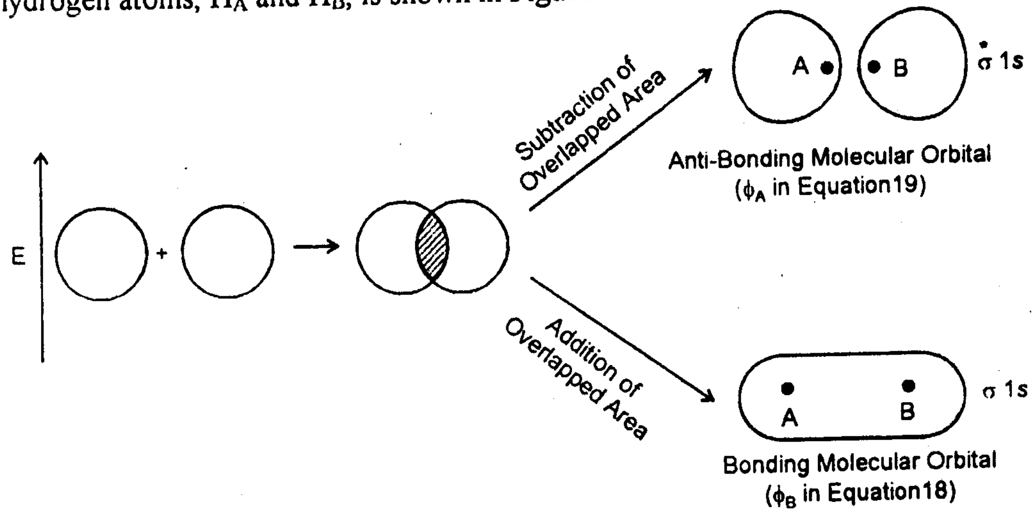


Fig. 4.15. Molecular orbital of σ-symmetry formed by the linear combination of 1s atomic orbitals of hydrogen.

Similar considerations would apply to linear combination of p-type atomic orbitals. Let us consider first the combination of two $2p_x$ atomic orbitals having the x-axis as the internuclear axis. In this case, the bonding and anti-bonding molecular orbitals can be described in terms of wave functions ϕ_B and ϕ_A, respectively. The values of ϕ_B and ϕ_A are:

$$\phi_B = \psi_A(2p_x) + \psi_B(2p_x), \text{ termed } \sigma\, 2p_x \qquad \ldots\ldots \qquad (20)$$

$$\phi_A = \psi_A(2p_x) - \psi_B(2p_x), \text{ termed } \sigma^*\, 2p_x \qquad \ldots\ldots \qquad (21)$$

The formation of molecular orbitals of σ-symmetry possessing wave functions ϕ_A and ϕ_B is shown in Figure 4.16.

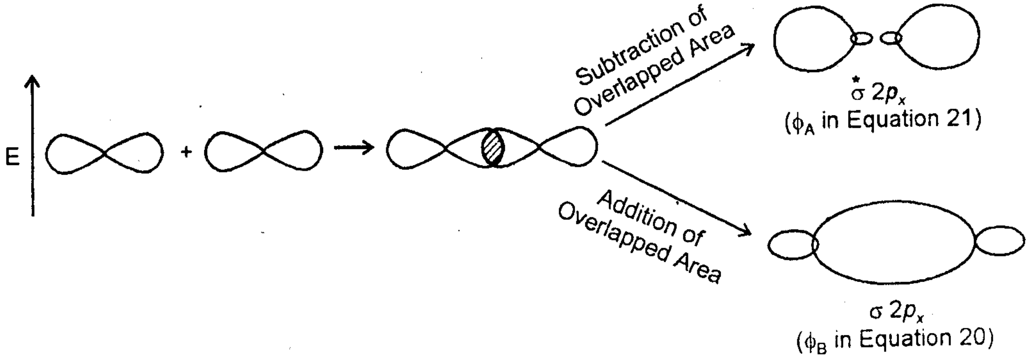


Fig. 4.16. Molecular orbitals of σ-symmetry formed by combination of $2p_x$ atomic orbitals.

The $2p_y$ or $2p_z$ atomic orbitals can have parallel overlap and combine to form molecular orbitals having a node on the internuclear x-axis. The molecular orbitals formed are said to possess π-symmetry. The molecular wave functions are again obtained by linear combination of atomic orbitals. Thus, the combination of two $2p_y$ atomic orbitals would be represented in terms of wave-functions as:

$$\phi_B = \psi_A(2p_y) + \psi_B(2p_y), \text{ termed } \pi_y\, 2p \qquad \ldots\ldots \qquad (21)$$

$$\phi_A = \psi_A(2p_y) - \psi_B(2p_y), \text{ termed } \overset{*}{\pi}_y\, 2p \qquad \ldots\ldots \qquad (22)$$

The $\pi_y\, 2p$ and $\overset{*}{\pi}_y\, 2p$ molecular orbitals are similar but oriented through 90° (Figure 4.17). The electrons occupying the bonding molecular orbital should have opposite spins but those occupying anti-bonding molecular orbital should be of same spin. The combination of $2p_z$ atomic orbitals is identical to the combination of $2p_y$ orbitals and would result in the formation of π-molecular orbitals.

$$\phi_B = \psi_A(2p_z) + \psi_B(2p_z), \text{ termed } \pi_z\, 2p \qquad \ldots\ldots \qquad (23)$$

$$\phi_A = \psi_A(2p_z) - \psi_B(2p_z), \text{ termed } \overset{*}{\pi}_z\, 2p \qquad \ldots\ldots \qquad (24)$$

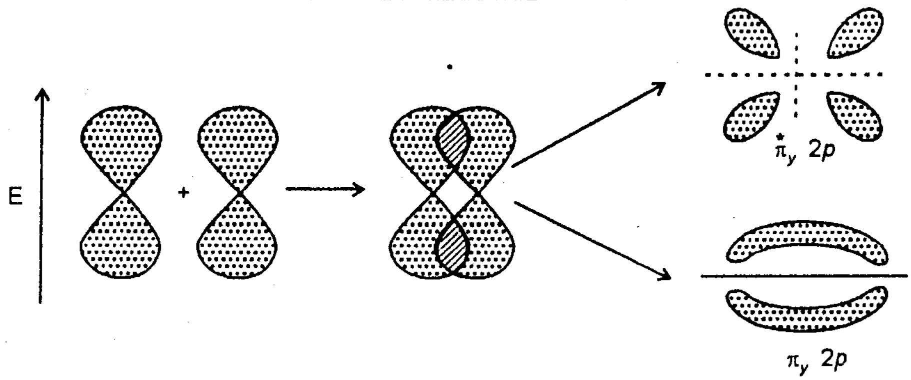


Fig. 4.17. Molecular orbitals of π-symmetry formed by the combination of $2p_y$ atomic orbitals.

In order to know about the filling of electrons in molecular orbitals it is necessary to find out the order of stability or energy states of their molecular orbitals. The order of stability has been obtained by the study of molecular spectra in the ultraviolet region. The order of stability for various molecular orbitals are:

$$\sigma\, 1s < \overset{*}{\sigma}\, 1s < \sigma\, 2s < \overset{*}{\sigma}\, 2s < \sigma\, 2p < \pi_y\, 2p = \pi_z\, 2p < \overset{*}{\pi}_y\, 2p = \overset{*}{\pi}_z\, 2p < \overset{*}{\sigma}\, 2p$$

σ 1s molecular orbital is the most stable and therefore possesses the least energy. In this series $\overset{*}{\sigma}$ 2p molecular orbital is the least stable and possesses the highest energy.

Molecular Orbital Valence Electron Configurations for Diatomic Molecules of the Second Period

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2$	0
B_2	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2\,(\pi_{2p},\ \pi_{2px})^2$	1
C_2	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2\,(\pi_{2py},\ \pi_{2px})^4$	2
N_2	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2\,(\pi_{2py},\ \pi_{2px})^4\,(\sigma_{px})^2$	3
O_2	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2\,(\sigma_{2px})^2\,(\pi_{2py},\ \pi_{2px})^4\,(\pi_{2py}\ ^*,\ \pi_{2px}{}^*)^2$	2
F_2	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)^2\,(\sigma_{2px})^2\,(\pi_{2py},\ \pi_{2px})^4\,(\pi_{2py}{}^*,\ \pi_{2px}{}^*)^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2\,(\sigma_{2s}{}^*)\,(\sigma_{2px})^2\,(\pi_{2py},\ \pi_{2px})^4\,(\pi_{2py},\ ^*,\ \pi_{2px}{}^*)^4\,(\sigma_{2ps}\ ^*)^2$	0

APPLICATIONS OF MOLECULAR ORBITAL THEORY:

Molecular orbital theory (MOT) treats the nuclei of the molecule as polycentric nucleus. Molecular orbitals are characterized by a set of quantum numbers, in a manner similar to the treatment of atomic orbitals in atoms. The electrons are added after the molecular orbitals (MO's) have been constructed. The lowest energy orbital is filled first and Hund's rule is obeyed.

MOLECULAR ORBITALS FOR HOMONUCLEAR DIATOMIC MOLECULES:

We shall discuss the construction of molecular orbitals of homonuclear diatomic molecules such as H_2, Li_2, F_2, O_2 and N_2. The possibility for the formation of helium molecules shall also be considered. We shall describe these molecules after constructing their molecular orbital diagrams.

1. Formation of H_2 Molecule:

Two 1*s* atomic orbitals of two hydrogen atoms would result in the formation of two molecular orbitals, as discussed above. The bonding molecular orbital (σ 1*s*) has less energy than the atomic orbitals as shown in molecular orbital diagram. The anti-bonding molecular orbital ($\overset{*}{\sigma}$ 1*s*) has higher energy than the combining atomic orbitals. As shown in Figure 4.18, both the electrons move to bonding molecular orbital and would result in the formation of a σ-bond (H – H) between two hydrogen atoms. The anti-bonding molecular orbitals refer to the extent of unstable nature of the bond. Any possibility of the shift of electrons to anti-bonding orbitals would mean the dissociation of a bond. As the atomic orbitals of two hydrogen atoms have the same energy the molecular hydrogen possesses predominating covalent bond, H – H.

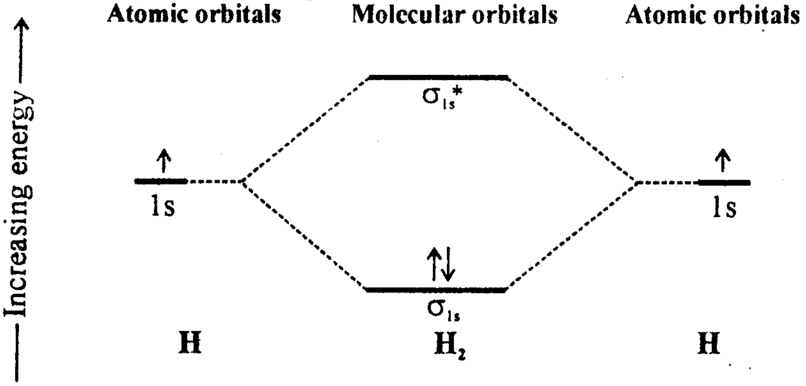


Fig. 4.18. Molecular orbital energy diagram for the dihydrogen molecule, H_2.

The bond order of H_2 molecule is one. Bond order is defined as the number of electron pairs which occupy the bonding molecular orbitals (MO's) minus the number of electron pairs in anti-bonding molecular orbitals. For hydrogen, the electron pairs in bonding MO's is one and in anti-bonding MO's is zero (no electron in $\overset{*}{\sigma}$ 1*s*). Thus the bond order of H_2 molecule is 1 – 0 = 1.

$$H_A(1s)\,H_B(1s) \longrightarrow H_2[(\sigma 1s)^2] \text{ or } H-H$$

2. Formation of MO's for He_2:

Let us see how molecular orbital theory is able to explain the non-existence of He_2 molecules. Each He atom (At. no. 2) has electronic configuration $1s^2$. Thus the $1s$ atomic orbital of each He atom would contain two electrons. Overlapping of two atomic orbitals would result in the formation of two molecular orbitals *e.g.*, bonding (ϕ_B) and anti-bonding (ϕ_A) type. Two out of a total of four electrons (derived from AO's) would go to bonding molecular orbitals and the other two would be promoted to anti-bonding molecular orbitals. As a result of this, the stability gained by two electrons moving to low energy molecular orbitals would be lost by the other two electrons moving to the anti-bonding molecular orbitals as shown in Figure 4.19. Thus, the bond forming capacity would become equal to bond breaking possibility. In other words, the bond order would be 1 – 1 = 0. ***The molecule is unstable and no bond will be formed between two helium atoms.*** That is why helium exists in atomic state in contrast to the existence of other gases which are present in diatomic states.

$$He_2\,[(\sigma\,.\,1s)^2\ \ (\sigma^*\,1s)^2]$$

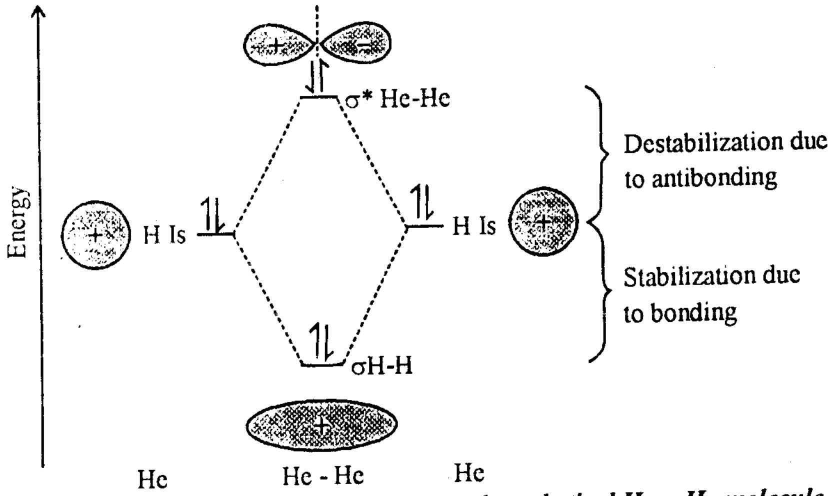


Fig. 4.19. Molecular orbital diagram for a hypothetical He – He molecule.

3. Formation of MO's for Li_2:

The electronic configuration for each lithium atom (At. no. 3) is $1s^2\ 2s^1$. Only $2s^1$ orbital would be responsible for the bond formation. The bonding molecular orbital formed from atomic orbitals of two lithium atoms would take up both the electrons. The electrons in bonding molecular orbital would be more stable than in atomic orbitals because of low energy. None of the $2s$ electrons is available for anti-bonding orbitals due to its high energy state (compared to even atomic orbitals). The bond order would be 1 – 0 = 1. So there is a possibility of bond formation among lithium atoms. The molecular orbital diagram is shown in Figure 4.20.

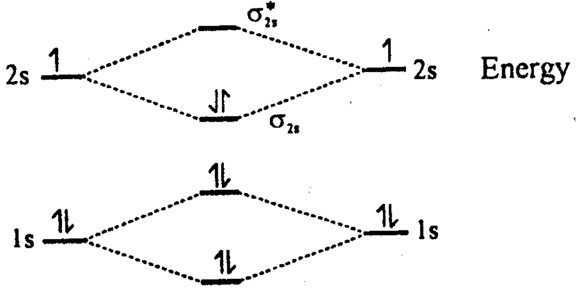


Fig. 4.20. Molecular orbital diagram for Li_2.

The configuration of Li_2 may be represented as:

$$2Li\ (1s^2\ 2s^1) \longrightarrow Li_2\ [KK(\sigma\ 2s^2)]$$

4. Formation of O_2 Molecule:

The electronic configuration of oxygen atom (At. no. 8) is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. It is obvious from the electronic configuration of oxygen that only $2p_x$ and $2p_y$ atomic orbitals would contribute to the bonding between two oxygen atoms forming O_2 molecules. As $1s^2$ and $2s^2$ orbitals will not contribute to bonding, we will not discuss these orbitals. Let us draw the molecular orbital diagram for O_2 molecule starting from $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of two oxygen atoms (see Figure 4.21).

It can be seen from π_y*2p and π_z*2p molecular orbitals (anti-bonding) that they are singly occupied with electrons of parallel spins. This would also explain the paramagnetic behaviour of O_2 because the number of unpaired electrons are related to paramagnetism. The explanation of this well-known paramagnetic property of O_2 was one of the major successes of molecular orbital theory.

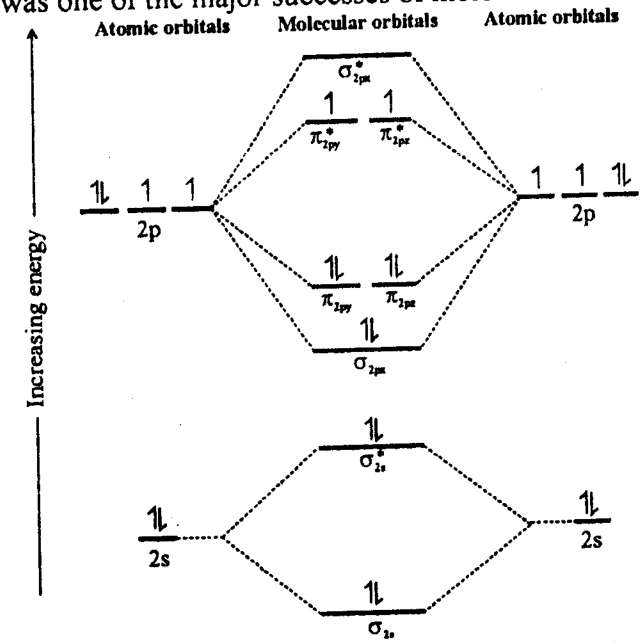


Fig. 4.21. Molecular orbital energy diagram for the valence orbitals of the dioxygen molecule, O_2

The electronic arrangement in O_2 molecule is:

$$O_2\ [KK(\sigma\ 2s)\ (\sigma^*\ 2s)^2\ (\sigma\ 2p_x)^2\ (\pi_y\ 2p)^2\ (\pi_z\ 2p)^2\ (\pi^*_y\ 2p)^1\ (\pi_z^*\ 2p)^1]$$

The bond order in O_2 molecule is $3 - 1 = 2$. One of the O = O bonds is a bond represented by $\sigma\ 2p_x$ and the other is a bond formed by $2p_y$ atomic orbital overlap of one oxygen atom with $2p_y$ AO of the second one. Thus, one of the double bonds present in O_2 molecule is a σ-bond and the other one, a π-bond.

5. Formation of N_2 Molecule:

The electronic configuration of nitrogen atom (At. No. 7) is $1s^2\ 2s^2\ 2px^1\ 2py^1\ 2pz^1$. All the three 2p orbitals are capable of bond formation between two nitrogen atoms of the molecule. The molecular orbital diagram of nitrogen molecule is given in Fig. 4.22. It depicts three bonds between two nitrogen atoms in N_2 involving on σ_{2p} and two π2p orbitals.

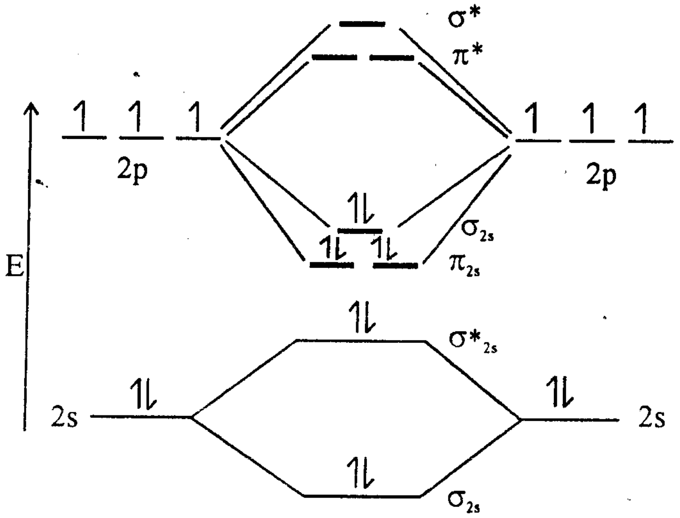


Fig. 4.22. Molecular Orbital Diagram of Nitrogen Molecule.

6. Formation of F_2 molecule:

The electronic configuration of a fluorine atom (At. no. 9) is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$ (for convenience, all *p* orbitals are equivalent and equi-energic). The overlap of $2p_y$ atomic orbitals of two fluorine atoms results in the formation of one bonding molecular orbital and one anti-bonding molecular orbital. Both the electrons from $2p_x$ atomic orbitals go to bonding molecular orbital $(\sigma\ 2p_x)^2$ resulting in the formation of a σ-bond between two fluorine atoms. The $2p_y$ and $2p_z$ atomic orbitals and resulting molecular orbitals do not contribute to the bond formation because of the presence of equal number of electrons in bonding and anti-bonding molecular orbitals (Figure 4.23).

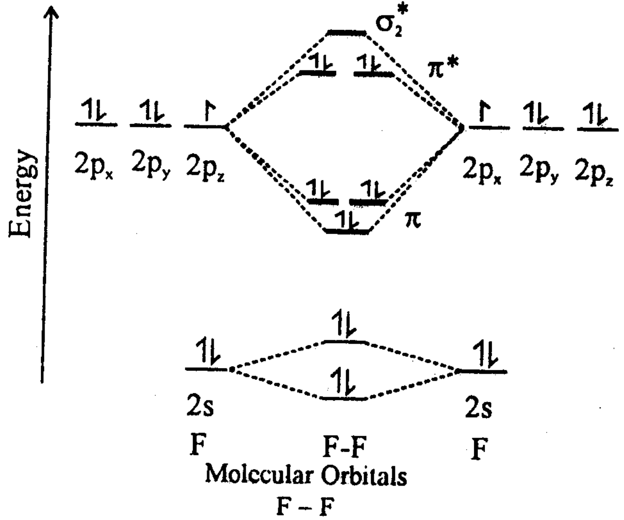


Fig. 4.23. Formation of F_2 molecule and relative energies of orbitals.

The electronic arrangement in F_2 molecule is:

$$F_2\ [KK(\sigma\ 2s)^2\ (\sigma^*\ 2s)^2\ (\sigma\ 2p_x)^2\ (\pi_y\ 2p)^2\ (\pi_z\ 2p)^2\ (\pi_y^*\ 2p)^2\ (\pi_z^*\ 2p)^2]$$

Cl_2 and Br_2 have analogous arrangements. The bond order in F_2 is $3 - 2 = 1$, a σ-bond existing between two fluorine atoms, F $\underline{\sigma}$ F.

HETERONUCLEAR DIATOMIC MOLECULES:

The molecular orbital theory can be applied to explain the bonding in heteronuclear (having different nuclei or atoms) diatomic molecules such as HF. The electronic configuration of hydrogen and fluorine atoms are:

H $1s^1$

F $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

The molecular orbitals which can describe the H – F bond must be formed by linear combination of the $1s$ atomic orbitals of H and $2p$ atomic orbitals of F. The $1s^2$ and $2s^2$ orbitals of F are not capable of bond formation because they are filled to capacity and too low lying to participate in this process. (The atomic orbitals of more electronegative elements have relatively lower energies). The $2p$ orbitals of F have suitable energy and are involved in bond formation.

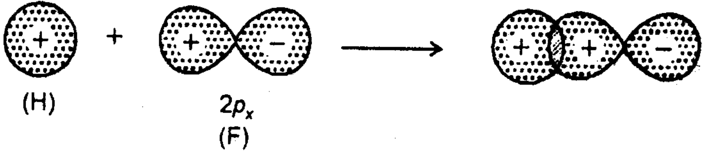


Fig. 4.24. Combination of 1s orbital of H and $2p_x$ orbital of F.

Now let us see which of the $2p$ orbitals is able to overlap more effectively so as to form a stable bond. The $2p_x$ atomic orbital of F combines with $1s$ atomic orbital of H to form an effective s-bond overlap as shown in Figure 4.24 (+ and – signs indicate the wave amplitudes or sign of the wave function). The maximum overlap is possible in this way forming a stronger bond. On the other hand, if $2p_y$ or $2p_z$ orbitals of F are involved in overlap with 1*s* atomic orbital from H, the overlap from the positive lobe (positive wave amplitude) will be counterbalanced by the negative lobe. This overlapping is thus cancelled out as shown in Figure. 4.25.

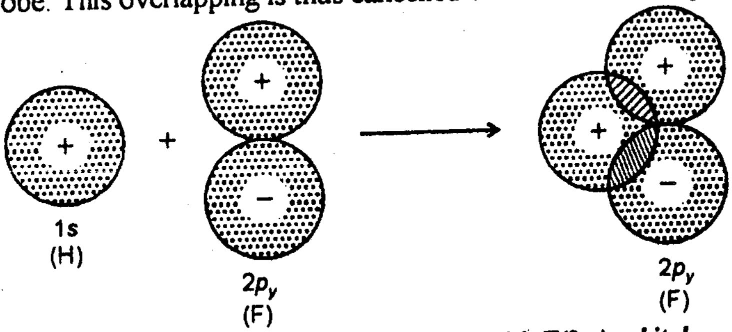


Fig. 4.25. Combination of H(1s) orbital with F($2p_y$) orbital.

It may now be concluded that only $2p_x$ atomic orbital is responsible for the bond formation between H and F. Let us now consider the molecular orbital diagram for HF molecule. HF is formed by the linear combination of atomic orbitals of H(1*s*) and F($2p_x$). Each one of the orbitals possesses one electron. Forgetting about the energies of the atomic orbitals, we get the molecular orbital diagram shown in Figure 4.26. The $2p_x$ orbitals of F are shown at a relatively lower energy state due to the greater electronegativity of F.

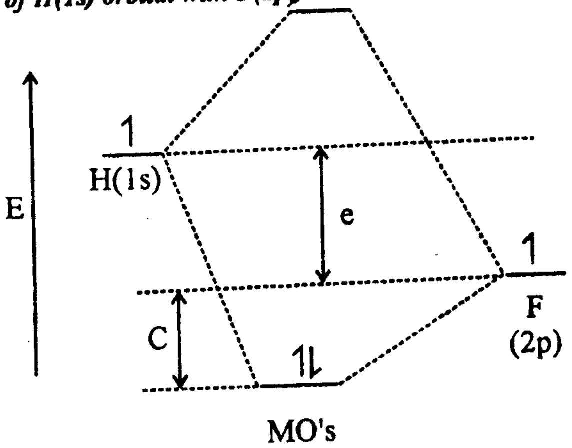


Fig. 4.26. Formation of H – F.

A single bond is expected in H – F molecule because the bond order would be 1 – 0 = 1. It must be noticed in the molecular orbital diagram given in Figure 4.26, that the energy difference '*e*' between atomic orbitals corresponds to the extent of ionic bond in HF which depends upon the difference in electronegativities between two atoms. The covalent character of the bond is determined by the energy difference 'C' and would indicate the extent of overlap. Therefore, the molecular orbital theory is able to predict the nature of the chemical bond to be expected from a molecule. This is another advantage of the molecular orbital theory.

It should be pointed out over here that the molecular orbital theory is decisively more comprehensive and rational.

COMPARISON OF ATOMIC AND MOLECULAR ORBITALS

Atomic Orbitals	**Molecular Orbitals**
1. Nucleus of the atom is fixed in space.	1. Nuclei of the constituent atoms of the molecule are fixed in space at their proper relative orientations.
2. In filling atomic orbitals, Aufbau principle is followed.	2. In filling molecular orbitals, the Aufbau principle is followed.
3. Pauli's exclusion principle is obeyed in filling the AO's with electrons.	3. While filling molecular orbitals with electrons, Pauli's exclusion principle is obeyed.
4. The filling of AO's obeys Hund's rule.	4. Hund's rule is obeyed by molecular orbitals while filling with electrons.
5. The chemistry of atoms is mainly concerned with electrons in high energy AO's. VBT	5. The chemistry of molecules is also concerned with electrons present in relatively higher energy orbitals.

COMPARISON OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES:

Both the valence bond and molecular orbital theories make use of the variation principle. The overlap criterion is predominant in both concepts. However, the valence bond theory does not provide a clear pictorial representation of the energy changes involved during bond formation. Molecular orbital description is able to indicate even the minor energy changes during bond formation from which a lot of information may be collected, *e.g.*, the contribution of covalent and ionic character etc. Valence bond theory is useful in predicting the symmetry of the molecules using the idea of hybridization. For example, sp^3 hybridized structures are always tetrahedral and d^2sp^3 hybridization results in the formation of octahedral symmetry. The most common features with the valence bond and molecular orbital theories are:

1. The electron distributions for a given molecule are similar.
2. In both the theories, a normal covalent bond involves the sharing of electron density by both nuclei and concentration of electron density between the nuclei.
3. σ and π bonds can be distinguished in both the treatments.
4. In both descriptions, atomic orbitals of the atoms must overlap and should have appropriate symmetry about the molecular axis to form a bond.
5. Variation principle is utilized in both treatments.

The essential points of difference between the two theories are:

1. Different procedures are adopted in the mathematical calculations involved.
2. Where valence bond theory (VBT) utilizes the concept of resonance, the molecular orbital theory (MOT) gives an idea of the delocalization. The term delocalization energy is employed in MOT instead of resonance energy.
3. The valence bond concept treats the partial ionic character as:

$$\phi = \phi_{cov} + \lambda'\phi_{ionic}$$

where λ' refers to the degree to which the ionic character is possible. The ionic character is explained by molecular orbital treatment as:

$$\sigma = N(\psi_A + \lambda\psi_B)$$

The difference in electronegativities of the components and the difference in energy states of the atomic orbitals determine the ionic character (see Figure 4.25).

4. Molecular orbital theory is more convenient for the description of excited states in molecules. The electronic transitions that occur in the visible and ultraviolet region of the spectra involve these states and can be simply described by MO treatment. The excited states are not easily described by the valence bond theory.
5. The paramagnetic character of O_2 molecule can be easily explained by the molecular orbital theory but the valence bond approach is not able to explain such characteristics of the molecule.

Questions

1. Discuss the principles involved in the valence bond theory. How is this theory applied to explain the formation of chemical bond?
2. Write a brief account of the molecular orbital theory. Explain the bonding in the following molecules:

   H_2, N_2, O_2.
3. Formulate the bonding in the hydrogen halide molecules in terms of MO theory. Discuss the bond properties of these molecules.
4. Discuss the bond properties of N_2, O_2, F_2 and P_2 in terms of their electronic structures.
5. What do you understand by 'covalent pi(π) bond'? Give examples of compounds containing π bonds and sketch the orbitals involved in (a) the π bonds (b) accompanying σ bonds.
6. Discuss the reasons (in terms of VBT and MOT) why a molecule such as LiHe is unstable?
7. Give the electronic configuration of Li, C, N and O. Discuss the molecular orbital structures and bond order in the formation of their homonuclear diatomic molecules.
8. Explain the following terms:

   (a) Sigma (σ) bond (b) Pi (π) bond
9. Explain the paramagnetic character of O_2 molecule based upon molecular orbital theory.
10. What do you understand by hybridization of orbitals? Discuss the formation of *sp*, sp^2 and sp^3 hybrid orbitals. What are the rules applied for hybridization?
11. What are the general characteristics of the molecular orbitals? Describe the formation of molecular orbitals of N_2, Cl_2 and S_2.
12. Discuss the molecular orbital theory. How is it applied to explain the formation of heteronuclear diatomic molecules?
13. How would you compare the atomic and molecular orbitals?
14. Discuss the common features in valence bond and molecular orbital theories. What are the essential points of difference between them?
15. Predict the shapes of the following molecules:

    (a) SO_2 (b) H_2O (c) CH_4 (d) SF_6
16. What are hybrid orbitals? Discuss the conditions of their formation.
17. What is bond order? How is it correlated to bond formation in molecules.
18. How is molecular orbital theory applied to explain the ionic character of the bond in heteronuclear diatomic molecules?

19.. **Write short answers to the following questions:**

(i) What is the basic principle of Valence Bond Theory?

(ii) How is valence bond method capable of explaining the nature of the ionic bond?

(iii) What do you mean by electron exchange interaction?

(iv) How is valence bond concept able to explain the formation of O_2, N_2, Cl_2, F_2.

(v) What do you understand about the concept of hybridization?

(vi) Describe the formation of *sp* hybrid orbitals.

(vii) Discuss the formation of sp^2 hybrid orbitals.

(viii) How are sp^3 hybrid orbitals formed?

(ix) Give summary of hybridization rules.

(x) Discuss the formation of sigma (σ) and pi (π) orbitals.

(xi) Describe sigma and pi orbital formation in O_2 and N_2 molecules.

(xii) Describe the salient features of molecular orbital theory.

(xiii) Discuss the formation of bonding and antibonding orbitals in *s* and *p* orbtials.

(xiv) What are applications of molecular orbital theory?

(xv) Explain the formation of H_2 molecule on the basis of molecular orbital theory.

(xvi) How is formation of O_2 molecule explained on the basis of molecular orbital theory?

(xvii) Why O_2 is paramagnetic?

(xviii) How is formation of F_2 molecule explained on the basis of molecular orbital theory?

(xix) Explain the formation of HCl on the basis of molecular orbital theory.

(xx) Give a comparison of atomic orbitals and molecular orbitals.

(xxi) How will you proceed to compare valence bond and molecular orbital theories?

20.. **Give the suitable answer:**

(i) Valency is considered as:

(a) number of valence bonds formed by an atom

(b) number of valence bonds formed by a molecule

(c) number of valencies expressed by the compound

(d) number of valence bonds formed by a compound

(Ans: a)

(ii) Covalence or non-polar bond concept was developed by:

(a) Arrhenius (b) Pauling
(c) Lewis (d) Sommerfeld

(Ans: c)

(iii) The bond formed by complete transfer of electrons is called:

(a) covalent bond (b) electrovalent bond
(c) metallic bond (d) coordinate covalent bond

(Ans: b)

(iv) Important forces between atoms or groups of atoms are:

(a) covalent (b) electrostatic
(c) metallic (d) Van der Waals' type

(Ans: b)

(v) Sodium chloride has the crystal structure:

(a) body-centered cube (b) face-centered cube
(c) hexagonal (d) tetragonal

(Ans: b)

(vi) Limiting radius ratio assigned to closely packed hexagonal structure is:

(a) 0.155 (b) 0.73
(c) 0.414 (d) 1

(Ans: d)

(vii) Hybridization is a process of combination of orbitals by:

(a) addition (b) multiplication
(c) subtraction (d) division

(Ans: a)

(viii) $BeCl_2$ has the hybrid orbitals of the type:

(a) sp (b) sp^2
(c) sp^3 (d) dsp^2

(Ans: a)

(ix) sp^2 hybridization in BF_3 gives structure to it:

(a) triangular plane (b) angular
(c) trigonal pyramid (d) square plane

(Ans: a)

(x) Hybridization is a process of mixing of:

(a) electrons (b) orbitals
(c) atoms (d) orbits

(Ans: b)

(xi) A bond in which the electron distribution is concentrated along the internuclear axis and possesses axial symmetry is called:
(a) pi bond (b) sigma bond
(c) ionic bond (d) covalent bond

(**Ans**: b)

(xii) Molecular orbitals are:
(a) localised (b) delocalised
(c) self-consistent

(**Ans**: b)

(xiii) Bonding molecular orbitals are formed by:
(a) subtraction of overlapped area
(b) addition of overlapped area
(c) division of overlapped area

(**Ans**: b)

(xiv) Oxygen is paramagnetic because it:
(a) is a gas (b) is colourless
(c) has unpaired electrons in antibonding M.O.
(d) has unpaired electrons in bonding M.O.

(**Ans**: c)

(xv) Valence bond theory cannot explain:
(a) geometry of molecules
(b) number of bonds formed in a molecule
(c) nature of bond (d) bond order

(**Ans**: a)

❀ ❀ 4 ❀ ❀

5

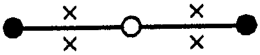
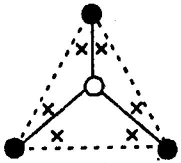
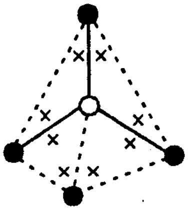
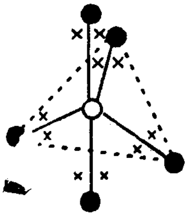
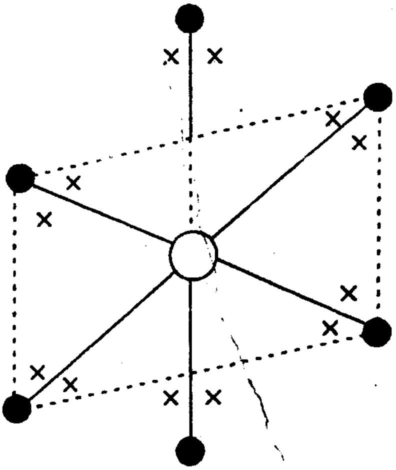
SHAPES OF INORGANIC MOLECULES

It has already been described that the chemical bonds are directed in space to form definite shapes of the molecules. In other words the electron-pairs forming the chemical bonds are distributed in space around the central atom along definite directions. The shared electron pairs as well as the lone pair of electrons appear to be responsible for the shapes of the molecules. Thus both the bonding pairs and lone pairs of electrons are responsible for the formation of molecular shapes. Sidgwick and Powell (1940) pointed out that the shapes of the molecules could be interpreted in terms of electron pairs present in the outer orbit of the central atom. ***Pairs of electrons occupy orbitals and the filled orbitals would repel each other and take up positions so as to remain as far apart as possible.*** The structures of solids and shapes of individual molecules have been ascertained by using instrumental techniques such as X-ray diffraction, electron diffraction, molecule spectra, magnetic susceptibility measurements and nuclear magnetic resonance spectroscopy etc.

Recently a simple theory has been put forward by Nyholm and Gillespie which is based on electron-pair repulsions between directed valences. This theory explains very well the shapes of the molecules containing non-transition elements. Accordingly, ***the shape or configuration of the molecules is mainly determined by the repulsive interaction between electron pairs present in the valence shell of the central atom.*** Such electron pairs are regarded as occupying localized orbitals. These orbitals are arranged in space in such a manner so that the distances between them are maximum and coulombic repulsion of electronic clouds is minimized.

In order to maintain a maximum separation between electron pairs, the following shapes of molecules are obtained (Table 5.1).

TABLE 5.1

No. of Electron Pairs		Shape of Molecules
2	Linear	
3	Plane triangle	
4	Tetrahedral	
5	Trigonal bipyramid	
6	Octahedral	

An important aspect to note over here is that if all the electron pairs are involved in bond formation with the same kind of atoms, we get regular shaped molecules as described in Table 5.1. But in the presence of lone pair of electrons in molecules or if different type of atoms join to form molecules, deviations from such regular shapes are to be expected.

The repulsion between electronic pairs in the valence shell decreases in the following order:

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair.

Nyholm and Gillespie theory is usually called the *valence shell electron pair repulsion* (VSEPR) concept. Let us elaborate this concept further and apply it to explain the shapes of various molecules.

Valence Shell Electron Pair Repulsion Concept (VSEPR):

In this concept, the arrangement of bonds around the central atom is considered to depend upon the number of valence shell electron pairs, and on the relative sizes and shapes of these orbitals. *These arrangements hold good for non-transition elements i.e.,* those elements which do not use electrons in bond formation. The geometrical shapes are actually result of the tendency of the electron-pairs to remain at a maximum distance apart so that the interaction between them is minimum. The repulsion between free electron-pairs will be obviously greater than that of repulsion between a bond pair and another bond pair. Let us sum up the essential features of this theory under the following rules:

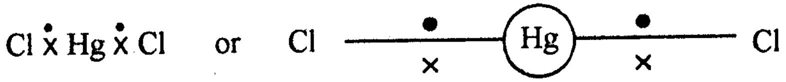
1. *The preferred arrangement of a given number of electron pairs in the valence shell is that which makes them to remain at a maximum distance apart.*
2. *A non-bonding pair (lone pair) of electrons is capable of making more space on the surface of an atom than a bonding pair.* This is because the non-bonding electron pair is under the influence of one nucleus only but the bonding electron pair is constrained by two nuclei.
3. *The influence of a bonding electron pair decreases with the increasing value of electronegativity of an atom forming a molecule.*
4. *The two electron pairs of a double bond (or the three electron pairs of a triple bond) take up more space than the one electron pair of a single bond.*

Applications of Valence Shell Electron Pair Repulsion Concept:

Let us now apply the valence shell electron pair repulsion concept to explain the shapes of the molecules. In other words, the effect of electron pair repulsion on molecular structure will be discussed. *The shapes of the molecules and ions of non-transition elements* will now be described in terms of this theory. The molecules will be classified according to the number of electron pairs present in them, irrespective of the fact whether they are of bonding or non-bonding type.

Shapes of Molecules Containing Two Electron Pairs (AB_2):

Mercuric chloride is a typical example of molecules which contains two electron pairs. Hg has the electronic configuration in which the valency shell has two electrons in 6*s* orbitals, $6s^2$. These two electrons are utilized to form two covalent bonds with two chlorine atoms to form $HgCl_2$. The two bond pairs of electrons in $HgCl_2$ arrange themselves as far apart as possible in order to minimize the repulsion between them. The only arrangement which satisfies this condition is that in which the molecule is linear.



Similarly, Be, Zn, Cd etc., having two electrons in the valency shell, also form linear molecules of the type A – M – A. They exhibit *sp* hybridization which also predicts a linear structure. The complex ions, $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$, which contain Ag^+ have the completed $4d^{10}$ electronic configuration. Both would form linear structures.

$$[NC - Ag - CN]^- \ [NH_3 - Ag - NH_3]^+$$

Shapes of Molecules Containing Three Electron Pairs (AB_3):

Boron ($1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z$) has three valency electrons and would be in sp^2 valence state. Three covalent bonds are expected. The electron pairs of these three bonds are arranged at the greatest possible distances from one another.

BF_3 contains three electron pairs as bond pairs which are situated at the corners of an equilateral triangle representing minimum interaction at maximum possible distance from one another as shown in Figure 5.1. Boron has one *s* and two *p* orbitals ($2s^2\ 2p_x^1\ 2p_y^1\ 2p_z$) or sp^2 hybrid orbitals which are bonded to three fluorine atoms.

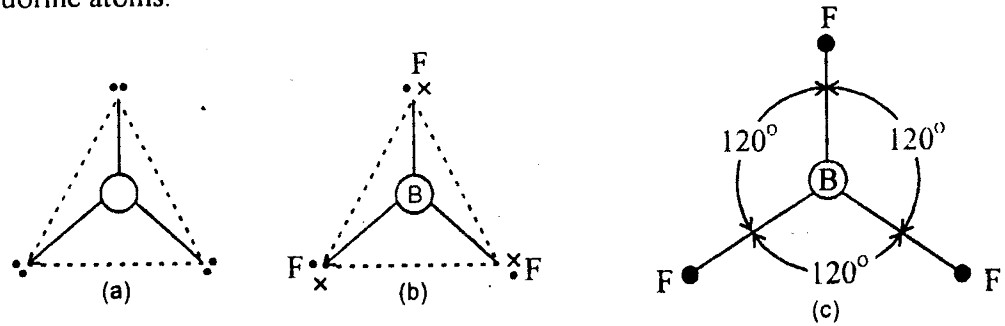


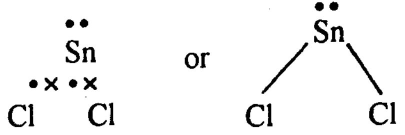
Fig. 5.1. Triangular shape.

(a) Triangular arrangement of three electron pairs.

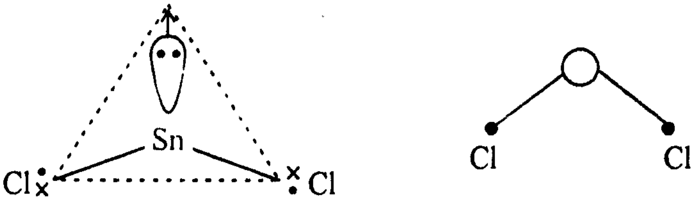
(b) Triangular shape of BF_3.

(c) Symbolic representation of plane triangular molecule.

In case of stannous chloride $SnCl_2$, Sn has valency electrons $5s^2\ 5p^2$. Two electrons present in 5*s* orbitals remain non-bonding (as a lone-pair) and do not take part in bond formation. The two electrons in 5*p* orbitals remain unpaired and form two covalent bonds by interaction with chlorine atoms. The lone pair present in the stannous chloride molecule occupies one corner of the triangle.



The other two corners of the triangle are occupied by two bond pairs as shown in Figure 5.2. The lone pair (non-bonding) of electrons exerts a greater repulsion on the bond pairs resulting in the shortening of Cl – Sn – Cl angle. Thus the effective molecular shape in the vapour phase of $SnCl_2$ is V-shaped and arrangement is called angular.



(a) (b)

Fig. 5.2. Distortion in triangular molecule.

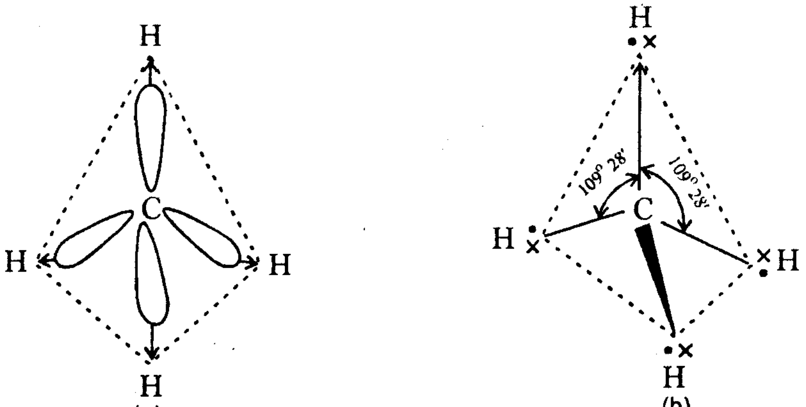
(a) V-shaped $SnCl_2$ due to the presence of a lone pair in a plane triangular symmetry.

(b) Representation of $SnCl_2$.

One *s* and two *p* atomic orbitals are involved in the formation of three molecular orbitals. Two of the molecular orbitals are of bonding type and the third one is non-bonding (containing lone pair of electrons).

Shapes of Molecules Containing Four Electron Pairs (AB_4):

The electrostatic repulsion between four pairs of electrons is minimum when these are situated at the corners of a regular tetrahedron, *e.g.*, CH_4 and $TiCl_4$ etc. Carbon and titanium, both have four unpaired electrons which share with four electrons (either supplied by four H atoms or Cl atoms, respectively) to form four electron bond pairs arranged in a tetrahedral manner as shown in Figure 5.3. The angles between tetrahedrally arranged bonds are 109° 28′ (each).



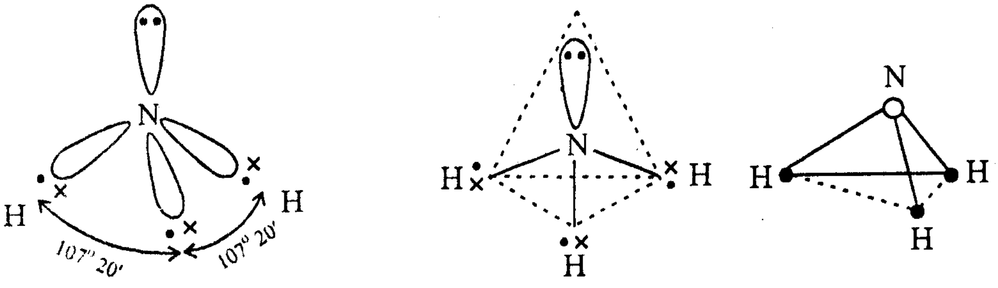
(a) (b)

Fig. 5.3. Tetrahedral shape.

(a) The effect of electron pair repulsion on bond angles.

(b) Tetrahedral arrangement of 4-electron pairs in CH_4.

However, it has been shown that the H – N – H bond angle is 107° 20′ in NH_3 which is less than that present in a tetrahedral arrangement (109° 28′). The decrease in angle may be considered to be due to the influence of lone pair of electrons. The electron cloud represented by the lone pair spreads out in space and causes more repulsive interaction between bonding electron pairs. Consequently, the three N – H bond pairs are pushed closer together and the bond angle decreases (107° 20′). As a result, NH_3 does not show the expected tetrahedral electronic arrangement but instead possesses a trigonal pyramidal molecular structure or geometry (Figure 5.4).



(a)

(b)

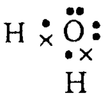
Fig. 5.4. Shape of NH_3 molecule.

(a) Effect of electron pair repulsion on the bond angles.

(b) Trigonal pyramidal structure or geometry.

If the three hydrogen atoms of ammonia are replaced by F(which is more electronegative than H), more electronic charge is shifted towards F atoms in NF_3. The lone pair on N in NF_3 will be able to exert more repulsive interaction on bond pairs. As a result, N – F bonds will shrink further giving F – N – F angle in NF_3 as 102.1°. But NF_3 like NH_3 will have triangular pyramidal shape.

Looking into the electron distribution in water molecule we find four electron pairs around oxygen — *two lone pairs and two bond pairs.*



$$\mathrm{H} \overset{\bullet}{\times} \underset{\substack{\bullet\times \\ \mathrm{H}}}{\ddot{\mathrm{O}}}:$$

The four electron pairs are arranged along the corners of a regular tetrahedron — two corners occupied by the two lone pairs and the other two corners by two bond pairs. The two lone pairs would have greater repulsion not only between themselves but also on the two bond pairs. As a result of this, the two O – H bonds in H_2O will be forced to come closer together than N – H bonds in NH_3. The electronegativity of oxygen will also play its role. The water molecule becomes V-shaped (Figure 5.5) and bond angle H – O – H will be decreased to 104.5°.

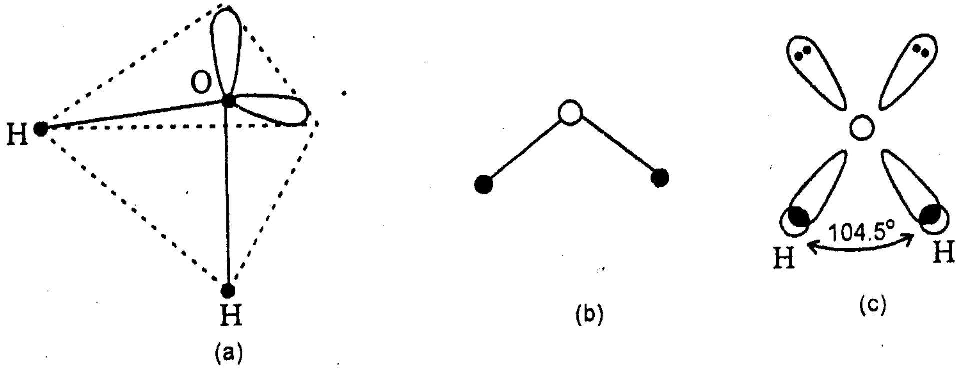


Fig. 5.5. Distortion in tetrahedral molecule due to two lone pairs.
(a) V-shape of H_2O.
(b) Representation of V-shaped molecule.
(c) Shape of water molecule.

F_2O molecule has situation analogous to H_2O.

Shapes of Molecules Containing Five Electron Pairs (AB_5):

With the increasing number of electron pairs it becomes increasingly difficult to visualize the true shapes of the molecules. Thus a central atom containing five electron pairs presents a more complicated system. A trigonal bipyramid arrangement (Figure 5.6a) represents a structure in which five electron pairs can have minimum repulsion. In PCl_5, there are five electron pairs in the valency shell of phosphorus atom. All of them are bonding pairs and thus PCl_5 molecule adopts trigonal bipyramidal structure (Figure 5.6b).

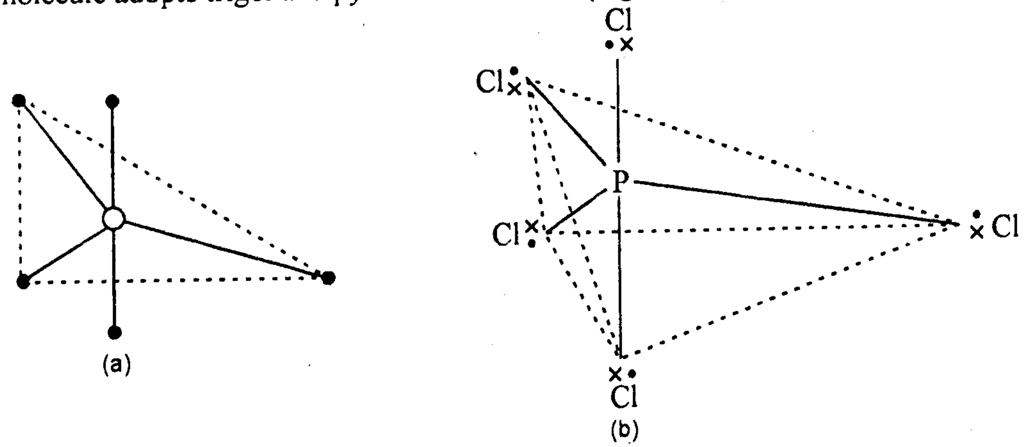


Fig. 5.6. Shapes arising out of five electron pairs around a central atom.
(a) Trigonal bipyramidal arrangement.
(b) Trigonal bipyramidal shape of PCl_5.

Chlorine Trifluoride, ClF_3 has five pairs of valency electrons around the Cl atom. Two of them are lone-pairs and the rest of three are bond-pairs. The presence of five pairs will give a trigonal bipyramidal shape to the molecule. The two lone-pairs would set up repulsive interactions with the bond-pairs and will distort its symmetry from true trigonal bipyramidal arrangement. The structure of ClF_3 is T-shaped, one F – Cl – F bond has bond angle 180° and two F – Cl – F have bond angles of 90° each. This structure gives minimum repulsion and the 'T' shaped structure of ClF_3, has also been experimentally verified (Figure 5.7).

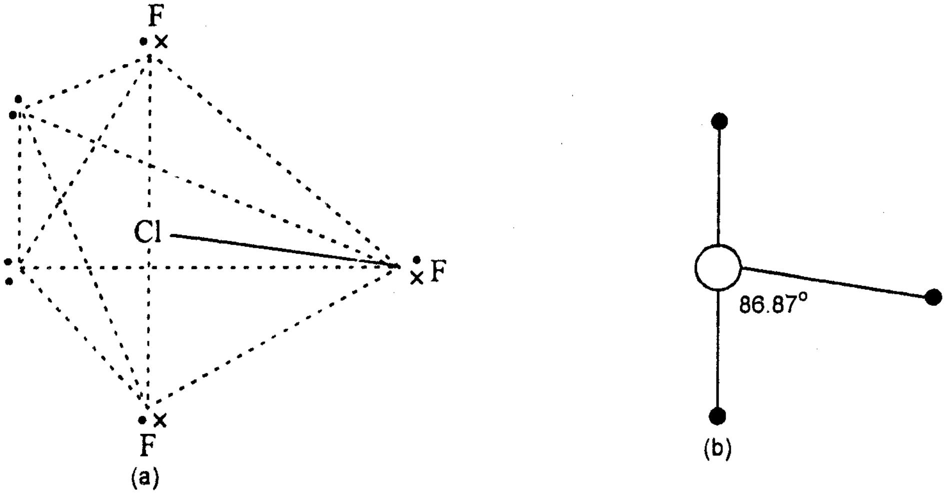


Fig. 5.7. Distortion in trigonal bipyramidal shape due to two lone pairs.
(a) T-shaped ClF_3.
(b) Representation of T-shaped molecule.

When the number of lone pairs increases from two to three in trigonal bipyramidal structure with a total of five electron pairs as in ICl_2^- or I_3^- ion (in KI_3), the only possible arrangement for the three lone pairs are the equatorial positions in which there is minimum of repulsion. The bond-pair electrons would thus be at an angle of 180°. The structure of I_3^- has, therefore, I – I – I bonds at an angle of 180° as shown in Figure 5.8. A similar structure for ICl_2^- is proposed.

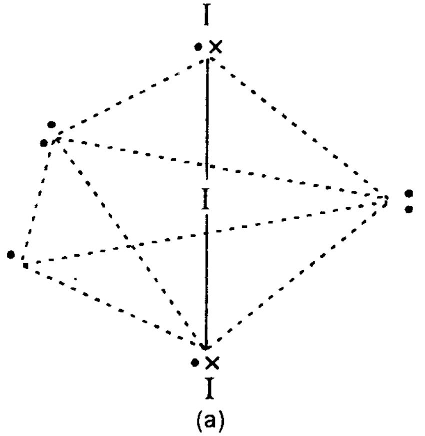


Fig. 5.8. Distortion in trigonal bipyramidal shape due to three lone pairs. Linear shape of I_3^- ion.

Shapes of Molecules Containing Six Electron Pairs (AB_6):

Molecules, in which the central atom has six electron pair bonds, adopt the *octahedral structure*. The examples of such type molecules or ions are: SF_6, MoF_6^- and PCl_6^- etc. The electrostatic repulsion is minimum when six electron pairs arrange in octahedral manner having all bond angles as 90° (Figure 5.9). In terms of hybridization, d^2sp^3 or sp^3d^2 hybrid orbitals would be arranged in octahedral symmetry.

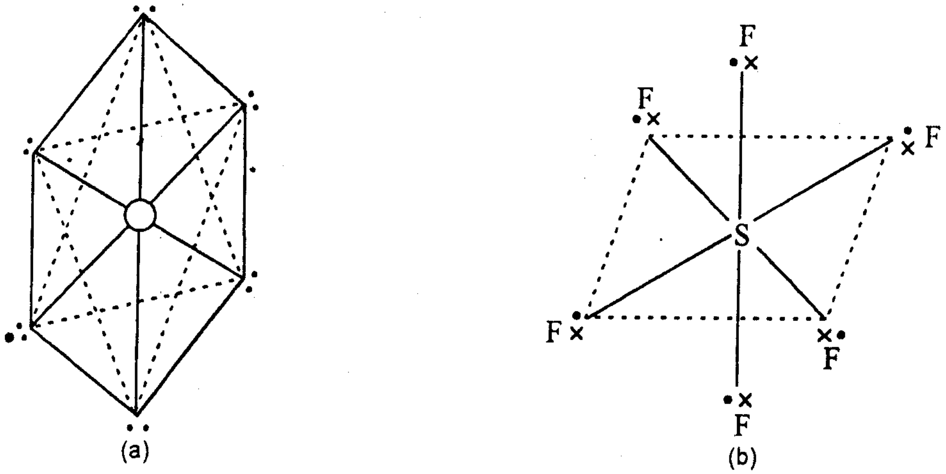


Fig. 5.9. Octahedral shape.
(a) Octahedral arrangement of six electron pair bonds.
(b) Shape of SF_6 molecule.

If six electron pairs consist of *one lone pair* and *five bond pairs*, the molecule will assume the square pyramid shape as shown in Figure 5.10. Thus IF_5, BrF_5 and $SbCl_5^{2-}$ etc., containing one lone pair would adopt square pyramidal shape.

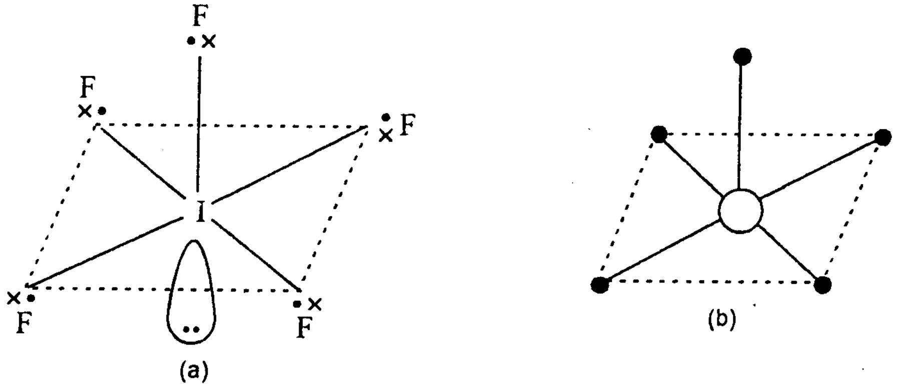


Fig.5.10. Distortion in octahedral shape in presence of one lone pair of electrons.
(a) Square pyramidal shape of IF_5.
(b) Representation of a square pyramid.

The molecule containing *two lone pairs* and *four bond pairs* have minimum repulsion when the two lone pairs of electrons are situated at an angle of 180° to each other placed at opposite corners. This leaves four positions in the square plane for the bond pairs. Thus molecules of this type would assume *a square planar shape i.e.*, ICl_4^-, BrF_4^- etc. (Figure 5.11)

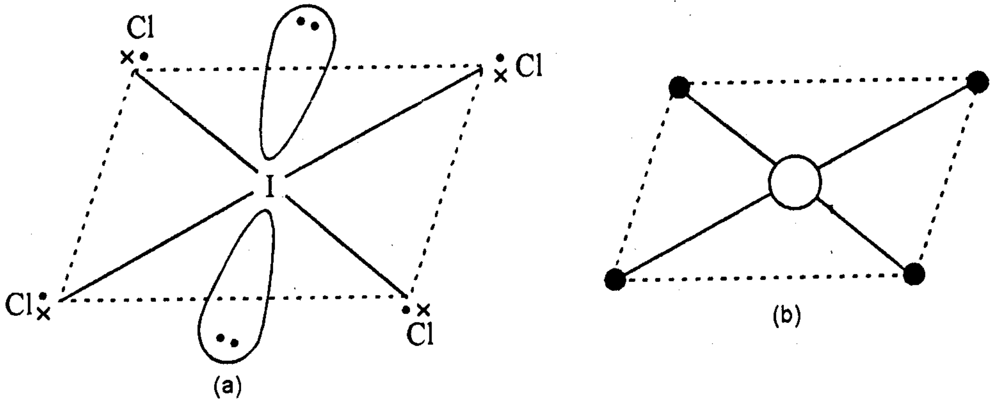


Fig. 5.11. Distortion of octahedral shape in presence of two lone pairs.

(a) ICl_4^- molecular ion.

(b) Representation of a square planar shape.

The compounds having **seven electron pair bonds** show **pentagonal bipyramidal** structures as shown in Figure 5.12. The typical examples of such type molecules and ions are IF_7 and ZrF_7^{2-} ion. If one of the bond pairs is a lone pair, as in $[SbBr_6]^{3-}$ ion, the shape becomes distorted to irregular octahedron.

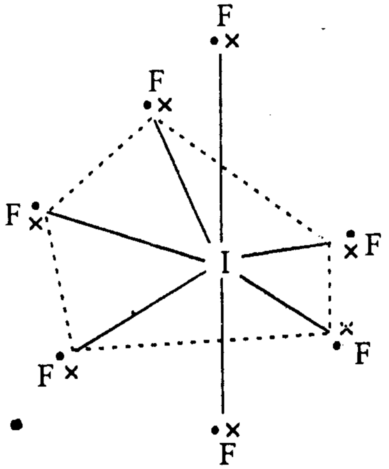


Fig. 5.12. Pentagonal bipyramidal shape of IF_7.

The various shapes of molecules based upon the number of electron pairs in the valency shell are summarised in Table 5.2.

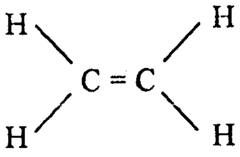
TABLE 5.2

Shapes of Molecules on the Basis of Electron Pairs

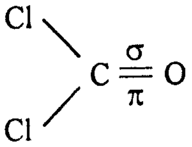
No. of electron pairs in valency shell	Stereo-chemistry	No. of bond pairs	No. of lone pairs	Shapes of molecules	Examples
2	Linear	2	0	Linear	$HgCl_2$, $[Ag(NH_3)_2]^2$
3	Equilateral triangle	3	0	Triangular plane	BF_3, BCl_3
		2	1	V-shaped	$SnCl_2$, $PbCl_2$
4	Tetrahedron	4	0	Tetrahedral	CH_4, BF_4^-, SnX_4
		3	1	Trigonal pyramid	NH_3, PCl_3, AsH_3
		2	2	V-shaped	H_2O, F_2O, H_2S
5	Trigonal bipyramid	5	0	Trigonal bipyramidal	PCl_5, $SbCl_5$
		4	1	Irregular tetrahedron	SeF_4, $TeCl_4$
		3	2	T-shaped	ClF_3, BrF_3
		2	3	Linear	ClF_2, I_3^-
6	Octahedron	6	0	Octahedral	SF_6, $PbCl_6^{2-}$
		5	1	Square pyramid	IF_5, BrF_5
		4	2	Square planar	ICl_4^-
7	Pentagonal bipyramid	7	0	Pentagonal bipyramidal	IF_7
		6	1	Irregular octahedron	$[Sb\ Br_6]^{3-}$

Shapes of Molecules Containing Double and Triple Bonds:

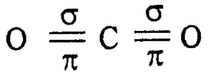
The molecules containing double and triple bonds have almost similar shapes as those represented by corresponding single bonds. The double and triple bonds have the σ and π-bond characters. However, the shape of the molecules containing double and triple bonds are determined only by the pairs of electrons forming σ-bonds. The effect of π-bonds is ignored because of their superimposition on the σ-bond pairs. Ethylene molecule has a plane triangular shape with the two carbon atoms placed at two centres of the two triangles joined by a double bond. The reason for such type of molecular symmetry is that σ-bond pairs are situated along a plane triangle.



Similarly, $COCl_2$ has a planar triangular shape.

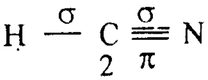


The linear structure of CO_2 is explained on the basis of two σ-bond pairs at an angle of 180° which show minimum repulsive interactions in this direction.



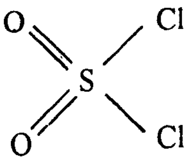
$$O \overset{\sigma}{\underset{\pi}{=}} C \overset{\sigma}{\underset{\pi}{=}} O$$

The two π-bonds present in the structure are ineffective. Similarly, HCN molecule has a linear structure because it has two σ-bonds which adjust themselves at an angle of 180° to have minimum repulsive interaction.

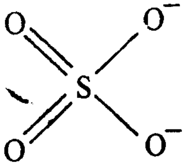


$$H \overset{\sigma}{-} \underset{2}{C} \overset{\sigma}{\underset{\pi}{\equiv}} N$$

The SO_2Cl_2 molecule has a tetrahedral shape because of the presence of four σ-bond pairs of electrons around central sulphur atom. A double bond present between sulphur and oxygen atoms consists of two electron pairs, which set up greater repulsion among themselves and thus the angle between two adjacent double bonds become greater than that between two single bonds. As a result of this, the angle O = S = O is larger than Cl – S – Cl in SO_2Cl_2.

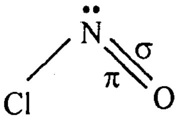


The arguments given for SO_2Cl_2 also apply for SO_4^{2-} ions.

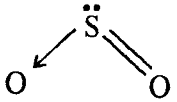


Molecules Containing Double Bonds and Lone Pairs:

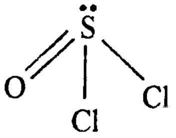
Molecules which contain double bonds as well the lone pair of electrons have strong tendency to distortions. However, the shapes of such molecules depend mostly on the number of σ-bond pairs and lone pairs. The σ-bond pair-lone pair repulsion and lone pair-lone pair repulsion are quite important in determining the shapes of the molecules. Thus, NOCl assumes a V-shaped or angular structure because two σ-bond pairs and one lone pair present in the molecule would give the minimum repulsion in plane triangular symmetry.



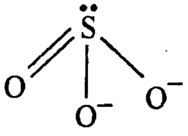
SO_2 molecule also possesses one lone pair and two σ-bond pairs and therefore, it has the following structure:



It has already been mentioned that molecules containing four σ-electron pairs will show tetrahedral shapes. But the presence of one or more lone pairs would distort the symmetry. The π-bonds as usual will not affect the shapes. Thus in the molecules or ions of the type $SOCl_2$ and SO_3^{2-}, there are three σ-bond pairs and one lone pair. The presence of one lone pair would distort the tetrahedral shape to triangular pyramidal shape giving the structures:

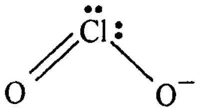


($SOCl_2$)



(SO_3^{2-})

Let us now consider a molecular ion which has two σ-bond pairs and two lone pairs. Such a molecule would be distorted from true tetrahedral to V-shaped structure.



(ClO_2^-)

The distortion in structures of molecules containing five or six σ-electron pairs will take place from trigonal bipyramidal and octahedral shapes in the presence of lone pair of electrons. A few examples of the shapes of molecules containing double bond are given in Table 5.3.

TABLE 5.3

Shapes of Molecules Containing Double and Triple Bonds

No. of σ-electron pairs	Possible structure	No. of σ-bond pairs	No. of lone pairs	Shape of molecules	Examples
2	Linear	2	0	Linear	CO_2, HCN
3	Equilateral triangle	3	0	Plane triangular	$COCl_2$, SO_3, C_2H_4, NO_3^-
		2	1	V-shaped	SO_2, NOCl
4	Tetrahedral	4	0	Tetrahedral	SO_2Cl_2, SO_4^{2-}
		3	1	Triangular pyramid	$SOCl_2$, SO_3^{2-}
		2	2	V-shaped	ClO_2^-

Thus the shapes of the molecules containing double and triple bonds can be predicted based upon the number of σ-bond pairs present in them. The π-electron pairs in double and triple bonds are ignored while determining the shapes of the molecules.

In short, the shapes of the molecules can be predicted based upon the following points:

1. The σ-bond pairs and lone pairs of electrons present in a molecule arrange themselves in such a manner that repulsion between them is minimized.
2. The lone pair-lone pair repulsive interaction is much greater than bond pair-bond pair repulsion so as to give maximum distortion.
3. Lone pair-bond pair distortion is also possible and plays important role in distortion.
4. The repulsion of a double bond pair with another double bond pair is more than the repulsion between single bond pairs or a double bond pair with a single bond.
5. Repulsion between bond pairs is influenced by the electronegativity of atoms forming the bonds. The repulsion decreases with the increase in electronegativity values.
6. Generally, π-bond pairs of electrons do not determine the shapes of the molecules.

Questions

1. Why does $AlCl_3$ exist as Al_2Cl_6 molecules? Discuss the shape of its molecule.
2. What type of geometry may be predicted for a molecule containing two σ-bond pairs and one lone pair of electrons? Discuss the structure of $SnCl_2$ in light of Valence Shell Electron Pair Repulsion concept.
3. Discuss the influence of double and triple bonds on the shapes of molecules.
4. Predict the shape of the following on the basis of electron pair repulsion theory:

   N_2O, CCl_4, XeF_4, $PbCl_2$, $SnCl_4$, PF_5, H_2S, SeF_6
5. What shape may be assigned to SO_2 and SO_3? Why SO_3 has zero dipole moment? Comment with respect to its structure.
6. Describe in general the effect of the lone pair of electrons on the shapes of the molecules.
7. Discuss the principles underlying the valence shell electron pair repulsion concept. What are the applications of this theory in determining the shapes of the molecules?
8. The presence of π-bonds is generally ignored in determining the shapes of molecules. Why?
9. Discuss shapes of molecules containing four σ-bond pairs. How is the change in symmetry brought about by the presence of lone pairs?
10. Discuss the shapes of molecules containing six electron pairs. How the distortion in molecules is brought about by the addition of lone pair of electrons?

11. **Write short answers to the following questions:**

(i) Give salient features of Valence Shell Electron Pair Repulsion (VSEPR) concept.

(ii) How does Valence Shell Electron Pair Repulsion (VSEPR) concept explain the shapes of molecules containing two electron pairs?

(iii) How does Valence Shell Electron Pair Repulsion (VSEPR) concept explain the shapes of molecules containing three electron pairs?

(iv) How does Valence Shell Electron Pairs Repulsion (VSEPR) concept explain the shapes of molecules containing four electron pairs?

(v) How does Valence Shell Electron Pair Repulsion (VSEPR) concept explain the shapes of molecules containing five electron pairs?

(vi) How does Valence Shell Electron Pairs Repulsion (VSEPR) concept explain the shapes of molecules containing six electron pairs?

(vii) Explain the shapes of molecules containing double and triple bonds.

(viii) Explain the shapes of molecules containing double bonds and lone pairs.

12. **Give the correct answer:**

(i) What will be the shape of a molecule which contains two sigma bond pairs and one lone pair of electrons?

(a) linear (b) V-shaped
(c) tetragonal (d) triangular

(**Ans**: b)

(ii) What will be the shape of a molecule which contains four bond pairs with one lone pair of electrons?

(a) tetrahedral (b) trigonal
(c) V-shaped (d) triangular

(**Ans**: b)

(iii) What will be the shape of a molecule which contains six bond pairs with no lone pair of electrons?

(a) octahedral
(b) tetrahedral
(c) trigonal bipyramidal
(d) pentagonal bipyramidal

(**Ans**: a)

(iv) Shape of ammonia molecules is:

(a) tetrahedral
(b) octahedral
(c) trigonal pyramidal
(d) monoclinic

(**Ans**: c)

(v) PCl_5 has the structure:

(a) tetrahedral
(b) T-shaped
(c) trigonal bipyramidal
(d) hexagonal

(**Ans**: a)

(vi) H_2O has the structure:

(a) tetrahedral
(b) trigonal bipyramidal
(c) T-shaped
(d) square planar

(**Ans**: a)

(vii) $SnCl_2$ has the structure:

(a) linear
(b) V-shaped
(c) trigonal pyramid
(d) triangular plane

(**Ans**: a)

(viii) SO_2 has the structure:

(a) linear
(b) V-shaped
(c) tetrahedral
(d) plane triangular

(**Ans**: b)

(ix) ICl_4^- has the structure:

(a) tetrahedral (b) square planar

(c) triangular plane (d) V-shaped

(Ans: b)

(x) ClF_3 has the structure:

(a) T-shaped (b) tetrahedral

(c) triangular plane (d) V-shaped

(Ans: a)

ICl_4^- planar [illegible] square

❀ ❀ 5 ❀ ❀

6

ACID-BASE EQUILIBRIA

VARIOUS CONCEPTS OF ACIDS AND BASES:

A brief review of the various concepts regarding acids and bases are given here.

1. THE ARRHENIUS (CLASSICAL) CONCEPT (1884):

According to this an **acid** is defined as *a hydrogen containing substance which gives* H^+ *ions (i.e.,* H_3O^+ *hydronium ions) when dissolved in water.*

A ***base*** is *a substance which contains OH groups and gives hydroxyl ions* OH^- *when dissolved in water.*

Arrhenius concept is based upon ionic dissociation of compound in water. For example, HCl is an acid because it produces H_3O^+ ions in water but CH_4 is not. Similarly, NaOH is a base because it furnishes OH^- ions, whereas C_2H_5OH is not a base.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$NaOH + H_2O \longrightarrow Na^+ + OH^-$$

The process of neutralization of an acid by a base can be represented by the reaction to form neutral water.

$$H^+ + OH^- \longrightarrow H_2O$$

Advantages:

With this concept, many aspects of acid-base behaviour were understood. For instance, the constant heat of neutralization of a strong acid by a strong base can readily be explained in terms of Arrhenius concept because the reaction *involves* only the combination of a hydrogen ion and a hydroxyl ion in all such neutralization reactions.

This theory also leads to the quantitative determinations of acid or base strengths from the equilibrium relation such as:

$$K = \frac{a_{H^+} \cdot a_{B^-}}{a_{HB}}$$

It explains the catalytic properties of acids. Arrhenius theory affords a correlation between the electrolytic dissociation and the concentrations of the hydrogen ion. The mobility of the hydrogen ions parallel the catalytic activity of the solution if the hydrogen ion is truly the source of the catalytic properties.

Shortcomings:

According to this theory, all the acid-base reactions are limited to aqueous medium only. It does not explain the acid-base reactions taking place in non-aqueous solvents such as liquid ammonia.

It also cannot explain the reactions in gas phase where no solvent is present.

Similarly, the definition of a base under this concept is restricted to compounds containing hydroxyl ions only, whereas many organic compounds as well as ammonia which exhibit basic properties cannot be explained by this definition. Similarly, there are many acidic compounds which do not contain hydrogen and cannot be explained on the basis of Arrhenius concept. Hence new concepts were put forward to explain more general cases of acids and bases.

2. THE PROTONIC OR LOWRY-BRONSTED CONCEPT (1923):

According to Bronsted:

An acid is defined as *a species (a compound or an ion) which donates or tends to donate a proton (H^+ ion).*

A base is *a species which accepts or tends to accept a proton.*

Acid-base reaction is the transfer of a proton from an acid to a base.

The dissociation of an acid HA can be represented as:

$$\underset{\text{Acid}}{HA} \longrightarrow \underset{\text{Base}}{A^-} + \underset{\text{proton}}{H^+}$$

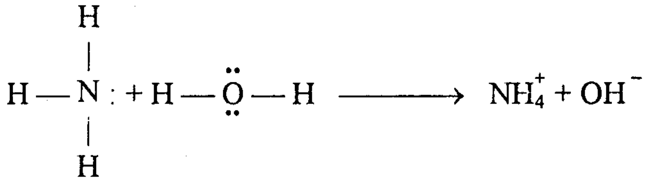
$$\underset{\text{Acid}}{CH_3COOH} \longrightarrow \underset{\text{Base}}{CH_3COO^-} + \underset{\text{Proton}}{H^+}$$

According to this definition, any negatively charged ion (anion) acts as a base. Thus, CH_3COO^- is a base and is said to be *conjugate base of acetic acid.*

In an acid-base reaction, an acid yields a base (conjugate) and base after accepting proton yields a conjugate acid. The acid-base reaction is represented as:

$$\begin{array}{ccccccc} A_1 & + & B_2 & \longrightarrow & B_1 & + & A_2 \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{Bronsted} & & \text{Bronsted} & & \text{Conjugate} & & \text{Conjugate} \\ \text{acid} & & \text{base} & & \text{base} & & \text{acid} \end{array}$$

The conjugate acid-base pairs are species on opposite sides of an equation that differ by a proton. The weaker acids have stronger conjugate base pairs and stronger acids have weaker conjugate base. Some conjugate acid-base pairs are given in Table 6.1. Ammonia is weak base and reacts with water (acting as weak acid) to give NH_4^+.



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}: + H-\ddot{\underset{..}{O}}-H \longrightarrow NH_4^+ + OH^-$$

Examples:

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \longrightarrow \underset{\text{Conjugate Base}}{Cl^-} + \underset{\text{Conjugate Acid}}{H_3O^+}$$

$$HCl + NH_3 \longrightarrow Cl^- + NH_4^+$$

In auto-ionization of water, it acts as an acid and a base because it can give and accept protons. Water is therefore said to be amphiprotic.

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{H_2O} \longrightarrow \underset{\text{Conjugate Base}}{OH^-} + \underset{\text{Conjugate Acid}}{H_3O^+}$$

$$\underset{\text{Acid}}{HSO_4^-} + \underset{\text{Base}}{OH^-} \longrightarrow SO_4^{2-} + H_2O$$

Thus Cl^-, SO_4^{2-}, OH^- are conjugate bases of HCl, HSO_4^- and H_2O, respectively. Similarly, H_2O, HSO_4^- and HCl are conjugate acids of the bases OH^-, SO_4^{2-} and Cl^-, respectively.

The following species may be regarded as acids:

Molecular Species: HCl, H_2SO_4, CH_3COOH, HCN, H_2S, H_2O etc.

Anionic Species: HSO_4^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, HS^- etc.

Cationic Species: H_3O^+, NH_4^+, $[Cu(H_2O)_4]^{2+}$ etc.

The following species may be regarded as bases:

Molecular Species: H_2O, NH_3, CH_3NH_2 etc.

Anionic Species: OH^-, HS^-, S^{2-}, HCO_3^-, HSO_4^-, Cl^- etc.

Cationic Species: $[Fe(H_2O)_5OH]^{2+}$, $[Cu(H_2O)_3\,OH]^+$ etc.

From the above examples, it is found that some of the species act both as acids and bases depending upon the *manner* they behave in the given reaction.

Amphiprotic Species: A species that acts both as a proton donor and a proton acceptor is said to be amphiprotic. For example:

(i) H_2O is amphiprotic. It loses proton to a base such as NH_3 or accepts a proton from an acid such as HCl.

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \longrightarrow NH_4^+ + OH^-$$

$$\underset{\text{Base}}{H_2O} + \underset{\text{Acid}}{HCl} \longrightarrow H_3O^+ + Cl^-$$

(ii) The proton-containing negative ions are amphiprotic. For example:

$$\underset{\text{Acid}}{HS^-} + \underset{\text{Base}}{OH^-} \longrightarrow S^{-2} + H_2O$$

$$\underset{\text{Base}}{HS^-} + \underset{\text{Acid}}{H_3O^+} \longrightarrow H_2S + H_2O$$

(iii) The conjugate base and acid are shown as:

$$\begin{tikzcd}
 & OH^- \text{ Conjugate base of water} \\
\overset{-H^+}{\underset{+H^+}{H_2O}} \arrow[ur] \arrow[dr] & \\
 & H_3O^+ \text{ Conjugate acid of water}
\end{tikzcd}$$

$$\begin{tikzcd}
 & CO_3^{2-} \text{ Conjugate base of } HCO_3^- \\
\overset{-H^+}{\underset{+H^+}{HCO_3^-}} \arrow[ur] \arrow[dr] & \\
 & H_2CO_3 \text{ Conjugate acid of } HCO_3^-
\end{tikzcd}$$

(iv) Amphoteric hydroxides react with both acids and bases because they are equally amphiprotic.

$$\underset{\text{Acid}}{Al(H_2O)_3\,(OH)_3} + \underset{\text{Base}}{OH^-} \longrightarrow Al(H_2O)_2\,(OH)_4^- + H_2O$$

$$\underset{\text{Base}}{Al(H_2O)_3\,(OH)_3} + \underset{\text{Acid}}{H_2O^+} \longrightarrow Al(H_2O)_4\,(OH)_2^+ + H_2O$$

Polyprotic Acids: Acids containing one proton which can be donated are *monoprotic acids* Those acids which contain more than one donatable proton are known as "Polyprotic acids" *e.g.*, HCl, HNO_3, HCN etc. are monoprotic, whereas H_3PO_4, H_2SO_4, H_3AsO_4 are Polyprotic.

Non-aqueous solutions also lose or gain protons and fit into the Bronsted acids and bases For example, water is dissolved in liquid ammonia

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \longrightarrow OH^- + NH_4^+$$

When perchloric acid is dissolved in concentrated H_2SO_4 acid-base reaction occurs.

$$\underset{\text{Acid}}{HClO_4} + \underset{\text{Base}}{H_2SO_4} \longrightarrow ClO_4^- + H_3SO_4^+$$

Similarly, when concentrated H_2SO_4 is dissolved in glacial acetic acid, we again have acid-base reaction.

$$\underset{\text{Acid}}{H_2SO_4} + \underset{\text{Base}}{CH_3COOH} \longrightarrow HSO_4^- + CH_3CO\overset{+}{O}H_2$$

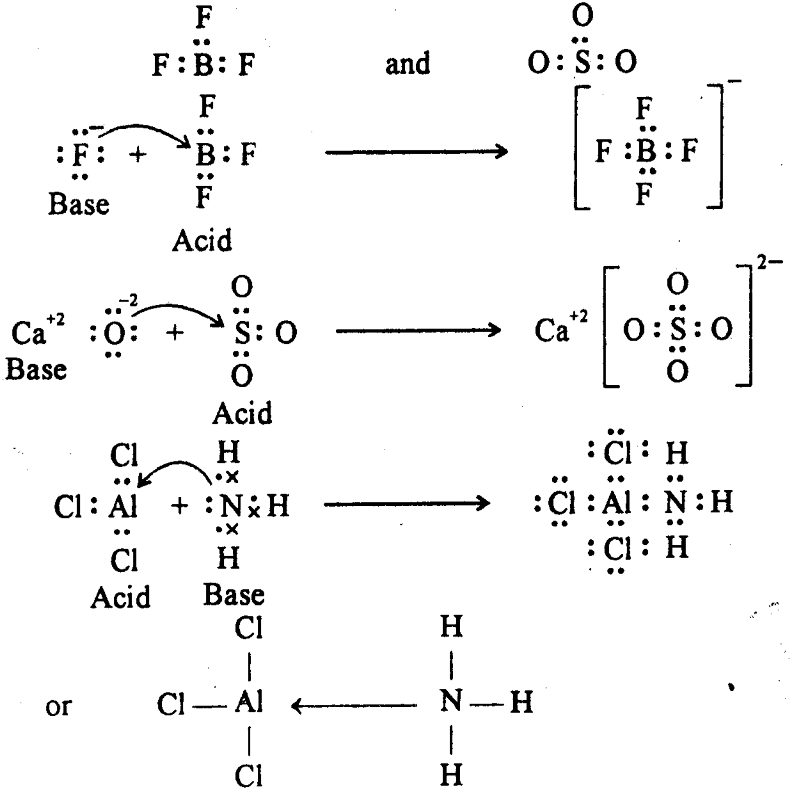
3. THE LEWIS CONCEPT:

According to Lewis, *'An acid is defined as a species (molecule or ion) which can accept a pair of electrons and a base is a species which can donate a pair of electrons.*

An acid is an electrophile (electron-loving) and a base is a nucleophile (nucleus-loving).

An acid-base reaction involves donation of a pair of electrons from a base to an acid with the formation of a coordinate bond between the two. For example:

(i) *Compounds having less than a full octet of electrons behave as Lewis acids e.g.,* BF_3 and SO_3, $AlCl_3$,

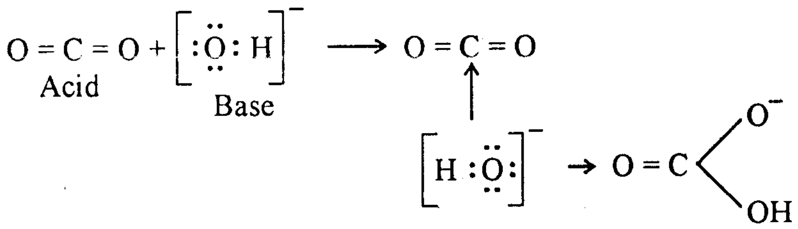


(ii) Positive ions are often considered as acids.

$$\underset{\text{Acid}}{Ag^+} + \underset{\text{Base}}{2:NH_3} \longrightarrow [Ag(:NH_3)_2]^+$$

$$\underset{\text{Acid}}{Co^{3+}} + \underset{\text{Base}}{6:NH_3} \longrightarrow [Co(:NH_3)_6]^{3+}$$

(iii) Compounds having double bonds (except C = C) behave as Lewis acids.



(iv) Other examples are:

$$SnCl_4 + 2\,:\ddot{\underset{\cdot\cdot}{Cl}}:^- \longrightarrow [SnCl_6]^{2-},$$

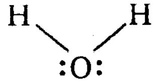
$$\underset{\text{Acid}}{SiF_4} + \underset{\text{Base}}{2\,:\ddot{\underset{\cdot\cdot}{F}}:^-} \longrightarrow [SiF_6]^{2-}$$

Similarly, Lewis bases can also be grouped as :

(i) Molecules containing an atom with unshared electron pairs, *e.g.*, the number of unshared electron pairs in HF, H_2O and NH_3 determines their basic properties and reactions:

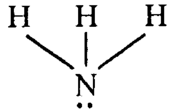
$H:\ddot{\underset{\cdot\cdot}{F}}:$ very weakly basic with 3 unshared pairs.

H_2O



base with 2 unshared pairs.

NH_3



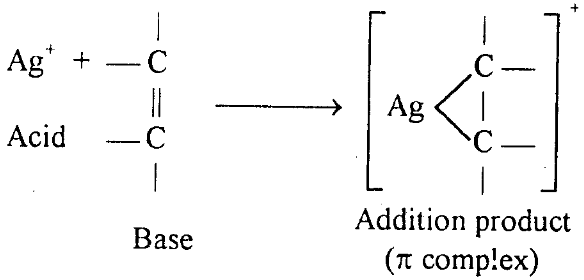
strongly basic with 1 unshared pair.

(ii) Negative ions are Lewis bases *e.g.*,

$$\underset{\text{Base}}{:\ddot{\underset{\cdot\cdot}{Cl}}:^-} + \underset{\text{Acid}}{H_3O^+} \longrightarrow HCl + H_2O$$

$$\underset{\text{Base}}{H:\ddot{\underset{\cdot\cdot}{O}}:^-} + \underset{\text{Acid}}{H_3O^+} \longrightarrow H_2O + H_2O$$

(iii) Compounds containing C = C double bonds also act as Lewis bases *e.g.*, reaction of Ag^+ ion with unsaturated hydrocarbons.



4. THE LUX-FLOOD CONCEPT:

The protonic concept cannot be applied to the species having no protons, for example, oxide systems. According to the Lux-Flood concept:

A base is defined as any species which gives up an oxide ion (O^{-2}), and

An acid is defined as any species which gains or takes up oxide ions. Hence,

$$\text{Base} \rightleftharpoons \text{Acid} + \text{Oxide } (O^{2-})$$

For example, CaO is a base, because it *gives* up O^{2-} ions.

$$CaO \rightleftharpoons Ca^{2+} + O^{2-}$$

SO_4^{2-} is a base because it gives up O^{2-} ions.

$$SO_4^{2-} \rightleftharpoons SO_3 + O^{2-}$$

Ca^{2+} and SO_3 are acids since they take up oxide ions as shown above.

The strength of acids is determined by the magnitude of the equilibrium constant,

$$K = \frac{[\text{Acid}] \times [O^{2-}]}{[\text{Base}]}$$

According to this concept, the strength of acids are given in the following order:

$$PO_4^{3-} > BO_2^{-} > SiO_3^{2-} > TiO_3^{2-}$$

5. THE USANOVICH CONCEPT:

According to this concept:

An **acid** is defined as any species

(i) capable of giving up cations,

(ii) combining with anions or electrons,

(iii) neutralizing a base to give a salt.

A **base** is defined as any species:

(i) capable of giving up anions or electrons,
(ii) combining with cations,
(iii) neutralizing an acid to give a salt.

This definition includes all previous acid-base definitions including oxidation-reduction reactions as a special class of acid-base reactions.

Examples:

Acid	Base	Salt	Justification
SO_3	Na_2O	Na_2SO_4	Na_2O give O^{2-} ion SO_3 combines with O^{2-}
$Fe(CN)_2$	KCN	$K_4Fe(CN)_6$	KCN gives CN^- $Fe(CN)_2$ combines with CN^-
Cl_2	Na	NaCl	Na loses an electron Cl gains an electron
HCl	NH_3	NH_4Cl	HCl gives H^+ NH_3 combines with H^+
NH_4^+	OH^-	$NH_3 + H_2O$	NH_4^+ gives H^+ OH^- combines with H^+

RELATIVE STRENGTHS OF ACIDS AND BASES:

According to Bronsted, the strength of an acid is measured from its tendency to donate a proton and that of a base from its tendency to accept a proton. Strengths are generally expressed in terms of dissociation constants (K*a*) and *p*K*a* values of acids. Let us consider a protonic acid HX. In aqueous solution it constitutes the following equilibrium,

$$HX + H_2O \longrightarrow X^- + H_3\overset{+}{O}$$

According to Law of Mass Action, we have,

$$K = \frac{[X^-][H_3\overset{+}{O}]}{[HX][H_2O]}$$

where K is an equilibrium constant and the quantities within the square brackets denote molar concentrations and to be more exact thermodynamically, activities of the reactants and products. As water is always in excess, its concentration is constant and we have,

$$\frac{[X^-][H_3\overset{+}{O}]}{[HX]} = K[H_2O] = Ka.$$

K*a* is called dissociation constant of acids and represents the extent to which an acid is dissociated. Greater the value of K*a*, stronger is the acid and vice versa. $\frac{1}{Ka}$ represents the strength of the base X^-. The strength of an acid can also be expressed in terms of its *p*K*a* where

$$pKa = \log\left(\frac{1}{Ka}\right) = -\log(Ka).$$

A large value of *p*K*a* means the acid is little dissociated (weak acid) and a small value means that acid is highly dissociated (strong acid). Thus HCl is a stronger acid than HNO_3 and its dissociation constant (10^7) is greater than that of HNO_3 (10^3) and its *p*K*a* value (– 7.0) is less than that of HNO_3 (– 3.0).

For very weak acids the *p*K*a* values are very high. For example, it is 11.8 in case of H_2O_2 (Table 6.1).

The strength of an acid is related to that of its conjugate base. If the acid is strong, its conjugate base is weak. For example, HCl is strong acid as it has got a great tendency to lose a proton, its conjugate base Cl^- ion is a weak base as it has got a little tendency to accept a proton. Reverse is true, if the conjugate base is strong.

The acid strength depends upon the solvent chosen. Thus in Bronsted definition we need to specify solvent while comparing the relative strengths of acids and bases.

All the strong acids like $HClO_4$, H_2SO_4, HCl, HNO_3 have very close *p*K*a* values. They appear to have nearly equal strengths in aqueous solutions. This phenomenon is called *Levelling effect*. All the acids which are completely dissociated in aqueous solutions are represented by H_3O^+ ion, as it is the strongest acid known. The same effect is noticed in case of the solutions of bases. The strongest base which can exist in water is OH^- ion. The bases O^{2-} and NH_2^- are fairly strong, therefore when Na_2O and $NaNH_2$ are dissolved in water, their reactions are

$$O^{2-}_{(aq)} + H_2O \longrightarrow 2OH^-_{(aq)}$$

$$NH^-_{2(aq)} + H_2O \longrightarrow NH_{3(aq)} + OH^-_{(aq)}$$

The reaction goes to completion and thus basic strength of O^{2-} or NH_2^- is levelled to the strength of OH^- ion and they behave as equally strong bases in aqueous solution.

The order of decreasing strengths of the stronger mineral acids has been found to be

$$HClO_4 > HBr > HCl > H_2SO_4 > HNO_3$$

TABLE 6.1

Approximate *p*K*a* Values of Some Acids

Acids	*p*Ka	Acids	*p*Ka
H_2O	16	HClO	7.2
HF	3	HBrO	8.7
HCl	– 7	HIO	11.0
HNO_3	– 1	H_2O_2	11.8
HBr	– 9	HNO_3	– 1.4
HI	– 10	$HClO_3$	– 1
H_2SO_4	– 3	HIO_3	0.8
$HClO_4$	– 10	H_3PO_3	– 2.1

RELATION BETWEEN ACID-BASE AND OXIDATION-REDUCTION BEHAVIOUR

According to Lewis concept of acids and bases, an acid is a species which accepts a lone pair of electrons from a base.

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{:NH_3} \longrightarrow NH_4^+$$

An oxidising agent also accepts complete transfer of electrons from other species. Oxidising agent is itself reduced. Reduction is a process in which electrons are gained.

$$\underset{\text{(oxidizing agent)}}{Cu^{2+}} + 2e^- \longrightarrow Cu$$

A base donates a pair of electrons to form a coordinate covalent bond.

$$\underset{\text{Base}}{:NH_3} + \underset{\text{Acid}}{H_3O^+} \longrightarrow NH_4^+ + H_2O$$

A reducing agent also transfers electrons and is oxidized. Oxidation is a process which involves loss of electrons.

$$Zn^\circ - 2e^- \longrightarrow Zn^{2+}$$

(Reducing Agent)

CHEMICAL REACTIVITY OF ACIDS AND BASES – TYPES OF ATTACKS AND DISPLACEMENTS

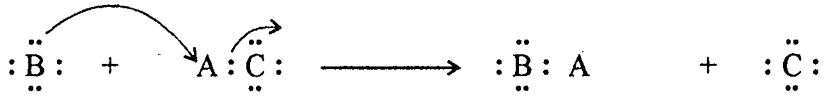
Lewis acids are also called electrophiles or electrophilic reagents because they are attracted to the electron-rich parts of basic molecules. Similarly, Lewis bases are called nucleophiles or nucleophilic reagents because they seek electron deficient regions of acids with which they react.

A Lewis acid-base reaction may be described as a nucleophilic attack of base on acid or an electrophilic attack of acid on base.

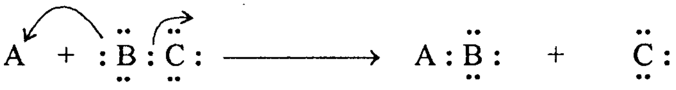
$$\underset{\text{Base}}{H_3N:} + \underset{\text{Acid}}{BF_3} \xrightarrow{\qquad} H_3N : BF_3$$

In this reaction, nitrogen of ammonia has a nucleophilic attack on boron or electrophilic attack of boron on nitrogen.

There are many reactions that result in the formation of a new covalent bond and the rupture of an old one. The bond breaking reagent may be either an acid or a base. These reactions are called displacement reactions.



nucleophilic displacement



electrophilic displacement

pH (HYDROGEN ION CONCENTRATION):

The acidity or basicity of an aqueous solution depends on the relative numbers of hydronium ions and hydroxide ions present in it. Pure water contains equal number of hydronium and hydroxide ions. In water, the product of hydronium ion concentration and hydroxide ion concentration is always 1.00×10^{-14} (at 25° C) and is called ionic product constant.

$$H_2O + H_2O \rightleftharpoons [H_3O^+] + [OH^-]$$

$$[H_3O^+] \times [OH^-] = 1.00 \times 10^{-14}$$

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$$

If hydronium and hydroxide ions are not equal the solution is either acidic or basic. In order to avoid numbers with negative exponents a convenient scale for measuring acidity or basicity is devised. It is called pH. The pH of a solution is a measure of its hydronium ion concentration. It ranges between 0 – 14.

The pH of solution may be defined as *the logarithm of the reciprocal of the hydrogen ion concentration*. Since the logarithm of 1 is O, pH may also be defined as the negative logarithm of the hydrogen (hydronium) ion concentration in moles/litre.

Thus

$$pH = \log\left(\frac{1}{H^{+]}}\right) = -\log[H^+] \text{ or } -\log[H_3O^+]$$

The logarithm (log) of a number is the power to which 10 must raised in order to equal the given number.

Number	**Logarithm of number**
10^{-2}	$\log(10^{-2}) = -2$
10^{-1}	$\log(10^{-1}) = -1$
$10^0 = 1$	$\log 10^1 = 0$
$10^1 = 10$	$\log 10^1 = 1$
$10^2 = 100$	$\log 10^2 = 2$

H^+ and pH are interconvertable

$$[H^+] = 10^{-pH} = \text{anti}\log(-pH)$$

For a neutral solution, therefore

$$[H^+] = 1.0 \times 10^{-7}$$
$$pH = -\log(10^{-7}) = -(-7)$$
$$pH = 7$$

For pH 9.67 of a solution hydrogen ion concentration $[H^+]$ can be calculated as:

$$-\log[H^+] = 9.67$$
$$[H^+] = 10^{-9.67} = 10^{-10} \times 10^{0.33}$$
$$[H^+] = 2.1 \times 10^{-10}\ M$$

pOH can also be defined in the same way as *the negative logarithm of the $\overline{OH}$ ion concentration*. Such values generally are not quoted; the pH value of a solution is used to define the acidity or alkalinity of the solution. However, it is frequently convenient to use pOH in calculations involving alkaline solutions or solutions for which the hydroxide ion concentration is known.

$$pH + pOH = 14 \quad \text{or} \quad pOH = 14 - pH$$

Problem:

Calculate pH and pOH of 5.0×10^{-2} M solution of NaOH.

$$[OH^-] = 5.0 \times 10^{-2}\ M$$
$$pOH = -\log[OH^-] = -\log 5.0 \times 10^{-2}$$
$$= 2 - \log 5.0 = 2.0 - 0.70$$
$$= 1.30$$

$$pH + pOH = 14$$
$$pH = 14 - pOH = 14 - 1.30 = 12.70$$

Thus for a 0.01 M solution of NaOH, the pOH is 2. Since the sum of the pH and the pOH equals 14, the pH of this solution is 12.

Exercise:

What is the pH of a solution for which

$$[OH^-] = 0.15\ M.$$

Solution:

$$\begin{aligned}
[OH^-] &= 1.5 \times 10^{-1} \\
\log [OH^-] &= \log 1.5 + \log 10^{-1} \\
&= 0.2 - 1.0 = -0.8 \\
pOH &= 0.8 \\
pH &= 14 - 0.8 = 13.2
\end{aligned}$$

An alternative solution is

$$\begin{aligned}
[H^+][OH^-] &= 1.0 \times 10^{-14} \\
[H^+] &= \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-1}} \\
&= 6.7 \times 10^{-14} \\
\log [H^+] &= \log 6.7 + \log 10^{-14} \\
&= 0.8 - 14.0 \\
&= -13.2
\end{aligned}$$

Thus $pH = 13.2.$

Exercise:

What is the $[H^+]$ of a solution with a pH of 10.6.

Solution:

$$\begin{aligned}
\log [H^+] &= -10.6 = 0.4 - 11.0 \\
[H^+] &= \text{anti-log } 0.4 \times \text{anti-log } (-11) \\
[H^+] &= 2.5 \times 10^{-11}
\end{aligned}$$

It should be kept in mind that pH relates to the power of 10. Hence, a solution of pH = 1 has a hydronium ion concentration 100 times that of a solution of pH = 3 (not three times). Furthermore, since the pH is related to a negative exponent, the lower the pH value, the larger the concentration of hydronium ion. At pH = 7, a solution is neutral. Solutions with pH below 7 are acidic, those with pH above 7 are alkaline (Table 7.1).

Measurements of pH:

More common methods frequently used to determine the pH of a solution are:

1. By the use of an indicator.
2. Colorimetric method.
3. Potentiometric method.

1. **By the Use of an indicator:** The indicators may be used in liquid form or as indicator papers commonly called pH papers which are available commercially. Indicators cannot, however, be used in case of coloured solutions.

2. **Colorimetric Method:** A rough determination of acidity or basicity is made using a pH paper impregnated in solution. Colour is compared with the standard.

For more accurate determination the colour of a test solution to which a few drops of indicator are added is compared with standard buffer solutions containing the same indicator. pH accurate to 0.5 pH can be made.

3. **Potentiometric Method:** The potentiometric method permits measurements which are accurate to 0.005 pH unit or better. The electrode potentials of many redox couples depend on the hydronium ion concentration.

The Nernst equation for the hydrogen electrode at 25°C and 1 atm. hydrogen pressure is:

$$\varepsilon = \varepsilon^\circ - 0.0592 \log \frac{1}{[H_3O^+]} = -0.0592 \text{ pH}$$

The pH of a solution can be determined by measuring in potential of a cell consisting of a hydrogen electrode combined with a suitable reference electrode, such as calomel electrode.

Calomel Electrode:

$$\text{Pt} \mid H_2 (\text{g, 1 atom}) \mid H_3O^+ (\text{xM}) \parallel \text{KCl (sat)}\ Hg_2Cl_2 \mid \text{Hg}$$

Where H_3O^+ (xM) represents the solution of unknown hydronium ion concentration.

The cell potential is given by

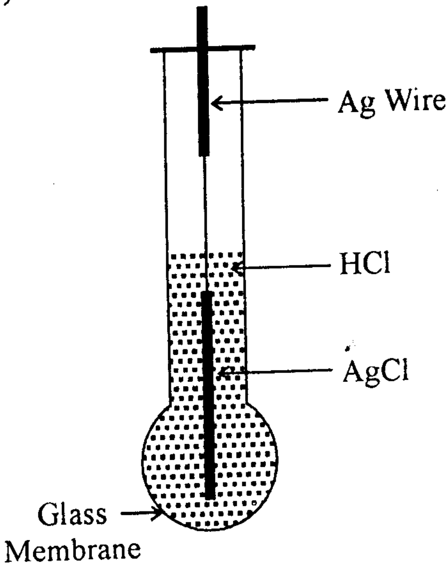
$$\varepsilon \text{ cell} = \varepsilon_{cal} - \varepsilon = \varepsilon_{cal} + 0.0592 \text{ (pH)}$$

$$\text{pH} = \frac{\varepsilon \text{ cell} - \varepsilon \text{ cal}}{0.0592} \text{ (at 25°C).}$$

Glass electrodes are more convenient to measure pH. H_2 electrode is easily destroyed due to reaction with acid or Pt.

Glass Electrode:

A glass electrode consists of Ag/AgCl electrode immersed in a dilute HCl solution contained in a thin walled glass bulb. The glass electrode and calomel electrode are placed in the solution whose pH is to be measured and a cell of the following type is produced.



$$\text{Ag} \mid AgCl_{(s)} \mid HCl_{(aq)} \mid \text{Glass} \parallel \text{Unknown solution} \parallel KCl_{(Sat.)} \mid Hg_2Cl_{2(s)} \mid \text{Hg.}$$

The observed potential arises from the following:

1. The potential of Ag/AgCl couple.
2. The potential of calomel electrode.
3. The potential between the glass and the HCl solution within the glass electrode.
4. The junction potential between the calomel electrode and the unknown solution.
5. The potential between the glass membrane and the solution of unknown pH.

For a given cell the first three sources of potential are fixed as constant. The fourth potential is compensated by adjusting the potentiometer when the electrodes are immersed in a buffer solution of known pH. Thus the observed potential will depend only on the pH of an unknown solution. A special glass which has high affinity for water is used to construct the glass membrane. A pH meter is shown in Figure 6.1.

INDICATORS:

Indicators are coloured organic compounds that change colour in solution as the pH of the solution changes. For example, methyl orange is red in solution of pH below 3.1 and yellow in solutions of pH above 4.5; the colour of this indicator is a varying mixture of yellow and red in the pH range between 3.1 and 4.5. Table 6.2 shows different indicators with different colours in acidic and alkaline media over a varied range of pH.

TABLE 6.2

Indicator	Acid colour	pH range of colour	alkaline colour
Thymol blue	red	1.2 — 2.8	yellow
Methyl orange	red	3.1 — 4.5	yellow
Bromcresol green	yellow	3.8 — 5.5	blue
Methyl red	red	4.2 — 6.3	yellow
Litmus	red	5.0 — 8.0	blue
Bromthymol blue	yellow	6.0 — 7.6	blue
Thymol blue	yellow	8.0 — 9.6	blue
Phenolphthalein	colourless	8.3 — 10.0	red
Alizarin yellow	yellow	10.0 — 12.1	lavender

Indicators are weak acids or weak bases. Since they are intensely coloured, only a few drops of a dilute solution of an indicator need be employed in any determination. In order to know a point at which a reaction is complete, a suitable indicator is used which changes its colour when chemically equivalent amount of the two reacting substances are present. The choice of an indicator depends upon the nature of the reaction under study. There are different types of indicators used:

1. Acid-Base indicators
2. Redox indicators
3. Precipitation indicators

1. Acid-Base Indicators:

According to Ostwald, an acid-base indicator is a weak organic acid. Let the symbol HIn stand for the litmus molecule (red) and the symbol In^- stand for the anion (blue) derived from the weak acid, the equation for the litmus equilibrium may be written as

$$\underset{\text{(red)}}{HIn} \longrightarrow \underset{\text{(blue)}}{H^+ + In^-}$$

The following equilibrium is established between an ionized and un-ionized particles.

$$In = \frac{[H^+][In^-]}{[HIn]}$$

According to the principle of Le-Chatelier, increasing the concentration of H^+ shifts the equilibrium to the left, and the red (or acid) colour of HIn is observed *i.e.*, un-ionized form. On the other hand, addition of OH^- decreases the concentration of H^+; the equilibrium shifts to the right, and the blue (or alkaline) colour of In^- is observed *i.e.*, ionized form. The above relation can be expressed as

$$[H^+] = \frac{K_{In} \times [H_{In}]}{[In^-]} = K_{In} \times \frac{\text{Un-ionized form}}{\text{Ionized form}}$$

From this relation it is seen that the colour of the solution depends upon the ratio of $\frac{[HIn]}{[In^-]}$ and this ratio depends upon H^+ or pH of the solution.

When two colours are present as in methyl orange, the colour is red in acids and yellow in the basic form. It is not possible for the eye to distinguish 100 % pure red colour from 95% red plus 5% yellow; and there exists an uncertainty unless the ratio of $\frac{[HIn]}{[In^-]}$ is 1 : 10 to distinguish from the basic (In^-) colour or 10 : 1 to distinguish from acid colour. If the ratio is greater than 10, the eye gets the pure acid colour and if the ratio is less than 0.1 the eye distinguishes the basic colour. So the eye registers the colour between the ratios 10 : 1 and 1:10.

Now taking the above equation

$$[H^+] = K_{In} \times \frac{[HIn]}{[In^-]} = K_{In} \times \frac{\text{Un-ionized form}}{\text{Ionized form}}$$

or $$pH = \log\frac{(In^-)}{(HIn)} + pK_{In}$$

So $$pH\ (\text{basic colour}) \geq pK_{In}^{+1}$$

$$pH\ (\text{acid colour}) \leq pK_{In}^{-1}$$

The colour change interval is

$$pH = pK_{In}^{+1}$$

or 2 pH units. This pH range is called the "Transition range" of the indicator. Within this range, the indicator changes from one colour to the other; and the change is gradual because it depends upon the ratios of the concentrations of the two colour forms.

The colour change of an indicator is due to the structural change. For example, phenolphthalein and methyl orange can be shown as:

Example:

An indicator is a weak acid and the pH range of its colour change is 3.1 to 4.5. If the neutral point of the indicator is in the centre of this pH range, what is the ionization constant of the indicator?

Solution:

The centre of range is formed by averaging the corresponding concentrations of H^+, however, when

$$pH = 3.1$$

$$\log [H^+] = -3.1 = 0.9 - 4.0$$

$$[H^+] = 7.9 \times 10^{-4} \qquad \cdots\cdots \quad (i)$$

when $$pH = 4.5$$

$$\log [H^+] = -4.5 = 0.5 - 5.0$$

$$[H^+] = 3.2 \times 10^{-5} \qquad \cdots\cdots \quad (ii)$$

To average (i) and (ii), the hydrogen ion concentrations, we must express both to the same power of 10. Thus

$$\frac{79.0 \times 10^{-5} + 3.2 \times 10^{-5}}{2} = 4.1 \times 10^{-4}$$

When $[H^+] = 4.1 \times 10^{-4}$ M, $K = [H^+]$,

Therefore

$$K = 4.1 \times 10^{-4}.$$

2. **Redox Indicators:**

These are dyes which undergo a reversible change on oxidation or reduction. They show different colours in the oxidised and reduced states. The general indicator reaction is

$$\underset{\text{Reduced form}}{\text{Ind}} \rightleftharpoons \underset{\text{Oxidised form}}{\text{Ind}^{n+}} + ne$$

Where Ind stands for indicator and e for electron, n is usually 1 – 2.

An oxidation potential is associated with each redox indicator. For example, in the titration of ferrous solution against a standard ceric solution, at the equivalence point, the potential of the system is shown as:

$$E_{\text{eq. pt}} = \frac{E^\circ_{Ce} - E^\circ_{Fe}}{2}$$

$$= \frac{1.45 - (-0.78)}{2} = 1.12 \text{ volts.}$$

This means that with Ce^{+4} solution used as an oxidising agent, the indicator should have an oxidation potential approximately 1.12 volts. In the Table 6.3 are given commonly used redox indicator.

TABLE 6.3

Indicator	Colour in reduced form	Colour in Oxidised form	emf
1 Diphenylamine	Colourless	violet	– 0.76
2. Diphenyl benzidine	Colourless	violet	– 0.76
3 Diphenylamine Sulphonic Acid (Sodium and Barium salts)	Colourless	Reddish violet	– 0.84
4. Ferroin	Red	pale blue	– 1.14
5. Nitroferrion	Red	pale blue	– 1.25

Sometimes oxidising and reducing agents may also serve as their own indicators; if the reagents are highly coloured and undergo reaction into colourless compounds. The end point will be observed by the appearance of colour when even one drop is added in excess *e.g.*, $KMnO_4$ added to a reducing solution is converted into colourless manganous compounds until no reductant is left. One excess drop will then impart pink colour to the whole solution.

3. Precipitation Indicators:

There is no suitable indicator for the precipitation reactions. However, the formation of a coloured precipitate may indicate the end point. For example, K_2CrO_4 is used as an indicator in the titrations of chloride with $AgNO_3$. Similarly, in Volhard's method, a soluble coloured compound results for the same estimation. Ag^+ is titrated against KCNS solution. AgCNS (solid) is precipitated.

$$Ag^+ + CNS^- \longrightarrow AgCNS_{(s)}$$

When end point is passed, thiocyanate concentration increases so much that the ion may be detected by its reaction with ferric ion if present.

$$Fe^{+3} + 6\ SCN^- \longrightarrow \underset{\text{(coloured)}}{Fe[SCN)_6]^{-3}}$$

Ferric alum is used as an indicator in this titration.

Sometimes adsorption indicator can also be used in the precipitation reactions. For example, fluorescein or dichlorofluorescein can be used effectively for titration of Cl^- against Ag^+. When fluorescein ion is adsorbed on the surface of the precipitate particles, its structure is changed to form a coloured substance that coats each particle. It should be remembered that the indicator ion should have a charge opposite to the ion used for titration. It should not be adsorbed too strongly. For this purpose dextrin is added sometimes.

BUFFERS:

It is sometimes necessary that a solution of a definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If the solution comes in contact with the air, it will absorb CO_2 and become more acidic. If the solution is stored in a glass bottle, alkaline impurities leached from the glass may alter the pH. Solutions can be maintained close to a certain value of pH by means of buffers. Buffer solutions are capable of maintaining their pH at some fairly constant value even when small amounts of the acid or base are added. Thus *"A buffer solution is one that tends to maintain its pH when an acid or alkali is added to it."* The buffer solution resists changes in pH when small amounts of acids and bases are added.

A buffer solution usually consists of a weakly dissociating acid and the salt of that acid or a weak base and its salt. For example, $NaHCO_3/H_2CO_3$, and NaH_2PO_4/H_3PO_4. Suppose HCl is added to a buffer system containing $NaHCO_3$ and H_2CO_3. The following reaction will take place.

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$

Thus HCl which is a strong acid and is expected to raise the H^+ ion concentration reacts with a base to yield H_2CO_3 (a weak acid due to an incomplete dissociation); and a neutral salt, NaCl, with the result that provided HCl is not added in very large amounts there would be only a little change in the original pH of the buffer solution.

In the same way, if NaOH is added to this buffer solution it reacts with the H_2CO_3 as follows:

$$NaOH + H_2CO_3 \longrightarrow NaHCO_3 + H_2O$$

Since $NaHCO_3$ is a much weaker base than NaOH, the resulting rise in pH will be quite small.

A solution containing a weak base *e.g.*, NH_4OH and its salt NH_4Cl can also act as a buffer.

Consider an acetic acid-acetate buffer.

$$HOAc \rightleftharpoons OAc^- + H^+$$

$$Ka = \frac{[H^+][OAc^-]}{[AcOH]} \quad \text{or} \quad [H^+] = Ka\frac{[HOAc]}{[OAc^-]}$$

Taking logarithm of each side

$$-\log[H^+] = -\log Ka - \log\frac{[HOAc]}{[OAc^-]}$$

$$pH = pKa + \log\frac{[OAc^-]}{[HOAc]}$$

or $$pH = pKa + \log\frac{[Salt]}{[Acid]}$$

This is called Handerson-Hazelback equation.

Applications of Buffers:

The use of buffers is an important part of many industrial processes. Examples are electroplating and the manufacture of leather, photographic materials and dyes.

In bacteriological research, culture media are generally buffered to maintain the pH required for the growth of the bacteria being studied.

Buffers are used extensively in analytical chemistry and are used to calibrate pH. Human blood is buffered to a pH of 7.4 by means of bicarbonate, phosphate and complex protein systems. For human body to function normally, the blood pH must stay within the range 7.35 to 7.45. If the pH of a person's blood drops below 7.35, one is said to have acidosis or low blood pH. It can cause disorientation and coma. An anxiety attack or hysteria can cause a person to breathe rapidly. Under these conditions, the blood pH may rise to 7.6 or 7.7 within minutes, resulting in alkalosis which causes vomiting. Common buffers with their pH values are:

Buffer	pH	Buffer	pH
NH_4^+, NH_3	9	CH_3COOH, CH_3COO^-	3.5
$H_2PO_4^-$, HPO_4^{-2}	7		

Example:

A buffer solution contains 1 mole per litre each of acetic acid and sodium acetate. Find the pH.

Solution:

The equilibrium in a buffer containing sodium acetate and acetic acid is given by

$$K = \frac{[H^+][OAc^-]}{[HOAc]}$$

Since most of the OAc⁻ ion is provided by the NaOAc, we can write,

$$K = \frac{[H^+][\text{salt}]}{[\text{acid}]}$$

$$\text{or} \quad [H^+] = K \times \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{Thus} \quad [H^+] = 1.8 \times 10^{-5}\,\frac{1}{1} = 1.8 \times 10^{-5}\,\text{M.}$$

$$\text{or} \quad \text{pH} = -\log(1.8 \times 10^{-5})$$

$$= -(0.26 - 5) = 4.74.$$

Example:

How many moles of sodium acetate must be added to 1 litre of 0.2 M HOAC solution to make buffer of pH 5.

Solution:

$$[H^+] = 1.8 \times 10^{-5} \times \frac{[\text{acid}]}{[\text{salt}]}$$

Since we specify a pH of 5, $[H^+] = 10^{-5}$ M.

Substituting this, we get

$$10^{-5} = 1.8 \times 10^{-5}\,\frac{[\text{acid}]}{[\text{salt}]}$$

Solving we get

$$\frac{[\text{salt}]}{[\text{acid}]} = \frac{1.8 \times 10^{-5}}{10^{-5}} = 1.8.$$

Since the concentration of acid is 0.2 M.

Therefore,

$$[\text{salt}] = 1.8 \times 0.2 = 0.36\,\text{M.}$$

Since we have a litre of solution, we add 0.36 mole NaOAc to obtain a salt concentration of 0.36 M.

What is pH of a solution of 0.400 M formic acid and 1.00 M sodium formate.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

$$Ka = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.77 \times 10^{-4}$$

$$[HCOO^-] = M\ HCOO^- = 1.00$$

$$[HCOOH] = M\ HCOOH = 0.400$$

$$[H_3O^+] = 1.77 \times 10^{-4} \times \frac{0.400}{1.00} = 7.08 \times 10^{-5}$$

$$pH = \log(7.08 \times 10^{-5}) = 4.12$$

Effect of Dilution:

pH of the buffer solution remains essentially independent of dilution until concentration is decreased beyond a limit.

Example:

Calculate pH of the buffer of HCOOH and HCOONa with pH = 4.15, if solution is diluted to (a) 50 times (b) 10,000 times (HCOOH is 0.400 M and HCOONa solution is 1.00 M; Ka = 1.77 × 10^{-4}).

Solution:

(a) On dilution to 50 ml., $M\ HCOOH = \frac{0.400}{50} = 8.00 \times 10^{-3}$

$$M\ HCOONa = \frac{1.00}{50} = 2.00 \times 10^{-2}$$

$$Ka = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

$$\frac{[H_3O^+] \times 2.00 \times 10^{-2}}{8.00 \times 10^{-3}} = 1.77 \times 10^{-4}$$

$$[H_3O^+] = 7.08 \times 10^{-5}$$

$$pH = -\log[H_3O^+] = -\log 7.08 \times 10^{-5} = 4.15.$$

(b) Upon dilution to a factor of 10,000,

$$M\ HCOOH = \frac{0.400}{10,000} = 4.00 \times 10^{-4}$$

$$M\ HCOO\ Na = \frac{1.00}{10,000} = 1.00 \times 10^{-4}$$

$$\frac{[H_3O^+] \times 1.00 \times 10^{-4}}{4.00 \times 10^{-4}} = 1.77 \times 10^{-4}$$

$$[H_3O^+] = 2.36 \times 10^{-5}$$

$$pH = 4.63.$$

The pH remains within the range.

Addition of Acids and Bases to Buffers:

The resistance of buffer mixtures to pH changes from added acids or bases is conveniently illustrated

Calculate pH change that takes place when 100 ml of (a) 0.0500 M NaOH and (b) 0.05 M HCl are added to 400 ml of a buffer solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl.

$$NH_3 + H_2O \rightleftharpoons NH_3^+ + OH^-$$

$$[NH_3] = 0.200\ M$$

$$[NH_4^+] = 0.300\ M$$

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K = \frac{[0.300][OH^-]}{0.200} = 1.76 \times 10^{-5}$$

$$pH = 14.00 - (-\log 1.17 \times 10^{-5}) = 9.07.$$

(a) Addition of NaOH converts part of NH_4^+ in the buffer to NH_3.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

$$M\ NH_3 = \frac{400 \times 0.200 + 100 \times 0.05}{500} = 0.170$$

$$M\ NH_4Cl = \frac{400 \times 0.300 + 100 \times 0.05}{500} = 0.230$$

$$[OH^-] = \frac{K \times M\ NH_3}{M\ NH_4^+} = \frac{1.76 \times 10^{-5} \times 0.170}{0.230} = 1.30 \times 10^{-5}$$

$$pH = 14.00\ (-\log 1.30 \times 10^{-5}) = 9.11$$

Change in pH = 9.11 – 9.07 = 0.04.

(b) Addition of HCl converts part of NH_3 to NH_4^+

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

$$M\ NH_3 = \frac{400 \times 0.2 - 100 \times 0.005}{500} = 0.150$$

$$M\ NH_4^+ = \frac{400 \times 0.300 + 100 \times 0.05}{500} = 0.250$$

$$[OH^-] = 1.76 \times 10^{-5} \times \frac{0.150}{0.250} = 1.06 \times 10^{-5}$$

$$pH = 14.00\ (-\log 1.06 \times 19^{-5}) = 9.02$$

Change in pH = 9.02 – 9.07 = – 0.05.

Buffer Capacity:

The ability of a buffer to prevent significant change in pH is directly related to the total concentration of the buffering species as well as their concentration ratios.

The buffer capacity of a solution is defined as the number of equivalents of strong acid or base needed to cause 1.00 *l* of the buffer to undergo 1.00 unit change in pH. The ~~buffer capacity is dependent upon~~ the concentration of conjugated acid-base pair.

SOFT AND HARD ACID AND BASE CONCEPT (SHAB):

Principle:

In order to understand the Soft and Hard Acid-Base concept, it is essential to know the meanings of Lewis Acids and Lewis Bases. A Lewis base is a lone pair electron donor and a Lewis acid is a lone pair electron acceptor.

When a Lewis acid (E) combines with a Lewis base (N), a chemical bond results *e.g.*,

$$E + :N \longrightarrow E:N \quad \text{or} \quad E \longleftarrow N$$

When a pair of electrons is held by a σ bond between two different atoms which differ widely in size, electronegativity etc., the bonding pair will be held more tightly to one core than to the other. A bond of this type is generally highly polar and relatively labile and is referred to as coordinate bond.

When the rates of reactions are considered, the Lewis acids are called *Electrophiles* and Lewis bases are known as *Nucleophiles*. The Lewis acids include most of the cations while the Lewis bases are mostly the anions and neutral spacies. If we break an organic molecule conceptually, we see that it is also a combination of Lewis acid and a Lewis base *e.g.*, C_2H_5OH, where $C_2H_5^+$ is a Lewis acid and OH^- is a Lewis base. Hence all carbonium ions (although may not exist freely) are considered to act as Lewis acids (Electrophiles), since they contain such a structure which can accept a pair of electrons from the Lewis base. Similarly, OH^- ions act as Lewis base (Nucleophile).

Classification of Acceptor and Donor Atoms and Ions:

In 1958, Chatt and Coworkers divided Lewis Acids (***acceptor molecules and ions***) into two classes.

Class (a):

Those Lewis acids which form their most stable complexes with the first member of Group V, VI & VII in the Periodic Table *i.e.*, N, O, F (which act as donor atoms or ligands).

Class (b):

Those Lewis acids which form their most stable complexes with the donor atoms (ligands) of the subsequent elements of these groups *i.e.*, P, S, Br, etc.

The donor atoms and ions (Lewis Bases) were classified on the basis of electronic affinity, coordinating ability, effective charge, ionic size and polarization considerations.

The electron affinity sequences of various groups of electron pair donor atoms and ions (ligands) with respect to the class (a) and class (b) electron pair acceptors (Lewis acids) is given below:

Class (a)	**Class (b)**
$F \gg Cl > Br > I$	$F \ll Cl < Br < I$
$O \gg S > Se > Te$	$O \ll S \sim Se \sim Te$
$N \gg P > As > Sb$	$N \ll P > As > Sb$

It is observed that greater the values of electron affinities between donor-acceptor atoms or ions greater will be their coordinating affinities. Thus, in general more stable complexes of donor atoms *i.e.*, F, O, N, etc., will be formed with class (a) acceptors and class (b) acceptors (Lewis Acids) will form less stable complexes with F, O, N in their respective oxidation states. Polarization of the donors (ligands) by the acceptor also plays an important role in determining the stabilities of the complexes.

Based on the polarization considerations, Pearson introduced the idea of HARD and SOFT acids and bases. According to him, the Lewis bases (ligands) which are more polarizable are 'Soft', and those which are less polarizable are 'Hard'. For example, the atoms F, O, and N are the hardest Lewis bases. Hence, Pearson's concept of Hard and Soft acids and bases is in close agreement with class (a) and (b) acceptors given by Chatt and Coworkers, Class (a) refers to hard acids and class (b) to soft acids.

Pearson, based on the concept of polarizability, divided the Lewis acids and bases as defined below:

Hard Bases:

The donor atoms of low polarizabilities, high electronegativities and associated with empty orbitals of high energy are classed as hard bases. They are hard to oxidise.

Soft Bases:

The donor atoms of high polarizabilities, low electronegativities and associated with empty orbitals of low energy are termed as soft bases. They are easy to oxidize.

Hard Acids:

These are acceptor atoms of high positive charge, small size and do not have outer electrons which can be easily excited.

Soft Acids:

These are acceptor atoms of low positive charge, large size and have several outer electrons which can be easily excited.

Based on these considerations, Pearson classified the Lewis acids and Lewis bases as hard and soft as given below:

Classification of Lewis Bases:

Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{-3}, SO_4^{-2}	I^-, SCN^-, $S_2O_3^{-2}$
Cl^-, CO_3^{-2}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6, H^-, R^-

Border line

$C_6H_5NH_2$ C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{-2}, N_2

Classification of Lewis Aci

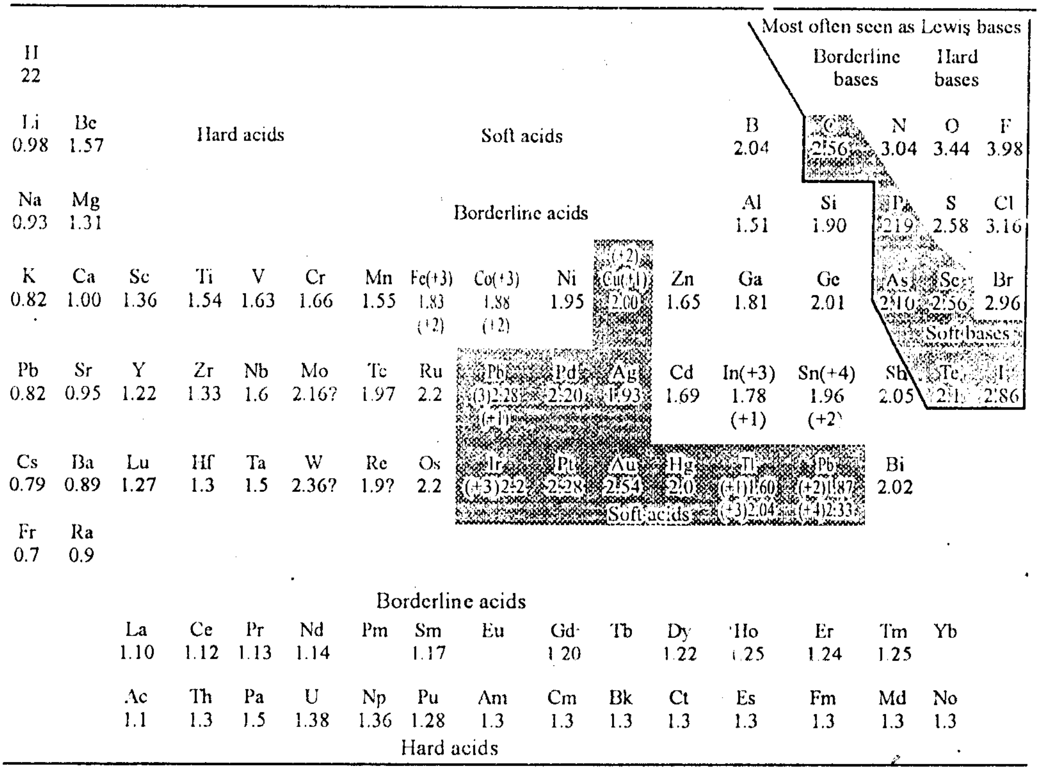
Hard	Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+
Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}	Pd^{+2}, Cd^{+2}, Pt^{+2}, Hg^{+2}
Mn^{+2}	CH_3Hg^+, $Co(CN)_5^{-2}$, Pb^{+4}, Te^{+4}
Al^{+3}, Sc^{+3}, Ga^{+3}, In^{+3}, La^{+3}	Te^{+3}, $Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$
N^{+3}, Cl^{+3}, Gd^{+3}, Lu^{+3}	$GaCl_3$, GaI_3, $InCl_3$
Cr^{+3}, Co^{+3}, Fe^{+3}, As^{+3}, CH_3Sn^{+3}	RS^+, RSe^+, RTe^+
Si^{+4}, Ti^{+4}, Zr^{+4}, Th^{+4}, U^{+4}	I^+, Br^+, HO^+, RO^+
Pu^{+4}, Ce^{+3}, Hf^{+4}, WO^{+4}, Sn^{+4}	I_2, Br_2, ICN etc.
UO_2^{+2}, $(CH_3)_2Sn^{+2}$, VO^{+2}, MoO^{+3}	trinitrobenzene, etc.
$BeMe_2$, BF_3, $B(OR)_3$	chloranil, quinones etc.
$Al(CH_3)_3$, $AlCl_3$, AlH_3	tetra cyanoethylene etc.
RPO_2^+, $ROPO_2^+$	O, Cl, Br, I, N, RO, RO_2
RSO_2^+, $ROSO_2^+$, SO_3,	M^0 (metal atoms)
I^{+7}, I^{+5}, Cl^{+7}, Cr^{+6}	bulk metals
RCO^+, CO_2, NC^+	CH_2, carbenes.
HX (hydrogen bonding molecules)	

Border Line

Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, Sn^{+2}, Sb^{+3}, Bi^{+3},

Rh^{+3}, Ir^{+2}, $B(CH_3)_3$, SO_2, NO^+, Ru^{+2}, Os^{+2}, R_3C^+, $C_6H_5^+$

The trend of soft and hard acids and bases in the Periodic Table is given below:



Most often seen as Lewis bases
Borderline bases
Hard bases

H 22																
Li 0.98	Be 1.57		Hard acids					Soft acids				B 2.04	C 2.56	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31							Borderline acids				Al 1.51	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe(+3) 1.83 (+2)	Co(+3) 1.88 (+2)	Ni 1.95	(+2) Cu(+1) 2.00	Zn 1.65	Ga 1.81	Ge 2.01	As 2.10	Se 2.56	Br 2.96
Pb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16?	Tc 1.97	Ru 2.2	Pb (3)2.28 (+1)	Pd 2.20	Ag 1.93	Cd 1.69	In(+3) 1.78 (+1)	Sn(+4) 1.96 (+2)	Sb 2.05	Te 2.1	I 2.86
Cs 0.79	Ba 0.89	Lu 1.27	Hf 1.3	Ta 1.5	W 2.36?	Re 1.9?	Os 2.2	Ir (+3)2.2	Pt 2.28	Au 2.54	Hg 2.0	Tl (+1)1.60 (+3)2.04	Pb (+2)1.87 (+4)2.33	Bi 2.02		
Fr 0.7	Ra 0.9															

Soft acids
Soft bases

Borderline acids

La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.25	Er 1.24	Tm 1.25	Yb
Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3

Hard acids

Consider a displacement reaction:

$$CH_3OH + HS^- \longrightarrow CH_3SH + OH^-$$

$$CH_3F + I^- \longrightarrow CH_3I + F^-.$$

$\overset{+}{CH_3}$ prefers HS^- in the first reaction and prefers I^- in the second reaction. It means that $\overset{+}{CH_3}$ is soft acid. The general conclusion is that the methyl carbonium ion is fairly soft but not as extremely soft as CH_3Hg^+.

If we arrange the donor atoms of the most common bases in the order of an increasing electronegativity, we will have As, P < C, Se, S, I < Br < N, Cl O < F. Soft Lewis Acids will form more stable complexes with donor atoms of low electronegativities, and Hard Lewis Acids will form more stable complexes with donor atoms of high electronegativities. Hence a simple rule can be framed which states that:

"Hard acids prefer to combine with Hard Bases and Soft Acids prefer to combine with Soft Bases."

This is known as the principle of Soft and Hard Acids and Bases (SHAB).

Common Features of Hard and Soft Acid:

1. **The hard acids** coordinate to various donors mainly by the *electrostatic interactions existing* between charges of the opposite signs. The higher the charge and the smaller the radius of the acceptor and of the donor atom to be coordinated, the stronger are generally the complexes formed *e.g.*, Be^{+2}, Al^{+3}, Ti^{+4} prefer donor atoms like F, O, N. *Acids termed soft* have opposite behaviour.
2. **The coordination of uncharged ligands** (soft bases) such as CO, olefines, acetylenes and aromatic hydrocarbons is preferred with soft acids (transition metals in low oxidation states).
3. **The rates of nucleophilic** displacements depend much on polarizability.
4. **Solvents** tend to bring out class (b) (soft) character for acids compared to the gas phase.

Common Features of Hard and Soft Bases:

1. The hard or soft base character is based on the polarizability of the donor atom or ion. The more polarizable is the donor, the most soft character it has. A decrease in electronegativity will increase the polarizability and consequently a stronger tendency to form a covalent bond.
2. Besides a high polarizability, a ligand must possess empty orbitals on suitable energy levels to accommodate the *d* electrons from the acceptors. The more available these orbitals, the softer the ligand.
3. Extreme softness is connected with the presence of *p*-orbitals of particularly favourable energy
4. The soft ligands like the hard ligands tend to flock together.

APPLICATIONS OF SOFT AND HARD ACIDS AND BASES (SHAB):

Although the principle of SHAB is qualitative in nature, yet it can be useful to provide some information about the chemical reactions. The various applications can be enumerated briefly as below:

1. Stability of the complexes: Consider two complexes for comparison *e.g.*, sulphenyl iodide (R S I) which is stable and sulphenyl fluoride which is unstable. The reason is that RS is a soft acid. Iodide is also a soft base and has large size, whereas the fluoride ion is a hard base and has small size, therefore a soft combination *i.e.*, **R S I** would give a stable complex than the soft-hard combination according to the SHAB principle.

Another example is that BH_3CO is a stable complex but BF_3CO is not known. Since CO is a typical soft base and soft BH_3 group holds strongly the soft CO group, BH_3CO is stable. On the other hand, BF_3 is a typical hard acid and CO is a typical soft base. So the complex BF_3CO cannot be stable according to the SHAB rule. BF_3 can form stable complexes like $BF_3 \cdot NR_3$ or BF_3 . OR, a hard-hard combination.

2. Prediction of Reaction Rates: The principle is also useful in predicting the rates of many chemical reactions *e.g.*, electrophilic or acid substitution reactions and nucleophilic or base substitution reactions. In such cases the rates of the reactions depend upon the hard or soft character of the various acid and base centres.

Consider a reaction,

$$X^- + A:Y \longrightarrow A:X^- + Y$$

If A is a hard centre, then hard base X^- will react fast, if A is a soft centre, then soft bases X^- will react fast.

In the case of esters and ketones, CH_3CO^+ is the hard centre. So it is found that the hard bases attack this group rapidly *i.e.*, ester hydrolysis.

Similarly, rates of nucleophilic substitution can be predicted *e.g.*, isopropyl bromide $i - C_3H_7Br$ has three different acidic sites or electrophilic centres. These sites are CH_3, CH_2 carbon atom and the bromine atom regarded as Br. It is seen that the behaviour of $i - C_3H_7Br$ towards a hard base such a OH^- is quite different from that towards a soft base such as malonic ester anion, even though both OH^- and $(C_2H_5OOC)_2CH^-$ are bases of very similar strength.

3. **Choice of Catalysts:** Consider the reaction of the type

$$X^- + A:B \longrightarrow X^-:B + A$$
$$Y^- + A:B \longrightarrow A:Y^- + B$$

The choice of the hard or soft acid or base catalyst is dictated by the hard or soft nature of Acid or Base. In the case of first reaction a basic catalyst is used which binds X effectively to speed up the rate of reaction. Similarly, in the second case, an acid catalyst is used which binds Y effectively.

4. **Biological Applications:** Most of the hard acids and bases are not poisons, while most of the soft acids and bases are poisons to the living organisms. This poisoning is brought about by the formation of complexes with the soft bases and acids that are present in small amounts in the bodies *e.g.*, the heavier elements and sulphide groups. The substances that are poisonous heterogenous catalysts are also poisons for the living things. Carbon monoxide is a poisonous gas because it is soft and reacts readily with iron of the haemoglobin in the blood.

5. **Prediction of the sign of ΔH:** The principle of soft and hard acids and bases (SHAB) may be used to predict the sign of ΔH for reactions of the type

$$AB + CD = AD + CB$$

6. **Symbiosis:** According to Jorgenson, soft ligands or bases tend to flock together on a central metal atom, and hard ligands tend to flock together. This mutual stabilizing effect is called the symbiosis.

Generally the piling up soft bases on an acceptor atom makes it soft and piling up hard bases on an acceptor atom makes it hard, *e.g.*, BF_3 is a hard acid and BH_3 is a soft acid. In both the compounds, boron is in plus (+) three oxidation state but different behaviour is noted in the above two compounds. The presence of hard fluoride ion in BF_3 makes it easy to add other hard bases. The hard F^- is largely ionic and forms complex with BF_3 to give BF_4^-.

7. **Thermodynamic Stabilities of the Compounds:** The concept of SHAB may be used to rationalize the thermodynamic stabilities of many kinds of organic molecules. Consider a gas phase reaction,

$$CH_3OH_{(g)} + HB_{(g)} \rightleftharpoons CH_3B_{(g)} + H_2O_{(g)}$$

In the above reaction CH_3^+ prefers the soft base and H^+ prefers the hard base e.g. OH^-. H^+ is intrinsically a much stronger acid than CH_3^+.

It has been found that the equilibrium constants are quite high for the soft bases such as CH_3^-, I^-, CH_3S^-. For hard bases such as CH_3O^- and $C_6H_5O^-$, the equilibrium constant is much smaller and for F^- ion, the equilibrium constant is less than unity. The equilibrium constants in order of decreasing softness are as follows:

$$H^- > CN^- > CH_2COCH_3^- > CH_3^- > I^- > SH^- > Br^- > Cl^-$$
$$> ONO^- > NH_2^- > CH_3O^- > F^-$$

8. Solubility of Halides: Water is a hard Lewis base with oxygen donor atom and a hard Lewis acid with hydrogen atom.

The ionic reaction of Ag^+ and Cl^- in aqueous solution with silver chloride precipitation reaction can be written as:

$$Cl^- : H_2O + Ag^+ : OH_2 \rightleftharpoons AgCl(s) + H_2O : H_2O$$

The HSAB principle favours the products. The soft Ag^+ in the reactant is coordinated by hard oxygen donor atoms of water molecules. Likewise, Cl^- in aqueous solution are in the form of $[Cl(H_2O)_n]^-$ which is a combination of Cl^-, a borderline base and H^+ of H_2O which is a hard acid. So the reaction will proceed in the forward direction to get soft acid-borderline base combination Ag^+Cl^- which being insoluble in water appears as precipitate. We can predict that the chlorides, bromides and iodides of the soft acids e.g; Ag^+, Hg^+, Pb^{2+}, Pd^{2+}, Pt^{2+} are insoluble. Similarly pseudohalides e.g, S^{2-}, Se^{2-} form insoluble salts with the soft and borderline acids e.g; Ag^+, Hg^{2+} etc.

9. The Qualitative Scheme for Metal Ions: During your practical work, you may have spent many weeks in laboratory learning to separate and identify the metal ions present in a solution, via the qualitative analysis scheme for the cations. The metal ions commonly present are first separated into six groups.

Group I Cations:	Precipitated with dil. (0.3 M) HCl
Group II Cations:	Precipitated with H_2S from acidic solution
Group III Cations:	Precipitated with NH_4Cl and NH_4OH
Group IV Cations:	Precipitated with H_2S from basic solution
Group V Cations:	Precipitated with $(NH_4)_2CO_3$ from basic solution
Group VI Cations:	Those which remain in aqueous solution

The cations of Group I scheme i.e; Ag^+, Hg_2^{2+}, Pb^{2+} are soft acids. These metal ions combine with borderline base, the chloride ion, to give insoluble chlorides.

The group reagent, H_2S for Group II metal ions is a soft and stronger base than the chloride ion. So it combines with these metal ions to give insoluble sulphides. Had the cations of Group I not removed with Cl^-, these would also have precipitated by H_2S in acidic solution.

The Group III involves cations, i.e. Fe^{3+}, Al^{3+}, Cr^{3+} which are hard acids and would prefer to combine with OH^-, a hard base to give insoluble hydroxides.

The Group IV cations, i.e; Co^{2+}, Ni^{2+}, Zn^{2+} are borderline acids which will be able to combine with soft S^{2-} to form insoluble sulphides from basic solution.

The Group V cations are mild hard acids, i.e; Ba^{2+}, Sr^{2+} and are precipitated with moderately basic carbonate ions.

Questions

1. Discuss Arrhenius concept of acids and bases. What are the drawbacks of this theory?
2. What are acids and bases according to Lowry Bronsted concept? Explain the terms conjugate acids and bases.
3. 'Lewis theory of acids and bases is a more generalised concept than the previous concepts'. Comment upon this statement.
4. What are the modem theories of acids and bases? Discuss with suitable examples.
5. Write a critical review on Soft and Hard Acid-Base concept.
6. (a) Define the following giving suitable examples:
    (i) Soft acid (ii) Soft base
    (iii) Hard acid (iv) Hard base
   (b) Discuss principles underlying soft and hard acid-base concept.
   (c) Describe the characteristic features of soft and hard acids and bases.
7. How is the soft and hard acid-base concept applied to explain the various chemical phenomena and reaction kinetics?
8. Arrange the following in order of increasing acidities giving reasons:
   HCl, H_2SO_4, $HClO_4$, CH_3COOH, H_2CO_3, $Cl_3C\ COOH$
9. An acid dissociates according to the equation $HA \rightleftharpoons H^+ + A^-$. A one-molar solution of the acid is 1 per cent ionized. What is the value of K*a*? **Ans.** 0.0001
10. The ionization of one-molar solution of HCN is 0.0[illegible]0 per cent at 18°C. Calculate K*a*. **Ans.** 1.0×10^{-8}
11. A one-molar solution of HC1 is about 92 per cent ionized at room temperature. Calculate K*a* for HCl.
12. A solution containing 0.275 g of NaOH requires 35.5 ml. of HCl for neutralization. What is the normality of HCl? **Ans.** 0.19N
13. What will be the pH of 0.1 N solution of NaOH assuming it to be completely dissociated? **Ans.** pH = 13
14. What is the pH of 0.2 mole HCl added to 1 litre of the buffer of acetic acid and sodium acetate.
    pH = 4.57
15. You have a buffer solution that contains 1 mole NH_4Cl and 1 mole NH_4OH per litre.
    (a) Calculate the pH of this solution.
    (b) Calculate the pH of the solution after the addition of 0.1 mole of solid NaOH to a litre.
    (c) Calculate the pH of this solution after the addition of 0.1 mole HCl gas to a separate 1 litre portion of the buffer.

(d) Calculate the pH of a solution made by adding 0.1 mole HCl gas to 100 ml H_2O. **Ans.** (a) 9.26 (b) 9.34 (c) 9.17 (d) 14

16. What is the pH of a solution containing 0.050 MH^+ ions? **Ans.** pH = 1.3

17. Given a pH 2.19, find $[H^+]$ ion concentration.

18. **Give the correct answer:**

(i) A base is a substance which contains:
(a) H_3O^+ ions (b) OH groups
(c) CO_3 ions (d) NH_3 group (**Ans**: b)

(ii) A base is a substance which accepts:
(a) an electron (b) a proton
(c) a neutron (d) a positron (**Ans**: b)

(iii) An acid is a species which donates or tends to donate:
(a) a proton (b) an electron
(c) a neutron (d) a positron (**Ans**: a)

(iv) One of the following is an acid:
(a) OH^- (b) NH_3
(c) HCO_3^- (d) S^{2-} (**Ans**: c)

(v) One of the following is a base:
(a) $\overset{+}{H_3O}$ (b) S^{2-}
(c) $\overset{+}{NH_4}$ (d) HSO_4^- (**Ans**: b)

(vi) One of the following is a Lewis base:
(a) BF_3 (b) NH_3
(c) $AlCl_3$ (d) CO_2 (**Ans**: b)

(vii) One of the following is a Lewis acid:
(a) H_2O (b) NH_3
(c) H^+ (d) Cl^- (**Ans**: c)

(viii) pH range of methyl orange indicator is:
(a) 1.2 – 2.2 (b) 1.2 – 2.8
(c) 3.1 – 4.5 (d) 5.0 – 8.0 (**Ans**: c)

(ix) Lewis acid is also called:
(a) electrophile (b) nucleophile
(c) electrolyte (d) non-electrolyte(**Ans**: a)

(x) One of the following is a hard acid:
(a) H^+ (b) Hg^+
(c) Pt^{2+} (d) Ag^+ (**Ans**: a)

(xi) One of the following is a soft base:
(a) H_2O (b) Ca^{2+}
(c) $S_2O_3^{2-}$ (d) H^+ (**Ans**: c)

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7

THEORETICAL PRINCIPLES OF INORGANIC ANALYSIS AND EVALUATION OF ANALYTICAL DATA

THE LAW OF MASS ACTION:

This law was put forward by Cato Guldberg and Peter Waage in 1864. It states that *"at constant temperature, the rate at which a substance reacts is proportional to its active mass or active concentration and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances."* For example,

Consider a general reaction

$$A + B \rightleftharpoons C + D$$

Let [A], [B], [C] and [D] be the active masses (the active molecular concentrations) of A, B, C and D, respectively at the equilibrium point.

Rate of combination of A and B α $[A] \times [B]$

$\therefore$ Rate of forward reaction $= K_1 [A] \times [B]$

where K_1 is called the velocity constant and would be the rate of reaction when [A] and [B] are both equal to one.

Similarly, the rate of formation of C and D α $[C] \times [D]$

or Rate of backward *reaction* $= K_2 [C] \times [D]$

At equilibrium point,

Rate of forward reaction = Rate of backward reaction

$$\therefore \quad K_1 [A] \times [B] = K_2 [C] \times [D]$$

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{K_1}{K_2} = K_e \text{ (at constant temperature)}$$

where K_e is called the equilibrium constant.

It may vary a little with temperature or pressure. The expression for equilibrium constant can be generalized by considering a general reaction

$$aA + bB + cC + \cdots \rightleftharpoons pP + qQ + rR + \cdots$$

Thus K_e is given by the expression

$$K_e = \frac{[P]^p\,[Q]^q\,[R]^r \times \cdots}{[A]^a\,[B]^b\,[C]^c \times \cdots}$$

APPLICATIONS OF THE LAW OF MASS ACTION:

The law of mass action can be applied to:

(a) the dissociation of weak electrolytes.

(b) the solubility of a sparingly soluble salt.

(a) The Dissociation of Weak Electrolytes:

A substance which ionizes to a very small extent is called a weak electrolyte.

Consider 1 gm mole of a weak binary electrolyte "AB" dissolved in "V" litres of solution. Let x be its degree of dissociation.

$$\begin{array}{cccccc} 1 \text{ mole} & & 0 \text{ mole} & & 0 \text{ mole} \\ AB & \rightleftharpoons & A^+ & + & B^- \\ (1-x) \text{ moles} & & x \text{ moles} & & x \text{ moles} \end{array}$$

The concentration at equilibrium will be:

$$[A^+] = \frac{x}{V}$$

$$[B^-] = \frac{x}{V}$$

$$[AB] = \frac{1-x}{V}$$

Hence the rate of ionization is $\alpha \dfrac{1-x}{V}$

$$= K_1 \frac{1-x}{V}$$

The rate of combination $\alpha \dfrac{x}{V} \times \dfrac{x}{V}$

$$= K_2 \frac{x}{V} \times \frac{x}{V}$$

At equilibrium the rate of ionization and combination are equal.

$$K_1 \times \frac{1-x}{V} = K_2 \frac{x}{V} \times \frac{x}{V}$$

or $$\frac{\frac{x}{V} \times \frac{x}{V}}{\frac{1-x}{V}} = \frac{K_1}{K_2} = K$$

or $$\frac{x^2}{(1-x)\,V} = K$$

The "K" is called the dissociation constant and the equation representing the variation of degree of dissociation with dilution is called *Ostwald's dilution law*.

In case of weak electrolytes the value of "x" is very small as compared with 1 and hence it is negligible and ignored in the denominator of the above expression.

Thus

$$\frac{x^2}{1 \times V} = K \qquad \text{or} \qquad x^2 = KV$$

or $$x = \sqrt{KV} \qquad \text{or} \qquad x \propto \sqrt{V}$$

In other words, the degree of dissociation for weak electrolytes is proportional to the square root of dilution.

(b) The Solubility of a Sparingly Soluble Salt (Solubility Product):

The law of mass action can also be applied to the study of the solubility of sparingly soluble salt.

Consider a sparingly soluble salt BA present in the solid phase in equilibrium with its saturated solution in water. The equilibrium can be represented as,

$$\underset{\text{Solid}}{BA} \rightleftharpoons \underset{\text{Dissolved}}{BA} \rightleftharpoons B^+ + A^-$$

The dissolved portion in solution dissociates and constitutes an ionic equilibrium.

$$K = \frac{[B^+][A^-]}{[BA]}$$

Where $[B^+]$ = Active mass or concentration of B^+

$[A^-]$ = Active mass or concentration of A^-

$[BA]$ = Active mass or concentration of BA

and K is the equilibrium constant.

As the salt is sparingly soluble, the concentration of [BA] does not change much. It is thus considered to be constant. Thus

$$K = [B^+] \times [A^-] = \text{Constant} = K_S$$

where K_S is called solubility product. It is constant at a constant temperature. It can be defined as:

> ***"the product of the concentrations of the constituent ions in a saturated solution raised to the appropriate powers."***

Now let us consider the solubility of a sparingly soluble salt. Let it be S gm. moles per litre. As the concentration of the salt is very low, it is said to be completely ionized. Thus S gm. moles of the salt 'BA' will ionize to form S gm. mole of B^+ and S gm. moles of A^-.

$$BA \rightleftharpoons B^+ + A^-$$
$$[B^+] = [A^-] = [S]$$
$$[B^+][A^-] = [S][S] = K_S$$
$$\text{or} \quad [S] = \sqrt{K_S}$$

Thus the solubility of a sparingly soluble salt is always equal to the square root of the solubility product at a given temperature and is expressed in gm. moles per litre. A few examples of solubility product are given below:

(a) $AgCl \rightleftharpoons Ag^+ + Cl^-$

$$K_S = [Ag^+][Cl^-]$$
$$\text{Solubility} = \sqrt{[Ag^+][Cl^-]} = \sqrt{K_S}$$

(b) $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$

$$K_S = [Pb^{2+}][Cl^-]^2$$
$$\text{Solubility} = \sqrt{[Pb^{2+}][Cl^-]^2} = \sqrt{K_S}$$

(c) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$$K_S = [Ag^+]^2[CrO_4^{2-}]$$
$$\text{Solubility} = \sqrt{[Ag^+]^2[CrO_4^{2-}]} = \sqrt{K_S}$$

Example:

At 25°C, 0.00188 g of AgCl is dissolved in 1 litre of water. What is the K_S of AgCl.

Solution:

The molar solubility of AgCl (molecular weight of AgCl is 143) is calculated as

$$\text{Moles of AgCl} = 0.00188 \text{ g. AgCl}\left[\frac{1}{143 \text{ g. AgCl}}\right]$$
$$= 1.31 \times 10^{-5} \text{ mole AgCl}$$

For each mole of AgCl dissolving, 1 mole of Ag^+ and 1 mole of Cl^- are formed.

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

1.31×10^{-5} M of Ag^+ and 1.31×10^{-5} M of Cl^-

$$\begin{aligned} K_S &= [Ag^+][Cl^-] \\ &= [1.31 \times 10^{-5}]^2 \\ &= 1.7 \times 10^{-10} \end{aligned}$$

Example:

At 25°C, 7.8 × 10^{-5} mole of Ag_2CrO_4 dissolves in 1 litre of water. What is the K_S of Ag_2CrO_4.

Solution:

For each mole of Ag_2CrO_4 that dissolves 2 moles of Ag^+ and 1 mole of CrO_4^{2-} are formed. Therefore,

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$2(7.8 \times 10^{-5})$ M of Ag^+ and 7.8×10^{-5} M of CrO_4^{2-}

$$\begin{aligned} K_e &= [Ag^+]^2[CrO_4^{2-}] \\ &= [1.56 \times 10^{-5}]^2[7.8 \times 10^{-5}] \\ &= 1.9 \times 10^{-12} \end{aligned}$$

The solubility of a solid is increased by the presence of the ions of another salt in the solution. This is called the salt effect and increases the degree of ionization of soluble weak electrolytes. This effect is due to inter-ionic attractions which do not depend upon the nature of the dissolved ions but on their concentrations and charges. Therefore, foreign ions reduce the activities of the ions of the substance under study.

PRECIPITATION AND THE SOLUBILITY PRODUCT:

The numerical value of the solubility product of a salt gives a quantitative limit of the solubility of the salt. For a particular solution of a salt, ***the product of concentration of the ions, each raised to the appropriate power, is called ionic product.*** Thus, for a saturated solution in equilibrium with excess solid, the ionic product equals the K_S. If the ionic product of a solution is less than the K_S, the solution is unsaturated. Additional solid ionic product can dissolve in this solution. On the other hand, if the ionic product is greater than the K_S, the solution is momentarily supersaturated, precipitation will occur until the ionic product equals the K_S.

Example:

Will a precipitate form if 10 ml. of 0.010 M $AgNO_3$ and 10 ml. of 0.00010 M NaCl are mixed? Assume that the final volume of the solution is 20 ml.

For AgCl, $K_S = 1.7 \times 10^{-10}$.

Solution:

Diluting a solution to twice its original volume reduces the concentrations of ions in the solution to half their original value. Therefore, if there were no reaction, the ionic concentrations would be

$$[Ag^+] = 5.0 \times 10^{-3}\ M$$
$$[Cl^-] = 5.0 \times 10^{-5}\ M$$

The ionic product is

$$[Ag^+][Cl^-] = ?$$
$$[5.0 \times 10^{-3}][5.0 \times 10^{-5}] = 2.5 \times 10^{-7}$$

Therefore, the ionic product is larger than the Ks (1.7×10^{-10}). and the precipitation of AgCl will occur.

Example:

Will a precipitate of $Mg(OH)_2$ form in a 0.0010 M solution of $Mg(NO_3)_2$ if the pH of the solution is adjusted to 9.0? The K_e of $Mg(OH)_2$ is 8.9×10^{-12}.

Solution:

If the pH = 9.0

$$[OH^-] = 1.0 \times 10^{-5}\ M$$

Since $[Mg^{2+}] = 1.0 \times 10^{-3}$, the ionic product is

$$[Mg^{2+}][OH^-]^2 = ?$$
$$(1 \times 10^{-3})(1 \times 10^{-5})^2 = 1 \times 10^{-13}$$

Since the ionic product is less than 8.9×10^{-12}, the solubility product, no precipitation will occur.

IONIZATION OF WATER:

Pure water is itself a very weak electrolyte and ionizes according to the equation

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

In simplified form, this is

$$H_2O \rightleftharpoons H^+ + OH^-$$

The ionization constant K is given by the expression

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

In dilute solutions, the concentration of water is virtually a constant and we may combine $[H_2O]$ with the constant K. Thus

$$K[H_2O] = [H^+] OH^-]$$

This constant $K[H_2O]$, is called the ionic product of water or the water constant, and is given by the symbol K_w.

$$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$

In pure water

$$[H^+] = [OH^-] = x$$

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M.}$$

COMMON ION EFFECT:

In a 0.1 M solution of acetic acid, methyl orange gives red colour. If sodium acetate is added to this solution, the colour changes to yellow, showing that this addition causes the acidity of the solution to decrease.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

According to Le-Chatelier, the equilibrium is shifted to the left by the addition of acetate ion from the sodium acetate and the concentration of the hydronium ion correspondingly decreases. Since acetic acid and sodium acetate have the acetate ion in common, this phenomenon is called the *Common-ion effect*. The degree of ionization is suppressed by addition of another electrolyte having a common ion. Similarly, the ionization of $NH_4^+ + OH^-$ is suppressed by addition of NH_4Cl which produces common NH_4^+ ions.

Application in Analytical Chemistry:

The principle of common ion effect has proved very useful in analytical chemistry. The following are some of its common applications:

1. Purification of Common Salt:

The common salt (NaCl) can be purified by passing dry HCl gas through saturated salt solution. Sodium chloride in the saturated state ionizes as:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

According to the law of mass action

$$K_e = \frac{[Na^+][Cl^-]}{[NaCl]}$$

If HCl is passed, it ionizes to give

$$HCl \rightleftharpoons H^+ + Cl^-$$

Cl^- ion which is common ion with Cl^- ion of NaCl in water. As a result, the concentration of Cl^- ion increases. To keep K constant the amount [NaCl] is increased. Thus more and more of sodium chloride molecules are formed and get precipitated. The salt is filtered and obtained in the pure form.

2. Use of HCl in Group II of Salt Analysis:

The cations of second group of the salt analysis are precipitated by passing H_2S gas in the acidic medium. The function of HCl is to suppress the ionization of H_2S gas due to common ion effect. The common ions of H_2S and HCl are

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
$$HCl \rightleftharpoons H^+ + Cl^-$$

Due to provision of H^+ ions more and more of S^{2-} ions combine with H^+ ions to form undissociated H_2S. Thus the ionization of H_2S gas is suppressed. Whatever the sulphide ions are left ionized, these form metallic sulphides with the cations of the second group. The cations of both the second and fourth groups are capable of forming sulphides. The sulphides of the former group are sparingly soluble and those of the latter *i.e.*, 4th group are fairly soluble. That is why the sulphides of second group are precipitated by H_2S in acidic medium and those of 4th group remain in solution and are not precipitated along with the sulphides of second group.

Example:

A solution that is 0.30 M in H^+, 0.050 M in Pb^{2+}, and 0.050 M in Fe^{2+} is saturated with H_2S; should PbS and/or FeS precipitate? The K_S of PbS is 7×10^{-29} and the K_S of FeS is 0×10^{-19}.

Solution:

For any saturated solution of H_2S

$$[H^+]^2 [S^{2-}] = 1.1 \times 10^{-22}$$

Since this solution is 0.30 M in H^+

$$(3.0 \times 10^{-1})^2 [S^{2-}] = 1.1 \times 10^{-22}$$
$$[S^{2-}] = 1.2 \times 10^{-21} \text{ M}$$

Both Pb^{2+} and Fe^{2+} are 2+ ions, and the form of the ionic product is

$$[M^{2+}] [S^{2-}]$$

where M^{2+} stands for either metal ion. Since both are present in concentrations of 0.050 M.

$$[M^{2+}] [S^{2-}]$$
$$(5.0 \times 10^{-2}) (1.2 \times 10^{-21}) = 6.0 \times 10^{-23}$$

This ionic product is greater than the K_S of PbS; therefore PbS will precipitate. However, the ionic product is less than the K_S of FeS; the solubility of FeS has not been exceeded; no FeS will form.

3. Use of NH_4Cl in Salt Analysis:

NH_4Cl is added to the solution of the salt to be analysed after the second group. Its function is to suppress the concentration of OH^- ions due to common NH_4^+ ion in NH_4Cl and NH_4OH (the group reagent for third group).

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Hydroxides of third group are sparingly soluble and those of the succeeding groups are fairly soluble. That is why the hydroxide of third group are precipitated in third group and those of succeeding groups remain in solution.

Similarly, the addition of NH_4Cl shows the same function in all the succeeding groups.

4. Use of NH_4OH in 4th Group of Salt Analysis:

The function of NH_4OH is to provide OH^- ions which remove H^+ ions and thus enhance the ionization of H_2S. More the formation of S^{2-} ions, more is the precipitation of sulphides

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \qquad H^+ + OH^- \longrightarrow H_2O$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

CO-PRECIPITATION (Contamination of Precipitates):

Contamination of precipitates is the presence of various impurities in the precipitates. Usually they are foreign substances. Contamination may also be due to the substances which are normally soluble under the conditions of precipitation. Such type of contamination is called co-precipitation *e.g.*, the precipitation of $BaSO_4$.

$$Ba^{2+} + 2Cl^- + 2K^+ + SO_4^{2-} \longrightarrow BaSO_{4(s)} + 2K^+ + 2Cl^-$$

In the above reaction $BaSO_4$ contains some amount of K_2SO_4 which is normally freely soluble.

In the case of ferric hydroxide precipitation some aluminium may also be precipitated as hydroxide. This contamination is not due to the co-precipitation. It is simply because the solubility product of $Al(OH)_3$ is exceeded. Co-precipitation may be due to the following conditions:

(i) Adsorption.
(ii) Occlusion.

Following types of co-precipitation have been recognised:

1. The Impurity is Isomorphic and Miscible with the Host:

Isomorphic compounds are those which possess the same type of formula and crystal structure. One of the compounds acts as a host. The host crystal may incorporate large amounts of the isomorphic impurities. The two compounds may form mixed crystals in this way; and the impurities are distributed throughout the host crystal uniformly or non-uniformly.

Example:

Let us consider the two isomorphic compounds $BaSO_4$ and $PbSO_4$. By the addition of SO_4^{2-} ions to a solution of Ba^{2+} and traces of Pb^{2+} in concentrations insufficient to exceed K_S of $PbSO_4$, $BaSO_4$ is precipitated, and Pb^{2+} is adsorbed upon its surface. Since $PbSO_4$ is isomorphic with $BaSO_4$ and impure $BaSO_4$ crystals readily grow, with Pb^{2+} randomly occupying lattice positions that are normally occupied by Ba^{2+} in a pure crystal.

2. The Impurity is Soluble in the Host:

The two compounds are soluble to some extent in each other if they have the same crystal form but different lattice spacings *e.g.*, KH_2PO_4 and (NH_4) H_2PO_4. Both are monoclinic crystals. In this case the crystal symmetry and structure of the host is not lost although it may carry the impurity.

3. The Impurity is Adsorbed on the Surface of the Host:

The contaminations may be adsorbed by the precipitate potentially on its surface. The impurities are distributed over the surface of the precipitated particles. This type of co-precipitation has an importance where the particles have large specific surfaces *e.g.*, gelatinous hydrated oxides. Impurities in large excess can be removed by simple washing, but traces may remain after even considerable washings.

4. The Impurity is Occluded by the Host:

Occlusion or internal adsorption is the process in which foreign particles or ions are trapped within the rapidly growing crystals. Sometimes impurities are entrapped in the spaces between the particles in aggregates. These spaces may trap not only impurities adsorbed on the surface of the precipitates but also mother-liquor with its impurities whether they are adsorbable or not.

FRACTIONAL PRECIPITATION:

Sometimes a mixture of ions is separated by the same precipitating agent. Their separation is brought about by the fractional precipitation which is based on the solubility product of the ions. For example, a mixture of chloride and iodide ions can be separated as

The solubility product of $[Ag^+] \times [Cl^-] = 1.2 \times 10^{-10}$

The solubility product of $[Ag^+] \times [I^-] = 1.7 \times 10^{-16}$

from the above values, it is obvious that AgI is less soluble than AgCl and therefore shows precipitate first. AgCl will not precipitate until the Ag ions have the concentration

$$\frac{k\text{AgCl}}{[\text{Cl}^-]} = \frac{1.2 \times 10^{-10}}{[\text{Cl}^-]}$$

when the silver ions are in equilibrium with both the Cl^- and I^- ions, then

$$\frac{[\text{I}^-]}{[\text{Cl}^-]} = \frac{k\text{AgI}}{k\text{AgCl}} = \frac{1.7 \times 10^{-16}}{1.2 \times 10^{-10}} = 1.4 \times 10^{-6}$$

For example, if the metal concentration of chloride and iodide ions are 0.1 M each then AgCl will be precipitated when the iodide has the concentration

$$\begin{aligned}[\text{I}^-] = 1.4 \times 10^{-6} \times 0.1 &= 1.4 \times 10^{-7} \\ &= 1.4 \times 10^{-7} \times 127 \\ &= 1.8 \times 10^{-5} \text{ gms/litre.}\end{aligned}$$

By *finding out the point at which iodide* precipitation is complete, it is possible to separate the chloride from the iodide.

The concentration of both of the ions of water are equal to 1.0×10^{-7} M in pure water or in any neutral solution at 25°C. Hence, in 1 litre, only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

In any aqueous solution, both hydronium and hydroxide ions exist. In an acid solution, the concentration of hydronium ions is larger than 1.0×10^{-7} M and larger than the hydroxide ion concentration. In an alkaline solution, the hydroxide ion concentration is larger than 1.0×10^{-7} M (larger than the hydronium ion concentration).

Example:

What are $[H^+]$ and $[OH^-]$ in a 0.020 M solution of HCl?

The quantity of $[H^+]$ ions obtained from the ionization of water is negligible compared to that derived from HCl.

Solution:

Since HCl is a strong electrolyte

$$\begin{aligned}\therefore \quad [\text{H}^+] &= 0.020 \text{ M} \\ [\text{H}^+][\text{OH}^-] &= 1.0 \times 10^{-14} \\ [2.0 \times 10^{-2}][\text{OH}^-] &= 1.0 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1.0 \times 10^{-4}}{2.0 \times 10^{-2}} \\ [\text{OH}^-] &= 5.0 \times 10^{-13} \text{ M.}\end{aligned}$$

EVALUATION OF ANALYTICAL DATA:

Everything around us is made of chemicals. Analytical chemistry deals with the chemical characterization of matter. It involves separation, identification and determination of the relative amounts of the components in a sample of matter. The chemical composition of substances involve both qualitative and quantitative methods of analysis. Analytical chemistry plays an important role in nearly all aspects of chemistry, for example, organic, inorganic, nuclear, agricultural, clinical, forensic, pharmaceutical, environmental and metallurgical chemistry. The measurements of chemical constituents in a sample is a necessary part of quality control. Chemical analysis has played a significant role in the development of chemistry.

Some terms used to present the analytical data are introduced here so that one may get familiarity with the fundamental concepts of analysis.

THE MOLE:

The atoms and molecules are extremely small. There are a larger number present in a macroscopic sample. The very large numbers involved in counting microscopic particles are inconvenient to think about. Therefore chemists have chosen to count atoms and molecules using a unit called the **mole.** One mole (abbreviated mol) is 6.022×10^{23} of the small particles i.e., atoms. This is called Avogadro number, N.

The idea of using a large number as a unit with which to measure the number of objects is not unique to chemistry. Eggs and many other things are sold by the dozen. The pencils are ordered in units of 144, the gross. The paper is packaged in reams, each of which contains 500 sheets.

Similarly

1 mol H contains 6.022×10^{23} H atoms; with mass $= 1.008$ g
1 mol C contains 6.022×10^{23} C atoms; with mass $= 12.000$ g
1 mol O contains 6.022×10^{23} O atoms; with mass $= 15.999$ g

The mass of a mole of molecules can be obtained from atomic weights. Just as a dozen eggs will have a dozen white and a dozen yolks, a mole of CO molecule will contain a mole of C atoms and a mole of O atoms.

The mass of mole of CO is:

Mass of 1 mol C+ mass of 1 mol O = mass of 1 mol CO
12.000 g + 15.999 g = 27.999 $\approx$ 28.0 g

The quantity of a substance in one gram atom or one gram molecule or one gram ion or one gram formula weight is called mole.

The atomic mass of an element expressed in grams is called gram atom or simply mole. The molecular mass of a substance expressed in grams is called gram molecular mass or gram mole or simply a mole. The ionic mass of an ion expressed in gram is called gram ion or mole of the ion.

The number of atoms, molecules or ions present in one gram atoms, one gram molecule or one gram ion respectively is called **Avogdaro's number**. It is denoted by N_A and has the value 6.022×10^{23}.

ACTIVITY AND ACTIVITY COEFFICIENT:

In order to describe the effect of ionic strength on equilibria in quantitative terms, concentration is expressed in terms of activity. The effective concentration of ions of an electrolyte is called activity of the ion.

$$a_i = C_i f_i$$

a_i is the activity of ion, C_i is the concentration of ion and f_i is called its activity coefficient. The concentration is usually expressed as molarity and activity has the same units as concentration. Activity coefficient is dimensionless and in dilute solutions with 10^{-4} m concentration the activity coefficient of a simple electrolyte is unity. As the concentration of an electrolyte increases, the activity coefficient generally decreases and activity becomes less than concentration.

For dissociation of acetic acid, we write:

$$CH_3COOCH + H_2O \rightleftharpoons CH_3COO^- + H_3\overset{+}{O}$$

$$K_a = \frac{[H_3\overset{+}{O}]\,[CH_3COO^-]}{[CH_3COOH]} \quad \text{(expressed as molar concentration)}$$

$$K_a = \frac{a_{H_3O^+} \cdot a_{CH_3COO^-}}{a_{CH_3COOH}}$$

$$= \frac{[H_3\overset{+}{O}]\,[CH_3COO^-]}{[CH_3COOH]} \times \frac{f_{CH_3COO^-} \times f_{H_3O^-}}{f_{CH_3COOH}}$$

It is obvious that activity coefficient is a function of the total electrolyte concentration of the solution. In 1923, Debye and Hickel derived a theoretical expression for calculating activity coefficients. The equation known as Debye-Hickel equation, is:

$$-\log f_i = \frac{0.51\, Z_i^2 \sqrt{\mu}}{1 + 0.33\, \alpha_i \sqrt{\mu}}$$

0.51 and 0.33 are constants for water at 25°C

α_i is the ion size parameter

μ = ionic strength

Z_i = ionic charge

For practical purposes the equation is simplified as:

$$-\log f_i = \frac{0.51\, Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

Problem:

Calculate the ionic strength of a solution of 0.30 M NaCl and 0.20 M Na_2SO_4.

Solutions:

$$\mu(\text{ionic strength}) = \frac{C_{Na^+} . Z^2_{Na^+} + C_{Cl^-} . Z^2_{Cl^-} + C_{SO_4^{2-}} . Z^2_{SO_4^{2-}}}{2}$$

(C = Concentration of ions; Z = charge on ions)

$$= \frac{(1 \times 0.30 + 2 + 0.20) \times 1^2 + 0.30 \times 1^2 + 0.20 \times 2^2}{2}$$

$$= 0.90$$

Problem:

Calculate the activity coefficients and activities for K+ and SO_4^{2-} in a 0.0020 M solution of potassium sulphate.

Solution:

$$\mu = \frac{C_{K^+} . Z^2_{K^+} + C_{SO_4^{2-}} . Z^2_{SO_4^{2-}}}{2}$$

$[K^+] = 0.0040\ M \quad [SO_4^{2-}] = 0.0020\ M$

Charge on $\overset{+}{K}_{(Z)} = 1$ Charge on SO_4^{2-} $(Z) = 2$

$$\mu = \frac{0.0040 \times 1^2 + 0.0020 \times 2^2}{2} = 0.00604$$

$$-\log f K^+ = \frac{0.51\, Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

$$= \frac{0.51 \times 1^2 \sqrt{0.00604}}{1 + \sqrt{0.00604}} = 0.037$$

$$f K^+ = 10^{-0.037} = 10^{-1} \times 10^{0.963} = 0.918$$

$$a_{K^+} = 0.918 \times 0.0020\ M = 0.001836$$

(activity)

$$-\log SO_4^{2-} = \frac{0.51 \times 2^2 \sqrt{0.0060}}{1 + \sqrt{0.0060}} = 0.147$$

$$f\, SO_4^{2-} = 10^{-0.147} = 10^{-1} \times 10^{0.853} \doteq 0.713$$

(activity coefficient)

$$a\, SO_4^{2-} = f_i(C_i) = 0.713 \times 0.002\ M = 0.001426$$

(activity) (activity coefficient × concentration)

General Principles about Activity and Activity Coefficient:

(1) The activity coefficient values become less accurate with increase in concentration of solution.

(2) The calculated activity coefficient values of ions in mixed electrolyte solution is less accurate than the single electrolyte solution.

(3) Activity coefficients of non-electrolytes are unity upto 0.1 M concentration.

(4) The activity coefficient of a given ion describes its effective behaviour in all equilibria in which it participates.

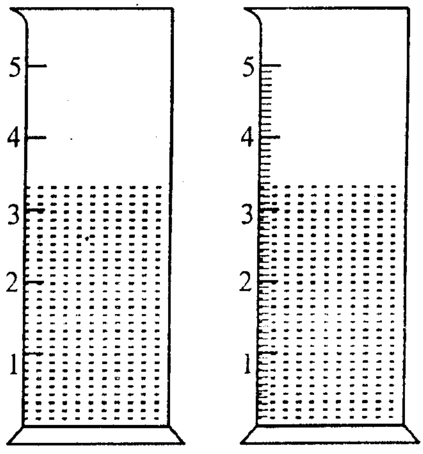
(5) The activity coefficients of ions of the same charge are approximately equal.

(6) The activity coefficient is independent of the nature of the electrolyte and dependent only upon the ionic strength in a fairly dilute solution.

SIGNIFICANT FIGURES:

Consider a volume of solution measured with two different graduated cylinders. In cylinder 'a' reading may be to an accuracy of 3.4 mL (slightly less than 3.5). In cylinder 'b' reading may be taken upto 3.45 mL (volume between 3.4 – 3.5 mL).

When values are reported with the proper number of significant (figures which matter) we get quality of the measurement. In cylinder 'a' the reading has uncertainity of ± 0.1 mL and lies between 3.3 and 3.5 mL. According to the measurement in cylinder 'b' the uncertainity is ± 0.01 mL and the volume is between 3.44 and 3.46 mL.



(a) (b)

The number of digits necessary to express results of a measurement with the measured precision is called significant figure. Since there may be uncertainity (imprecision) in any measurement, the number of significant figures includes all the digits that are known plus the first uncertain one.

Example:

List the proper number of significant figures in the following numbers.

0.234, 95.6, 500.0, 0.0560, 1400, 0.06318

Solution:

0.234	Three significant figures
95.6	Three significant figures
500.0	Four significant figures
0.0560	Three significant figures
0.06318 or 63.18×10^{-3}	Four significant figures

Rounding off Data:

(1) If last digit is 5 the data is rounded off to even number

8.65 = 8.6
8.75 = 8.8
8.55 = 8.6

(2) If the last figure is less than 5 the number is rounded to the value prior to the last figure

8.63 = 8.6
1.064 = 1.06

(3) If the last figure is greater than 5, number is rounded up to the next higher digit.

6.37 = 6.4
5.008 = 4.01

Addition and Subtraction:

The answer of an addition or subtraction is known to the same number of units as the number in the least significant unit.

12.2	Three significant figures
0.3652	Four significant figures
1.04	Three significant figures
13.6052	

The total 13.6052 is rounded off to 13.6 with three (least) significant figures.

Example:

Calculate the formula weight of Ag_2CrO_4 from following atomic weights.

Ag	107.87
Ag	107.87
Cr	51.996
O	15.9994
O	15.9994
O	15.9994
O	15.9994
	331.8156

Molecular weight of Ag_2CrO_4 = 331.82
(Five significant figures which is the least of all figures)

Multiplication and Division:

The answer is expressed in least significant figure:

$$\frac{40.1 \times 0.1633}{204.228} = 0.0320638208$$

$$= 0.0321 \text{ or } 3.21 \times 10^{-2}$$

(Three significant figures which is the least of all significant figures)

Example:

Compute the answer to:

$$\frac{21.6 \times 0.317}{4.10} + 16.037$$

$$= 1.67004 + 16.037$$

$$= 1.67 + 16.037$$

$$= 17.707 = 17.7 \qquad \text{(Three significant figures)}$$

Logarithm:

In changing from logarithms to antilogarithms and vice-versa, the number being operated on and the logarithm mantissa have the same number of significant figures. All zeros are significant.

Example:

Calculate pH of 2.0×10^{-3} M solution of HCl

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{H}^+ = 2.0 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log 2.0 \times 10^{-3}$$

$$= -(-3 + 0.30) = 2.70$$

CONCEPTS OF MEAN AND MEDIAN:

Mean is the arithmetic mean or average ($\bar{x}$) of all analytical values

$$\bar{x} = \frac{\sum_{i=1}^{N} X_i}{N}$$

The symbols $\Sigma_{x=i}$ means addition of all values, x_i for the replicates.

The median of a set of data is the middle value of data arranged in increasing or decreasing order.

Example:

Calculate the mean and median for the data:

19.4, 19.5, 19.6, 19.8, 20.1 and 20.3 ppm.

$$\text{Mean, } \bar{x} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6}$$

$$= 19.78 \approx 19.8 \text{ ppm.}$$

$$\text{Median} = 19.4, 19.5, 19.6 \mid \qquad \mid 19.8, 20.1, 20.3$$

$$= \frac{19.6 + 19.8}{2} = 19.7$$

Ideally, the mean and median are identical. Frequently they are not, particularly when the number of measurements in a set is small.

ACCURACY:

Accuracy indicates the closeness or nearness of a measurement to its true or accepted value and is expressed by the error. Accuracy measures agreement between a result and its true value.

The difference between the true result and the measured value is expressed as error. The actual difference between the true result and the measured value is called absolute error.

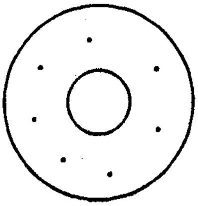
Relative error may be computed and is expressed as a percentage of measured value or in parts per thousand.

Gross error is that which occurs occasionally. Splitting of solutions, wrong scale of instrument, wrong recording, arithmetic mistake, use of reverse of sign are examples of gross erorr.

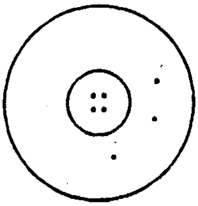
PRECISION:

Precision describes the agreement among several results measured in the same way. It also indicates the variability in results.

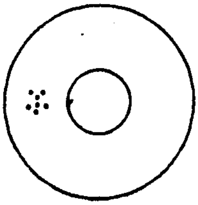
If values are expressed as dots, following may be the possibilities.



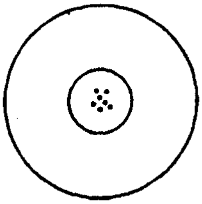
Low accuracy
Low precision



High accuracy
Low precision



Low accuracy
High precision



High accuracy
High precision

STANDARD DEVIATION:

Each set of analytical results should be accompanied by an indication of the precision of analysis. This can be expressed in terms of standard deviation.

For finite number of set of data the standard deviation, S is given by:

$$S = \sqrt{\frac{\Sigma(x_i)^2 - \Sigma(x_i)^{2/N}}{N-1}}$$

x_i = individual measurement
N = No. of measurements

Standard deviation for infinite number of data more than 30, is calculated as:

$$S = \frac{\sqrt{\Sigma x_i - \mu^2}}{N}$$

x_i = individual measurements
μ = mean of infinite number of measurements

Standard deviation of mean $= \dfrac{S}{\sqrt{N}}$

Standard deviation can also be calculated as:

$$S = \frac{\sqrt{\Sigma(x_i - \bar{x})^2}}{N - 1}$$

x_i = individual measurement

$\bar{x}$ = mean value of all measurements

Problem:

Calculate standard deviation of readings:

15.67, 15.69, 16.03

Solution:

$$\Sigma x_i = 15.67 + 15.69 + 16.03 = 47.39$$

$$\Sigma x_i^2 = 245.55 + 246.18 + 256.96 = 748.69$$

$$S = \sqrt{\frac{\Sigma\, 748.6 - (47.39)^{2/3}}{3 - 1}} = \pm 0.21$$

Problem:

The following replicate weighings were obtained:

29.8 mg, 30.2 mg, 28.6 mg, 29.7 mg

Calculate standard deviation of the mean.

Solution:

x_i	$x_i - \bar{x}$	$(x_i - x)^2$
29.8	0.2	0.04
30.2	0.6	0.36
28.6	1.0	1.00
29.7	0.10	0.01
Σ118.3	Σ1.9	Σ1.41

$$\bar{x} = \frac{118.3}{4} = 29.6$$

As per simple formula:

$$S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N - 1}} = \sqrt{\frac{\Sigma\, 1.41}{4 - 1}}$$

$$= 0.69 \text{ mg} = \pm 0.69$$

$$S(\text{mean}) = \frac{S}{\sqrt{N}} = \frac{0.69}{\sqrt{4}} = 0.34$$

Relative Standard Deviation or Coefficient of Variation $= \dfrac{S}{\bar{x}} \times 100 = \%$

So coefficient of variation or relative standard deviation of the above data would be:

$$\text{Coefficient of variation} = \frac{S}{\bar{x}} \times 100$$

$$= \frac{0.69}{29.6} \times 100 = 2.3\ \%$$

$$\textbf{Coefficient of relative variation} = \frac{\text{Standard deviation of mean}}{\text{Average value}} \times 100$$

$$= \frac{0.34}{29.6} \times 100 = 1.1\ \%$$

Exercise:

A student performed quantitative analysis of gasoline and obtained the amount of isooctane as follows:

Determination No.	Percent of isooctane
1	3.83
2	3.97
3	3.94
4	3.88
5	3.94
6	3.90

Calculate the standard deviation.

Solution:

$$\bar{x} = \frac{3.83 + 3.97 + 3.94 + 3.88 + 3.94 + 3.90}{6}$$

$$\bar{x} = 3.91$$

x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
3.83	0.08	0.0064
3.97	0.06	0.0036
3.94	0.03	0.0009
3.88	0.03	0.0009
3.94	0.03	0.0009
3.90	0.01	0.0001

$\Sigma = 0.0128$

$$\text{Standard deviation,}\quad S = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{N - 1}}$$

$$S = \sqrt{\frac{0.0128}{6 - 1}} = \pm\ 0.051$$

Questions

1. What do you understand by the "law of mass action"? How is it applied to the solubility of a sparingly soluble salt?
2. Discuss the use of common ion effect in analytical chemistry.
3. Define solubility product. Discuss the relationship involved to get K.
4. Write notes on:
   (a) Co-precipitation.
   (b) Fractional precipitation.
   (c) Ionization of water.
   (d) Theory of indicators.
5. What do you understand by the term "Hydrogen ion concentration" or pH? How is it determined for a certain solution? Define negative pH.
6. What are buffers? Discuss the applications of buffers.
7. A solution is 0.10 M in Cl^- and 0.10 M in CrO_4^{2-}. If solid $AgNO_3$ is gradually added to this solution, which will precipitate first, AgCl or Ag_2Cl_4? Assume that the addition causes no change in volume. For AgCl, $K_S = 1.7 \times 10^{-10}$; for Ag_2CrO_4, $K_S = 1.9 \times 10^{-12}$.

   [Ans: AgCl]
8. What must be the hydronium ion concentration of a solution that is 0.050 M in Ni^{2+} to prevent the precipitation of NiS when the solution is saturated with H_2S? The K_S of NiS is 3×10^{-21}.

   [Ans: $[H^+] = 0.04$ M]
9. A solution containing Mn^{2+} and Cd^{2+} ions in 0.2 M HCl is saturated with H_2S. Calculate the concentration of two ions at equilibrium.

   [Ans: $[Cd^{2+}] = 3.1 \times 10^{-9}$ M.
   $[Mn^{2+}] = 3.0 \times 10^{3}$ M.]
10. The solubility of $Mg(OH)_2$ is 0.0009 g per 100 ml. at 18°C. Calculate the K_S value.

    [Ans: 13.5×10^{-12}]
11. What are $[H^+]$ and $[OH^-]$ in a 0.0050 M solution of NaOH.
12. What do you understand by:
    mean, median, accuracy, precision, significant figures.
13. (a) What is activity and activity coefficient? How are these correlated with concentration?
    (b) Under what conditions do you expect the value of activity coefficient as unity?
    (c) Enumerate general principals of activity and activity coefficient.

14. What is standard deviation, standard deviation of the mean relative standard deviation? How would you proceed to calculate these values?

15. **Give the correct answer:**

(i) Guldberg and Waage stated:

(a) acid-base equilibrium (b) periodic law

(c) rule of maximum of multiplicity

(d) law of mass action

(Ans: d)

(ii) Purification of common salt by passing dry HCl gas is based on:

(a) solubility product principle (b) ionization

(c) co-precipitation (d) common ion effect

(Ans: d)

(iii) NH_4Cl is used in salt analysis because of:

(a) solubility in water (b) volatility

(c) common ion effect (d) ionization solution

(Ans: c)

(iv) HCl is used in Group II salt analysis because of:

(a) common ion effect (b) solubility in water

(c) ionization in solution (d) being acid

(Ans: a)

(v) Co-precipitation may be due to one of the following:

(a) occlusion (b) common ion effect

(c) high solubility product (d) absorption

(Ans: a)

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8

TYPES OF CHEMICAL REACTIONS

A large number of different types of chemical reactions occur which can be distinguished from one another. Although some of these reactions are interrelated but they may be classified on the following basis:

(a) Reactions among similar atoms and molecules.

(b) Reactions among different kinds of atoms and molecules.

(c) Miscellaneous reactions.

Let us discuss various chemical reactions under the same classification.

(a) Reactions Among Similar Atoms and Molecules:

1. **Association:** In such reactions two or more molecules combine together to form large aggregates There is no change in chemical characteristics of the substance as a result of association. For example, water is an associated liquid in which H_2O molecules associate to form $(H_2O)_x$ linked through hydrogen bonding. Due to this reason water is a liquid but H_2S is not because the later molecule does not associate.

2. **Dissociation:** This process involves degradation of the molecules. Dissociation processes are of two types:

(i) Thermal dissociation (ii) Ionic dissociation in solution

(i) In **thermal dissociation,** the substance decomposes on heating but the products recombine on cooling. For example, ammonium chloride on heating dissociates into ammonia and HCl which recombine on cooling to form NH_4Cl.

$$NH_4Cl \underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftharpoons}} NH_3 + HCl$$

Similarly, PCl_5 dissociates reversibly to PCl_3 and Cl_2.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Thus dissociation is a reversible process in which the dissociated substance and the dissociated products are present in a state of equilibrium.

(ii) **Ionic dissociation** represents a process in which a substance breaks up into cations and anions in solution. The two ions recombine on removing the solvent.

$$NaCl \underset{Dry}{\overset{Water}{\rightleftharpoons}} NH^+ + Cl^-$$

3. **Decomposition:** In this reaction, the molecule of a substance breaks up into two or more molecules, irreversibly. For example:

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

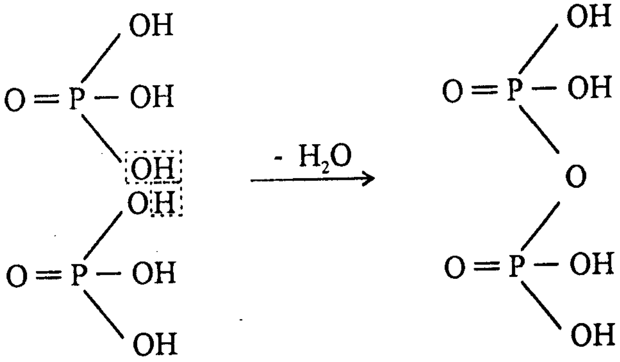
$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

4. **Disproportionation:** When a compound undergoes simultaneously the oxidation and reduction reactions due to its variable valency, the process is called disproportionation. Thus, a compound breaks up into two new substances, one containing element in the lower valency and the other having higher valency.

$$\overset{I}{Cu_2Cl_2} \longrightarrow \overset{II}{CuCl_2} + Cu$$

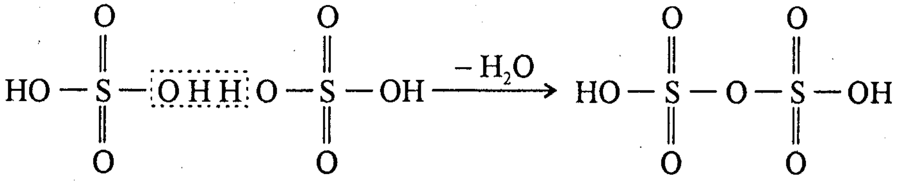
$$3\overset{I}{AuCl} \longrightarrow \overset{III}{AuCl_3} + 2Au$$

5. **Condensation:** This type of reaction represents the formation of a more complicated molecule by the combination of two or more simple molecules with the elimination of water. The combination of two phosphoric acid molecules to form pyrophosphoric acid with the elimination of one molecule of water is a typical example of this type.



Orthophosphoric acid Pyrophosphoric acid

Similarly, two molecules of sulphuric acid condense to form pyrosulphuric acid.



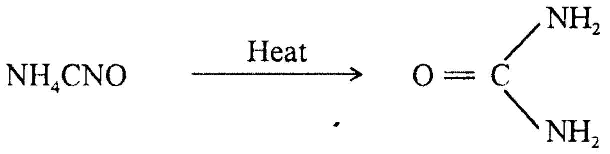
$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\boxed{OH\;H}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \xrightarrow{-H_2O} HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

Pyrosulphuric acid

6. Polymerisation: This process is said to take place when a large number of small molecules of the same kind combine to form a large macromolecular product or polymer. Thus ethylene, C_2H_4, polymerises to polyethylene polymer, $(-CH_2-CH_2-)_n$. Similarly, sulphur trioxide forms a trimer $(SO_3)_3$ and phosphorus pentoxide gives a dimer $(P_2O_5)_2$.

7. Depolymerisation: A polymer or a complex molecule breaks up to give two or more molecules of the same type. Thus N_2O_4, a dimer, breaks up to give two molecules of NO_2.

8. Isomeric Rearrangement: In isomeric rearrangement the atoms in the molecule of a substance undergo rearrangement producing a new substance of same composition but having different properties. The conversion of ammonium cyanate, NH_4CNO into urea, $CO(NH_2)_2$, by heat is a typical example of isomeric change.



Urea

(b) Reactions Among Different Kinds of Atoms and Molecules:

1. Synthesis: The combination of atoms or molecules to produce a new compound is known as synthesis or synthetic reaction. Formation of FeS on heating iron and sulphur is an example of a synthetic reaction.

$$Fe + S \longrightarrow FeS$$

$$CaO + CO_2 \longrightarrow CaCO_3$$

2. Substitution or Simple Displacement: In this process one element displaces or substitutes another element from a compound.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$

3. Double Decomposition: This process involves the mutual displacement of atoms from reacting species.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

4. **Neutralization:** Acids and bases react with one another to form salts and the solvent molecule is given out. Thus neutralization of NaOH with HCl in water as solvent can be represented as:

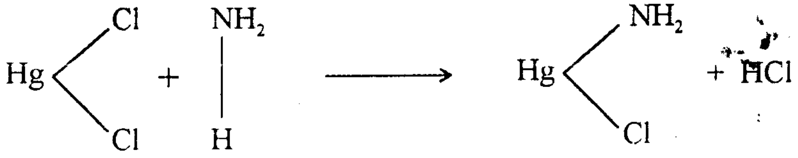
$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{(solvent)}}{H_2O}$$

In liquid ammonia as a solvent, NH_4Cl acts as an acid and $NaNH_2$, a base and both react to form NaCl (a salt) and liberate NH_4 (solvent molecules). This type of reaction is called ammonolysis as compared to reactions in water, called hydrolysis.

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \xrightarrow{\text{Liquid } NH_3} NaCl + 2NH_3$$

5. **Solvolysis:** This reaction is generally defined as a process in which an ion reacts with the solvent to form the products containing cations and anions of solvent.

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$$



(c) **Miscellaneous Reactions:**

Large number of chemical reactions cannot be classified and may be discussed separately. Some of them are of great importance in chemistry and discussed below:

1. **Addition Reactions:** Such reactions involve the addition of atoms or molecules to unsaturated molecules containing double or triple bonds. This addition of H_2 to ethylene to form ethane is an example of such type of reactions.

2. **Pyrolysis or Cracking:** In this process, large molecules decompose to form small molecules. The typical example is the cracking of higher petroleum hydrocarbons to lower hydrocarbons in the formation of gasoline.

3. **Chain Reactions:** These reactions include such processes in which the products of the reactions initiate and carry the reaction further. For example, the reaction between chlorine and hydrogen molecules takes place in the presence of sunlight giving rise to the following chain reaction:

$$Cl_2 \xrightarrow{\text{Light}} 2Cl$$

$$Cl + H_2 \longrightarrow HCl + H$$

$$H + Cl_2 \xrightarrow{\hspace{2em}} HCl + Cl$$

$$Cl + H_2 \xrightarrow{\hspace{2em}} HCl + H$$

4. **Catalytic Reactions:** Such types of reactions take place in the presence of catalysts which remain unchanged at the end of the reaction. Some reactions do not proceed smoothly or are too slow in the absence of catalysts. However, catalysts or catalytic agents can accelerate or retard the rate of chemical reactions.

Synthesis of ammonia from N_2 and H_2 is carried out in the presence of tungsten or iron catalyst.

$$N_2 + 3H_2 \xrightarrow{\text{W or Fe}} 2NH_3$$

Sulphur dioxide can only be converted to SO_3 in the presence of Pt or V_2O_5 catalyst.

$$2SO_2 + O_2 \xrightarrow[V_2O_5]{\text{Pt or}} 2SO_3$$

5. **Endothermic and Exothermic Reactions:** *Reactions accompanied by the absorption of heat are known as endothermic reactions.* Reactions of this type require a constant supply of energy from outside to let them go smoothly.

$$H_2 + I_2 \xrightarrow{\hspace{2em}} 2HI\ (-\ 5\ \text{kJ/mol})$$

Reactions accompanied by the evolution of heat are said to be exothermic reactions. Thus, burning of magnesium or carbon in air is an exothermic reaction.

$$2Mg + O_2 \xrightarrow{\hspace{2em}} 2MgO\ \ (+619\ \text{kJ/mole})$$

$$C + O_2 \xrightarrow{\hspace{2em}} CO\ (+405\ \text{kJ/mole})$$

6. **Oxidation and Reduction Reactions:** The reactions involving electron transfers are called oxidation-reduction or redox reactions. Every oxidation process is accompanied by the reduction or vice versa. ***The loss of electrons or gain of positive charge is called oxidation.***

$$Fe^{2+} - e \xrightarrow{\text{Oxidation}} Fe^{3+}$$

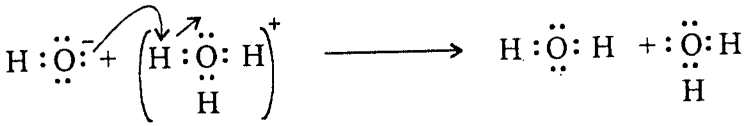
The process of gaining electrons or loss of positive charge is called reduction.

$$Cl + e \xrightarrow{\text{Reduction}} Cl^-.$$

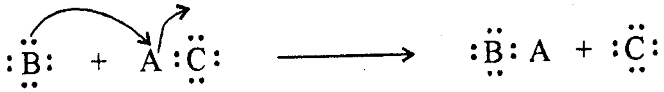
7. **Electrophilic and Nucleophilic Reactions:** Both the electrophilic and nucleophilic terms are used with reactions of compounds containing covalent bonds. Lewis acids (electron pair acceptors) are generally referred to electrophilic (electron-liking) reagents because they are attracted to the electron rich molecules. Lewis bases (electron pair donors) behave as nucleophilic (nucleus-liking) reagents because they attack the electron poor region of the acid molecules. Let us consider the reaction:

$$H_3N: + BF_3 \longrightarrow H_3N : BF_3 \text{ or } H_3N \longrightarrow BF_3$$

This reaction takes place by the nucleophilic attack of ammonia on boron trifluoride or electrophilic attack of BF_3 on ammonia. The reaction of H_3O^+ with OH^- represents a nucleophilic displacement reaction. This reaction represents the nucleophilic displacement of water by OH^- on hydrogen.

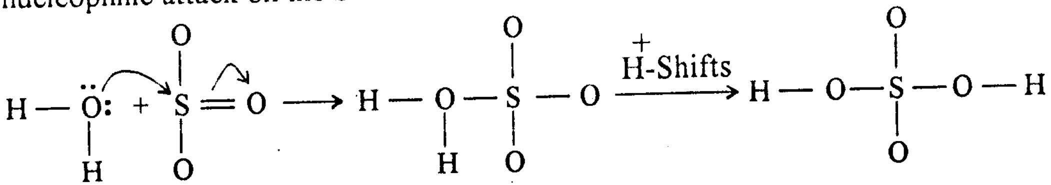


The nucleophilic displacement reaction can be represented in the general form as:



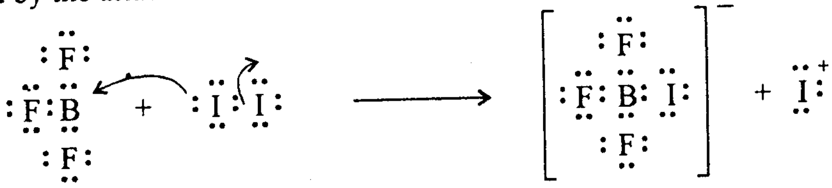
The nucleophilic attack on double bond would be.

The reaction of water on sulphur trioxide is an example of the nucleophilic attack on the S = O bond.

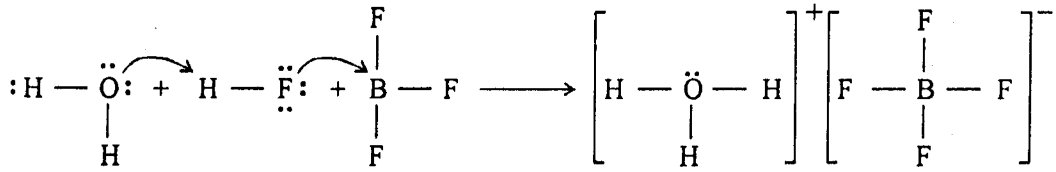


The electrophilic displacement is generally represented as:

A typical electrophilic displacement occurs when the iodonium ion (I^+) is prepared by the attack of molecular iodine on BF_3.



A *concerted displacement* which is also called *push-pull reaction* sometimes occurs. We will consider the example of a reaction of aqueous HF with boron trifluoride.



$$:\mathrm{H}-\underset{\mathrm{H}}{\underset{|}{\ddot{\mathrm{O}}:}} + \mathrm{H}-\underset{\cdot\cdot}{\ddot{\mathrm{F}}:} + \overset{\mathrm{F}}{\overset{|}{\underset{\mathrm{F}}{\underset{|}{\mathrm{B}}}}}-\mathrm{F} \longrightarrow \left[\mathrm{H}-\underset{\mathrm{H}}{\underset{|}{\ddot{\mathrm{O}}}}-\mathrm{H}\right]^{+}\left[\mathrm{F}-\overset{\mathrm{F}}{\overset{|}{\underset{\mathrm{F}}{\underset{|}{\mathrm{B}}}}}-\mathrm{F}\right]^{-}$$

The reactions described above involve the shift of electrons in pairs. But certain atoms or group of atoms attack only through unpaired electrons. Since the atoms or molecules bearing unpaired electrons are called *radicals*, the displacements involving breaking up of electron pairs are called *radical displacements i.e.*,

$$:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\dot{} + \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \longrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:\mathrm{H} + :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\dot{}$$

The terms 'electrophilic', 'nucleophilic', 'concerted', and 'radical displacement' are extensively used by organic chemists but it should be noted over here that such terms are now conveniently used to describe inorganic reaction mechanisms also. However, further discussion is beyond the scope of this book.

Questions

1. How are the chemical reactions classified? Describe some important chemical reactions giving examples.

Write notes on:

(a) Condensation reactions.

(b) Polymerization.

(c) Catalytic reactions.

Differentiate between the following set of chemical reactions. Give examples to support your answer:

(a) Polymerisation and Condensation.

(b) Association and Polymerisation.

(c) Ammonolysis and Hydrolysis.

(d) Endothermic and Exothermic.

(e) Dissociation and Decomposition.

4. Write an essay on different types of chemical reactions.

5. Discuss the mechanisms of the following reactions:

(a) $H^{-}: + H_2O \longrightarrow H_2 + OH^{-}$

(b) $I^{-} + HgCl^{+} \longrightarrow HgI^{+} + Cl^{-}$

(c) $FeCl_3 + Br_2 \longrightarrow FeCl_2Br^{-} + Br^{+}$

(d) $Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + \cdot\underset{\cdot\cdot}{\ddot{O}}:H$

6. **Give the correct answer:**

(i) Identify the disproportion reaction:

(a) $KClO_3 \longrightarrow 2KCl + 3O_2$

(b) $2P_2O_5 \longrightarrow (P_2O_5)_2$

(c) $NH_4Cl \rightleftharpoons NH_3 + HCl$

(d) $Cu_2Cl_2 \longrightarrow CuCl_2 + Cu$

(**Ans**: d)

(ii) Identify the double decomposition reaction:

(a) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

(b) $HCl + NaOH \longrightarrow NaCl + H_2O$

(c) $NH_4Cl + NaNH_2 \longrightarrow NaCl + 2NH_3$

(d) $Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$

(**Ans**: a)

(iii) Identify the endothermic reaction:

(a) $H_2 + I_2 \longrightarrow 2HI$

(b) $2Mg + O_2 \longrightarrow 2MgO$

(c) $2C + O_2 \longrightarrow 2CO$

(d) $2SO_2 + O_2 \longrightarrow 2SO_3$

(**Ans**: a)

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9

HYDROGEN AND HYDRIDES

Hydrogen is the first member of the Periodic Table. It was first recognized by Cavendish in 1766. Lavoisier named the gas hydrogen (water producer). Hydrogen stands next to oxygen in abundance in nature.

Hydrogen atom consists of one proton and one electron in 1*s* orbital. The ionization potential of 1*s* electron is very high (13.54 ev). Hydrogen atom is non-metallic element and would form hydride ion, H^-, by acquiring one electron. Hydrogen is a reactive element and forms more compounds than any of the other elements, including carbon.

With electronic configuration $1s^1$, hydrogen almost always forms covalent bonds. But loss of electrons leaves the proton, H^+. The H^+ exerts a strong positive field and is not able to exist alone, especially in presence of polarizable molecules. Thus in water, H^+ becomes solvated as H_3O^+ and in ammonia, it forms NH_4^+.

ORTHO AND PARA-HYDROGEN:

The hydrogen atoms combine to form the very stable molecule, with an energy drop of 426 kJ per mole.

$$2H\,(1s^1) \longrightarrow H_2\,(\sigma\ 1s^2)$$

Heisenberg showed that H_2 molecule can have two types of nuclear spins. This indicates the presence of two forms or isomers of hydrogen. Like electronic spins the protons or neutrons (or both) in the nucleus also have directed spins.

The hydrogen molecule H_2, has two protons which may be spinning in the same direction (both clockwise or both anti-clockwise) or in opposite directions (one clockwise, the other anti-clockwise) as shown in Figure 9.1.

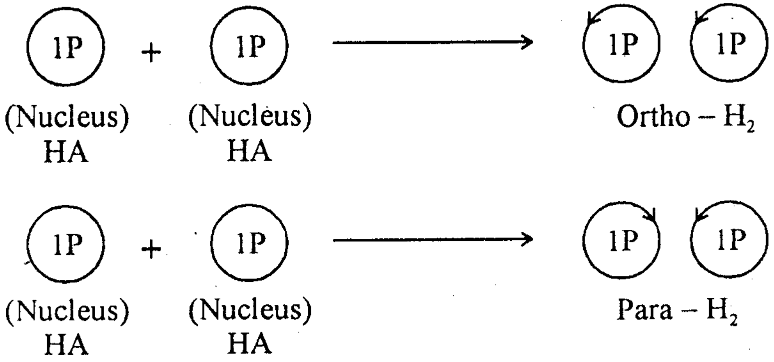


Fig. 9.1. Ortho and Para-hydrogen.

The hydrogen molecule having parallel nuclear spins is called ortho-hydrogen and H_2 molecule which possesses anti-parallel or opposed nuclear spins is called ***para-hydrogen***. The physical properties of ortho-hydrogen are different from para-hydrogen. Ordinary hydrogen gas at room temperature is found to contain ortho and para-hydrogen in the ratio of 3 :1.

Inter conversion of ortho and para-hydrogen:

At very low temperature the para form (with opposed nuclear spins) is the more stable. With increase in temperature, the ratio of ortho-hydrogen increases and mixture becomes richer in ortho-H_2. The concentration of ortho-hydrogen beyond its limiting ratio 3 : 1 (75%) is impossible. The mechanism of conversion, from ortho to para-hydrogen which is an exothermic process, involves dissociation and recombination during which the nuclear spins recouple in parallel or anti-parallel manner.

The para-hydrogen of 99.8% purity is obtained in presence of activated charcoal at 20°K (– 253°C). At absolute zero, hydrogen exists as 100% para-hydrogen.

TABLE 9.1

Proportions of Ortho-hydrogen and Para-hydrogen

Temperature °K	% of Ortho-hydrogen	% of Para-hydrogen
20	0.2	99.8
50	23.1	76.9
100	61.5	38.5
200	74.0	26.0
273	74.87	25.13
298	74.9	25.1
Higher temperature	75.0	25.0

Although ortho-para ratio is temperature dependent, sudden temperature changes will not cause a rapid change in absence of a catalyst. Methods which are capable of breaking and remaking the H — H bonds offer a path to equilibrium. The passage of electric discharge, addition of atomic hydrogen or catalysts are able to do so. The proportions of ortho and para-hydrogen present at equilibrium is found to be temperature dependent as shown in Table 9.1.

Physical Properties:

The most interesting physical property of H_2 is its specific heat, which is lower than expected from the Kinetic Theory of Gases. This low value is depicted by the existence of two modifications (isomers) of hydrogen known as o- and p-hydrogen. Both ortho and para-hydrogen have identical chemical properties but show difference in physical properties such as specific heat, melting and boiling points etc., (See Table 9.2).

TABLE 9.2

Physical Properties of Ortho and Para-Hydrogen

Property	Ortho-hydrogen	Para-hydrogen	Equilibrium Mixture
M.P. (°K)	13.93	13.88	13.92
B.P. (°K)	20.41	20.29	20.38
Specific heat at 298°K (25°C)	1.838	2.186	1.925

The magnetic moment of the molecule of para-hydrogen is zero because the anti-parallel spins counterbalance each other. Since the nuclear spins are parallel in ortho-hydrogen, they add to each others effect. As a result, the molecule of ortho-hydrogen has twice the value of magnetic moment as that of a proton. However, the magnetic moment due to nucleus is much less than due to electrons.

Thermal conductivities of ortho- and para-hydrogen are also different.

The rate of conversion of para-hydrogen to the equilibrium mixture is taken as a measure of the concentration of free hydrogen atoms in a gas. Thus the concentration of hydrogen atoms in photochemical reactions is measured in this way.

The evaporation of liquid hydrogen is considered to be due to the conversion of $o - H_2$ to $p - H_2$ which is an exothermic reaction and releases sufficient energy to evaporate 64 % of the original liquid.

Atomic Hydrogen:

At high temperatures the hydrogen molecule dissociates into atoms:

$$H_2 \overset{5000°C}{\rightleftharpoons} 2H$$

Hydrogen consisting of separate atoms and not the H_2 molecules is called monatomic hydrogen. Atomic hydrogen can also be produced by passing electric discharge at low pressure. Total recombination of hydrogen atoms does not occur on collision because during this process 103 Kcal per mole of energy is liberated which causes immediate dissociation of some molecules. Thus a third body is necessary to absorb the excess of energy.

Hydrogen atoms are much more reactive than H_2 molecules. It reduces many metal oxides at ordinary temperatures and directly combines with S, N, and As to form hydrides.

$$2H + S \longrightarrow H_2S$$
$$2H + O_2 \longrightarrow H_2O_2$$
$$3H + As \longrightarrow AsH_3$$
$$8H + BaSO_4 \longrightarrow BaS + 4H_2O$$

Atomic hydrogen reduces many metals to lower oxidation states.

$$H + FeCl_3 \longrightarrow FeCl_2 + HCl$$

Usefulness:

Reunion of atomic hydrogen to form molecular hydrogen liberates a large amount of heat energy. Hydrogen torches are based on this principle. A jet of hydrogen gas on passing through an electric arc (struck between two tungsten electrodes) is decomposed into hydrogen atoms. The atomic hydrogen thus produced recombines at a short distance from the arc, liberating heat and producing a very hot flame. Thus high temperature of the flame is not due to the combustion of hydrogen but to the recombination of hydrogen atoms into molecules.

ISOTOPES OF HYDROGEN:

Three isotopes of hydrogen have been recognized:

1.	Protium or ordinary hydrogen	${}_1H^1$	or	P
2.	Deuterium or heavy hydrogen	${}_1H^2$	or	D
3.	Tritium	${}_1H^3$	or	T

All these isotopes have the same atomic number (protons) but differ in their atomic weights. Naturally occurring hydrogen contains 0.0156 % deuterium, while tritium is believed to be of the order of 1 part in 10^{17} parts of hydrogen. Tritium is usually formed in the upper atmosphere by nuclear reactions induced by cosmic rays.

(1) PROTIUM OR ORDINARY HYDROGEN:

Ordinary hydrogen is present in the atmosphere in free state. It forms $\frac{1}{9}$th of the weight of water, and is present in petroleum and in all animal and vegetable matter in the combined state.

Preparation:

It can be prepared from its three main sources: water, acids and alkalies.

(i) **From Water:** Hydrogen can be obtained by electrolysis of water or by action of metals.

$$3H_2O + E \xrightarrow{\text{Elect.}} 2H_{2(g)} + O_{2(g)} \quad \text{(decomposition and redox)}$$

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \quad \text{(displacement and redox)}$$

$$Mg + H_2O \longrightarrow MgO + H_2 \quad \text{(displacement and redox)}$$

(ii) **From Acids:** Most of the metals decompose dilute acids to liberate hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

(iii) **From Alkalies:** Zinc, tin and aluminium reacts with alkalies to liberate hydrogen.

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium Zincate}}{Na_2ZnO_2} + H_2$$

Properties:

Hydrogen is a colourless gas and lightest of all elements known. A litre of the gas at N.T.P. weighs 0.0899 gram. It liquefies at –253°C and solidifies at –259°C. Atomic weight of protium is 1.008.

Hydrogen is [illegible] reactive gas and undergoes the following general type reactions:

(i) **Combination with Oxygen:** Hydrogen burns in air or oxygen to give water.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

(ii) **Combination with Other Elements:** Hydrogen directly combines with halogens, nitrogen, sulphur, carbon and certain metals to form compounds called hydrides. These compounds will be discussed subsequently.

$$C + H_2O \xrightarrow{\Delta} CO + H_2 \text{ (water gas)}$$

Hydrogen is used in various chemical industries. Thus, it is used in the hydrogenation of oils for the manufacture of vanaspati ghee, in the manufacture of ammonia (Haber Process) etc.

The oxy-hydrogen flame produces a temperature of 2,800°C.

It is also used (its being lightest) in large quantities for filling airships and balloons.

(2) DEUTERIUM OR HEAVY HYDROGEN:

Deuterium isotope has one proton and a neutron in the nucleus having atomic weight 2.014. It is usually present in the form of D_2O (heavy water; density 1.1059 at 20°C) in ordinary water, H_2O (density 0.9982 at 20°C) in small amounts. Deuterium has B.P. – 249.4°C and M.P. – 254.5°C.

Preparation:

(i) **Electrolysis:** Electrolysis of ordinary water is carried out in presence of sodium hydroxide. As a result, light hydrogen comes off first leaving water more and more concentrated with heavy water. The residual water containing relatively more amounts of D_2O would liberate ***Deuterium***, D_2 at later stages.

On treating heavy water with reactive metals like sodium, deuterium can be obtained.

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$

(ii) **Fractional Distillation** of a mixture of ordinary hydrogen and deuterium separates deuterium from the other isotope.

Ortho and para-deuterium, just like ortho and para-hydrogen also exist but in a ratio 2:1, respectively.

Reactions:

The reactions of D_2 and D_2O are similar to H_2 and H_2O.

Deuterium would combine with nitrogen to form ND_3. Similarly, it reacts with other elements in exactly the same manner as H_2.

$$2D_2 + O_2 \longrightarrow 2D_2O$$

It would also show reducing properties similar to that of H_2.

$$D_2 + 2AgF \longrightarrow 2Ag + 2DF$$

Let us study the chemistry of deuterium oxide D_2O, in order to learn the behaviour of D_2 similar to H_2.

$$D_2O + H_2O \longrightarrow 2HDO$$

$$3D_2O + P_2O_5 \longrightarrow 2D_3PO_4$$

$$D_2O + SO_3 \longrightarrow D_2SO_4$$

$$D_2O + CaC_2 \longrightarrow CaO + D_2C_2 \quad \text{(Deuterated acetylene)}$$

$$6D_2O + Al_2C_3 \longrightarrow 2Al_2O_3 + 3CD_4 \quad \text{(Deuterated methane)}$$

$$3D_2O + Mg_3N_2 \longrightarrow 3MgO + 2ND_3 \quad \text{(Deuterated ammonia)}$$

Just like water of hydration, compounds can also carry heavy water of crystallization as in copper sulphate.

$CuSO_4 . 5H_2O$	$CuSO_4 . 5D_2O$
(Blue)	(Green)

When H_2 and D_2 are mixed at sufficiently high temperature, exchange reaction occurs:

$$H_2 + D_2 \longrightarrow 2HD$$

$$D + H_2 \longrightarrow HD + H$$

$$H + D_2 \longrightarrow HD + D$$

Heavy water D_2O can exchange deuterium with compounds containing labile hydrogen.

$$NH_4^+ + D_2O \rightleftharpoons NH_3D^+ + HDO$$

$$CH_3NH_2 + D_2O \rightleftharpoons CH_3NHD + HDO$$

$$CH_3OH + D_2O \rightleftharpoons CH_3OD + HDO$$

(3) TRITIUM:

Tritium isotope contains one proton and two neutrons making its mass number 3. The atomic weight is 3.016.

It occurs in very minute quantities in the upper atmosphere obtained through nuclear reactions. It is radioactive form of hydrogen and has half-life of 12.5 years.

Preparation:

(i) Rutherford (1934) prepared this isotope of hydrogen by bombarding deuterium on deuterium compounds.

$$_1H^2 + {_1H^2} \longrightarrow {_1H^3} + {_1H^1}$$

(Tritium)

(ii) It can also be prepared by bombarding beryllium with deuterium particles.

$$_4Be^9 + {_1H^2} \longrightarrow 2\,{_2He^4} + {_1H^3}$$

(iii) Tritium can also be obtained by the bombardment of lithium with slow neutrons.

$$_3Li^6 + {_0n^1} \longrightarrow {_2He^4} + {_1H^3}$$

Tritium is absorbed in uranium to separate it from helium.

Tritium is radioactive and decays (β emission) with a half-life of 12.5 years and is used as tracer.

$$_1H^3 \xrightarrow{\beta} {_2He^3}$$

Detection of Hydrogen:

Free hydrogen may be detected by the fact that it burns in air with nearly colourless flame to form water vapours. The hydrogen gas can be separated from other gases by adsorption over finely divided palladium from which it can be regenerated by heating.

Chemically combined hydrogen can be detected by heating the compound with copper (II) oxide. The formation of water vapours indicates the presence of a compound containing hydrogen. Hydrogen can be quantitatively estimated by absorbing the water vapours on a weighed amount of $CaCl_2$ or P_2O_5. From the amount of moisture content, the amount of hydrogen can be estimated.

TYPES OF HYDROGEN COMPOUNDS:

Hydrogen enters into chemical combination with many non-metals to form covalent compounds. The atoms of non-metals and hydrogen contribute one electron each to form a shared electron pair that constitutes the covalent bond.

The ionic compounds of hydrogen are formed by electron transfers to form H^+ or H^- ions.

(1) Compounds of Hydrogen with Non-metals:

Hydrogen combines with all non-metallic elements except the noble gases. Many of such compounds formed are gases or liquids.

The chemistry of these type of derivatives depends upon the nature of element to which hydrogen is attached. The compounds BH_3, SiH_4, NH_3, H_2O and HF belong to this class of compounds formed through electron pair or covalent bonds. Hydrogen molecule (H_2) is a homopolar molecule and forms true covalent bond among two hydrogen atoms. All other molecules of the type H — X possess polar character to some extent. This may be attributed to the difference in electronegativities of H and X. If X is more electronegative than H the charge density will shift more to X and polarity in the molecule would be observed. The possibility of such molecules to behave as polar species along with their covalent character can be explained on the basis of molecular orbital theory. (See Chapter 4).

(2) Formation of Hydrogen Ions: The $1s^1$ electron from hydrogen atom may be lost to give proton or hydrogen ion, H^+. Due to the small size of H^+, it is capable of distorting the electron cloud from the surrounding atoms or solvent molecules. Thus, proton H^+ is not able to exist independently but would associate with other atoms or molecules.

$$H^+ + H_2O \longrightarrow H_3O^+$$
$$H^+ + NH_3 \longrightarrow NH_4^+$$
$$H^+ + CH_3OH \longrightarrow CH_3OH_2^+$$

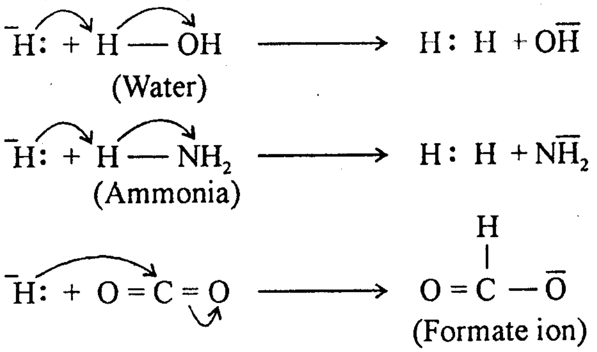
(3) Formation of Hydride Ions: The hydrogen atom can gain one electron to acquire $1s^2$ (helium) configuration and forms hydride ion, H^-. The ion can exist as such and combines with alkali metals and alkaline earth metals. In these metal hydrides the electropositive metal ions and the negative hydride ions H^-, are held together in the crystal lattice by ionic attraction. We shall now discuss the chemistry of the hydrides of metals in detail.

HYDRIDES:

The binary compounds of hydrogen with other elements are called hydrides. Typical examples of hydrides are: NaH, CaH_2, B_2H_6, SiH_4, NH_3, H_2S, H_2O etc. Hydrogen atom is bonded to more electropositive elements in its binary compounds as H^- ion. However, it combines with more electronegative elements through sharing of electron pairs to form covalent bonds. Hydrides can be classified into various groups on the basis of the nature of bonds between hydrogen and the other elements as well as their structures and properties.

Mechanism of Reactions of the Hydride Ion:

The hydride ion, H^-:, is a very strong Lewis base and would react with compounds containing acidic hydrogen to liberate H_2. It should react with Lewis acids. Hydride ion can attack a double bond, acting both as a Lewis base and a reducing agent. The typical reactions of H^-: are:



$$\bar{H}: + H-OH \longrightarrow H:H + \overline{OH}$$

(Water)

$$\bar{H}: + H-NH_2 \longrightarrow H:H + \overline{NH}_2$$

(Ammonia)

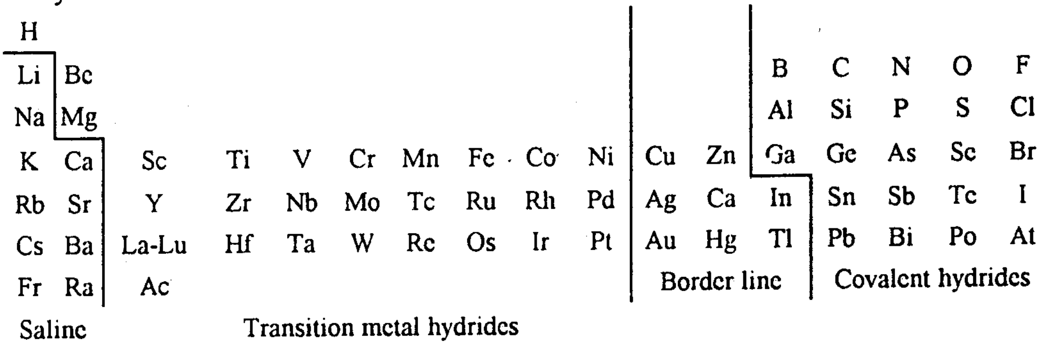
$$\bar{H}: + O=C=O \longrightarrow O=\overset{\overset{\Large H}{|}}{C}-\bar{O}$$

(Formate ion)

The reactions with water and ammonia indicate that hydride ion, H^- is a stronger base than OH^- or NH_2^-. The reaction with CO_2 involves an attack of H^- (Lewis base) on the double bond and attachment of one hydrogen atom to carbon of CO_2 converts the double bond to a single bond with the formation of formate ion.

CLASSIFICATION:

Hydrides may be broadly classified as saline, covalent and metallic. Saline hydrides are formed by alkali and alkaline earth metals and the lanthanides. Elements of A subgroups from Groups III to VII give covalent hydrides. Transition elements form metallic hydrides which do not observe the valency rules and usually lack the stoichiometric composition of normal chemical compounds. Other type of hydrides have also been recognised. The classification of hydrides in terms of the Periodic Table of elements is shown in Figure 9.2.



H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Ca	In	Sn	Sb	Te	I
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac														

Fig. 9.2. A classification of hydrides.

The following types of hydrides have been recognised:

1. **Saline or Salt-Like Hydrides:**

The hydrides of alkali and alkaline earth metals represent this class of hydrides. These hydrides show ionic character in which electropositive metals are bonded to hydrogen present as H^- (hydride ion). Such hydrides are thermally very stable and possess high melting and boiling points. They conduct electricity in the molten state like various metal salts.

2. **Covalent Hydrides:**

The elements of Group III A, IV A, V A, VI A and VII A are capable of forming hydrides in which their atoms are linked to hydrogen through shared pair of electrons or covalent bonds. The elements forming such type of hydrides have low electropositivities or high values of electronegativities.

Such type of hydrides are volatile in nature and are mostly gases or low boiling liquids. They show considerable difference in bond polarities.

3. **Metallic Hydrides:**

The binary compounds of hydrogen with transition metals are called metallic hydrides. Some of the transition metals are inert to the action of hydrogen and would not form true chemical compounds. However, they may occlude hydrogen due to the adsorption of hydrogen (having very small atomic size) in the interstices of the metal lattices and hence referred to interstitial hydrides. The hydrogen atoms sit within the holes created by the metal structures. Thus the interaction of transition metals with hydrogen is not a true chemical process but a physical phenomenon involving simple adsorption of a gas on solid. Such hydrides do not have a definite metal to hydrogen ratio. They can be represented by non-stoichiometric compositions, *i.e.*, $Ti\,H_{1.7}$, $Zr\,H_{1.22}$ and $Ta\,H_{0.78}$, depending upon the physical conditions.

4. **Polymeric Hydrides:**

The hydrides of beryllium and magnesium polymerize through hydrogen bonds and are termed polymeric hydrides. These hydrides have the character intermediate between ionic and covalent hydrides.

5. **Borderline Hydrides:**

These compounds represent relatively unstable hydrides. This class of hydrides appears to have properties intermediate between covalent and metallic hydrides. Hydrides of copper, cadmium, mercury etc., are representative examples of borderline hydrides.

6. **Complex Hydrides:**

The addition of two or more than two hydrides form complex derivatives called complex hydrides. Thus, LiH and AlH_3 would give $LiAlH_4$ and NaH and BH_3 form $NaBH_4$. The complex hydrides are of industrial importance and form a large group of compounds.

Now the chemistry of ionic (saline), metallic, polymeric and covalent hydrides will be discussed in detail.

SALINE OR IONIC HYDRIDES:

When hydrogen combines with strongly electropositive elements the former behaves as a member of halogen family and gains one electron to form hydride ion, H^-. But the formation of H^- is an endothermic process as compared to the formation of halide ion, X^- which involves the exothermic process *e.g.*,

$$\frac{1}{2} H_{2(g)} + e \longrightarrow H^- \qquad (\Delta H = +146 \text{ kJ/mole})$$

$$\frac{1}{2} F_{2(g)} + e \longrightarrow F^- \qquad (\Delta H = -269 \text{ kJ/mole})$$

The formation of H^- is, therefore, an energetically unfavourable process. But in presence of strongly electropositive elements of Group IA and IIA, hydride ion (H^-) may be formed due to the easy availability of valence electrons in alkali and alkaline earth metal atoms to be taken up by hydrogen. The positive and negative ions produced by transfer of electrons from electropositive metal atoms to hydrogen atoms will be highly polar and would be bonded together by the strong electrostatic forces of attraction. Such compounds will, therefore, show high melting and boiling points and crystalline state similar to salts or ionic compounds.

HYDRIDES OF ALKALI METALS:

All alkali metal hydrides have similar properties and other general characteristics. Therefore, they will not be discussed individually. The hydrides of all the alkali metals are known and have general formula MH (M = Li, Na, K, Rb, Cs).

Preparation:

These hydrides can be prepared by the direct combination of metals with hydrogen at high temperature.

$$2Li + H_2 \xrightarrow{600^\circ C} 2LiH$$

$$2Na + H_2 \xrightarrow{300-400^\circ C} 2NaH$$

$$2K + H_2 \xrightarrow{300-400^\circ C} 2KH$$

$$2Rb + H_2 \xrightarrow{700^\circ C} 2RbH$$

$$2Cs + H_2 \xrightarrow{600^\circ C} 2CsH$$

The metals are taken in fine state in order to avoid the formation of a film over metals which causes passivity. Thus sodium metal is dispersed in a hydrocarbon solvent, say kerosene oil, and treated with hydrogen under high pressure.

Potassium hydride may be prepared by passing an electric arc between potassium electrodes in presence of a stream of hydrogen.

Properties:

The alkali metal hydrides are white crystalline solids. They have high melting and boiling points and conduct electricity in molten state like metal salts.

Reactions:

They are chemically reactive compounds which is obvious from the following reactions, the reactivity increases with increasing atomic number.

(i) **Reaction with Water:** All alkali metal hydrides are decomposed rapidly by water liberating hydrogen and reaction is exothermic.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

$$LiH + H_2O \longrightarrow LiOH + H_2$$

(ii) **Thermal Decomposition:** These hydrides are thermally unstable and decompose on heating to liberate hydrogen.

(iii) **Solubility in Organic Solvents:** They are insoluble in organic solvents due to the ionic nature except LiH (it has covalent character) which is soluble in ether and dioxane.

(iv) **Stability to Air and Oxygen:** All the hydrides of alkali metals are unstable in air and react with oxygen. Sodium hydride, for example, in finely divided state would spontaneously ignite due to the heat evolved during hydrolysis.

$$2NaH + O_2 \longrightarrow 2NaOH$$

(v) **Reaction with NH_3:** Sodium hydride and others are insoluble in liquid ammonia but they react with ammonia at higher temperatures to form sodamide etc

$$NaH + NH_3 \longrightarrow NaNH_2 + H_2$$

(vi) **Reaction with Alcohols:** These hydrides react with alcohols to form alcoholates.

$$NaH + ROH \longrightarrow NaOR + H_2$$

(sodium alcoholate)

(vii) **Reaction with Benzaldehyde and Methylacetate:** Benzaldehyde can be condensed with acetic esters in presence of these hydrides.

$$C_6H_5CHO + CH_3COOCH_3 + NaH \longrightarrow C_6H_5CH = CHCOOCH_3 + NaOH + H_2$$

(Methyl cinnamate)

(viii) Reduction of Benzophenone: Alkali metal hydrides, for example NaH, can reduce benzophenone to diphenylcarbinol.

$$(C_6H_5)_2CO + NaH \xrightarrow{145°C} (C_6H_5)_2CHONa \xrightarrow{H_2O} (C_6H_5)_2CHOH$$

Similarly, these hydrides can be used in the catalytic hydrogenation of hydrocarbons and reduction of many other organic compounds.

(ix) Reduction of Halides: Transition metal halides can be easily reduced in presence of hydrides of alkali metals. Thus, sodium hydride reduces titanium tetrachloride to titanium metal at 400°

$$TiCl_4 + 4NaH \longrightarrow Ti + 4NaCl + 2H_2$$

(x) Reaction with Boron Halides: Reduction and hydrogenation is brought about by the alkali metal hydrides when treated with halides of boron. For example, if vapours of boron trifluoride are passed over sodium hydride at 200°C, diborane is formed.

$$2BF_3 + 6NaH \longrightarrow B_2H_6 + 6NaF$$

(xi) Alkali Metal Hydrides, especially NaH would reduce H_2SO_4 to H_2S and free sulphur. Sodium hydride reacts with sulphur on heating to form sodium sulphide and free hydrogen.

$$2NaH + S \longrightarrow Na_2S + H_2$$

(xii) Catalytic Reactions: Alkali metal hydrides act as polymerization catalysts. Sodium hydride polymerizes butadiene to rubber-like polymers.

Structure:

The crystal structures of alkali metal hydrides are built up of positively charged metal ions and negatively charged hydride ions, H^-. Electrolysis of fused mass of these hydrides liberate hydrogen at the anode and an equivalent amount of metal is deposited at the cathode. This indicates that hydrogen ions are negatively charged.

The crystal lattice of alkali metal hydrides is made up of positively charged alkali metal ions, M^+ and negatively charged hydride ions, H^- to give ***face-centred cubic structure*** of NaCl type. The structures of alkali metal hydrides are more compact than the corresponding metals.

Uses:

(i) Alkali metal hydrides are widely used in synthetic organic chemistry.

(ii) They are used in various metallurgical operations as descaling agents.

(iii) They are used as portable source of hydrogen

(iv) They are used as sensitive elements in photo cells

(v) Lithium hydride may be used as a drying agent, or desiccant

HYDRIDES OF ALKALINE EARTH METALS:

The members of these hydrides are CaH_2, SrH_2 and BaH_2. They are all brittle solids which are insoluble in organic and inorganic solvents.

Preparation:

(i) Like alkali metal hydrides, they can be prepared by the direct combination of metals and hydrogen at elevated temperature.

$$Ca + H_2 \xrightarrow{250-300^\circ} CaH_2$$

The finely divided calcium dissolved in liquid ammonia reacts with hydrogen to form CaH_2 at 0°C.

(ii) **Indirect methods:** CaH_2 can be prepared by action of calcium oxide with magnesium in presence of hydrogen at higher temperatures.

$$CaO + Mg + H_2 \longrightarrow CaH_2 + MgO$$

The calcium salts of cresols, naphthols and picric acid react at room temperature with hydrogen under pressure to form calcium hydride (200 atm. pressure).

Strontium hydride has been obtained by distilling a Cd – Sr alloy in hydrogen, or by distilling an amalgam of strontium in mercury in presence of hydrogen.

Properties:

These hydrides are less reactive than alkali metal hydrides but have similar behaviour as is evident from the following reactions.

Reactions:

(i) Decomposition: On heating, the hydrides of alkaline earth metals decompose to liberate hydrogen and free metal. Strontium hydride volatilizes at 1000°C because of partial decomposition to give Sr metal which is also volatile.

$$CaH_2 \longrightarrow Ca + H_2$$

$$SrH_2 \xrightarrow{1000^\circ} Sr + H_2$$

(ii) Reaction with Air or Oxygen: Calcium hydride does not react with dry oxygen or nitrogen at 400° to 500°C. However, on ignition these hydrides react to give oxides and water. CaH_2 is inflammable in moist air.

$$CaH_2 + O_2 \xrightarrow{500^\circ} CaO + H_2O$$

With nitrogen, these hydrides react to form nitrides.

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + 3H_2$$

(iii) Reaction with Halogens: These hydrides do not react with halogen under ordinary conditions. But strontium hydride reacts with chlorine when strongly heated. Barium hydride reacts more easily because the reactivity increases with increasing atomic numbers.

$$SrH_2 + 2Cl_2 \longrightarrow SrCl_2 + 2HCl$$

Bromine and iodine react at red heat to form corresponding halides.

$$SrH_2 + Br_2 \xrightarrow{\text{red hot}} SrBr_2 + H_2$$

$$SrH_2 + I_2 \xrightarrow{\text{red hot}} SrI_2 + H_2$$

(iv) Reaction with Sulphur: These hydrides react with sulphur at red heat to form corresponding sulphides. On the basis of this reaction, CaH_2 is used to estimate sulphur in oils and rubbers.

$$CaH_2 + S \longrightarrow CaS + H_2$$

$$SrH_2 + S \longrightarrow SrS + H_2$$

(v) Reaction with Water: These hydrides react with water less vigorously than the alkali metal hydrides. Strontium hydride is more reactive than CaH_2 but less reactive than BaH_2.

$$SrH_2 + 2H_2O \longrightarrow Sr(OH)_2 + 2H_2$$

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

(vi) Reduction of Covalent Halides: These hydrides of alkaline earth metals reduce many covalent hydrides as shown by the following reactions. Calcium hydride reacts with CCl_4 at 400° to form HCl, $CaCl_2$ and carbon.

$$CaH_2 + CCl_4 \longrightarrow CaCl_2 + 2HCl + C$$

$$3CaH_2 + 2BCl_3 \longrightarrow 3CaCl_2 + B_2H_6$$

(vii) Reduction of Metal Halides: The hydrides reduce metal halides to give either the corresponding hydrides or free metals. As transition metal hydrides are unstable, free metals are isolated in presence of these hydrides.

$$2NaCl + CaH_2 \longrightarrow CaCl_2 + 2NaH$$

(viii) Reduction of Metal Oxides: On heating, an intimate mixture of finely divided metal oxide and an excess of these hydrides, say CaH_2, at 600 – 1000°C, free metal is obtained in state of high purity. Thus metal oxides are reduced to free metals.

$$MO_2 + 2CaH_2 \longrightarrow M + 2CaO + 2H_2$$

(M = Ti, V, Ta, Fe, Cu, Mn, Sn, Pb, W, etc.)

(ix) Reaction with Alcohols: These hydrides can react with alcohols to form alcoholates but the reaction is less vigorous than of alkali metal hydrides.

$$2ROH + CaH_2 \longrightarrow (RO)_2\,Ca + 2H_2$$

(x) Reaction with Oxidizing Agents: These hydrides react with oxidizing agents, such as chlorates, chromates and perchlorates with explosive violence if slightly heated.

(xi) Condensation Reactions: Various organic compounds can undergo condensation reactions in presence of these hydrides. Thus ***acetone*** is condensed at its boiling point to ***mesitylene oxide*** in presence of CaH_2, ***quinoline to biquinoyl*** at 220°, and diphenyl oxide to diphenyl (in presence of CaH_2 at 450°C).

Structure:

The structure of calcium hydride is orthorhombic with unit cell comprising of four calcium ions and eight hydride ions. The structures of SrH_2 and BaH_2 are also similar to that of CaH_2.

Uses:

The alkaline earth metal hydrides have number of important applications:

(i) Calcium hydride is an important portable source of hydrogen and has been used under various trades names such as ***Hydrolith*** and ***Hydrogenite***. It was used in World War II as a source of hydrogen for signals and meteorological balloons.

(ii) **As Drying Agents:** Calcium hydride (including SrH_2 and BaH_2) is very powerful drying agent and is often used as a desiccant for drying ethers and various solvents.

(iii) **As Reducing Agents:** They are used as powerful reducing agents to get metals in the free state.

(iv) Calcium hydride and others are efficient reagents for organic reductions and condensation reactions under various trade names.

POLYMERIC HYDRIDES:

The hydrides of beryllium and magnesium are members of polymeric hydrides. They may be considered a bridge between ionic hydrides and covalent hydrides because their properties are intermediate between these two groups. However, these two hydrides have more covalent character.

HYDRIDES OF BERYLLIUM AND MAGNESIUM:

Although these hydrides have covalent nature but resemble closely to LiH.

Preparation:

Beryllium hydrides can be obtained by the following methods:

(i) **By thermal decomposition of Be alkyls:** The alkyls of beryllium decompose to give BeH_2.

$$(Me_3C)_2Be \xrightarrow{210°C} BeH_2 + \text{Hydrocarbons}$$

(ii) **By the action of $LiAlH_4$:** BeH_2 can also be prepared by the action of lithium aluminium hydride on dimethyl beryllium.

$$(CH_3)_2Be + LiAlH_4 \longrightarrow BeH_2 + LiAlH_2(CH_3)_2$$

Beryllium hydride is usually difficult to isolate in the pure state. ***Magnesium hydride*** is obtained in the following manner:

(i) **By thermal decomposition of Mg dialkyls:** The hydrolysis of magnesium dialkyls or Grignard reagent gives magnesium hydride.

$$Mg(C_2H_5)_2 \xrightarrow{175-200°C} MgH_2 + 2C_2H_4$$

$$2Mg(C_2H_5)I \xrightarrow{200°C} MgH_2 + MgI_2 + 2C_2H_4$$

(ii) **By the action of a reactive hydride:** Magnesium hydride can be prepared by the reaction of Mg dialkyl with a reactive hydride, such as diborane or $LiAlH_4$.

$$MgR_2 + LiAlH_4 \longrightarrow MgH_2 + LiAlH_2R_2$$

$$3MgR_2 + B_2H_6 \longrightarrow 3MgH_2 + 2BR_3$$

(iii) **By direct interaction:** On heating magnesium or Mg_2Cu alloy in atmosphere of hydrogen, MgH_2 is obtained.

$$Mg + H_2 \xrightarrow{300°C} MgH_2$$

(iv) **From magnesium halides:** Sodium hydride reacts with $MgBr_2$ in diethyl ether to form MgH_2.

$$MgBr_2 + 2NaH \longrightarrow MgH_2 + 2NaBr$$

Properties:

They are white non-volatile solids, insoluble in organic solvents which gives a clue towards their polymeric nature.

Reactions:

The most common reactions of beryllium and magnesium hydrides are:

(i) **Thermal Stability:** BeH_2 is stable up to 80°C but decomposes rapidly at 125°C. Magnesium hydride is surprisingly more stable and decomposes only above 283°C.

(ii) **Reaction with Water:** Magnesium reacts vigorously with water to produce $Mg(OH)_2$ and H_2.MgH_2 reacts with water instantaneously even at −186°C.

$$MgH_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2H_2$$

(iii) **Reaction with alcohols:** These hydrides react to form metal alcoholates.

$$MgH_2 + 3CH_3OH \longrightarrow Mg(OCH_3)_2 + 2H_2$$

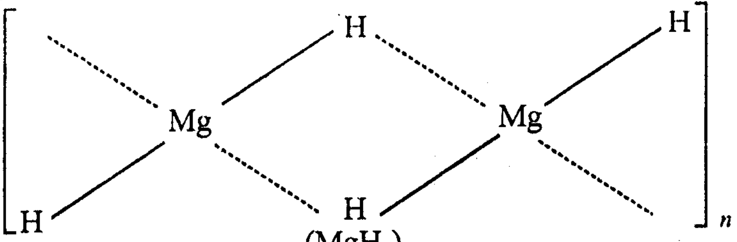
(iv) **Reducing action:** Like other hydrides, beryllium and magnesium hydrides are good reducing agents.

$$TiCl_4 + 2MgH_2 \longrightarrow Ti + 2MgCl_2 + 2H_2$$

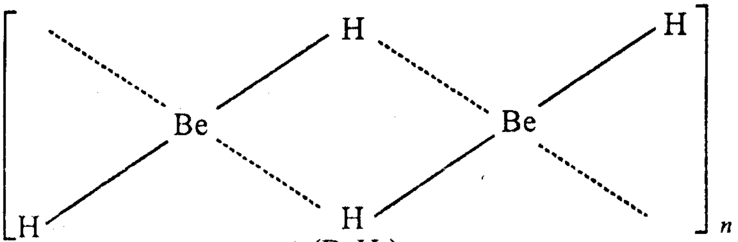
Structure:

Due to the electron acceptor capacity of beryllium and magnesium, their hydrides are polymeric in nature.

The polymerization of their molecules takes place through hydrogen as shown in Figure 9.3.



$(MgH_2)_n$



$(BeH_2)_n$

Fig. 9.3. Polymeric nature of BeH_2 and MgH_2.

METALLIC HYDRIDES:

The binary compounds of hydrogen with transition metals are called metallic hydrides or interstitial hydrides. Some of the transition metals react vigorously with hydrogen but others do not. A few transition metals can only adsorb or occlude hydrogen without undergoing any chemical reaction. The reaction of metals Ti, Zr, Hf and lanthanides with hydrogen is exothermic and can be formed easily. But Mo, W, Mn, Fe, Co, Ru, Pt, etc., react with hydrogen endothermically indicating their slow reactivity. Therefore, the hydrides of these metals are either unstable or unknown.

There are three types of metallic hydrides in general:

(a) The hydrides are formed by the adsorption of hydrogen within the interstices or holes present in metallic structures. The stoichiometry is not in accordance with laws of chemical combinations.

(b) The hydrides which are obtained by physical adsorption of hydrogen at definite positions within the crystal lattice. The properties of hydrides formed remain those of metals.

(c) The metal hydrides formed by reactive metals have crystal structure quite different from the metals. The hydrides, in such cases, appear definite to be loose chemical compounds. Even in these metallic hydrides the chemical composition is variable.

These metal hydrides are usually represented by true formulae. When the ratio of hydrogen for one metal atom varies between 1.5 to 2.4 they are represented as dihydrides with general formula MH_2. The ratio of hydrogen to metal in the range of 2.5 - 3.0 is represented by formula MH_3.

Preparation:

(i) **By direct combination of metal and hydrogen:** The transition metals when heated in presence of hydrogen atmosphere form metallic hydrides.

$$2La + 3H_2 \xrightarrow{\text{above } 300^\circ} 2LaH_3$$

(ii) **From halides:** The hydrides of nickel, cobalt, iron and chromium are obtained by passing hydrogen gas through the suspension of anhydrous metal chlorides in organic solvents in presence of Grignard reagents.

$$NiCl_2 + 2C_6H_5MgBr \longrightarrow Ni(C_6H_5)_2 + MgBr_2 + MgCl_2$$

$$Ni(C_6H_5)_2 + 2H_2 \longrightarrow NiH_2 + 2C_6H_6$$

(iii) **By the action of $LiAlH_4$:** The hydrides of zinc and cadmium etc., are prepared by treating their dimethyls with $LiAlH_4$.

$$Zn(CH_3)_2 + LiAlH_4 \longrightarrow ZnH_2 + LiAlH_2(CH_3)_2$$

$$Cd(CH_3)_2 + LiAlH_4 \longrightarrow CdH_2 + LiAlH_2(CH_3)_2$$

Properties:

The absorption of hydrogen by a transition metal causes a partial loss of its metallic character. These metal hydrides *i.e.*, hydrides of lanthanides and actinides are dark coloured compounds. Most of the metallic hydrides are pyrophoric and ignite spontaneously when exposed to air.

The composition of some of these metal hydrides are:

$$LaH_{2.76},\ TiH_{1.62},\ ZnH_{1.92},\ CeH_{2.69},\ UH_3$$

These metal hydrides are also good reducing agents and reduce H_2SO_4 to SO_2, S and H_2S.

Some of these hydrides are used as catalysts for certain organic reactions. Thus, titanium hydride can be used as a catalyst for hydrogenation of olefins, reduction of nitrobenzene to aniline, and nitriles to amines.

COVALENT HYDRIDES:

The hydrides of elements of Group IIIA to VIIA are called covalent hydrides. These hydrides are binary compounds of hydrogen with other elements linked through electron pair bonds and are volatile gases or liquids under normal conditions. Now chemistry of these hydride will be discussed group-wise.

1. HYDRIDES OF GROUP III-A ELEMENTS:

The hydrides of elements of Group III-A include boron hydride, aluminium hydride and gallium hydride. Let us discuss them one by one.

Hydrides of Boron or Boranes:

Two types of boron hydrides have been distinguished bearing the general formulae B_nH_{n+4} and B_nH_{n+6}. The hydrides of composition B_nH_{n+4} are stable and those resorting to the general formula B_nH_{n+6} are relatively more unstable.

The well characterised hydrides of boron are given in Table 9.3.

TABLE 9.3

Formula	Name of the hydride	Type of formula
B_2H_6	Diborane	B_nH_{n+4}
B_4H_{10}	Tetraborane	B_nH_{n+6}
B_5H_9	Pentaborane	B_nH_{n+4}
B_5H_{11}	Pentaborane-II	B_nH_{n+6}
B_6H_{10}	Hexaborane	B_nH_{n+4}
B_9H_{15}	Enneaborane	B_nH_{n+6}
$B_{10}H_{14}$	Decaborane	B_nH_{n+4}

The other hydrides of boron *i.e.*, B_3H_7, B_6H_{12}, B_9H_{13} and $B_{10}H_{16}$, have been reported but not well established.

Preparation:

Following methods are commonly used to prepare boron hydrides. The mixture can be separated by fractional distillation.

(i) **Stock's Method:** The hydrolysis of metal borides, such as magnesium boride, in acid solutions gives mixture of boron hydrides which can be easily separated.

$$Mg_3B_2 + HCl \longrightarrow B_2H_6 + \text{other boranes}$$

(ii) **From Boron Trifluoride:** Reduction of BF_3 with $LiAlH_4$ or LiH yields diborane.

$$3NaAlH_4 + 4BF_3 \longrightarrow 3NaAlF_4 + 2B_2H_6$$

$$6LiH + 8BF_3 \longrightarrow 6LiBF_4 + B_2H_6$$

Diborane is converted to higher boron hydrides by heating B_2H_6 with or without hydrogen at 200 – 250°C.

$$3B_2H_6 \xrightarrow{200^\circ - 250^\circ C} 2B_3H_9$$

(iii) **By Electric Discharge:** When a mixture of boron trichloride and hydrogen is passed through high voltage discharge, a reduction reaction occurs and diborane is formed.

$$2BCl_3 + 6H_2 \longrightarrow B_2H_6 + 6HCl$$

(iv) Diborane can also be prepared when boron halide and hydrogen are passed through a bed of finely divided electropositive metal.

$$2BX_3 + 6M + 3H_2 \longrightarrow B_2H_6 + 6MX$$

Thermal Stability:

As already pointed out, the boranes bearing the general formula B_nH_{n+4} are more stable. The unusual behaviour of boranes is based on the fact that on heating at moderate temperatures they form more complex condensed systems. However, the ultimate products at high temperatures are boron and hydrogen.

Diborane is converted to higher boranes and hydrogen at moderate temperatures. The hydrogen released during the reactions appears to act as inhibitor for further decomposition to elements. However, above 300°C, diborane decomposes to boron and hydrogen.

$$B_6H_6 \xrightarrow{300^\circ} 2B + 3H_2$$

Tetraborane, B_4H_{10} belongs to B_nH_{n+6} category and is found to decompose slowly even at room temperature. Decaborane $B_{10}H_{14}$ is very stable borane and can be kept at 150° for long periods without decomposition.

The interconversion of boranes is very interesting. The kinetics of the pyrolysis of diborane has been studied and following mechanism is suggested based upon the observed products.

$$B_2H_6 \longrightarrow 2BH_3$$

$$B_2H_6 + BH_3 \longrightarrow \text{(Intermediate products)}$$

$$\text{(Intermediate products)} + B_2H_6 \longrightarrow B_5H_{11} + 2H_2$$

$$B_5H_{11} \longrightarrow B_5H_9 + H_2$$

$$B_5H_{11} \longrightarrow B_2H_6 + \text{higher boranes}$$

It has also been observed that diborane can condense reversibly to tetraborane with the liberation of hydrogen.

$$2B_2H_6 \rightleftharpoons B_4H_{10} + H_2$$

Reactions of Boranes:

The reactions of boranes can be interpreted keeping in mind the following special features of these compounds:

(a) The boron atom is a good Lewis acid and can form products with Lewis bases.

(b) Boron is relatively electropositive element and would combine with strongly electronegative elements (oxygen and halogens) with release of energy.

(c) The bond between boron and hydrogen becomes relatively weaker than the coordinate bond formed between boron (Lewis acid) and the electron pair donor (Lewis base).

Let us now study various reactions of diborane:

(i) **Oxidation:** All diboranes burn vigorously in air or oxygen. The heat of combustion of diborane (B_2H_6) is twice that of C_2H_6.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

The boranes with general formula B_nH_{n+4} can be easily handled as they are stable at room temperature to the action of air and oxygen. However, tetraborane and others are unstable and would ignite on mixing with air.

(ii) **Halogenation:** Diborane reacts vigorously with free chlorine to form boron trichloride and HCl as the end products.

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

Diborane reacts very slowly with Br_2 and I_2, and these reactions can be controlled to capture intermediate products B_2H_5Br and B_2H_5I.

Reaction of BCl_3 with diborane yields B_2H_5Cl.

$$5B_2H_6 + 2BCl_3 \rightleftharpoons 6B_2H_5Cl$$

Diborane also reacts with hydrogen halides. The reaction is slow and requires longer time even at high temperature.

$$B_2H_6 + HBr \xrightarrow{AlBr_3} B_2H_5Br + H_2$$

(iii) **Hydrolysis:** Diborane reacts with water to give boric acid and liberates hydrogen.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

The rate at which diborane can be hydrolysed varies with boranes.

(iv) **Formation of coordination compounds:** Diborane behaves as Lewis acid and would readily combine with Lewis bases such as ammonia.

$$\underset{\text{(Lewis acid)}}{B_2H_6} + \underset{\text{(Lewis base)}}{:NH_3} \longrightarrow B_2H_6 \cdot (NH_3)_2$$

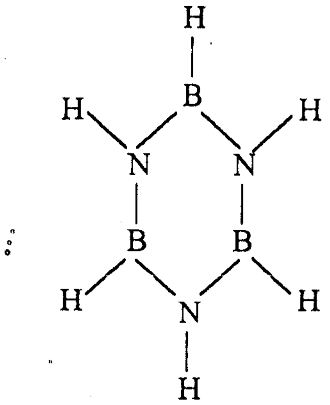
or

$$2(H_3B \longleftarrow NH_3)$$

Borane — ammoniate is converted to borazole on heating.

$$3B_2H_6 \cdot (NH_3)_2 \longrightarrow \underset{\text{(Borazole)}}{2B_3N_3H_6} + 12H_2$$

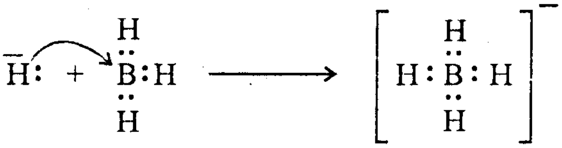
The structure of borazole is:



An interesting coordination complex is formed between borine, BH_3 and carbon monoxide.

$$H_3B + CO \longrightarrow H_3B \longleftarrow CO$$

The formation of a coordinate bond between a borine molecule (Lewis acid) and hydride ion (Lewis base) results in the formation of *borohydride ion.* For example, LiH will form $LiBH_4$.



(v) **Reaction with Alkali Metals:** Boranes react with alkali metals (as amalgams) to form ionic compounds such as:

$$B_2H_6 + 2Na \longrightarrow Na_2[B_2H_6]$$

(vi) **Reaction with Hydrocarbons:** On mixing diborane with ethylene or acetylene an exothermic reaction starts which yields a variety of polymeric products. However, at low temperatures a smooth reaction will take place and trialkyls of boron are obtained.

$$BH_3 + 3R\,CH = CH_2 \longrightarrow (R\,CH_2\,CH_2)_3B$$

Diaborane attacks benzene at 100°C to undergo substitution reaction.

$$3C_6H_6 + BH_3 \longrightarrow (C_6H_5)_3B + 3H_2$$

(vii) **Substituted Derivatives of Boranes:** The alkyl substituted derivatives are obtained by reacting diborane with trialkyl borine (BR_3). In this way, a series of derivatives of the type B_2H_5R, $B_2H_4R_2$, $B_2H_3R_3$ etc., are obtained. They hydrolyse to give boric acid and organoboric acid.

$$B_2H_5R + 5H_2O \longrightarrow B(OH)_3 + RB(OH)_2 + 5H_2$$

(viii) **Reaction with Alcohols:** Diborane reacts with alcohols to give substituted products.

$$B_2H_6 + 4CH_3OH \longrightarrow 2(CH_3O)_2BH + 4H_2$$

(ix) **Reaction with Alkalies:** If lower boranes are treated with solid alkalies or their concentrated solutions, a partial decomposition takes place.

$$B_2H_6 + 2KOH \longrightarrow K_2[B_2H_4(OH)_2] + H_2$$

(x) **Miscellaneous Reactions:**

$$B_2H_6 + F^- \longrightarrow H_3BF^-$$

$$B_2H_6 + CN^- \longrightarrow H_3BCN + BH_3^-$$

$$NH_4^+ + B_2H_6 + SCN^- \xrightarrow{0°C} NH_4^+BH_3\ SCN^- \xrightarrow{0°C} H_3NBH_2\ SCN$$

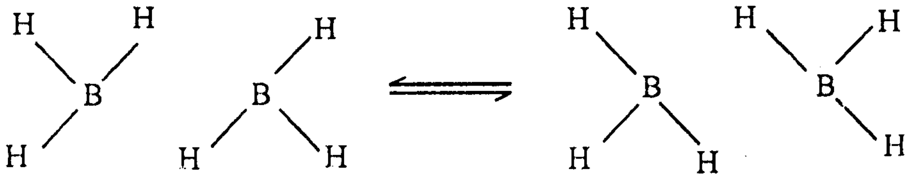
STRUCTURAL ASPECTS OF ELECTRON DEFICIENT MOLECULES:

Boranes are electron deficient compounds. In other words, there are more bonding orbitals than the available electrons to fill these orbitals. Therefore, multicentre bonds are expected in these compounds.

Reaction of diborane gives alkyl substituted products, $B_2H_2R_4$. If one or two alkyl groups are attached to each boron atom of diborane, the product $B_2H_2R_4$ should be dimeric. However, attempts to substitute the rest of the two hydrogen atoms result in the formation of alkylated monomeric *borine*, BR_3. It shows that at least two hydrogen atoms are required to establish dimeric structure of diborane.

Boron has electronic configuration $1s^2\ 2s^2\ 2p^1$ which indicates the presence of three electrons in valency shell. The diborane molecule, B_2H_6 is made up of two borine (BH_3) units. But each boron atom in the formation of BH_3 utilizes all the three electrons to form three covalent bonds with three hydrogen atoms and none of the electrons is left for forming a B — B bond.

Now, let us see the way in which two boron atoms are linked to form diborane B_2H_6. To solve this enigma hydrogen bridge structure was proposed by Dilthey in 1921. The nature of the hydrogen bridge was not taken into consideration. It was proposed later that hydrogen bridge structures were formed because two hydrogen atoms could 'resonate' between two probable but equivalent structures. But these resonating structures do not account for bond lengths and bond angles which are experimentally found. The presence of two kinds



of B – H bond is indicated by Raman spectrum and through the chemical evidence of the formation of $B_2H_2R_4$. Thus a bridge structure (Figure 9.4) was proposed for diborane. Electron diffraction studies have shown that B – H_a = 1.19A°, B – H_b = 1.33A°, B – B = 1.77A°, angle H_aBH_a = 121.8° and angle H_bBH_b = 96.5°.

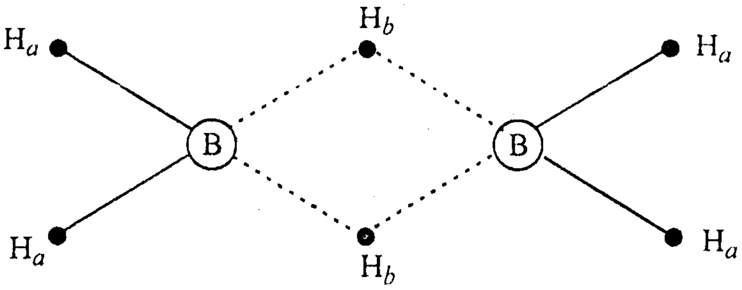


Fig. 9.4. Hydrogen bridge structure of diborane.

It has recently been further elaborated that sp^3 hybrid orbitals obtained from $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z$ of each boron overlap with three $1s$ orbitals of hydrogen as shown in figure 9.5. In the bridge, hydrogen bonds electrons are delocalised and charge density spreads over to two boron atoms. A total of four electrons are present in the hydrogen bridges, two electrons are provided by two bridge hydrogen atoms and the rest of the two electrons are contributed by two BH_2 groups (each carrying one electron for bridge bonds).

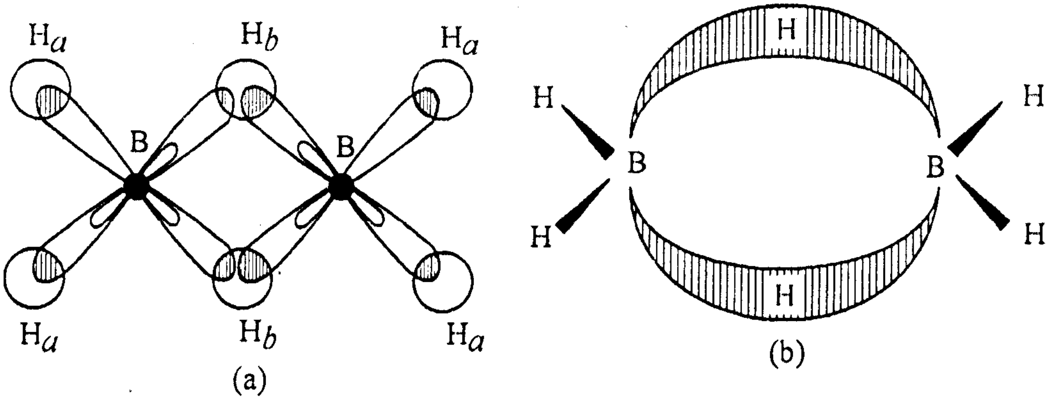
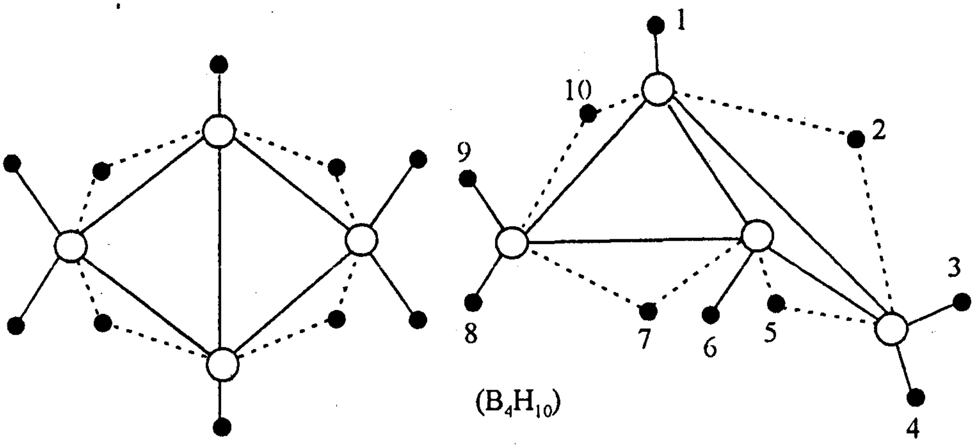


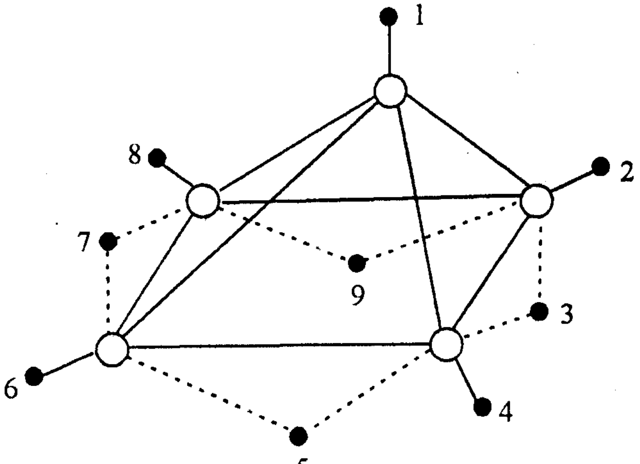
Fig. 9.5. (a) Tetrahedral sp^3 hybrid orbitals on each boron atom with 1s atomic orbitals of hydrogen: (b) Representation of delocalised two electron three-centred bond.

The measured specific heat and nuclear magnetic resonance (NMR) studies have favoured the bridge structure of diborane.

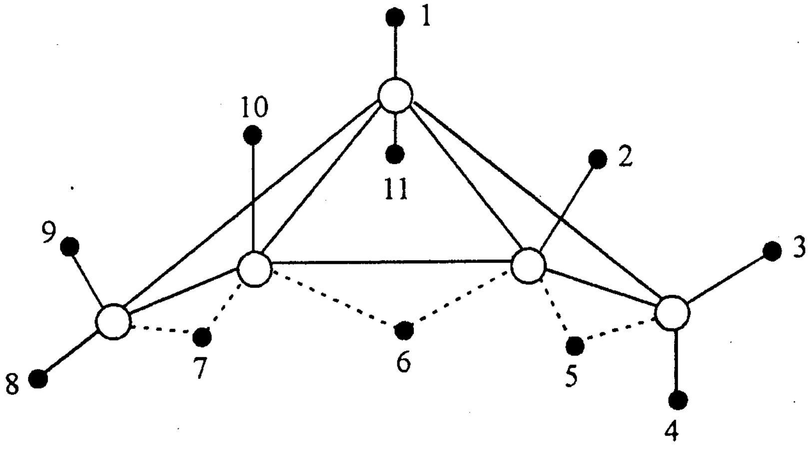
The structure of higher boranes are given in Figure 9.6.



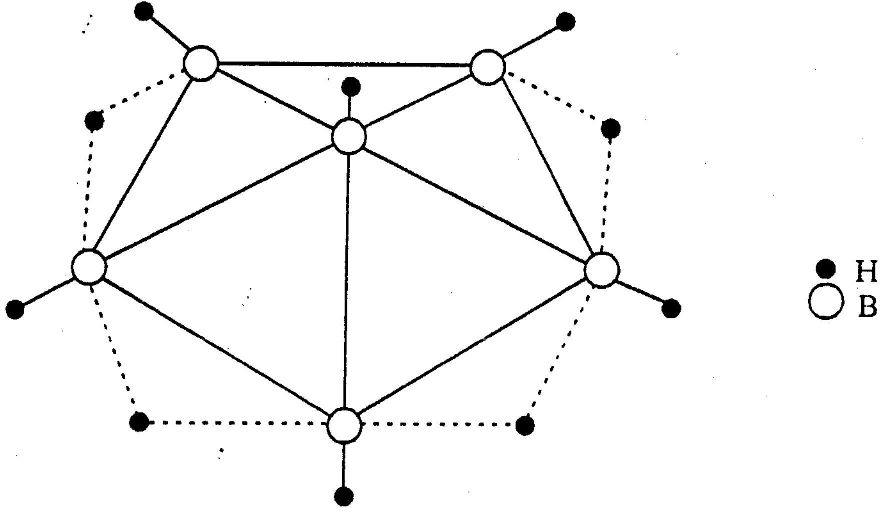
(B_4H_{10})



(B_5H_9)



(B_5H_{11})



(B_6H_{10})

Fig. 9.6. Structures of some boranes.

Applications:

(1) Metal Coating: On heating metals with boranes, element boron is deposited on metal surfaces. This renders the metal surfaces hard, abrasive and corrosion resistant.

(2) High Energy Fuels: Since boron and hydrogen both have high heats of combustion, oxidation of boron hydrides releases lot of energy. This makes them useful as fuel for rockets.

(3) In Polymer Chemistry: Boron hydrides can be used as vulcanizing agents for organic polymers and synthetic rubbers. Decaborane is superior to sulphur for vulcanizing rubber.

HYDRIDES OF ALUMINIUM AND GALLIUM:

Like boron hydrides the mononuclear hydrides of aluminium and gallium are not known. Whereas, aluminium hydride exists as a polymeric solid $(AlH_3)_x$, the simplest hydride of gallium is digallane, Ga_2H_6.

Preparation:

Aluminium hydride is prepared by the treatment of aluminium chloride with limited amounts of LiH.

$$AlCl_3 + 3LiH \longrightarrow (AlH_3)_x + 3LiCl$$

In presence of excess LiH the following reaction takes place and complex $LiAlH_4$ is obtained.

$$AlCl_3 + 3LiH \longrightarrow AlH_3 + 3LiCl$$
$$LiH + AlH_3 \longrightarrow LiAlH_4$$

Gallium hydride is conveniently obtained by the reaction of Li Al H_4 with gallium chloride.

$$4GaCl_3 + 3\,LiAlH_4 \longrightarrow 2Ga_2H_6 + 3LiCl + 3AlCl_3$$

Digallane can also be obtained by passing a mixture of trimethyl gallium and hydrogen through an electric discharge. The product is treated with triethylamine to liberate gallium hydride.

$$6Me_3Ga + 3H_2 \longrightarrow 3Ga_2\,Me_4\,H_2 + \text{Hydrocarbons}$$

$$3Ga_2\,Me_4H_2 + 4Et_3N \longrightarrow 4GaMe_3\,.\,NEt_3 + Ga_2H_6$$

Properties:

Aluminium hydride is a white solid and digallane is a colourless liquid.

Aluminium hydride is stable up to 100°C and gallium hydride up to 130°C. They decompose above these temperatures to elements and hydrogen.

$$Ga_2H_6 \xrightarrow[130^\circ]{\text{above}} 2Ga + 3H_2$$

Aluminium hydride is oxidised in air or oxygen to aluminium oxide and hydrogen. Digallane is spontaneously inflammable when exposed to air.

$$4(AlH_3)_x + 6O_2 \longrightarrow 2Al_2O_3 + 6H_2O$$

Aluminium and gallium hydrides are hydrolysed by water.

$$2(AlH_3)_x + 3H_2 \longrightarrow Al_2O_3 + 6H_2$$

Hydrogen of these hydrides can be substituted by alkyl groups. These hydrides are capable of forming complex metal hydrides.

$$(AlH_3)_n + B_2H_6 \longrightarrow Al(BH_4)_3$$

$$(AlH_3)_n + LiH \longrightarrow LiAlH_4$$

$$Ga_2H_6 + LiH \longrightarrow 2\,LiGaH_4$$

Aluminium hydride and digallane act as Lewis acid and would react with Lewis bases to form coordination compounds.

$$(AlH_3)_x + :NH_3 \longrightarrow H_3Al \leftarrow NH_3$$

$$Ga_2H_6 + 2:NH_3 \longrightarrow 2H_3Ga \leftarrow NH_3$$

These hydrides, like other hydrides, are good reducing agents.

Structure:

The structures of these hydrides involve the formation of hydrogen bridges as shown in Figure 9.7.

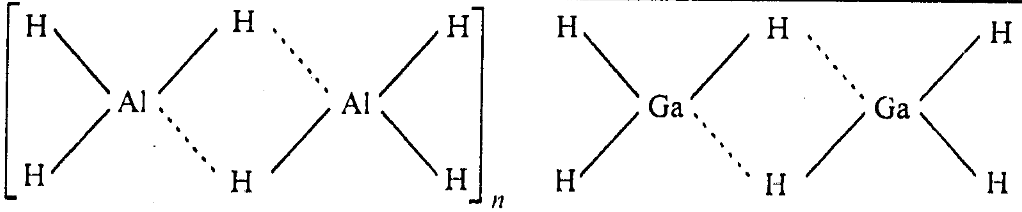


Fig. 9.7 Structure of aluminium hydride and digallane.

2. HYDRIDES OF GROUP IVA ELEMENTS:

The binary compounds of hydrogen with carbon, silicon, germanium and lead represent this class. The hydrides of carbon are called hydrocarbons and will not be discussed over here because they represent a class of organic compounds. The hydrides of silicon are called silanes and will first be discussed.

SILANES:

Silicon is capable of forming polynuclear hydrides similar to hydrocarbons. Silicon will show four co-valencies as is the case with carbon. In fact, silicon forms hydride compounds quite similar to hydrocarbons. The following hydrides of silicon with general formula Si_nH_{2n+2} are well known:

SiH_4	(Monosilane)
Si_2H_6	(Disilane)
Si_3H_8	(Trisilane)
Si_4H_{10}	(n – Tetrasilane)
Si_5H_{12}	(Pentasilane)
Si_6H_{14}	(Hexasilane)

Silanes are colourless gases or volatile liquids and miscible in organic solvents.

PREPARATION:

(i) From Magnesium Silicide: A mixture of silanes is prepared by hydrolysis of magnesium silicide, Mg_2Si in presence HCl.

$$Mg_2Si + H_2O \xrightarrow{HCl} \underset{(40\,\%)}{SiH_4} + \underset{(30\,\%)}{Si_2H_6} + \underset{(15\,\%)}{Si_3H_8} + \underset{(10\,\%)}{Si_4H_{10}} + \underset{(5\,\%)}{\text{higher hydrides}}$$

(ii) From Silicon Chloride: Reduction of $SiCl_4$ with LiH or $LiAlH_4$ affords monosilane.

$$SiCl_4 + 4LiH \longrightarrow SiH_4 + 4LiCl$$

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

(iii) From Calcium Silicide: Hydrolysis of calcium silicide in presence of HCl forms a polymeric hydride $(SiH_2)_n$ as brown solid. $(SiH_2)_n$ decomposes on heating to give silanes.

Reactions:

They are fairly stable compounds but on heating to 600°C they decompose to silicon and hydrogen. The stability decreases with increasing number of silicon atoms.

(i) Hydrolysis: Pure water has no effect on silanes but presence of acids or alkalies hydrolyse them to silicic acid and hydrogen.

$$SiH_4 + 4H_2O \xrightarrow[\text{alkalies}]{\text{acid or}} \underset{\text{(Silicic acid)}}{H_4SiO_4} + 4H_2$$

$$Si_2H_6 + 2H_2O + 4NaOH \longrightarrow 2Na_2SiO_3 + 4H_2$$

(ii) Reducing Action: Silanes are strong reducing agents and precipitate metals from their salts.

$$4AgNO_3 + SiH_4 \longrightarrow Si + 4Ag + 4HNO_3$$

$$2CuSO_4 + SiH_4 \longrightarrow Cu_2Si + 2H_2SO_4$$

Monosilane reduces potassium permanganate solution to manganese dioxide.

(iii) Halogenation: Silanes react with halogens to form halogenated silane derivatives. The reaction of hydrogen halides is also similar.

$$Si_2H_6 + HCl \xrightarrow{AlCl_3} Si_2H_5Cl + H_2$$

$$Si_2H_6 + Cl_2 \longrightarrow Si_2H_5Cl + HCl$$

The reaction with halogens is explosively violent.

$$SiH_4 + Cl_2 \longrightarrow SiH_3Cl \xrightarrow{Cl_2} SiH_2Cl_2 \xrightarrow{Cl_2} SiHCl_3$$

Disilane and trisilane react vigorously with chlorinating agents *i.e.*, CCl_4 or $CHCl_3$.

$$Si_2H_6 + 2CCl_4 \longrightarrow 2SiCl_4 + 2C + 3H_2$$

(iv) The silanes do not react with ammonia at ordinary temperatures. However, the chlorosilane reacts with ammonia at room temperature to yield trisilylamine, $(SiH_3)_3N$.

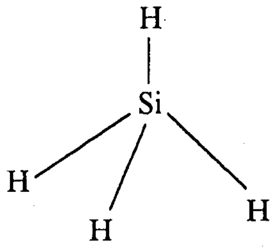
(v) Formation of Alkylamines: Monosilanes add to olefins such as ethylene or isobutylene to form alkylsilane derivatives.

$$SiH_4 + CH_2 = CH_2 \longrightarrow SiH_3(C_2H_2)$$

Silanes show resemblance to paraffin hydrocarbons in many respects.

Structure:

The structures of silanes are similar to corresponding paraffin hydrocarbons. Thus four hydrogen atoms of SiH_4 are directed along the corners of a regular tetrahedron involving sp^3 hybridization. Si — H bond length is 1.49°A and H — Si — H bond angle is 109°28′.



The polynuclear silanes consist of Si — Si chains. No silane is as yet known to possess double or triple bond between two silicon atoms.

USES:

(i) Monosilane is found to render various surfaces water-repellent.

(ii) Dischlorosilane and trichlorosilane are used as intermediates for the preparation of silicon polymers.

HYDRIDES OF GERMANIUM, TIN AND LEAD:

The hydrides of germanium, tin and lead form covalent hydrides similar to silanes. Tin and lead form only mononuclear hydrides, SnH_4 and PbH_4. But germanium forms the following four polynuclear hydrides in addition to the mononuclear hydride, GeH_4.

Ge_2H_6	(Digermane)
Ge_3H_8	(Trigermane)
Ge_4H_{10}	(Tetragermane)
Ge_5H_{12}	(Pentagermane)

Monogermane and digermane are gases and higher germanes are volatile liquids. The stannane and plumbane are gases which decompose even at room temperature.

PREPARATION OF GERMANES:

(i) Mono-, di-, and trigermanes are prepared by the action of dilute HCl on magnesium germanide

$$Mg_2Ge + 4HCl \xrightarrow{\qquad} \underset{(20 - 25\ \%)}{GeH_4} + 2MgCl_2$$

(ii) Monogermane is also prepared by the electrolysis of GeO_2 in concentrated H_2SO_4.

(iii) The higher germanes are obtained by circulating monogermane through ozoniser electric discharge tube at 78°C and 0.5 atmosphere pressure.

(iv) Monogermane can be prepared by the direct action of atomic hydrogen and elemental germanium.

$$Ge + 2H_2 \longrightarrow GeH_4$$

(v) The germanes can be prepared by the action of $LiAlH_4$ on germanium halides in a medium of dry ethyl ether at room temperature.

$$GeCl_4 + LiAlH_4 \longrightarrow GeH_4 + LiCl + AlCl_3$$

(vi) By the action of NH_4Br on Mg_2Ge in liquid ammonia, GeH_4 is obtained.

PREPARATION OF STANNANE AND PLUMBANE:

(i) The hydride of tin, SnH_4 (stannane) and of lead, PbH_4 (plumbane) are prepared by the action of dilute HCl on Mg — Sn alloy or Mg — Pb alloy.

(ii) The stannane is also prepared by the electrolysis of $Sn(SO_4)_2$ in concentrated H_2SO_4.

Plumbane is also prepared by the action of atomic hydrogen on metallic lead or by reduction of the dilute solution of lead acetate by metallic magnesium.

$$Pb + 4H \longrightarrow PbH_4$$

Reactions:

The chemistry of germanes, stannane and plumbane is similar to silanes in many respects. The following are salient features of their chemistry:

(i) **Thermal Stability:** The hydrides of lead and tin are more unstable than germanes. Germanes are stable at room temperature or even at higher temperatures. Monogermane decomposes only above 340°C.

$$GeH_4 \xrightarrow{340-360^\circ C} Ge + 2H_2$$

(ii) **Action of Water:** They are not affected by water even in presence of dilute acids or alkalies. However, they may be hydrolysed in presence of concentrated acids or alkalies.

(iii) **Action of Air or Oxygen:** Germanes are quite stable and have no action by air or oxygen under ordinary conditions. These are not inflammable in air like silanes.

(iv) **Halogenation:** Chlorination of germanes or treatment of germanes with hydrogen halides give chloroderivatives.

$$GeH_4 + Cl_2 \xrightarrow{Cl_2} H_3GeCl \xrightarrow{Cl_2} H_2GeCl_2 \longrightarrow HGeCl_3$$

The halogen derivatives of germanes are readily hydrolysed.

(v) **With Metals:** Monogermane reacts with sodium in liquid ammonia to liberate H_2.

$$GeH_4 + Na \longrightarrow NaGeH_3 + \frac{1}{2}H_2$$

If solution of sodium germanyl, $NaGeH_3$ is electrolysed in liquid ammonia, germane and nitrogen are liberated.

$$6GeH_3^- + 2NH_3 \longrightarrow 6GeH_4 + N_2 + 6e \text{ (at anode)}$$

Sodium germanyl, Na GeH_3 reacts with alkyl halides to form *alkyl germanes.*

$$NaGe\,H_3 + RX \longrightarrow RGe\,H_3 + NaX$$

Structure:

Germane, stannane and plumbane possess structures in which central atoms Ge, Sn or Pb are surrounded by hydrogen atoms in tetrahedral manner due to sp^3 hybridization of orbitals involved.

Uses:

(i) Germanes may be used to produce pure metallic germanium used as rectifier in electronic instruments.

(ii) Stannane is used in vapour phase tin plating.

The elements of Group VA, VIA and VIIA also form covalent hydrides: ammonia (NH_3), phosphine (PH_3), arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3) represent the hydrides of Group VA. In addition to these mononuclear hydrides, certain binuclear species are also obtained *i.e.*, N_2H_4, P_2H_4 etc.

The compounds H_2O, H_2S, H_2Se, H_2Te and H_2Po represent the hydrides of Group VIA. Similarly, hydrogen halides are considered to be belonging to the family of covalent hydrides. Although all these compounds are well known, but they would be better discussed along with the chemistry of particular groups.

Questions

1. Explain the terms ortho- and para-hydrogen. What is the basis for the existence of these two forms? How are they interconverted?
2. How many isotopes of hydrogen have been recognised? Discuss the chemistry of deuterium and deuterium oxide.
3. Write short notes on the following:

   (a) Atomic hydrogen (b) Tritium (c) Heavy water
4. What is heavy water? How does it differ from water?
5. Describe the chemistry of hydrogen or protium. What type of hydrogen compounds are generally recognised?
6. What are hydrides? How would you proceed to classify them?
7. Discuss the general chemistry of saline hydrides. Compare them with the behaviour of covalent hydrides.
8. Starting from heavy water, indicate the reactions used to prepare the following deuterium compounds:

   NaOD D_2S

   D_3PO_4 DOH

   DBr D_2O_2
9. Equal weights of aluminium metal, lithium metal, lithium hydride and calcium hydride are treated with an excess acid. If lithium metal liberates 1.0 gram of hydrogen, how much hydrogen the other compounds would evolve?
10. What type of polymeric hydrides have been recognised? Discuss their characteristics and structures.
11. What is diborane? How is it usually obtained? Discuss its chemistry based upon its structure.
12. Discuss the chemistry of boranes with special emphasis on their structures. What are the applications of boron hydrides?
13. Describe the general characteristics of metallic hydrides.
14. What are silanes? How are they generally obtained? Give in detail their reactions and compare their chemistry with paraffin hydrocarbons.
15. What type of hydrides have so far been recognised with members of Group IVA? Elaborate them with special reference to the chemistry and structures of silanes and germanes.

16. **Give short answers to the following questions:**

(i) What do you understand by ortho- and para-hydrogen?

(ii) How ortho- and para-hydrogen can be interconverted?

(iii) What is atomic hydrogen? How is it produced?

(iv) Describe the isotopes of hydrogen with regard to their preparation and characteristics.

(v) What type of compounds are formed by hydrogen?

(vi) What are hydrides? How are they classified?

(vii) Discuss alkali metal hydrides with reference to reactivities.

(viii) How are hydrides of beryllium and magnesium formed? Draw their structures.

(ix) Discuss covalent hydrides with reference to their thermal stability.

(x) What are boranes? How are these fomed?

(xi) Discuss the reactivity of boranes.

(xii) Discuss various aspects of structures of boranes.

(xiii) Describe the characteristic features of aluminium and gallium hydrides.

(xiv) What are silanes? How are they prepared?

(xv) Discuss various aspects of hydrides of germanium, tin and lead.

17. **Give the correct answer:**

(i) Hydrogen has number of isotopes:

(a) Two	(b) Three
(c) Four	(d) Five

(**Ans**: b)

(ii) Re-union of atomic hydrogen to form molecular hydrogen liberates:

(a) 103 Kcals per mole of energy

(b) 206 Kcals per mole of energy

(c) 13 Kcals per mole of energy

(d) 26 Kcals per mole of energy

(**Ans**: a)

(iii) Protium or ordinary hydrogen has:

(a) one proton and one neutron

(b) one proton and one electron

(c) one proton

(d) one proton and one positron

(**Ans**: c)

(iv) Deuterium or heavy hydrogen has:
- (a) one proton and one neutron
- (b) one proton and one electron
- (c) one proton
- (d) one proton and one positron

(**Ans**: a)

(v) Covalent hydrides belong to:
- (a) Group IIIA to VIIA
- (b) Group IIA to Group VIA
- (c) Group IIIA to Group VA
- (d) Group IVA to Group VIA

(**Ans**: a)

(vi) Boranes are:
- (a) saline hydrides
- (b) metallic hydrides
- (c) polymeric hydrides
- (d) electron deficient hydrides

(**Ans**: d)

(vii) Hydrogen resembles both halogens in that:
- (a) it can form H^-
- (b) it can form H^+
- (c) it can form H_3O^+
- (d) it can form HCl

(**Ans**: a)

(viii) An example of saline hydride is:
- (a) CaH_2 (b) NH_3
- (c) LiH (d) B_2H_6

(**Ans**: a)

(ix) Ortho- and para-hydrogen differ essentially in:
- (a) physical properties (b) chemical properties
- (c) spin of electrons (d) spin of protons

(**Ans**: d)

(x) One characteristic feature of an oxidizing agent is that it:
- (a) gains electrons (b) contains oxygen
- (c) is oxidised (d) is a metal

(**Ans**: a)

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10

THE ALKALI METALS (GROUP IA)

The group I(A) consists of alkali metals comprising six elements, lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). They are called alkali metals because hydroxides of sodium and potassium are since long known to be "alkalie". The metals are also obtained by electrolysis of alkalies in fused state.

The alkali metals are characterised by the presence of one electron in outermost (valency shell) '*s*' orbitals. The low ionization potential values for the atoms of these elements render them electropositive nature. They acquire the configuration of noble gases preceding them during the formation of electropositive ions. The electronic configuration of alkali metals is shown in Table 10.1.

TABLE 10.1

Electronic Configuration of Alkali Metals

Element	Shell: 1	2		3			4				5			6		7
	Orbital: *s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*	*s*
Li	2	1														
Na	2	2	6	1												
K	2	2	6	2	6		1									
Rb	2	2	6	2	6	10	2	6			1					
Cs	2	2	6	2	6	10	2	6	10		2	6		1		
Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1

The ammonium ion, NH_4^+ resembles ions of group IA elements in chemical properties. It is more close to K^+ with respect to its physical properties.

Both potassium and rubidium have radioactive isotopes. Potassium — 40 is a weak β-emitter with a half-life of 1.3×10^9 years. Radioactive potassium makes up about 0.012 % of the natural element. Rubidium — 87 is also radioactive with half-life 6×10^{10} years.

Occurrence:

Owing to their reactivity, the alkali metals occur in nature only in the combined state. Sodium and potassium are more abundant metals and constitute 2.40 % and 2.35 % of the earth's crust, respectively. These metals are usually present in various silicate-type minerals and rocks.

The most important minerals of the most common metals are:

(i) **For lithium:**

$LiAl(PO_4)F$	Amblygonite

(ii) **For Sodium:**

$NaCl$	Rock salt or common salt
$NaNO_3$	Chile saltpetre
Na_2CO_3	Natron or Taona
$Na_2B_4O_7 . 10H_2O$	Borax

(iii) **For Potassium:**

$KCl . MgCl_2 . 6H_2O$	Carnallite
KCl	Sylvite

Preparation:

Alkali metals are prepared by electrolysis of the fused chlorides. In order to lower the melting points and to overcome corrosion, impurities like $CaCl_2$ are added before electrolysis.

$$MCl \longrightarrow M^+ + Cl^-$$

$$M^+ + e^- \longrightarrow M \text{ (Alkali metal)}$$

$$Cl^- - e^- \longrightarrow \frac{1}{2} Cl_2$$

GENERAL CHARACTERISTICS:

Physical Properties: The alkali metals are very soft, malleable and light metals; the first three being light enough to float upon water. They can be easily cut with knife. The freshly cut surface has a bright silvery lustre. Some of the important physical constants of the alkali metals are given in Table 10.2.

TABLE 10.2

Physical Constants of Alkali Metals

Element	Li	Na	K	Rb	Cs	Fr
Atomic number	3	11	19	37	55	87
Atomic weight	6.94	22.99	39.09	85.46	132.91	223
Atomic radius (pm)	152	186	227	248	265	—
Ionic radius (pm)	78	98	133	148	169	—
Ionization Potential (ev)	5.4	5.1	4.4	4.2	3.9	—
Density (g/cm^3)	0.53	0.97	0.86	1.53	1.90	—
Melting point (°C)	180.5	97.8	63.7	38.98	28.6	—
Boiling point (°C)	1326	883	756	688	690	—

The above physical properties are linked with loose bonding of the only valence electrons present in '*s*' orbitals of alkali metals. The trend in the values of ionization potential indicates the decreasing effect of effective nuclear charge on the valency (*s*) electrons with increasing atomic numbers.

The relatively weaker binding forces between alkali metal atoms in the solid state result in low melting and boiling points. The free motions of the valence electrons is responsible for the high electrical conductivity of metals.

These metals or their salts on heating in Bunsen flame impart characteristic colour to the flame. Lithium imparts caramine red, sodium yellow, potassium violet and caesium blue colour. The colour is imparted due to the electronic transitions from higher to lower energy states. In this process, energy is released in the form of light waves of particular wavelength corresponding to the metal.

Reactions:

The easy removal of one electron from alkali metal atoms, due to low ionization potential values invariably would exhibit a valency of +1 in their compounds. The reactivity of these metals increases with increase in atomic number due to the increasing ease with which electrons may be lost. Because of the ready loss of electrons, the alkali metals act as good reducing agents. The following reactions are more common:

(i) Action of Air or Oxygen: All the alkali metals except Li readily react with oxygen and are quickly tarnished. Lithium reacts only on heating to form Li_2O.

$$2Li + \frac{1}{2}O_2 \longrightarrow Li_2O$$

Sodium reacts slowly at room temperature and vigorously on heating to form sodium peroxide Na_2O_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

Potassium forms superoxide, KO_2 even at room temperature. Rubidium and caesium react rapidly with oxygen even at room temperature to form RbO_2 and CsO_2.

(ii) Reaction with Water: The alkali metals react very vigorously with water. A large amount of energy is released during the reaction and due to low melting points of alkali metals (except lithium), reaction becomes more vigorous. As a result of this hydrogen thus liberated catches fire.

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

Lithium is as good a reducing agent as caesium. This is because of high standard electrode potential ($E° = 3.02$ volts) of lithium in spite of its high ionization potential value.

(iii) Reaction with Acids. The alkali metals react very vigorously with acids:

$$2Na + 2HCl \longrightarrow 2NaCl + H_2$$

(iv) Reaction with Hydrogen. The alkali metals combine directly with hydrogen on gentle heating forming crystalline colourless compounds called hydrides. They belong to the class of ionic hydrides.

$$2Na + H_2 \longrightarrow 2NaH$$

(v) Reaction with Halogens: Alkali metals react with halogens with explosive violence. Halogens are strongly electronegative elements and would gain electrons from alkali metals capable of losing them.

$$2M + X_2 \longrightarrow 2MX \qquad (X = F, Cl, Br, I)$$

$$2K + Br_2 \longrightarrow 2KBr$$

(vi) Reaction with Nitrogen: Alkali metals react with nitrogen in presence of electric discharge to form nitrides.

$$6Li + N_2 \longrightarrow 2Li_3N$$

The nitrides are readily hydrolysed with water to liberate NH_3.

$$Na_3N + 3H_2O \longrightarrow 3NaOH + NH_3$$

(vii) Reaction with Ammonia: On passing gaseous ammonia over heated sodium, sodamide is formed.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

However, alkali metals react with liquid ammonia to form blue coloured solutions due to solvation.

(viii) Reducing Agents: Alkali metals are powerful reducing agents and reduce most of the oxides to elements on heating.

$$MgO + 2Na \longrightarrow Mg + Na_2O$$

$$CO_2 + 4Na \longrightarrow C + 2Na_2O$$

The chlorides of metals can also be reduced:

$$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$$

Among elements themselves the more powerful reducing agents will displace less reactive metals from their salts.

$$Li_2O + 2Na \longrightarrow 2Li + Na_2O$$

(ix) Reaction with H_2S: With H_2S, alkali metal sulphides are obtained.

$$2Na + H_2S \longrightarrow Na_2S + H_2$$

(x) Reaction with Acetylene: Alkali metals react with acetylene to form acetylides by replacement of hydrogen atoms.

$$2Li + C_2H_2 \longrightarrow Li_2C_2 + H_2$$

$$2Na + 2C_2H_2 \xrightarrow{90°C} 2NaHC_2 + H_2$$

$$2NaHC_2 \xrightarrow{190°C} Na_2C_2 + C_2H_2$$

(xi) Reaction with Alcohol: Alkali metals react with alcohols to form alcohols or alcoholates.

$$2Na + C_2H_5OH \longrightarrow 2C_2H_5ONa + H_2$$

Applications:

Alkali metals are mostly used as reducing agents. Sodium and other alkali metals are used in photoelectric cells. The Na – Pb alloy is used in the production of tetraethyl lead used as anti-knock in petrol.

IMPORTANT COMPOUNDS OF ALKALI METALS:

Alkali metals form well-defined compounds. Most of them are colourless except their dichromates, permanganates, cobaltinitrites, nitroprussides etc., which are coloured.

COMPOUNDS OF LITHIUM:

Lithium minerals are usually processed to obtain Li_2CO_3 or LiCl to get other compounds. Lithium carbonate is obtained by the action of ammonium carbonate on LiCl.

$$2LiCl + (NH_4)_2CO_3 \longrightarrow Li_2CO_3 + 2NH_4Cl$$

Lithium carbonate is used in glass industry. Lithium hydroxide is usually obtained from Li_2SO_4.

$$Li_2SO_4 + Ba(OH)_2 \longrightarrow 2LiOH + BaSO_4$$

COMPOUNDS OF SODIUM:

Some of the important compounds are discussed, except Na_2CO_3 and NaOH which are described along with chemical industries.

Sodium Peroxide, Na_2O_2: The compound is manufactured by heating small pieces of sodium in aluminium trays in furnace heated at 300°C. A current of dry air or CO_2 free air is passed in the opposite direction to the movement of aluminium trays. The passage of air from opposite direction is based upon the "counter current principle".

Properties:

(i) Sodium peroxide is a yellow powder which turns white on exposure to air owing to the formation of a coating of sodium hydroxide and carbonate. It is hygroscopic.

(ii) **Action of heat:** On heating, sodium peroxide liberates oxygen.

(iii) **Hydrolysis:** It reacts with water or moisture to form superoxide NaO_2, and hydroxide.

$$3Na_2O_2 + 2H_2O \longrightarrow 2NaO_2 + 4NaOH$$

In presence of hot water, only hydroxide is obtained.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

(iv) **Reaction with alcohol:** Na_2O_2 reacts with absolute alcohol at 0°C to give sodium hydrogen peroxide.

$$Na_2O_2 + Et\,OH \longrightarrow NaO\,Et + NaO\,.\,OH$$

(v) **Oxidising agent:** Sodium peroxide is a powerful oxidising agent and converts $Cr(OH)_3$, into Na_2CrO_4, SO_2 into SO_3 and chromite, $Fe(CrO_2)_2$ into ferric oxide. Thus, it oxidizes Fe (II) to Fe (III), Cr (III) to Cr (VI) and Co (II) to Co (III) etc.

$$2Fe(CrO_2)_2 + 7Na_2O_2 \longrightarrow Fe_2O_3 + 4Na_2CrO_4 + 3Na_2O$$

Benzoyl chloride reacts with Na_2O_2 to form benzoyl peroxide.

$$2C_6H_5COCl + Na_2O_2 \longrightarrow (C_6H_5CO)_2O_2 + 2NaCl$$

It converts $Cr(OH)_3$ into sodium chromate.

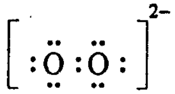
$$3Na_2O_2 + 2Cr(OH)_3 \longrightarrow 2Na_2CrO_4 + 2NaOH + 3H_2O$$

(vi) **Reaction with CO_2:** The peroxide, Na_2O_2 reacts with CO_2 to form carbonate.

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

Structure:

Sodium peroxide contains peroxide ions, O_2^{-2} which consist of chains of — O — O — in the molecular structure, Na — O — O — Na.



$$\left[:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:\right]^{2-}$$

The crystal structure is distorted trigonal prismatic.

Applications:

(i) It is used as oxidizing agent in chemical analysis.

(ii) It is used as an oxidizing and bleaching agent under the trade name 'oxone' for the preparation of oxygen and 'soda bleach' (Na_2O_2 and HCl) for bleaching of fibres.

(iii) It is also used for generating oxygen in hospitals and submarines.

Sodium Chloride, NaCl (Common Salt, 'Namak'):

Sodium chloride or common salt is present quite abundantly in nature. Rock salt and sea water (containing about 2.5 % NaCl) are the two main sources of sodium chloride. In Pakistan, large deposits of rock salt are present in salt range of Khewra. Rock salt deposits are also found in U.S.A. and Germany. The natural sodium chloride is usually associated with certain metal salts like $MgCl_2$ and $CaCl_2$ as impurities which render the commercial salt moist during humid weather.

Purification:

Pure sodium chloride is usually obtained by passing HCl gas through a saturated solution of commercial sodium chloride. Due to common ion effect the solid NaCl settles down.

$$Na^+\,Cl^- + H^+\,Cl^- \longrightarrow NaCl\downarrow + HCl$$

Pure sodium chloride is also called ***table salt***. It is a good source of a variety of other important compounds. Sodium chloride is an essential constituent in foods of animals and human beings.

Sodium nitrate, $NaNO_3$: This occurs in large quantities in Chile and is commonly known as ***Chile saltpetre***. The crude salt ***'caliche'*** is purified by crystallization. The mother liquor is mostly sodium iodate which is used as a source of iodine.

Sodium Nitrite, $NaNO_2$: Sodium nitrite is largely used as a source of azodyes and in other organic synthesis. It is commercially obtained from N_2 and O_2 of the air which are converted to NO in presence of electric spark. NO is converted to NO_2 simply by exposure to oxygen and later reacted with NaOH to form sodium nitrite.

$$2NO_2 + 2NaOH \longrightarrow 2NaNO_2 + H_2O + \tfrac{1}{2}O_2$$

Sodium nitrite can also be obtained from $NaNO_3$.

$$NaNO_3 + Pb \longrightarrow PbO + NaNO_2$$

It is a good reducing agent and liberates iodine from KI.

Sodamide, $NaNH_2$: When sodium is heated at about 300°C in presence of ammonia, sodamide is produced.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

Reactions:

(i) Sodamide is decomposed by water to liberate NH_3.

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

(ii) It reacts with CO_2 to form cyanamide.

$$2NaNH_2 + 2CO_2 \longrightarrow Na_2CO_3 + H_2O + \underset{\text{(Cyanamide)}}{NCNH_2}$$

(iii) On heating $NaNH_2$ with N_2O gas, sodium azide is formed.

$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O$$

(iv) When sodium amide is treated with $NaNO_3$ in liquid ammonia, sodium azide is formed.

$$NaNO_3 + 3NaNH_2 \longrightarrow NaN_3 + 3NaOH + NH_3$$

Sodium Cyanide, NaCN: It is formed by heating sodamide with red-hot charcoal.

$$NaNH_2 + C \xrightarrow{\text{Heat}} \underset{\text{(Sodium Cyanamide)}}{Na_2CN_2} \xrightarrow{\text{Heat}} NaCN$$

Sodium cyanide is very useful compound. It is used in electroplating and in the extraction of gold and silver. It is also an important chemical to carry out certain organic syntheses.

Sodium Tetraborate, $Na_2B_4O_7 . 10H_2O$ (Borax): Sodium tetraborate or borax is also called pyroborate and occurs in nature as *'tincal'*. It is obtained by,

(i) The mineral *tincal* is leached with water and crystallised to borax.

$$Na_2B_4O_7 . 10H_2O$$

(ii) The mineral ***'columenite'***, $Ca_2B_6H_{11}$ is treated with Na_2CO_3 to get borax.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

The byproduct $NaBO_2$ is also converted to borax by passing CO_2 through its solution.

$$4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

If crystallisation is carried out *below* 58°C, $Na_2B_4O_7 . 10H_2O$ is obtained but *above* 58°C, $Na_2B_4O_7 . 5H_2O$ is formed.

The concentrated solutions of borax liberate only boric acid and are acidic. However, large dilution renders the solution alkaline due to the formation of NaOH (a strong base) along with boric acid.

$$Na_2B_4O_7 + 3H_2O \longrightarrow 2NaBO_2 + 2H_3BO_3 \text{ (acidic)}$$

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3 \text{ (alkaline)}$$

Uses:

(i) Borax is used as a flux.

(ii) It is used for the manufacture of heat resisting glass (pyrex), glazes, enamels and soaps.

(iii) Leather industry utilises borax for soaking and cleaning hides.

(iv) It is applied in food preservations.

COMPOUNDS OF POTASSIUM:

The compounds of potassium are exactly similar to those of sodium and are also prepared by the same methods. The following important compounds of potassium will be discussed over here.

Potassium Superoxide, KO_2: It is prepared by the direct reaction between potassium metal and oxygen.

$$K + O_2 \longrightarrow KO_2$$

The superoxide is readily hydrolysed to give KOH and O_2.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

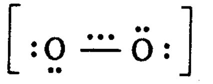
In presence of CO_2, carbonates are formed.

$$4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$$

The other superoxides behave exactly in the same manner. All the superoxides are paramagnetic and coloured.

Structure:

Potassium superoxide has calcium carbide structure and superoxide ion is represented as:



Potassium Nitrate (*Shora*), KNO_3: Potassium nitrate, nitre, is found as efflorescence on the surface of the earth in tropical countries like Pakistan and is usually called ***Shora*** or ***Kallar***. It is found that ammonia formed by the decay of nitrogenous matter of the soil is oxidised to HNO_3 under the influence of ***'nitrifying bacteria'*** of the soil. The acid reacts with potash present in the soil to form KNO_3.

Preparation:

(i) **From Nitrous Earth:** The salt is lixiviated with water and filtered. The clear solution is evaporated to get potassium nitrate crystals.

(ii) **From Chile saltpetre:** Large quantities of salt are obtained from chile saltpetre or $NaNO_3$ by double decomposition.

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl$$

It undergoes typical reactions of nitrates.

Applications:

It is not deliquescent and is used in fireworks. Large quantities of potassium nitrate are used in the manufacture of flint glass and as fertilizer.

Potassium Bromide, KBr: It is a white crystalline solid and has a sharp saline taste.

Preparation:

(i) It may be obtained by the action of HBr on KOH.

$$HBr + KOH \longrightarrow KBr + H_2O$$

(ii) **From Iron Bromide:** It may be obtained from iron bromide ($FeBr_2$. $2FeBr_3$) produced as byproduct during the manufacture of bromine. The ferric bromide is extracted with water and treated with K_2CO_3. The black precipitate of ferrosoferric hydroxide is filtered off and solution evaporated to get crystals of KBr.

$$FeBr_2 \, . \, 2FeBr_3 + 4K_2CO_3 + 4H_2O \rightarrow Fe(OH)_2 \, . \, 2Fe(OH_3)\downarrow + 8KBr + 4CO_2$$

(iii) **From Bromine:** Bromine dissolves in KOH to form potassium bromide and potassium bromate.

$$3Br_2 + 6KOH \longrightarrow 5KBr + KBrO_3 + 3H_2O$$

Potassium bromate formed as byproduct can also be converted to KBr either by direct heating or in presence of charcoal.

$$2KBrO_3 \longrightarrow 2KBr + 3O_2$$

$$KBrO_3 + 3C \longrightarrow KBr + 3CO$$

It undergoes the typical reactions of bromides, *i.e.*,

$$KBr + AgNO_3 \longrightarrow AgBr + KNO_3$$

$$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

Applications:

(i) Potassium bromide is used in medicine as sedative to remove nervousness and to induce sleep.

(ii) It is also used in photography.

Potassium Iodide, KI: It is similar in behaviour to KBr and is prepared by the action of I_2 with KOH.

$$3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 3H_2O$$

$$KIO_3 + 3C \longrightarrow KI + 3CO$$

The mass is extracted with water, filtered and evaporated to get crystals of potassium iodide.

It can also be obtained from Fe and I_2.

$$Fe + I_2 \xrightarrow{H_2O} FeI_2 \,.\, FeI_3 \xrightarrow[Boil]{K_2CO_3} KI$$

Potassium iodide undergoes the typical reactions of iodides, *i.e.*,

$$KI + AgNO_3 \longrightarrow AgI + KNO_3$$

KI is soluble in water and alcohol and is an oxidising agent.

Applications:

(i) It is used in medicine for the treatment of syphilitic and other diseases.

(ii) It is used as solvent for iodine.

$$KI + I_2 \longrightarrow KI_3$$

(iii) It is also used in photography.

Potassium Cyanide, KCN: It is obtained by the following methods:

(i) Potassium cyanide can be obtained by heating potassium ferrocyanide alone or in presence of metallic potassium.

$$K_4\,[Fe(CN)_6] \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$$

$$K_4\,[Fe(CN)_6] + 2K \xrightarrow{\Delta} 6KCN + Fe$$

(ii) It can also be obtained by heating KCl, carbon and calcium cyanamide in electric arc furnace.

$$CaNCN + C + 2KCl \longrightarrow 2KCN + CaCl_2$$

(iii) On heating K_2CO_3 and carbon in atmosphere of nitrogen at red hot, potassium cyanide is obtained.

$$K_2CO_3 + 4C + N_2 \longrightarrow 2KCN + 3CO$$

Properties:

Potassium cyanide is soluble in water and alcohol. It is deadly poisonous because of the reactivity of CN group for iron in blood which coagulates.

It forms complexes with transition metals like Fe, Ni, Cu etc., $K_4\,[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ are typical examples.

Applications:

Potassium cyanide is mainly used for the extraction of gold and as an analytical reagent.

Chrome Alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$: It is one of the important salts and is obtained in the laboratory by reducing an acidic solution of $K_2Cr_2O_7$ with SO_2.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 3H_2O \longrightarrow K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$$

Chrome alum is also obtained as a byproduct during the conversion of ethyl alcohol to acetaldehyde.

$$K_2Cr_2O_7+4H_2SO_4+3CH_3CH_2OH \longrightarrow K_2SO_4+Cr_2(SO_4)_3+3CH_3CHO+7H_2O$$

The dark green solution thus obtained is allowed to stand for a few days to get violet crystals of chrome alum.

Properties:

On heating, it melts at 89°C in its own water of crystallisation. It is a double salt and shows the same reactions as potassium sulphate and chromic sulphate.

Uses:

(i) It is used as a mordant in dyeing and calico-printing.

(ii) It is widely used in chrome tanning.

(iii) It is found useful in 'fixing bath' to harden the gelatin on photographic films and plates.

Potassium Dichromate, $K_2Cr_2O_7$ (*Surkh Kahi*):

(i) The compound can directly be obtained from *chromite* ore. The ore is roasted with lime and potassium carbonate. The lime keeps the mass porous and facilitates oxidation. The roasted mass is extracted with hot water. The solution is filtered and filtrate treated with sulphuric acid to convert chromate into dichromate. On cooling, orange red crystals of $K_2Cr_2O_7$ settle.

$$4FeO . Cr_2O_3 + 8K_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$$

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

(ii) Another method is to convert sodium dichromate into $K_2Cr_2O_7$ by using KCl. Potassium dichromate is far less soluble and separates out.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Reactions:

(i) Addition of an alkali to the solution of dichromate converts it into chromate with a colour change from orange to yellow.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

(ii) Potassium dichromate acts as an oxidizing agent in presence of sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow {}_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

It oxidises ferrous salts to ferric state.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

(iii) When potassium dichromate is heated with solid chlorides in presence of concentrated sulphuric acid, reddish brown vapours of chromyl chloride, CrO_2Cl_2 are evolved.

$$K_2Cr_2O_7 + 2KCl + 6H_2SO_4 \longrightarrow 6KHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

Applications:

(i) Potassium dichromate is used in the manufacture of other important chromium compounds *i.e.*, chrome alum, chrome yellow ($PbCrO_4$), zinc yellow ($ZnCrO_4$), etc.

(ii) It is a useful oxidising agent and is also used to convert ethyl alcohol to acetaldehyde or in the manufacture of anthraquinone.

(iii) It is also used in chrome tanning. The hides are first soaked in a weakly acidified solution of potassium dichromate and then immersed in a bath of reducing agents such as bisulphite or hypo. The precipitated hydrous chromic oxide settles within the pores of leather.

$$K_2Cr_2O_7 + 3NaHSO_3 + H_2SO_4 + 2H_2O \longrightarrow K_2SO_4 + 3NaHSO_4 + 2Cr(OH)_3$$

Potassium Permanganate, $KMnO_4$ (*Lal Dawaee or Potash*): It is very important compound and is obtained from manganese dioxide (pysolusite). A mixture of manganese dioxide and potassium hydroxide is fused in air to get green mass of potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

The green mass of potassium manganate is extracted with water and oxidised with ozone or chlorine to potassium permanganate.

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

The purple solution thus obtained is concentrated and allowed to stand when deep purple crystals of $KMnO_4$ with metallic lustre are obtained.

Reactions:

In presence of excess of dilute H_2SO_4, it acts as a good oxidising agent as is shown by the following reactions:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$5C_2O_4^{2-} + 5MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Uses:

(i) It is employed as a reagent in quantitative analysis.

(ii) Potassium permanganate is used as an important disinfectant.

RUBIDIUM AND CAESIUM COMPOUNDS:

The compounds are rare but similar to those of sodium and potassium. Caesium is the most electropositive of all alkali metals and CsOH is the strongest alkali of all hydroxides of this group. Rubidium and caesium salts are more soluble than corresponding potassium salts. They easily form superoxides. RbO_2 and CsO_2, in addition to other oxides.

COMPLEX COMPOUNDS:

(a) **Organometallic:** One of the most important fields of the chemistry of Group I elements is the organic derivatives of alkali metals. The most common and useful compounds are organolithium and organosodium. They are usually prepared from alkyl or aryl halides.

$$C_2H_5Cl + 2Li \longrightarrow C_2H_5Li + LiCl$$

Organolithium and sodium compounds react rapidly with oxygen and are readily inflammable in air and water. They are very reactive compounds and are widely used in organic synthesis.

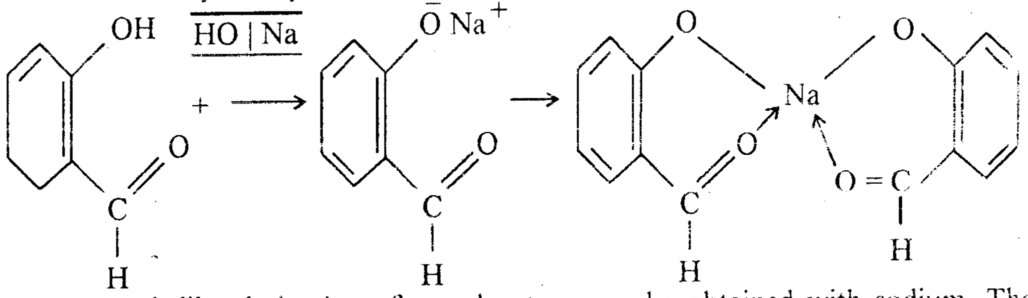
$$2Li + R_2Hg \longrightarrow 2RLi + Hg$$

The ethereal solution of phenyl lithium is oxidised by oxygen, with chemiluminescence, to diphenyl.

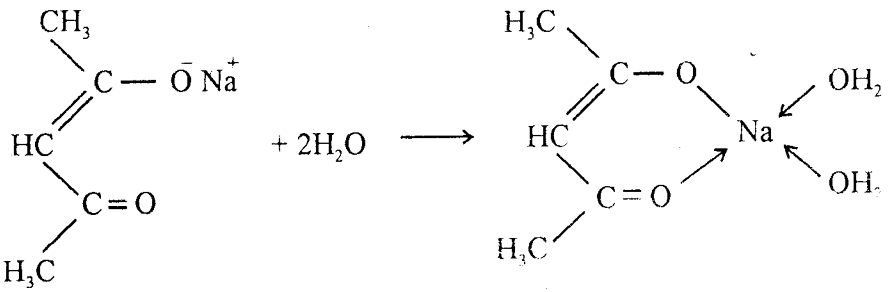
$$2LiC_6H_5 \quad O \longrightarrow C_6H_5 - C_6H_5 + Li_2O$$

LiC_6H_5 reacts with peroxide to give $LiOC_6H_5$.

(b) **Coordination Compounds:** The electronic configuration of alkali metals does not favour the formation of coordination compounds because of the absence of *d* orbitals. But chelating groups impose some acceptor properties on alkali metals. Thus saliylaldehyde forms a sodium derivative on treatment with NaOH.

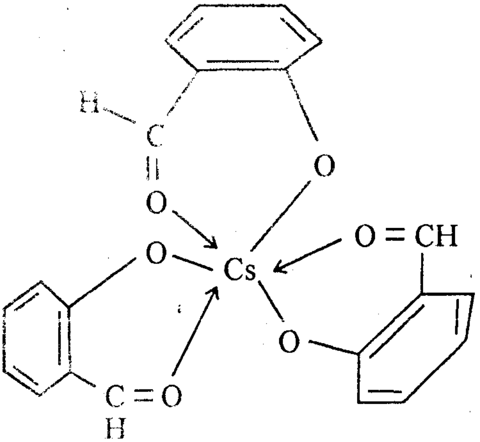


A salt-like derivative of acetylacetone can be obtained with sodium. The product is soluble in non-polar solvents such as toluene and is a dihydrate.



It should be pointed out that the alkali metals involve the next vacant orbitals for hybridization. In most of these complexes sp^3 hybridization takes place.

Potassium, rubidium and caesium form 6-coordinate covalent bonds, shown below:



DIAGONAL RELATIONSHIP BETWEEN LITHIUM AND MAGNESIUM:

The first few members of the first period show similar behaviour to elements of the next group belonging to the second period. This is called diagonal relationship or similarity. Thus lithium resembles magnesium, beryllium resembles aluminium and boron resembles silicon as regards the chemical behaviour.

1st group ⟶ Li Be B C

2nd group ⟶ Na Mg Al Si

The similarity between lithium and magnesium can be realised from the following points:

(i) Both lithium and magnesium form normal oxides on burning. Other alkali metals also form higher oxides.

(ii) The carbonates of lithium and magnesium are unstable and decompose to form oxides.

$$MgCO_3 \longrightarrow MgO + CO_2$$
$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

(iii) Both lithium and magnesium form the carbides and nitrides by direct combination of elements.

$$6Li + N_2 \longrightarrow 2Li_3N$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$

(iv) Both the carbonates and phosphates of lithium and magnesium are insoluble in water. Alkali metals form soluble carbonates and phosphates.

(v) Both metals show strong hydration of the ions.

(vi) The chlorides and some of other compounds of both are soluble in organic solvents.

Questions

1. Give an account of the general characteristics of alkali metals. How can we explain these properties based upon the atomic structure of alkali metals?
2. Explain the reactivity of alkali metals with examples.
3. Discuss the anomalies of lithium, and compare it with magnesium.
4. Explain why:
   (a) metallic sodium does not occur in the free state.
   (b) alkali metals can form complex compounds.
   (c) calcium chloride is added to electrolyse fused sodium chloride.
5. Discuss the reducing action of alkali metals.
6. Discuss the chemistry of the following:
   (a) Potassium permanganate.
   (b) Potassium dichromate.
   (c) Sodium peroxide.
7. Describe the chemistry and usefulness of some of the compounds of potassium and sodium.
8. Comment on the expected properties of caesium.
9. What is the tendency of covalent compound formation in the following set of metals:

   Li and Na ; Na and Rb
10. Why do alkali metals show low ionization potential values?
11. **Give short answers:**
    (i) Give names and electronic configuration of alkali metals.
    (ii) Give names of most important minerals of alkali metals.
    (iii) What are the general characteristics of alkali metals?
    (iv) Name important compounds of alkali metals.
    (v) Describe important compounds of sodium.
    (vi) Give preparation and important characteristics of potassium compounds.
    (vii) How is potassium dichromate prepared? Give some of its chemical reactions.
    (viii) How is potassium permanganate commercially prepared? Give its typical reaction in which it acts as an oxidizing agent.

(ix) Describe at least three typical coordination compounds of alkali metals.

(x) What is the diagonal relationship between lithium and magnesium?

12. **Give the correct answer:**

(i) Total number of alkali metals in Group I are:

(a) 4
(b) 5
(c) 6
(d) 7

(Ans: c)

(ii) Pure sodium chloride is prepared by:

(a) passing HCl gas
(b) adding HCl
(c) passing Cl_2
(d) adding more NaCl

(Ans: a)

(iii) Borax occurs in nature as:

(a) columenite
(b) carnalite
(c) chile saltpetre
(d) tincal

(Ans: d)

(iv) Iodine dissolves:

(a) in water
(b) KI solution
(c) NaI solution
(d) HCl

(Ans: b)

(v) Chrome alum has:

(a) 12 H_2O
(b) 16 H_2O
(c) 20 H_2O
(d) 24 H_2O

(Ans: d)

(vi) Li is the best reducing agent due to:

(a) low ionization energy
(b) small ionic radius
(c) low heat of sublimation
(d) high enthalpy of hydration

(Ans: a)

(vii) The covalent radius of potassium atom is 0.203 nanometer. The ionic radius of K^+ ion is:

(a) 0.013
(b) 0.254
(c) 0.133
(d) 0.231

(Ans: c)

(viii) Which of the following carbonates does not yield CO_2 on heating?

(a) Li_2CO_3 (b) Na_2CO_3

(c) $CaCO_3$ (d) $MgCO_3$

(**Ans:** b)

(ix) Baking powder is:

(a) $NaHCO_3$ (b) Na_2CO_3

(c) $KHCO_3$ (d) K_2CO_3

(**Ans:** a)

(x) Which is not correct?

(a) H_2O oxidizes Na (b) H_2 oxidises Li

(c) SO_2 reduces H_2S (d) H_2O_2 reduces Ag_2O

(**Ans:** b)

❀ ❀ **10** ❀ ❀

11

ALKALINE EARTH METALS (GROUP IIA)

The elements beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra) belong to Group IIA and are collectively known as the alkaline earth metals. Radium is radioactive. The electronic configurations (shown in Table 11.1) consist of a noble gas kernel plus a pair of '*s*' electrons in the valence shell of these elements. The atoms of these elements are somewhat smaller than those of the corresponding alkali metals in the same period. As a result of this, they show greater specific gravities, greater hardness and higher melting points. The variation in physical properties of these elements are not as regular as for the alkali metals. The reason for this being that the elements of this group do not crystallise with the same type of metallic lattice. Beryllium and magnesium crystallise in close-packed haxagonal lattices, calcium and strontium in face-centred cubic lattices, and barium in body-centred cubic lattices.

TABLE 11.1

Electronic Configuration of Elements of Group IIA

	1	2		3			4				5			6		7
Element	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*	*s*
Be	2	2														
Mg	2	2	6	2												
Ca	2	2	6	2	6		2									
Sr	2	2	6	2	6	10	2	6			2					
Ba	2	2	6	2	6	10	2	6	10	14	2	6		2		
Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2

The smaller atomic radii are responsible for higher values of ionization potentials than those for alkali metals. Except for beryllium, di-positive ions of these metals are readily formed. The alkaline earth metals are quite reactive but less than alkali metals. The small atomic size and resulting high ionization potential value of beryllium render it less reactive than other elements of this group. The overall effect is the greater difference in the chemistry of beryllium and other metals of this group (IIA) than that with alkali metals. Beryllium shows a diagonal relationship with aluminium (a member of Group III). It should be noted over here that electronegativities of both Be and Al are 1.5.

Occurrence:

The reactivity of the alkaline earth metals does not allow them to remain in free state. The compounds of these elements occur widely in nature. The most important minerals are:

(i)	**For beryllium:**	$Be_3Al_2(SiO_3)_6$	Beryl
		$BeO \cdot Al_2O_3$	Chrysoberyl
(ii)	**For magnesium:**	$KCl \cdot MgCl_2 \cdot 6H_2O$	Carnallite
		$MgCO_3$	Magnesite
		$MgCO_3 \cdot CaCO_3$	Dolomite
		$MgSO_4 \cdot 7H_2O$	Epsom salt
(iii)	**For calcium:**	$CaCO_3$	Limestone, Chalk, Marble (Sang-e-Marmar), Calcite.
		$CaSO_4 \cdot 2H_2O$	Gypsum
		$Ca_3(PO_4)_2$	Phosphorite
(iv)	**For strontium:**	$SrCO_3$	Strontianite
(v)	**For barium:**	$BaCO_3$	Witherite

Preparation:

Alkaline earth metals are themselves reducing agents and cannot easily be prepared by reduction of their oxides. The electrolysis in solution is also not possible because of the high oxidation potential of these metals. Moreover, the metals immediately react with water and cannot be isolated easily. ***The metals are usually obtained by the electrolysis of their fused chlorides.*** Some salts are added as impurities to reduce the melting points. They can be obtained by reduction of their oxides with Al.

$$3SrO + 2Al \longrightarrow Al_2O_3 + 3Sr$$

General Characteristics

Physical Properties: All metals have white colour, except beryllium which has steel grey colour. They are readily tarnished in air but with oxides formed initially on the surface protects them from further attack. Some of the important physical properties of these metals are given in Table 11.2.

TABLE 11.2

Physical Properties of Alkaline Earth Metals

Element	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic weight	9.012	24.312	40.08	87.62	137.54	226.05
Atomic radius (pm)	106	140	174	191	198	220
Ionic radius (pm)	34	78	106	127	143	157
1st Ionization Potential (ev)	9.32	7.64	6.11	5.69	5.21	5.28
Density (g/cm^3)	1.86	1.75	1.55	2.60	3.59	6.00
Melting point (°C)	1278	651	843	769	725	700
Boiling point (°C)	1500	1100	1487	1366	1537	1150

The higher values of densities and melting points are due to (i) higher nuclear charge, and (ii) the presence of two electrons in the valency shell.

The nuclear charge of alkaline earth metals is more than the corresponding alkali metals. Hence more attractive forces would come into play and atomic size would decrease.

The ionization potential values are more than alkali metals which can be expected from the greater nuclear pull of the electrons due to increase in the nuclear charge on the atoms of alkaline earth metals.

Ca, Sr and Ba form volatile salts and would impart characteristic brick red, red and green colours, respectively due to electronic excitations by supplying heat energy.

Reactions:

The reactivity of these elements increases with increasing atomic number. The two electrons present in outermost '*s*' orbitals are relatively easily lost. This renders these metals good reducing agents. They form dipositive colourless cations. The typical reactions of these metals are:

(i) Action of Air or Oxygen: The alkaline earth metals react readily on heating with oxygen and nitrogen of the air to form corresponding divalent oxides and nitrides.

$$2M + O_2 \longrightarrow 2MO$$

$$3M + N_2 \longrightarrow M_3N_2$$

Ba forms peroxides, BaO_2, owing to its greater reactivity.

(ii) Reaction with Hydrogen: Ca, Sr and Ba form corresponding hydride compounds when heated with hydrogen. Beryllium forms BeH_2 only on heating in the presence of atomic hydrogen.

$$Ca + H_2 \xrightarrow{\Delta} CaH_2$$

These hydrides are readily hydrolysed to liberate hydrogen

$$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + H_2$$

(iii) Reaction with water: The reaction of these metals with water is less violent than alkali metals. However, they react with water to form hydroxides and liberate hydrogen.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

The reaction becomes more and more vigorous with increase in atomic number. Thus barium reacts more rapidly than calcium or magnesium but less than sodium (a metal of 1st group). They react with alcohols to form alcoholates but with difficulty.

$$Ba + 2H_2O \longrightarrow Ba(OH)_2 + H_2$$

$$M + 2C_2H_5OH \longrightarrow M(OC_2H_5)_2 + H_2$$

(iv) Reaction with Acids: The metals react with acids quite vigorously but less than alkali metals.

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

(v) Reaction with Halogens: The alkaline earth metals directly combine with halogens to form hydrated halides. They are ionic compounds except Be halides.

$$M + X_2 \longrightarrow MX_2$$

(vi) Reaction with Nitrogen: All these metals combine with nitrogen to form corresponding nitrides. The nitrides liberate NH_3 on hydrolysis.

$$3M + N_2 \longrightarrow M_3N_2$$

(vii) Reaction with Carbon: Calcium, strontium and barium combine directly with carbon at high temperatures to form acetylides of the type MC_2. On hydrolysis they yield acetylene and probably contain $(C \equiv C)^{2-}$ ion.

$$Ca + 2C \longrightarrow CaC_2$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

Magnesium does not combine directly with carbon under any conditions.

(viii) Reaction with Alkalies: Only beryllium dissolves in cold, concentrated aqueous alkalies to form alkali metal beryllate (similar to aluminates).

$$Be + NaOH + H_2O \longrightarrow NaHBeO_2 + H_2$$

(ix) Reaction with Ammonia: Ca, Sr and Ba dissolve in liquid ammonia to form stable hexammine derivatives in solution.

$$Ca + 6NH_3 \longrightarrow [Ca\,(NH_3)_6]$$

(x) Reducing Agents: The alkaline earth metals are quite powerful reducing agents and would reduce many oxides and chlorides.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$
$$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$$

Applications:

(i) The light metals are used to prepare light alloys *i.e.*, magnalium, an alloy of magnesium (30%) and aluminium (70%) which is used to construct cheap balances, and pistons of motor engines.

(ii) The metals may be used as 'deoxidizer' to prepare copper, aluminium etc., from oxides.

(iii) Magnesium powder is used as an essential constituent of the flashlight, military star-shells and other light signals.

(iv) Calcium is used as a dehydrating agent for those organic compounds which are decomposed by sodium.

(v) Beryllium is transparent to X-rays and is used as window material of x-rays tubes.

(vi) Barium is used as a degassing agent in making vacuum tubes.

IMPORTANT COMPOUNDS OF ALKALINE EARTH METALS:

Alkaline earth metals form colourless compounds in which their oxidation states are +2. Some of the important compounds from commercial and academic point of view are discussed below.

Compounds of Beryllium: Compounds of beryllium are mostly covalent in nature. This is due to small size of its atom resulting in high values of ionization potentials. As a result, electron transfer becomes more difficult.

Beryllium halides are formed by passing halogens over a mixture of BeO and carbon at high temperatures.

$$BeO \quad C \quad Cl_2 \longrightarrow BeCl_2 + CO$$

Beryllium chloride is a linear molecule formed by *sp* hybridized orbitals of Be to form two equivalent bonds at an angle of 180°. The bonding is covalent in nature. The overlap of *p* orbitals of chlorine with *sp* hybrid orbitals are shown in Figure 11.1.

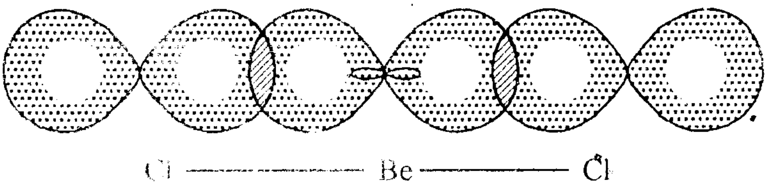


Fig. 11.1. Overlap of p orbitals of Cl atoms with sp hybrid orbitals of Be.

Compounds of Magnesium: The following compounds of magnesium have variety of interest and would, therefore, now be discussed.

Magnesium Carbonate, $MgCO_3$: This compound occurs in nature as *magnesite.* On adding a sodium carbonate solution to magnesium sulphate, a white precipitate of *basic carbonate,* $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ is formed. The basic carbonate is usually known as *magnesia alba* in commerce, and used in the manufacture of cosmetics and tooth paste.

It decomposes on heating to give MgO and CO_2.

$$MgCO_3 \longrightarrow MgO + CO_2$$

On passing excess CO_2 to the suspension of magnesium carbonate a clear ion

$$MgCO_3 + CO_2 + H_2O \longrightarrow Mg(HCO_3)_2$$

btained. Magnesium bicarbonate is usually known as 'fluid magnesia'. It is ent in hard water and is converted to insoluble basic carbonate on boiling.

gnesium Oxide, MgO: It is commonly known as magnesia.

eparation:

(i) By burning metallic Mg in air or oxygen, MgO is obtained.

$$2Mg + O_2 \longrightarrow 2MgO$$

(ii) On heating $MgCO_3$ or $Mg(OH)_2$ or $Mg(NO_3)_2$, magnesium oxide is obtained.

$$MgCO_3 \longrightarrow MgO + CO_2$$

$$Mg(NO_3)_2 \longrightarrow MgO + 2NO_2 + \tfrac{1}{2} O_2$$

Properties:

(i) MgO is a very light white powder and is a bad conductor

(ii) It is insoluble in water but reacts with it to form hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

(iii) It reacts with acids to form corresponding salts.

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

(iv) With reducing agents, it undergoes the following reactions:

$$MgO + C + S \longrightarrow MgS + CO$$

$$MgO + CO + Cl_2 \longrightarrow MgCl_2 + CO_2$$

(v) Reactions with CS_2 and CaC_2.

$$2MgO + CS_2 \xrightarrow{700^\circ - 900^\circ} 2MgS + CO_2$$

$$MgO + CaC_2 \xrightarrow{1300^\circ} Mg + CaO + 2C$$

Structure:

It has sodium chloride structure.

Applications:

(i) It fuses at high temperature and is used as furnace lining.

(ii) Magnesium oxide may be used in medicine to control hyperacidity.

(iii) A mixture of MgO and asbestos is used as "lagging" for steam pipes and boiler to reduce the loss of heat.

Magnesium Sulphate, $MgSO_4 . 7H_2O$: This is usually called Epsom salt and is prepared by the action of $MgCO_3$ or magnesite with H_2SO_4

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

Magnesium sulphate is less soluble in cold water but is freely soluble in hot water.

When magnesium sulphate is heated, water is lost and anhydrous magnesium sulphate is rendered as porous feathery material.

Applications:

(i) It is used in medicine as purgative.

(ii) The platinized magnesium sulphate is also used for the manufacture of H_2SO_4 by Grillo process.

(iii) A mixture of $MgSO_4$, NH_4Cl, NH_4OH is used in analytical chemistry under the name magnesia mixture.

Magnesium Chloride, $MgCl_2 . 6H_2O$: This is found in sea water and in the mineral carnallite. It is usually obtained by the action of HCl on MgO or $MgCO_3$.

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

Anhydrous magnesium chloride can only be obtained by heating Mg in chlorine.

Properties:

(i) Magnesium chloride is very soluble in water and can be recrystallised as $MgCl_2 . 6H_2O$. This hexahydrate is hygroscopic compound.

(ii) On heating it hydrolyses and forms MgO, HCl and H_2O.

$$MgCl_2 . 6H_2O \longrightarrow MgO + 2HCl + 5H_2O$$

Slow heating gives magnesium oxychloride which on strong heating liberates chlorine.

$$2MgCl_2 . 6H_2O \longrightarrow Mg_2OCl_2 + 5H_2O + 2HCl$$

$$2Mg_2OCl_2 + O_2 \longrightarrow 4MgO + 2Cl_2$$

Structure:

The magnesium chloride has $CaCl_2$ lattice. The structure of $BeCl_2$ is chain-like.

Applications:

(i) It is used as a constituent of Sorel's cement (MgO. $MgCl_2$), which is a hard, marble-like mass.

(ii) It may be used as a constituent for filling teeth.

Magnesium Phosphate, $Mg_3(PO_4)_2$: It is obtained by the addition of Na_3PO_4 to magnesium salt solution.

The magnesium halide is treated with Na_2HPO_4.

$$MgCl_2 + Na_2HPO_4 \longrightarrow MgHPO_4 + 2NaCl$$

When $MgHPO_4$ is treated with NH_3 and NH_4Cl, a white precipitate of magnesium ammonium phosphate is obtained, which on heating decomposes to magnesium pyrophosphate.

$$MgHPO_4 + NH_3 \longrightarrow MgNH_4PO_4$$

$$2MgNH_4PO_4 \longrightarrow \underset{\text{(magnesium pyrophosphate)}}{Mg_2P_2O_7} + H_2O + 2NH_3$$

Magnesium Silicate: The hydrated magnesium silicate is usually called Talc or Soapstone. It is greasy to touch and soft. It is commercially used in making face powder and household furniture.

Asbestos is a hydrated magnesium silicate with fibrous structure. It is used for making incombustible fabrics and hardboard.

Non-Chelate Complexes: The magnesium can be converted to alkyl derivatives. The ethereal solutions of alkyl magnesium halides RMgX, commonly known as Grignard reagents, have been extensively used for organic synthetic processes.

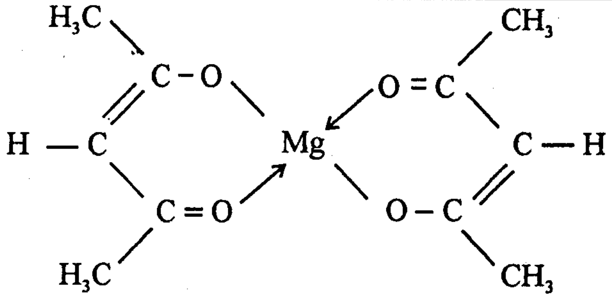
Cyclopentadienyl magnesium, $(C_5H_5)_2$ Mg, is prepared by the reaction of cyclopentadiene with C_2H_5MgBr or magnesium vapours. It is an ionic, colourless, crystalline compound.

The cationic and anionic complexes have also been prepared. The compounds of the type K_2MgF_4 and (Mg . $4NH_3$) Cl_2 represent this class and have been prepared.

Several coordination complexes of the following type have also been obtained.

$$(Mg\ .\ 6NH_3)\ Cl_2,\ (Mg\ 2Py\ .\ 4H_2O)\ (NO_3)_2,\ (Mg\ .\ 6CH_3CN)I_2.$$

Chelate Complexes: The bidendate and polydendate (chelating) ligands are able to react with magnesium to form various complexes. Such ligands include β-diketones, β-ketoesters etc. Thus, acetylacetone forms a stable complex:



(Magnesium acetylacetonate)

This possibility of complex formation supports the presence of magnesium and naturally occurring compounds. For example, chlorophyll (responsible for photosynthesis in plants) contains magnesium sitting in the centre of chelating ligands (porphin compounds) bearing nitrogen atoms.

COMPOUNDS OF CALCIUM:

Calcium forms almost similar compounds as those described for magnesium. The following compounds are more important and would now be discussed.

Calcium Oxide (*Anbujha Chuna*), CaO: Calcium oxide is commonly known as quicklime or lime. It is manufactured from limestone, $CaCO_3$, in a tall chimney-like furnace called "limekiln".

$$CaCO_3 \longrightarrow CaO + CO_2$$

The temperature must be kept low in order to avoid the possibility of forming fusible silicates of high temperatures.

Quicklime is a white amorphous powder. It melts at 2570°C and emits a bright light known as *'limelight'* on strong heating.

It reacts exothermally with water to form hydroxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Calcium oxide reacts with oxides to form corresponding salts.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

A mixture of CaO and coke reacts in electric furnace to form calcium carbide.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Applications:

(i) It is used as a cheap material for making slaked lime, bleaching powder, mortar, calcium carbide, cement and glass.

(ii) It is also used in the purification of sugar and coal gas.

(iii) It is also used in tanneries.

(iv) It is used to liberate ammonia from ammonium salts.

(v) A mixture of CaO and NaOH called 'Sodalime' is used to remove CO_2 and water vapour from atmosphere.

Calcium Hydroxide, $Ca(OH)_2$: It is also called slaked lime (*Bhuja hua chuna*) and is obtained pure by adding water to quicklime, CaO. The reaction is exothermic and converts water into steam. On adding excess of water a milky liquid is obtained called ***milk of lime.*** When solution is allowed to stand it becomes clear and is usually called lime water. The solubility of calcium hydroxide decreases with increase in temperature. The solution of lime is $\frac{N}{20}$ at 0°C but only $\frac{N}{50}$ at 100°C.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Calcium hydroxide reacts with CO_2 of the atmosphere and forms $CaCO_3$.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Applications:

(i) It is used in making hydraulic mortar and cement.

(ii) Lime is also used for white-washing.

(iii) Large quantities of lime are used in agriculture. The heavy soil becomes loose and water holding capacity of sand soil increases.

(iv) Lime is used in the manufacture of various chemicals such as bleaching powder, calcium carbide, glass, ammonia, caustic soda etc.

Calcium Carbonate, $CaCO_3$: It occurs in various forms. Limestone and marble occur widely in Pakistan and Himalaya ranges.

Pure calcium carbonate can be prepared by adding sodium carbonate to a solution of calcium salt.

$$CaCl_2 + Na_2CO_3 \longrightarrow 2NaCl + CaCO_3$$

Calcium carbonate dissolves in water in presence of CO_2, with the formation of *calcium bicarbonate.*

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

Applications:

It is used in cement utilised for the construction of buildings and for the manufacture of glass, washing soda and lime etc.

The formation of cement from limestone will be discussed later.

Calcium Carbide, CaC_2: It is usually prepared on a large scale by heating strongly a mixture of quicklime and powdered coke in an electric furnace.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

It is a hard, dark-grey crystalline solid and is decomposed by water to evolve acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

It is used as a source of acetylene and for the manufacture of cyanamide.

Calcium Sulphate: Calcium sulphate is abundantly found in the form of ***gypsum***, $CaSO_4 . 2H_2O$ and as anhydride, $CaSO_4$.

When gypsum, $CaSO_4 . 2H_2O$, is heated at 120° – 130°, it forms calcium sulphate hemihydrate, $(CaSO_4)_2 . H_2O$, known as *Plaster of Paris*. When Plaster of Paris is allowed to stand in water it sets to a solid mass, owing to regeneration of gypsum.

$$\underset{\text{Plaster of Paris}}{(CaSO_4)_2 . H_2O} + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2CaSO_4 . 2H_2O}$$

The conversion of Plaster of Paris to Gypsum is facilitated by the presence of a few particles of gypsum which act as nuclei.

Plaster of Paris is used for making casts, statues, blackboard chalk, etc.

Calcium Superphosphate, $Ca(H_2PO_4)_2$: Calcium superphosphate is manufactured from calcium phosphate, from bone ash or powdered phosphorite. A calculated quantity of H_2SO_4 is added to calcium phosphate to form a paste and allowed to stand for 24 – 36 hours. During this time, the temperature rises to 100° due to exothermic reaction.

$$Ca_3(PO_4)_3 + 3H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

It is soluble in water and is used as fertilizer to reinforce phosphorus content in the soil.

Bleaching Powder, CaCl (OCl): It is a useful compound and is usually accompanied by $CaCl_2 . Ca(OH)_2 . H_2O$ (basic chloride). It is prepared on industrial scale by the action of chlorine or dry slaked lime. The process for the manufacture of bleaching powder is based on *counter current principle* in which chlorine is passed in the opposite direction to lime.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaCl(OCl) + H_2O$$

Properties:

(i) Bleaching powder is a pale yellow powder having chlorine smell.

(ii) Due to the presence of basic chloride, $CaCl_2 . Ca(OH)_2 . H_2O$ along with it, four ions are found in solution, *i.e.*, Ca^{2+}, Cl^-, OCl^-, OH^-.

(iii) Bleaching powder is a good oxidising agent due to presence of hypochlorite ion, OCl^-.

$$OCl^- + 2H^+ + 2e \longrightarrow H_2O + Cl^-$$

Bleaching powder also acts as a bleaching and disinfecting agent due to this property.

(iv) The chloride ion produced by aqueous solution of bleaching powder has reducing properties. Thus addition of an excess of dilute acid would liberate whole of the chlorine.

$$\begin{array}{c} OCl^- + 2H^+ + 2e \longrightarrow H_2O + Cl^- \\ 2Cl^- \longrightarrow Cl_2 + 2e \\ \hline OCl^- + Cl^- + 2H^+ \longrightarrow H_2O + Cl_2 \end{array}$$

This is the amount of chlorine liberated in presence of acid and is called ***"available chlorine".*** The evaluation of bleaching powder is based on the amount of chlorine liberated.

(v) Bleaching powder is unstable in the presence of acids. But the presence of OH^- ions increases the stability of bleaching powder.

$$CaCl(OCl) + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

(vi) Bleaching powder loses its strength on exposure to air due to its reaction with CO_2.

$$Ca^{2+} + 2OH^- + CO_2 \longrightarrow CaCO_3 + H_2O$$

Applications:

(i) Bleaching powder is used for bleaching wood, cotton and linen. The bleaching of cotton is an automatic process. The cloth is first passed through bleaching powder solution and through a vat containing a dilute acid solution. The cloth is then passed through antichlor, *e.g.*, sodium bisulphite or hypo which destroys the excess chlorine otherwise cloth would be destroyed.

$$NaHSO_3 + H_2O + Cl_2 \longrightarrow NaHSO_4 + 2HCl$$

$$Na_2S_2O_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl + S$$

(ii) It is largely used as disinfectant and for sterilization of water.

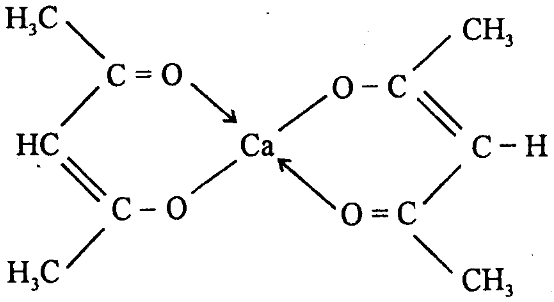
(iii) It is also used to prepare shrinkable wood.

Non-Chelate Complexes: Various Lewis bases (ligands) are capable of forming non-chelate complexes such as $[Ca(NH_3)_4]Cl_2$ and $[Ca(H_2O)_4](NO_3)_2$.

These compounds have tetrahedral arrangement.

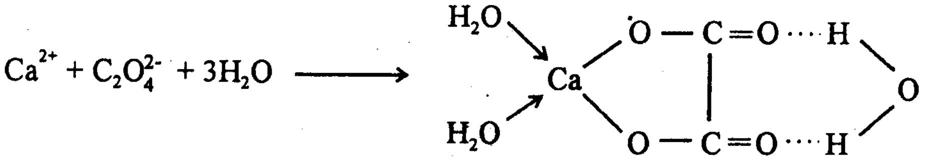
Chelate Complexes: Calcium forms chelate complexes with β-diketones, β-ketoesters and α-dicarboxylic esters.

An example of β-diketone complex is acetylacetonate of calcium obtained by treating Ca^{2+} with acetylacetone (acac).

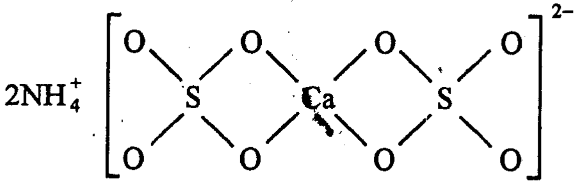


Acetoacetic ester and malonic ester react in a similar way.

Calcium salts react with oxalic acid to form a precipitate of calcium oxalate trihydrate.



Calcium sulphate dissolves in a concentrated aqueous ammonium sulphate solution owing to the formation of the following complex ion:



Magnesium and calcium form well defined complexes with ethylenediaminetetraacetic acid (EDTA). This complex formation is the basis of complexometric titrations of these metals. The structure of Ca-EDTA complex is given in Figure 11.2. EDTA acts as a hexadentate ligand.

Compounds of Sr, Ba and Ra: The compounds of these metals are similar to those of calcium. Their carbonates, sulphates and chromates are insoluble compounds. Barium sulphate is used in the manufacture of paints, pigments and in rubber industry.

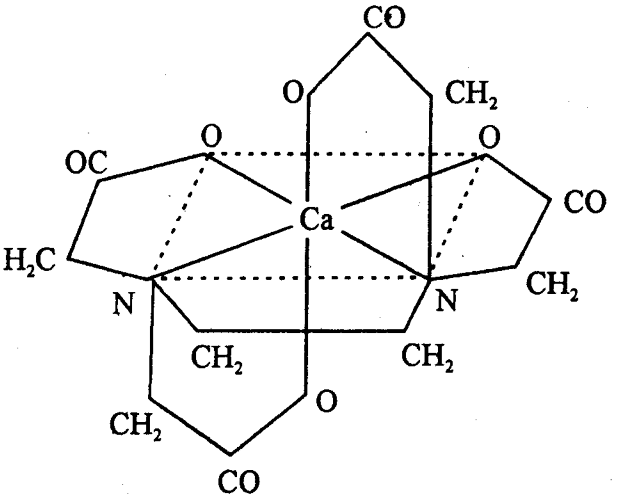


Fig. 11.2. Ca – EDTA complex.

Comparison of Alkali and Alkaline Earth Metals: The alkali and alkaline earth metals resemble in many respects and this may be due to the involvement of *s* orbital electrons in their chemistry.

The points of similarity are:

(i) Both alkali and alkaline earth metals are electropositive and have great chemical reactivity.

(ii) They do not occur in free state in nature.

(iii) Both are prepared by electrolysis of their fused chlorides.

(iv) Alkali and alkaline earth metals are soft and silvery white metals.

(v) They react with water to form hydroxides and liberate H_2.

(vi) The hydroxides of both are strong bases.

Points of Difference: The points of difference between alkali and alkaline earth metals arise mainly due to the presence of one and two electrons in valence shell, respectively. The M^{2+} ions formed by alkaline earth metals pull the electron cloud closer to the nucleus than M^+ ions of alkali metals. Thus greater reduction in size of alkaline earth metal ions takes place.

The following points of difference are noteworthy:

(i) The alkaline earth metals are harder and heavier than alkali metals.

(ii) The alkaline earth metals have higher melting and boiling points than those of alkali metals.

(iii) The increased charge and smaller ionic size of M^{2+} of alkaline earth metals lead to their greater polarizing power as compared to alkali metals. Therefore, oxides and hydroxides of M^{2+} are more covalent than the alkali metals.

(iv) Beryllium and magnesium can remain in contact with water without any change. Ca, Sr and Ba react less vigorously than alkali metals.

(v) Carbonates and sulphates of all alkaline earth metals are insoluble in water but those of alkali metals are fairly soluble (except Li_2CO_3 which is insoluble).

(vi) Phosphates of alkaline earth metals are not soluble in water whereas those of alkali metals are soluble (except Li_3PO_4 which is insoluble).

Beryllium and Magnesium differ from other members of this group as may be noted from the following points:

(i) Beryllium and magnesium do not react with pure, dry air.

(ii) All alkaline earth metals except Be and Mg react readily with water. Beryllium does not react with water even in the hot state.

(iii) The sulphates of beryllium and magnesium are soluble in water but other members (Ca, Sr, Ba, Ra) form insoluble sulphates. $BaSO_4$ is one of the most insoluble salts.

(iv) The compounds of Be and Mg do not impart any colour to the flame. But other metals of this group impart characteristic colours to flame. Calcium compounds impart brick-red colour, strontium a crimson colour, barium a persistent-green colour and radium a deep-red colour to the flame.

Diagonal Relationship between Beryllium and Aluminium:

Although Al^{3+} ion is larger than Be^{2+} but due to greater charge on aluminium ion its polarising power is of the same order as that of Be^{2+}. The similarities between Be and Al led earlier workers to place beryllium along with Al in the IIIrd group and low atomic heat of beryllium supported this idea.

The similarities between Be and Al are summarised as:

(i) Both metals do not react with dilute nitric acid.

(ii) Both dissolve in caustic alkalies to form beryllates and aluminates with the evolution of hydrogen. Thus beryllium forms Na_2BeO_2 and aluminium gives $NaAlO_2$ when dissolved in NaOH.

(iii) The halides of both metals are good Lewis acids and show similar solubilities in organic solvents.

(iv) Beryllium carbide, Be_2C, and aluminium carbide, Al_4C_3, liberate methane on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(v) The standard electrode potential of both the metals are of the same order (Be^{2+} / Be = – 1.70 V; Al^{3+} / Al = – 1.67 V).

Questions

1. What are alkaline earth metals? How would you compare them with alkali metals?
2. Why do alkaline earth metals form divalent cations? Is it possible to get their M^+ ions?
3. Discuss the chemistry of the elements of Group IIA of the Periodic Table. In what respect beryllium and magnesium differ from other members of the group?
4. Describe the important compounds of calcium. What are their applications in industry?
5. How is quicklime manufactured? How are the following obtained from it?
   - (a) Slaked lime
   - (b) Milk of lime
   - (c) Limewater
   - (d) Calcium carbide
6. Describe the commercial production of calcium carbide. Why is it considered technically important?
7. Discuss the chemistry of the following:
   - (i) Bleaching powder
   - (ii) Calcium carbide
   - (iii) Calcium superphosphate
   - (iv) Magnesium sulphate

   What are their commercial applications?
8. Give the electronic arrangement and the general trends of the alkaline earth metals. Explain the similarities in their chemical properties based upon the electronic configuration.
9. Discuss the anomalous position of Be in alkaline earth metals. Describe points which show diagonal relationship between beryllium and aluminium.
10. In what respect beryllium and magnesium differ from other members of this group?
11. Write short note on alkaline earth metals and their compounds.
12. Discuss the diagonal relationship between beryllium and aluminium quoting suitable examples.
13. Compare the behaviour of IA and IIA Group metals.
14. **Give short answers:**
    - (i) What are alkaline earth metals? Give their electronic configuration.
    - (ii) Give an account of occurrence of alkaline earth metals in nature.
    - (iii) What are the general characteristics of alkaline earth metals?
    - (iv) What are the reactions of alkaline earth metals with:
      (a) H_2O (b) H_2SO_4 (c) N_2 (d) C (e) NaOH (f) NH_3.
    - (v) Write a brief note on magnesium sulphate.
    - (vi) Write a brief note on magnesium chloride.

(vii) Discuss non-chelate complexes of magnesium.
(viii) Discuss chemical aspects of calcium carbonate.
(ix) What is bleaching powder? Give its characteristic features.
(x) Discuss chelate complexes of calcium.
(xi) Draw comparison between alkali and alkaline earth metals.
(xii) How do beryllium and magnesium differ?
(xiii) Discuss the diagonal relationship between beryllium and aluminium.

15. **Give the correct answer:**

(i) $BaSO_4$ is precipitated by adding $BaCl_2$ to sodium sulphate because:
(a) $BaCl_2$ is a sparingly soluble salt.
(b) $BaSO_4$ forms a covalent molecule.
(c) $BaSO_4$ is strongly hydrated.
(d) Ba^{2+} and SO_4^{2-} ionic product exceeds the solubility product.
(Ans: d)

(ii) Which of the following elements is likely to have an electronegativity similar to that of aluminium?
(a) barium (b) beryllium
(c) calcium (d) magnesium **(Ans: b)**

(iii) Which of the following statements is true?
(a) All nitrates of Group II metals decompose on heating to give NO_2.
(b) Group II metal nitrates are acidic.
(c) Group II metal nitrates are basic.
(d) Group II metal nitrates are insoluble in water. **(Ans: a)**

(iv) Which property of Group II (magnesium to barium) compounds increases with increasing atomic number?
(a) pH of aqueous chlorides
(b) solubility of sulphates in water
(c) stability of carbonates to heat
(d) tendency to form complex ions
(Ans: c)

(v) Strontium lies between calcium and barium in Group II in the Periodic Table. Which of the following properties could be predicted for strontium?
(a) It forms water soluble carbonate.
(b) It forms a sparingly soluble sulphate.
(c) Its nitrate decomposes on heating to give nitrite and oxygen.
(d) It is reduced by water to liberate hydrogen. **(Ans: b)**

(vi) In hospitals, barium sulphate is used in taking X-ray photograph of alimentary canal. It is mixed with food and eaten by patient prior for photograph taken because:

(a) Barium sulphate is non-poisonous and insoluble in water.
(b) Barium sulphate is white.
(c) Barium sulphate is heavy.
(d) Barium sulphate is resistant to oxidation.

(Ans: a)

(vii) What are the products of the thermal decomposition of magnesium nitrate?

(a) Magnesium nitride and oxygen
(b) Magnesium oxide and nitrogen
(c) Magnesium oxide, nitrogen and oxygen
(d) Magnesium oxide, nitrogen dioxide and oxygen

(Ans: d)

(viii) Which pair of 0.1 mol dm^{-3} aqueous solution is most likely to give a precipitate when added together?

(a) KBr and $MgSO_4$ (b) $NaNO_3$ and $CaCl_2$
(c) NH_3 and $BaCl_2$ (d) $MgSO_4$ and $SrCl_2$

(Ans: d)

(ix) Lithium resembles magnesium in its chemical properties. Which property of lithium compounds is unlikely to be correct?

(a) Lithium carbonate decomposes to give CO_2.
(b) Lithium nitrate gives oxygen on heating.
(c) Lithium oxide with water produces pH 7.
(d) Lithium sulphate is soluble in water.

(Ans: b)

(x) $CaSO_4$ decomposes into CaO and SO_3 and $CaCO_3$ decomposes at lower temperature to CaO and CO_2, why?

(a) $CaCO_3$ has higher lattice energy than $CaSO_4$.
(b) CO_2 is smaller molecule than SO_3.
(c) CO_3^{2-} is more easily polarized than SO_4^{2-}.
(d) Charge density of CO_3^{2-} is more than SO_4^{2-}.

(Ans: c)

❀ ❀ **11** ❀ ❀

CHEMISTRY OF ‘*p*-BLOCK’ ELEMENTS

Elements in which *p*-orbitals are in the process of filling in order to reach the 'inert gas' configuration are called *p*-BLOCK ELEMENTS. These elements have completely filled *ns*-orbitals and have np^{1-6} electronic configuration. The non-transition elements belonging to Group III, IV, V, VI, VII and inert gases are considered to be members of *p*-block elements.

Whereas *s*, *d* and *f*-block elements are almost all metals, the *p*-block elements include both metals and non-metals. The elements of *p*-block usually form covalently bonded, colourless compounds. Some of these elements are capable of showing variable valencies mostly due to the presence of inert pair of ns^2 electrons. Thus the heavy members of these series usually render ns^2 electrons inert and with the loss of *np* electrons result in the formation of ionic compounds. Members of the *p*-block elements show resemblance and gradual change in their properties across a period and also a group in the Periodic Table. The chemistry of *p*-block elements of Groups IIIA, IVA, VA, VIA and VIIA, (*The sub-group A indicates over here the non-transition or representative members of a group)* together with the inert gases will be discussed in Chapters 12 to 17.

12

BORON AND ALUMINIUM (GROUP IIIA)

Group IIIA includes boron, aluminium, gallium, indium and thallium. The chemistry of boron and aluminium will only be taken up in this text. Description of the rare elements of this group (gallium, indium and thallium) as well as those for the entire IIIB group including rare earth metals would appear in more advanced books.

GROUP TRENDS IN BORON AND ALUMINIUM:

The first two elements of Group IIIA are boron and aluminium. Both have the electronic configuration ns^2np^1 and are trivalent since promotion to ns^1np^2 occurs very readily. They form cations with an inert gas configuration much less readily than elements of Group IIA which precede them.

Group trends can be depicted by the following characteristic features of these elements:

1. The ionic radius of aluminium (50 pm) is 2.5 times that of boron (20 pm). The ionic values are in the ratio of about sixteen to one. These ratios make it easy to understand why boron in its oxidized form shows acidic behaviour, *e.g.*, boric acid than trivalent aluminium.
2. Boron is regarded as a typical metalloid, and aluminium is a metal.
3. Both form electron deficient molecules, but more so for boron.
4. Boron-boron bonds are shorter than aluminium bonds. So aluminium is more ionic in character.
5. Trivalent state is stable for both boron and aluminium but the univalent state becomes more stable with increase in atomic number.
6. The electron acceptor ability or Lewis acidity decreases with increase in atomic number.
7. Boron halides are monomeric but those of aluminium are dimeric.
8. Compounds of aluminium have trigonal-bipyramidal structures which are not possible for boron compounds.

The electronic configuration of elements of this group can be generalised as ns^2np^1. The electronic configuration for boron and aluminium is:

B (5) $1s^2$ $2s^2$ $2p^1$
Al (13) $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1$

The great majority of the compounds of boron and aluminium are in oxidation state 3 (The oxidation state of an element indicates the number of its own electrons which the atom of the element is using to form covalent or ionic bonds). The trivalent state of these elements is due to the promotion of electrons from *ns* to *np* state. It is possible because of the low ionization potential values of these elements. Thus boron in the excited state would acquire $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z$ configuration. Similarly, aluminium would have attained $3s^1$ $3p_x^1$ $3p_y^1$ $3p_z$ configuration. In any case, the inert gas configuration is not readily reached by the formation of cations (by loss of 3 electrons). The bonding is predominantly covalent.

Boron and aluminum atoms are electron-deficient since an octet is not normally present even after bond formation. There are three electron pairs present in the valence shell of their compounds obtaincd through covalency. They are short of electrons and electron-pair repulsions are smaller than usual. So the atoms of B and Al tend to be electron 'acceptors'. Simple molecules with an incomplete octet around the metal contain sp^2 hybrid bonds. The tendency to complete an octet is shown by the existence of tetrahedral compounds, $H_3B : CO$, in which sp^3 hybridisation is involved. The fourth hybrid orbital overlaps with orbitals of CO containing lone pair electrons.

Some of the physical properties of elements of Sub-Group IIIA are given in Table 12.1.

TABLE 12.1

Physical Properties of Group IIIA Elements

	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electronic Configuration	[He] $2s^2$ $2p^1$	[Ne] $3s^2$ $3p^1$	[Ar] $3d^{10}$ $4s^2$ $4p^1$	[Kr] $4d^{10}$ $5s^2$ $5p^1$	[Xe] $5d^{10}$ $6s^2$ $6p^1$
Atomic Weight	10.82	26.91	69.72	114.76	204.39
M.P. °C	2300	659.7	29.75	155	303.5
B.P. °C	2550	1800	~ 2000	1450	1650
Crystal lattice	Complex	Close-packed	Complex	Close-packed (Distorted)	Close-packed
Ionization Potential					
1st (kJ/mole)	800	580	580	560	590
Standard Electrode Potential $M^{3+}/M(v)$	—	1.7	0.5	0.34	—

BORON

The ionization potential values of boron are rather high. Therefore, the formation of B^{3+} ions is not possible. Consequently, loss of electrons to form cations is of less importance in boron chemistry. Instead, covalent bond formation is very common. That is why, boron compounds usually resemble those of other non-metals (*i.e.*, silicon) in properties and reactions.

The electronic arrangement $2s^2\ 2p^1$ in boron suggests that +1 oxidation state is possible. But for boron +1 oxidation state is not known. This may be attributed to relatively high value of first ionization potential for boron (8.29 ev) among members of the subgroup IIIB. Moreover, the total energy released in the formation of three bonds in BX_3 compounds is much more than the energy released during the formation of one bond in BX compounds. Thus stability gained during the formation of BX_3 type compounds is greater than BX type. Consequently, the formation of BX_3 becomes relatively an easy possibility. At the same time it should be noted that sufficient energy is available for the promotion of boron to a hybridised valence state of sp^2 ($2s^1\ 2p_x^1\ 2p_y^1\ 2p_z$) type.

Among the compounds in which boron atom is trigonally hybridised and third *p* orbital remains unused are BF_3, BCl_3 and BBr_3. The molecules of such compounds have been shown experimentally to have planar structures (XBX angle = 120°). The Group BX_3 containing a trigonally hybridised boron atom has three electron pairs only. By accepting another electron pair from a donor molecule (: NH_3, : CO etc.) the boron atom becomes tetrahedrally (sp^3) hybridised. As a consequence, BX_3 type compounds would behave as electron pair *acceptors* (Lewis acids) in which boron attains its maximum coordination through sp^3 hybridisation. Thus, various Lewis bases, such as amines, phosphines, ethers etc., would form 1 : 1 adducts with BX_3 type compounds.

Boron also completes an octet by forming complex anions *e.g.*, BF_4^-, BH_4^- $[B(C_6H_5)_4]^-$ and the chelate complexes. In both cases, the approaching anion and the chelating ligand donate lone pair of electrons to boron in order to complete the octet.

COMPARISON OF BORON WITH SILICON:

Elemental boron shows properties which place it between metallic and non-metallic elements. Thus it behaves as a semi-conductor and shows chemical characteristics which resemble silicon much more closely than aluminium. Boron has three electrons in the outer shell, and because of the small size of the atom (88 pm) these are difficult to remove. Thus, boron shows covalency in all of its compounds.

The diagonal relationship between boron and silicon can be explained by making use of Fajans' rules. A move to the right in the Periodic Table involves an increase in charge on the corresponding ion which leads to increase polarizing power. On moving down a group the size of the ion is increased showing thereby, decreased polarizing power. Across a diagonal, therefore, these two opposing factors approximately balance each others effect. Thus ion of the element placed diagonally would have similar polarizing powers and, therefore, similar properties are indicated. Boron and silicon are, therefore, very similar both in form and properties of the elements and compounds. Differences observed arise from the different electronic configurations and valencies of the two elements.

Some of the noteworthy **points of resemblance** between B and Si are:

(1) Boric acid and silicic acids are both weak acids. Boric acid, $B(OH)_3$ and silicic acid, $Si(OH)_4$ do not show amphoteric properties.

(2) The hydrides of B and Si are volatile, readily inflammable, and hydrolised. Due to electron deficient nature of boron its hydrides show unusual bonding (bridged structures) but in silicon hydrides normal covalent bonding is exhibited which is similar to saturated hydrocarbons.

(3) Boron halides BX_3 are readily hydrolysed (except BF_3) to give boric acid, $B(OH)_3$. Similarly, silicon halides (SiX_4) would hydrolyse to give silicic acid, $Si(OH)_4$.

$$BX_3 + 3H_2O \rightleftharpoons B(OH)_3 + 3HX$$

$$SiX_4 + 4H_2O \rightleftharpoons Si(OH)_4 + 4HX$$

(4) Both B_2O_3 and SiO_2 (oxides of boron and silicon) are acidic in nature. They readily dissolve with metallic oxides to form borates and silicates. Both the oxides readily form glasses which are difficult to crystallize.

(5) Oxo salts of boron and silicon are structurally similar. Thus $(BO_2)_n$ and $(SiO_3)_n$ would form linear structures in metaborates and pyroxene silicates, respectively.

(6) Boron and silicon resist the action of acids and alkalies. On fusion with alkalies both form silicates and borates evolving H_2.

(7) Boron and silicon form colourless gases. BF_3 and SiF_4 which are easily hydrolysed forming acids.

Dissimilarities Between Boron and Aluminium:

Due to the small size of the atom (88 pm) of boron as compared to aluminium atom (126 pm) and other analogues of this group, the properties of boron show some deviation from the overall behaviour of the group. Moreover, ionization potential values are also markedly different for boron as compared to other members of sub-group IIIA.

The main points of difference in chemical behaviour of boron from aluminium are:

1. Whereas the alkyls and halides of aluminium make up the electron deficiency through the formation of dimers with alkyl or halogen bridges, the boron compounds are not capable of forming dimeric structures. Probably, the size factor is very important in this respect. Thus, in BCl_3 or BBr_3, the small boron atom would not be able to coordinate strongly to four atoms of relatively large size *e.g.*, Cl or Br. Also, certain amount of B — X (Pπ — Pπ) bond energy would have to be sacrificed which would also lower the stability of dimers relative to monomers.
2. Boric acid, $B(OH)_3$ is a weak acid. $Al(OH)_3$ is mainly basic with some amphoteric behaviour.
3. Boron hydrides are usually volatile, gaseous or liquid products. Aluminium forms only a solid, polymeric hydride.
4. Boron halides are readily hydrolyzed in aqueous solutions to form boric acid. Aluminium halides are only partially hydrolyzed in water to give $Al(OH)_3$ which is basic in nature.

OCCURRENCE:

Boron occurs quite abundantly as soluble borates, particularly in desert parts of California and India *i.e.*,

Borax $Na_2B_2O_7 . 10H_2O$

Natural boron consists of two isotopes; B^{10} (18.83 %) and B^{11}(81.17 %).

ISOLATION:

It is very difficult to prepare boron in a high state of purity because of its high melting point and the corrosive nature of the liquid. However, various methods have been used to prepare boron in low purity (95 – 98 %). High-purity boron can also be obtained by special techniques. Some of the commonly used methods are:

1. **By Reduction of B_2O_3 with Mg:** Boron can be obtained in amorphous state by the reduction of B_2O_3 with magnesium. The product is thoroughly washed with alkali, hydrochloric acid and finally hydrofluoric acid.
2. **By Reduction of BCl_3 with H_2:** The reduction of BCl_3 with hydrogen is carried out by passing a mixture of H_2 and BCl_3 over a series of electrically heated graphite rods.

$$2BCl_3 + 3H_2 \longrightarrow 2B + 6HCl$$

3. **By Electrolysis:** Electrolysis of a solution containing sodium chloride, potassium chloride and potassium fluoroborates with boron carbide anodes gives boron of 99.8% purity at the cathode.

4. Impure boron can be obtained by heating potassium fluoroborate with Na, K etc.

$$KBF_4 + 3K \longrightarrow B + 4KF$$

CHEMICAL CHARACTERISTICS OF BORON:

The chemical reactivity of boron depends greatly upon whether the impure amorphous form or the crystalline form is involved. Thus, amorphous boron burns readily, on heating in air or oxygen, forming B_2O_3. Under similar conditions crystalline boron is only superficially oxidized even when heated to incandescence. Amorphous boron is vigorously oxidized by HNO_3 to boric acid and concentrated acid causes it to inflame but the crystalline form of boron is scarcely attacked even by concentrated acid.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

Similarly, hot concentrated sulphuric acid readily oxidizes amorphous boron but has little effect on the crystalline form.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

Fused sodium hyroxide dissolves amorphous boron liberating hydrogen. Crystalline boron undergoes only a slight change at about 500°C.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

Amorphous boron dissolves slowly in hot, concentrated aqueous alkalies, evolving hydrogen and forming a solution of the metaborate. Crystalline boron does not react under these conditions:

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

Carbon dioxide and SiO_2 react with amorphous boron on heating to deposit C and Si, respectively.

$$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$$

$$4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$$

Amorphous boron is attacked by various elements even under ordinary conditions to form corresponding products. Crystalline boron is not attacked by any of these elements.

$$2B + 3O_2 \longrightarrow B_2O_3$$

$$2B + 3S \xrightarrow{1200°C} B_2S_3$$

$$2B + 3Se \longrightarrow B_2Se_3$$

$$2B + 3F_2 \xrightarrow{\text{Room temp.}} 2BF_3 \text{ (inflamable)}$$

$$2B + 3Cl_2 \xrightarrow{410°C} 2BCl_3$$

$$2B + 3Br_2 \xrightarrow{700°C} 2BBr_3$$

$$2B + 3I_2 \xrightarrow{1250°C} 2BI_3$$

These differences in reactivity between two forms of boron are possibly due to differences in surface area. In general, if boron is mentioned in connection with any particular reaction it is assumed to be amorphous boron unless otherwise mentioned. Overall summary of the reactions of boron is given in Figure 12.1.

COMPOUNDS OF BORON:

We will now discuss the compound formation of boron based upon the type of hybridization involved. There are two general trends in the hybridization of boron:

(a) sp^2 **Hybridization:** (It involves compounds in which boron atom is trigonally hybridized).

(b) sp^3 **Hybridization:** (It involves those compounds in which the boron atom is tetrahedrally hybridized).

Let us now discuss various compounds of boron under such categories.

COMPOUNDS IN WHICH BORON ATOM IS TRIGONALLY HYBRIDIZED:

Boron forms many compounds in which the B atom is present in the trigonally hybridized state. Such compounds involve sp^2 hybridization of boron atoms where the third '*p*' orbital remains unused. The molecules of such compounds would show planar arrangement. We will restrict ourselves to such compounds only in which the boron atoms have three σ-bonds. Among these only BX_3 type compounds will be discussed below.

HALIDES OF BORON:

Among the various type of halides formed only trihalides would be taken up over here. Trihalides have the general formula, MX_3 (X, F, Cl, Br, I). All the trihalides of boron are covalent. The boron trihalide molecule is trigonal planar

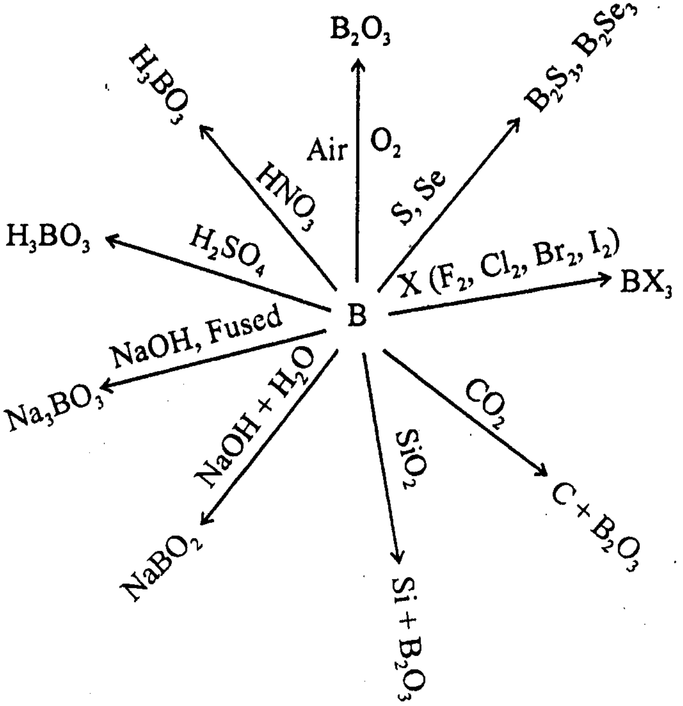
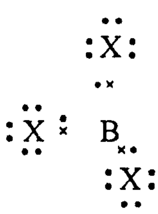
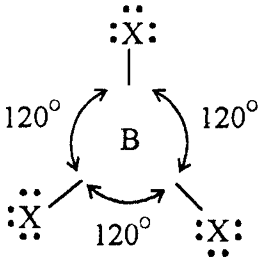


Fig. 12.1.

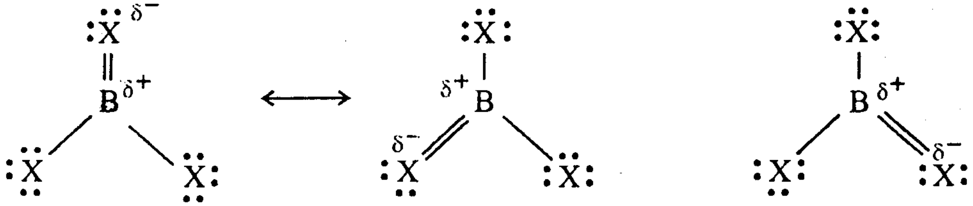
(D_3h symmetry) with angles of 120° between the bonds. The simplest concept about its electronic structure is:



OR



Although this shape involves sp^2 hybrid bonds and is correct, the measured bond lengths are shorter than expected for single (electron-pair) B — X bonds. If the third unoccupied p orbital in the valency shell of the excited boron atom is also utilized in bond formation, it is possible to conceive the BX_3 molecule as a resonance hybrid of the following structures:



The calculated bond lengths for such a structure (a resonance hybrid of these three forms) agree with the measured values.

Orbital model showing hybridized orbitals and forming σ-bonds with *p*-orbital of F in BF_3 is shown in Figure 12.2. Other halogens have similar structural aspects.

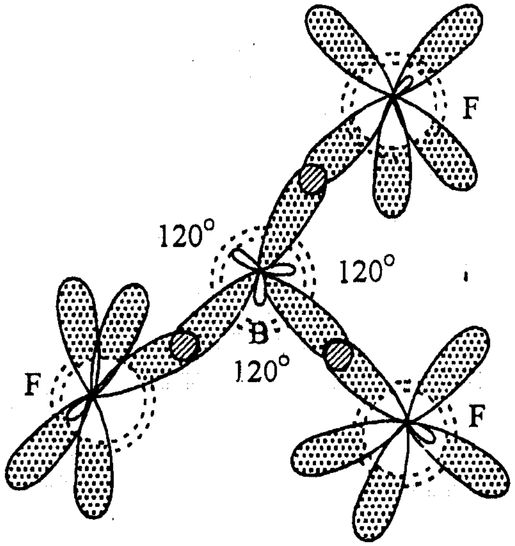


Fig. 12.2. Orbital model showing hybridized orbitals in BF_3.

Boron Trifluoride, BF_3:

It is a gas which fumes strongly in moist air (b.p. — 101°C).

Methods of Preparation:

1. **By the Direct Action of F_2 on Boron:** On passing fluorine over amorphous boron, the mixture spontaneously inflames with the formation of BF_3.

$$2B + 3F_2 \longrightarrow 2BF_3$$

2. **From Calcium Fluoride and Boric Oxide or Borax:** BF_3 can be obtained by heating a mixture of calcium fluoride, boric oxide and concentrated sulphuric acid.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 2NaHSO_4 + 6CaSO_4 + 7H_2O + 4BF_3$$

3. **From Potassium Fluoroborate and Boric Oxide:** On heating a mixture of potassium fluoroborate and boric oxide with concentrated sulphuric acid, BF_3 is obtained.

$$B_2O_3 + 6KBF_4 + 3H_2SO_4 \longrightarrow 8BF_3 + 2K_2SO_4 + 3H_2O$$

4. **From Boron Trichloride:** BF_3 can be obtained by heating boron trichloride with CaF_2 at 200°C or with SbF_3 and $SbCl_5$ below – 78°C.

$$2BCl_3 + 3CaF_2 \longrightarrow 2BF_3 + 3CaCl_2$$

Chemical Characteristics:

The reaction types shown by BF_3 are based upon its electron deficiency or replacement of flourine by other substituents. The following reactions would clearly indicate such type of behaviour shown by boron trifluoride.

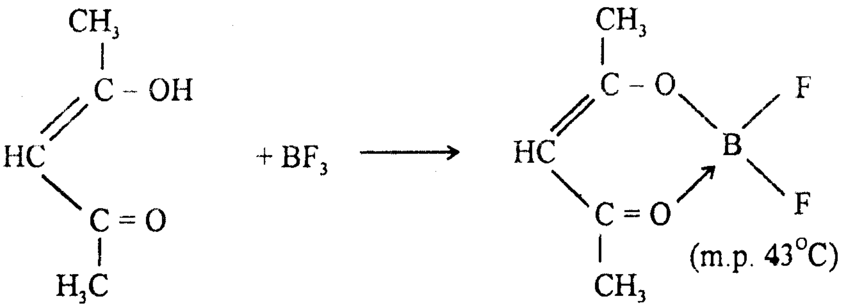
1. **Reactions Based Upon Lewis Acidity of BF_3:** Boron trifluoride forms additive compounds with ammonia and its derivatives, with ethers, esters and phosphines. All these molecules are good Lewis bases and would be able to donate lone pair of electrons to make up the deficiency of electrons by boron.

$$BF_3 + :NH_3 \longrightarrow F_3B \longleftarrow :NH_3$$

$$BF_3 + :PH_3 \longrightarrow F_3B \longleftarrow :PH_3$$

$$BF_3 + :O(CH_3)_2 \longrightarrow F_3B \longleftarrow :O(CH_3)_2$$

Boron trifluoride also reacts with certain organic molecules which carry lone-pair electron donor atoms to form chelate compounds. Thus it reacts with β-diketones such as acetylacetone in benzene solution to form semi-chelate neutral compound. All fluorine atoms cannot be replaced due to the high affinity of boron for flourine.



(m.p. 43°C)

2. **Other Reactions:** These reactions usually involve the partial or complete replacement of fluorine from BF_3 by other groups. Thus boron trifluoride reacts with a Grignard reagent to give a trialkyl or triaryl boron through an exchange reaction. Similarly, alkylhaloboranes can be obtained by reacting BF_3 with alkyl boranes.

$$BF_3 + 3MgC_6H_4Br \xrightarrow{\text{Ether}} B(C_6H_5)_3 + 3MgFBr$$

$$R_3B + 2BF_3 \xrightarrow{\text{Ether}} 3RBF_2$$

Boron trifluoride reacts with trimethyl boroxole at – 45°C.

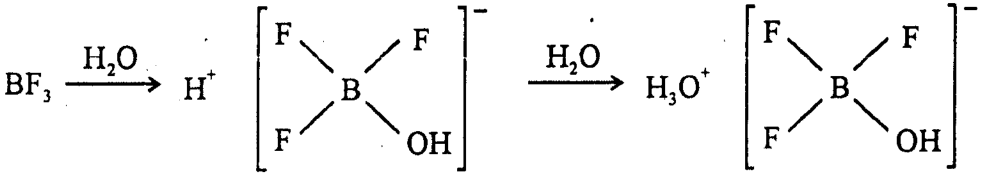
$$2BF_3 + (CH_3OB)_3 \longrightarrow 3CH_3BF_2 + B_2O_3$$

If boron trifluoride is passed into water, first a precipitate of boric acid is obtained which dissolves afterwards due to the formation of fluoroboric acid.

$$BF_3 + 3H_2O \longrightarrow B(OH)_3 + 3HF$$

$$BF_3 + HF \longrightarrow HBF_4$$

Boron trifluoride also forms 1 : 1 and 1 : 2 adducts with water. 1 : 2 adduct is quite stable and can be distilled without decomposition.



(1 : 2 adduct) (1 : 1 adduct)

Molecules of alcohols, aldehydes and ketones form addition compounds with BF_3.

$$2ROH + BF_3 \longrightarrow ROH_2^+ [BF_3OR]^-$$

3. Reactions with Metal Hydrides: Boron trifluoride reacts with metal hydrides in two ways. In one of such reactions, diborane is obtained and the other results in the formation of complex metal borohydride.

$$6LiH + 8BF_3 \xrightarrow{\text{Ether}} 6LiF + B_2H_6$$

$$4LiH + 4BF_3 \xrightarrow{\text{Ether}} 3LiBF_4 + LiBH_4$$

4. Catalytic Properties of Boron Trifluoride: The commercial value of BF_3 is due largely to its function as a catalyst. It is mostly used in organic syntheses. Thus in Friedel-Crafts synthesis the function of BF_3 is represented by the following steps:

$$RCOOCH_3 + BF_3 \longrightarrow RCOOCH_3 . BF_3$$

$$RCOOCH_3BF_3 \longrightarrow RCO^+ + CH_3OBF_3^-$$

$$RCO^+ + C_6H_6 \longrightarrow C_6H_5COR + H^+$$

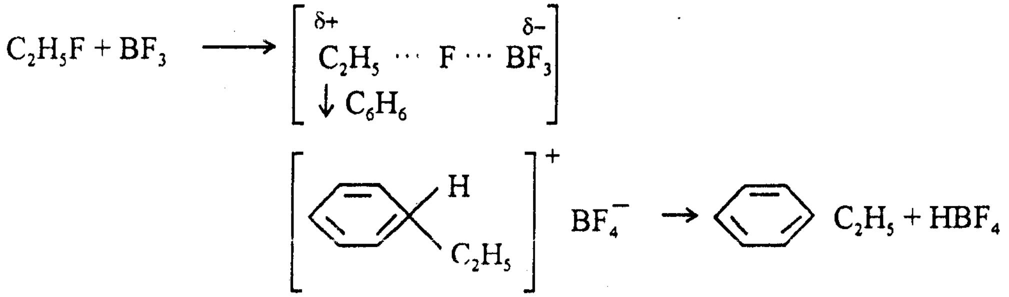
$$CH_3OBF_3^- + H^+ \longrightarrow CH_3OH + BF_3$$

One of the most interesting examples of catalytic nitration using boron trifluoride is the use of a complex $N_2O_5 . BF_3$ which ionizes to liberate $(NO_2)^+$.

$$O_2N — O — NO_2 + BF_3 \longrightarrow (NO_2)^+ + O_2NOBF_3^-$$

In such manner the nitration is obtained probably by electrophilic substitution on the aromatic molecule by the nitryl cation.

Ethylation of benzene by ethyl fluoride in presence of BF_3 proceeds in the following manner:



5. **Formation of Organoboron Compounds:** BF_3 reacts with diazomethane to form B – C linkage

$$BF_3 + CH_2N_2 \rightarrow F_3B^- - CH_2^+ + N_2 \rightarrow F_2B - CH_2F$$

OTHER BORON TRIHALIDES:

Boron trichloride, boron tribromide and boron triodide will be discussed under this heading. These trihalides are colourless liquids (BCl_3, b.p. 12.5°C; BBr_3, b.p. 91.3°C; BI_3, b.p. 210°C). However, boron tribromide and triodide become coloured when exposed to light. It is likely that both these compounds absorb strongly in the ultraviolet region of the spectrum. Structures of these trihalides are similar to BF_3.

Methods of Preparation:

The most common methods used to prepare trihalides will only be described over here.

Boron trichloride is prepared on a large scale by the chlorination of a mixture of elemental carbon and boric oxide or metal borate. Boron tribromide is prepared in an analogous manner.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 3CO + 2BCl_3$$

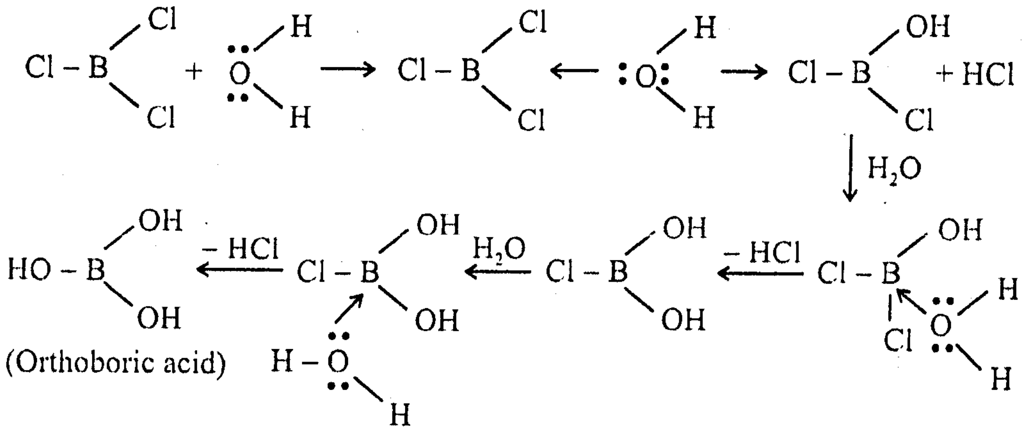
The most satisfactory preparation of BI_3 involves the treatment of $LiBH_4$ at 125°C, or sodium borohydride, $NaBH_4$ at 200°C with iodine.

Chemical Characteristics:

There are mainly two type of reactions given by trihalides of boron. In some reactions, BX_3 molecules may behave as Lewis acids due to their electron deficient nature. In other reactions, halogen substitution is the major phenomenon. Moreover, we will also take up representative halogen exchange catalytic reactions of boron trihalides.

1. **Reactions in which Boron Trihalides Act as Acid Halides:** Treatment of the boron trihalides except boron trifluoride with reagents containing an active hydrogen results in protonolysis of the boron-halogen bond. The following are the classified reactions of this type:

(i) **Hydrolysis:** Water reacts to form boric acid according to the following mechanism:



(Orthoboric acid)

(ii) **Alcoholysis:** Boron trichloride and tribromide react vigorously with lower alcohols and more slowly with higher alcohsols to form the borate esters.

$$3ROH + BX_3 \longrightarrow B(OR)_3 + 3HX$$

(iii) **Ammonolysis:** Ammonia reacts with BCl_3 and BBr_3 to give a wide variety of amines and imines as well as boron nitride. Boron trichloride reacts with ammonium chloride at 150°C to produce B-trichloro-borazine.

$$3NH_4Cl + 3BCl_3 \longrightarrow B_3N_3Cl_3 + 7HCl$$

(iv) **Other Protonolytic Reactions:** Boron trichloride reacts with methyl mercaptan and acetic acid (carboxylic acids) according to the following equations:

$$CH_3SH + BCl_3 \longrightarrow CH_3S-BCl_2 + HCl$$

$$5CH_3COOH + 2BCl_3 \rightarrow (CH_3COO)_2B\text{–}O\text{–}B(OOCCH_3)_2 + CH_3COCl + 5HCl$$

2. **Reactions in which the Boron Trihalides Behave as Lewis Acids:** Boron trifluoride is considered to be the strongest Lewis acid and the order of decreasing Lewis acidity is:

$$BF_3 > BCl_3 > BBr_3 > BI_3$$

This is the order which would be expected from considerations of difference in the inductive effect with the changing electronegativity of the halides. As fluorine is the most electronegative of all the halides, a greater positive charge would reside on the boron atom in boron trifluoride than in case of BCl_3 and other trihalides. Therefore, greater Lewis acidity will be shown by BF_3 due to its strong electron accepting behaviour. Same arguments will apply to other trihalides keeping in view the decreasing electronegative behaviour with the increase in atomic number in the halogen group.

The adducts or the complexes formed by boron trihalides will be more stable for BF_3 than BCl_3 and so on. Some of the reactions in which boron trihalides would behave as Lewis acids are given below:

(i) **With Amines:** Trimethylamine reacts with boron trichloride to form crystalline solid, m.p. 243 — 244°C.

$$(CH_3)_3N: + BCl_3 \longrightarrow (CH_3)_3N : BCl_3$$

(ii) **With Ethers:** Ethers form 1 : 1 complexes with boron trihalides, which on heating will give alkoxy derivatives.

$$R_2O: + BCl_3 \longrightarrow R_2O : BCl_3$$

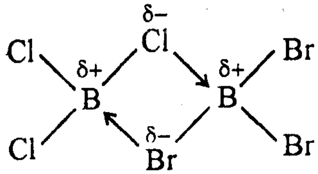
$$R_2O : BCl_3 \xrightarrow{\Delta} ROBCl_2 + RCl$$

3. **Substitution Reactions of Boron Trihalides:** Boron trihalides react with metal hydrides to form either diborane or a complex metal borohydride. With metal salts metathetic reactions are obtained. Alkyl and aryl derivatives of most metals react with the boron trihalides to undergo metathetic reactions resulting in the formation of the trialkyl and triaryl boranes.

4. **Exchange Reactions:** Boron trihalides are found to exchange their halogen atoms. Thus on keeping a mixture of BCl_3 and BBr_3 at 20°C for several hours, following reaction takes place.

$$BCl_3 + BBr_3 \rightleftharpoons BBrCl_2 + BBr_2Cl$$

Exchange reactions may be considered to proceed via halogen bridged structure such as:



Exchange reactions with other boron compounds are also possible.

5. **Reaction with Metals:** On passing boron trichloride vapours at low pressure through a mercury arc, diborane tetrahalides are formed.

$$2BCl_3 + 2Hg \longrightarrow B_2Cl_4 + Hg_2Cl_2$$

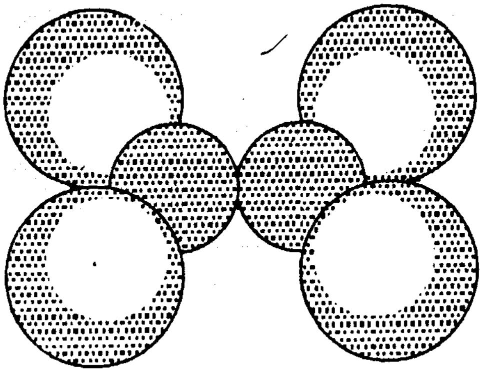


Fig. 12.3. Molecule of B_2Cl_4

Such compounds depict the boron — boron bond structure as shown in Figure 12.3.

OXYGEN COMPOUNDS OF BORON IN THE TRIGONAL VALENCE STATE:

Among such compounds, boric acid is important. It possesses a continuous layer structure in which $B(OH)_3$ units are held together by hydroxyl groups.

Boric Acid, $B(OH)_3$: It has been generally assumed that the boron and oxygen atoms of boric acid in solution form a planar arrangement of composition, $B(OH)_3$.

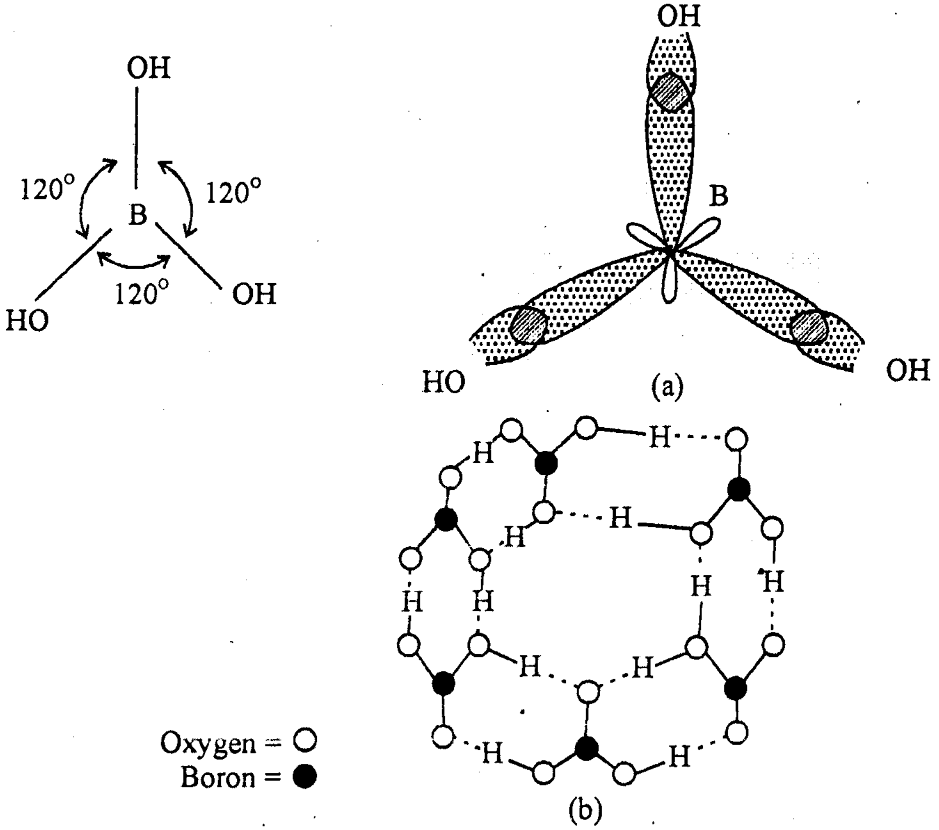


Fig. 12.4. Structure of Boric acid, $B(OH)_3$ (a) Molecular structure (b) Crystal structure.

On cooling, boric acid separates as white triclinic crystals. The crystals have a greasy touch due to the gliding of the $B(OH)_3$ sheets over one another. Crystal structure of boric acid shows a layer lattice containing $B(OH)_3$ groups which are linked by hydroxyl bonds.

This structure of boric acid is based on two assumptions: (i) the hydrogen atoms are situated at points on straight lines joining the oxygen atoms, and (ii) that the oxygen atoms are in the trigonal valence state. If oxygen atoms are in the trigonal valence state it is possible that the structure of boric acid may contain non-localised orbitals. This is possible because one out of three p orbitals does not involve in sp^2 hybridization and becomes available for the formation of non-localised π-bonds.

Methods of Formation:

Two methods commonly available for the preparation of boric acid are:

1. **From Borax:** A hot saturated solution of borax is treated with hydrochloric acid until strongly acid.

$$\underset{\text{Borax}}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

2. **From Boron Trihalides:** Hydrolysis of boron trihalides would yield boric acid. BCl_3, BBr_3 and BI_3 readily hydrolyse to give H_3BO_3.

$$BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX$$

General Characteristics:

(i) Boric acid is fairly soluble in water and is slightly volatile in steam.

(ii) On heating, it loses water molecules stepwise to give metaboric acid and finally B_2O_3.

$$B(OH)_3 \overset{1000°C}{\rightleftharpoons} HBO_2 \overset{\Delta}{\rightleftharpoons} B_2O_3$$

(iii) Boric acid is a weak acid (*pka* = 9.2). The dissociation at 25°C is 6×10^{-11}. The ionization may take place in one of the following ways:

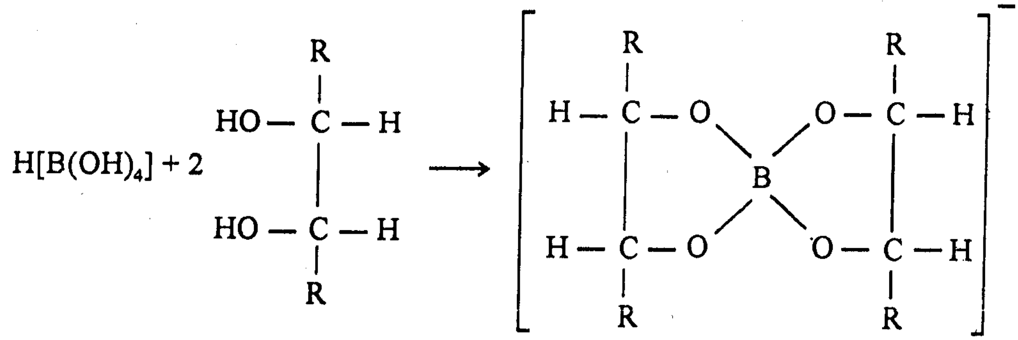
(a) $H_3BO_3 \rightleftharpoons H^+ + (H_2BO_3)^-$

(b) $H_3BO_3 \rightleftharpoons H^+ + BO_2^- + H_2O$

(c) $H_3BO_3 + H_2O \rightleftharpoons H^+ + [B(OH)_4]^-$

Boric acid is so weak an acid that its soluble salts are very easily hydrolysed. Thus sodium borate may be titrated as an alkali against a strong acid with methyl orange as indicator. Although boric acid is a very weak acid but the presence of glycerol or mannitol in the solution enhances the strength of the acid. So much so that it can be titrated against sodium hydroxide using phenolphthalein as indicator. The increase in strength of boric acid is due to the increased ionization which is caused by the formation a chelate compound. The complex ion is not able to accept proton without decomposition and the product therefore, provides more H^+ in solution. Another way to increase the strength of boric acid is to saturate its solution with a salt *i.e.*, calcium chloride (the mechanism of this change is not well known).

$$H_3BO_3 + H_2O \rightleftharpoons H[B(OH)_4]$$



$$\underset{\text{Mannitol}}{C_6H_8(OH)_6} + HB(OH)_4 \longrightarrow [C_6H_8(OH)_4BO_4]^- + H^+$$

Some of the important reactions of boric acid are given in Figure 12.5.

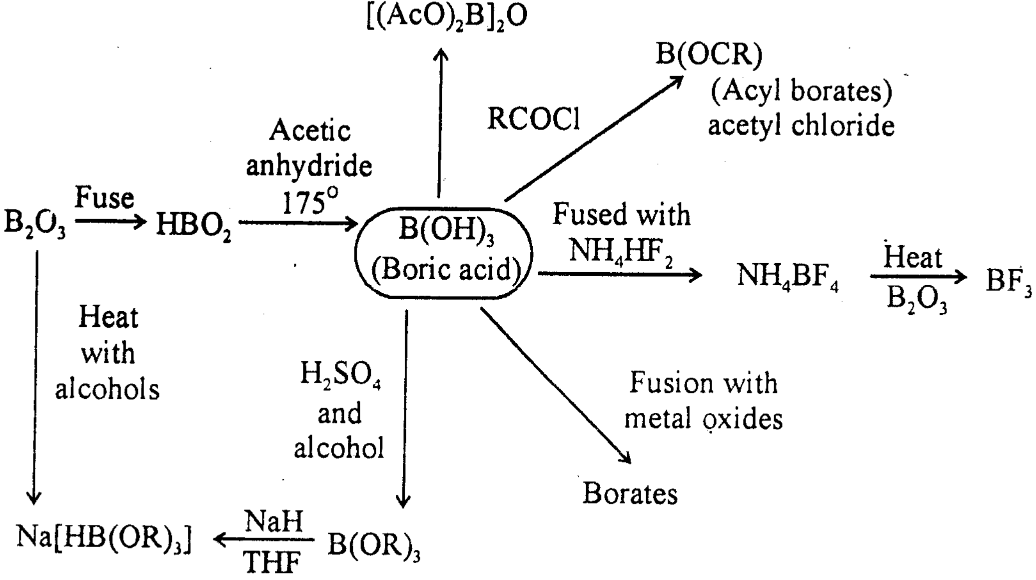


Fig. 12.5.

Fusion of metal oxides with boric acid results in the formation of metal borate. The hydrated borates can be crystallized from aqueous solutions. Many borates occur naturally, usually in hydrated states *i.e.*, borax, $Na_2B_4O_7 \cdot 10H_2O$.

Uses

Boric acid and borax are used in medicine and widely employed in soaps and cleansers and as fluxes in refining operations, welding, soldering etc.

COMPOUNDS IN WHICH THE BORON ATOM IS TETRAHEDRALLY HYBRIDIZED:

Boron can attain at the most a tetrahedral valence state. All types of tetrahedral compounds are formed by boron (except non-chelate compounds). Tetrahedrally hybridized compounds of boron can be further classified as:

1. Electron deficient compounds *i.e.*, The boron hydrides.

   (They have already been discussed in Chapter 9).
2. Non-chelate complex anions.
3. Chelate complexes.

In the following portion of boron chemistry, ***non-chelate complex anions*** will only be discussed with special reference to sodium borohydride, $NaBH_4$.

Sodium Borohydride, $NaBH_4$: It is a useful reducing agent in weakly alkaline solution. Reducing action can be destroyed by the addition of acid. It is less powerful reducing agent than $LiBH_4$ and can be used to reduce aldehydes and ketones to alcohols. It can reduce Fe(III) to Fe(II), Tl(III) to Tl(I) and Ag(I) to silver metal.

X-ray analysis has shown that $NaBH_4$ has a sodium chloride lattice in which BH_4^- plays the role of chloride ion. The distance Na — B is 3.03°A and B — B is 4.35 A°.

Preparation:

$NaBH_4$ can be prepared:

(i) By the action of sodium hydride on boric acid esters.

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

$$4NaH + NaB(OCH_3)_4 \longrightarrow NaBH_4 + 4NaOCH_3$$

(ii) By the action of boron hydrides (usually diborane) with sodium methoxide.

$$3NaOCH_3 + 4BH_3 \longrightarrow 3NaBH_4 + B(OCH_3)_3$$

Properties:

(i) Sodium borohydride is a white salt-like solid and stable up to 400°C in vacuum, and up to 300°C in air. It is soluble in liquid ammonia and isopropylamine but insoluble in ether and dioxane.

(ii) **Reaction with Water:** It slowly reacts with cold water but decomposes rapidly in presence of hot water.

$$3NaBH_4 + 6H_2O \longrightarrow Na_3[B_3O_6] + 12H_2$$

(iii) **Reaction with Acids:** It is attacked by acids and decomposed to liberate diborane and hydrogen.

$$2NaBH_4 + 2HCl \longrightarrow 2NaCl + B_2H_6 + 2H_2$$

(iv) **Reaction with Alcohols:** The reaction with alcohols is very rapid and proceeds even at – 40°C.

$$NaBH_4 + 4CH_3OH \longrightarrow NaB(OCH_3)_4 + 4H_2$$

(v) **Reaction with Iodine:** Sodium borohydride reacts with iodine at 200°C to give BI_3.

$$2NaBH_4 + 4I_2 \longrightarrow 2BI_3 + 2NaI + 4H_2$$

(vi) **Reducing Agent:** It is a powerful and useful reducing agent and reduces:

(a) aldehydes and ketone to alcohols.

(b) V (V) to V (IV).

(c) Fe (III) to Fe (II) (d) Tl (III) to Tl (I) (e) Ag (I) to Ag.

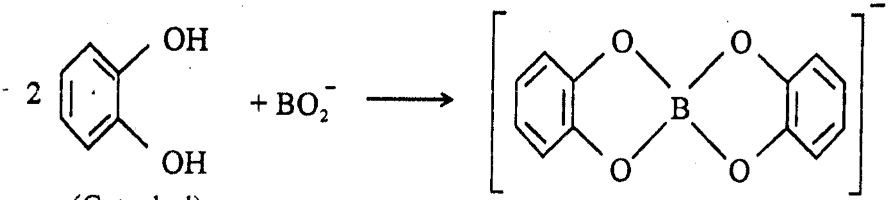
(vii) Sodium borohydride is a good starting material for other metallic borohydrides

$$NaBH_4 + LiCl \longrightarrow LiBH_4 + NaCl$$

$$NaBH_4 + KOCH_3 \longrightarrow KBH_4 + NaOCH_3$$

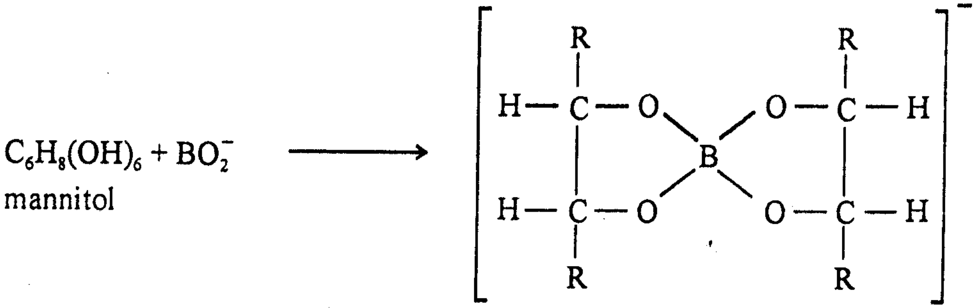
Chelate Complexes of Boron: Boron shows a strong tendency to form complexes having 4 covalencies. The BF_4^- ion and BH_4^- ion are tetrahedral in which boron atoms are tetrahedrally hybridised.

Catechol forms 4-covalent complex,

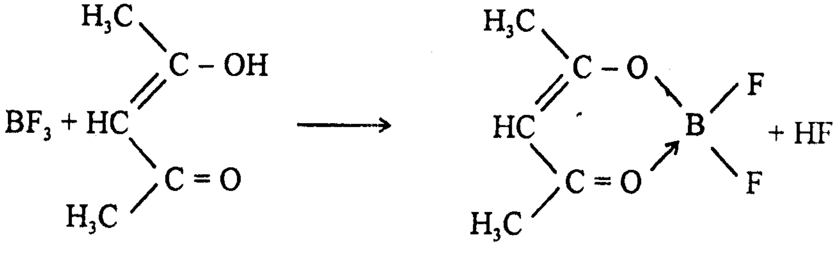


(Catechol)

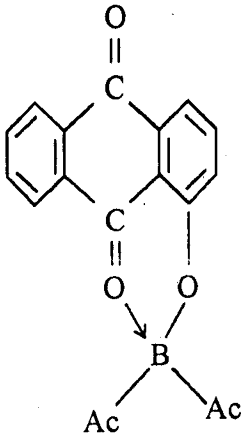
Similarly, mannitol forms a complex in which boron shows 4-covalency.



Acetylacetone reacts to form complex containing boronium ion.



Boron triacetate reacts with 1-hydroxy-anthraquinol to give the complex.



METALLURGY OF ALUMINIUM

Occurrence:

Aluminium does not occur in free state, but it is widely distributed in nature in the form of compounds. It comes third, after oxygen and silicon, in abundance.

The chief minerals of aluminium are either silicates or oxides.

1. **Silicates:** Aluminium occurs mostly as silicates and the most important among them are:

Kaolin,	$Al_2O_3 . 2SiO_2 . 2H_2O$
Potash feldspar,	$K_2O . Al_2O_3 . 6SiO_2$
Potash mica,	$K_2O . 3Al_2O_3 . 6SiO_2 . 2H_2O$

2. **Oxide:** Aluminium occurs in different forms as Al_2O_3.

Bauxite,	$Al_2O_3 . 2H_2O$
Corundum,	Al_2O_3
Diaspare,	$Al_2O_3 . H_2O$
Gubsite	$Al_2O_3 . 3H_2O$

Ruby (red), sapphire (blue) and emerald (green) are impure forms of Al_2O_3 (corundum).

3. **Fluorides:** The most important double fluoride of aluminium is ***cryolite***, Na_3AlF_6.

Extraction of Aluminium:

Aluminium is mainly prepared from the mineral *bauxite* by an electrolytic process discovered by American student, Hall in 1886 at the very young age.

The process involves two important steps:

1. Preparation of pure alumina from bauxite.
2. Electrolysis of alumina.

1. **Preparation of Pure Alumina from Bauxite:** The chief impurities in bauxite are ferric oxide and silica. Both these impurities must be removed because they render the metal brittle and liable to corrosion. The following two independent processes are used to purify bauxite:

(a) **Hall and Baeyer's Process:** This process is suitable for treating red bauxite (which contains large amounts of iron). The finely divided ore is treated with concentrated solution of caustic soda (NaOH) or sodium carbonate in autoclaves. Aluminium oxide present in bauxite goes into solution as sodium aluminate and partly as colloidal alumina. Calcium silicate and $Fe(OH)_3$ remain as residue.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$Al_2O_3 . 2H_2O + Na_2CO_3 \longrightarrow \underset{\text{(water soluble)}}{2NaAlO_2 + CO_2 + 2H_2O}$$

The solution thus obtained is slightly diluted with water and filtered to remove ferric oxide and other insoluble matter. CO_2 is passed through the solution and agitated when $Al(OH)_3$ precipitates. Large dilutions also give precipitates of $Al(OH)_3$.

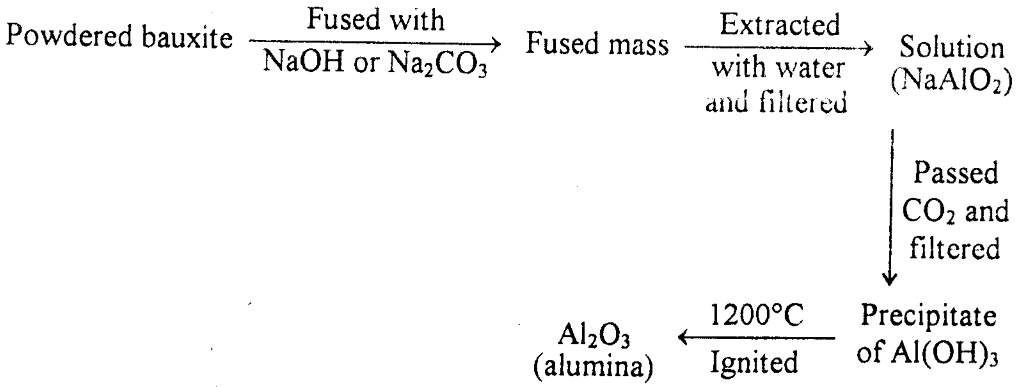
$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3\downarrow + Na_2CO_3$$

$$NaAlO_2 + 2H_2O \text{ (dilution)} \longrightarrow Al(OH)_3\downarrow + NaOH$$

The precipitate of $Al(OH)_3$ is filtered, washed and ignited to get Al_2O_3.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

The flow sheet for this process is:



(b) **Serpeck's Process:** This process is suitable for bauxite containing large amounts of silica. The ore is mixed with carbon and heated at 1800°C in a current of nitrogen when aluminium nitride is produced.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

Aluminium nitride thus obtained is decomposed with water to get $Al(OH)_3$.

Aluminium hydroxide is filtered, washed with water and ignited to get Al_2O_3.

Ammonia is obtained as a valuable byproduct in this process.

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

The silica present in bauxite is reduced to silicon, which being volatile at high temperatures volatilises off.

$$SiO_2 + 2C \longrightarrow 2CO + Si$$

2. Electrolysis of Alumina (Hall's Process): The pure and dry alumina obtained from either of the above processes is fused with cryolite, Na_3AlF_6. This molten mass is electrolysed in a steel tank (8 ft × 6 ft) lined with blocks of carbon which serves as the cathode (Figure 12.6). The anodes are rods of carbon hanging in the molten mass.

The resistance of the electrolyte to the current produces enough heat which keeps the mass in molten state. Liquid aluminium obtained at the cathode sinks to the bottom of the cell and is tapped off occasionally. Fresh amounts of bauxite are added when required.

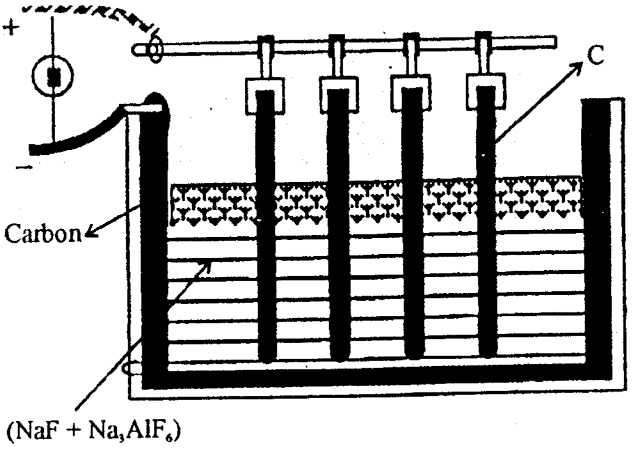


Fig. 12.6.

The raw material for this process is Al_2O_3 but Na_3AlF_6 provides AlF_3 first. Aluminium trifluoride liberates F_2 at the anode which reacts with Al_2O_3 forming AlF_3 again. Thus Al_2O_3 gets consumed in the process.

$$2Al^{3+} + 6e^- \longrightarrow 2Al \text{ (at cathode)}$$

$$6F^- - 6e^- \longrightarrow 3F_2 \text{ (at anode)}$$

The overall reaction may be shown as:

$$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

The liberated oxygen attacks carbon anode forming some CO and CO_2. Therefore, in modified method a mixture of composition, $2AlF_3 \,.\, 6NaF \,.\, 3CaF_2$ is used.

Al metal produced in this method is about 99% pure but contains trace impurities of Fe, Si, Al_2O_3 etc.

Refining of Aluminium (Hoopes Process): This process is based on electrolysis of a fused mixture of AlF_3, BaF_2 and NaF saturated with Al_2O_3. The bath consists of two layers (a) lower molten Al-Cu alloy and (b) upper molten fluorides. Aluminium metal is deposited at the top of the upper layer which contains hanging carbon cathodes. Crude Al is introduced at the bottom layer as shown in Figure 12.7.

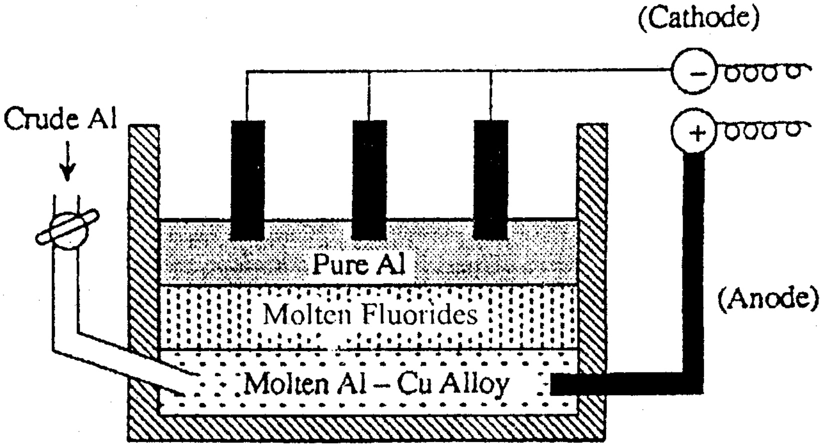


Fig. 12.7. Electrolytic refining of aluminium.

On electrolysis, Al from Al-Cu alloy goes into solution in the middle layer as Al^{3+} leaving impurities at the anode. Al^{3+} is reduced at the cathode and deposited at the top of molten fluorides. The aluminium layer grows and is drawn off occasionally.

Uses:

1. Aluminium is used for making utensils due to less weight, resistance to corrosion and good conductor of heat.
2. It is used for preparing aeroplane bodies and certain structural material.
3. Aluminium is used in reflecting mirrors for reflecting heat and light.
4. It is also used to prepare the electric goods.
5. It is used to prepare useful alloys.

Aluminium bronze is an alloy of Al (10%) and Cu (90%). It is used in imitation jewellary due to high tensile strength and golden colour.

Duralumin (Al, 92.5%; Mg, 1.5%; Cu, 2%; Ni, 4%) is an alloy of Al used in aircraft due to tensile strength (as high as that of steel) and light weight.

ALUMINIUM AND ITS COMPOUNDS:

The three electrons in the valence shell of aluminium almost always take part in bond formation. Although a few compounds are known to show aluminium in univalent state. Aluminium is moderately reactive metal and would react with acids and alkalies in hot state. It reacts with oxygen only on strong heating but the reaction is exothermic.

Aluminium is a useful metal. It is often used in making cooking utensils owing to its light weight and resistance to corrosion as well as being a good conductor. Various alloys of aluminium are used in making aeroplane bodies and for reflecting heat and light in the form of reflecting mirrors.

Aluminium forms the following three type of compounds:

1. Covalent compounds, *e.g.*, $AlCl_3$.
2. Compounds consisting of giant molecules, *e.g.*, Al_2O_3.
3. Non-chelate and chelate complexes in which aluminium is in the ionic state.

We shall discuss the compounds of aluminium under these categories.

1. Covalent Compounds:

Aluminium bearing the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ can provide three electrons for sharing with three other atoms to form three covalent bonds. In the process of this bond formation, aluminium attains only 6 electrons in the valency shell which means short of two electrons to complete the octet. The covalent compounds thus formed are *electron deficient.* The typical example is aluminium chloride, $AlCl_3$.

Aluminium Chloride, $AlCl_3$: It is a white, stable and volatile solid and is prepared by the following methods:

(i) **By Direct Combination of Al and Cl_2 or HCl:** Anhydrous aluminium chloride is prepared by passing dry chlorine or hydrochloric acid gas on heated aluminium metal. The compound $AlCl_3$ sublimes and is collected in a receiver.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

(ii) **From Alumina, Carbon and Chlorine:** On heating a mixture of alumina, carbon and chlorine at high temperature anhydrous $AlCl_3$ is obtained.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

(iii) Alumina heated with sulphur monochloride, S_2Cl_2 and chlorine gives aluminium chloride.

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 \longrightarrow 8AlCl_3 + 6SO_2$$

Properties

(i) Anhydrous aluminium chloride sublimes at 193°C and is soluble in organic solvents which indicates its covalent nature.

(ii) It is hygroscopic and from aqueous solutions crystals of $Al_2Cl_6 \cdot 12H_2O$ are obtained.

(iii) It acts as a Lewis acid due to electron deficiency and would readily combine with Lewis bases, *e.g.*, NH_3.

$$AlCl_3 + \underset{\text{(Lewis base)}}{NH_3} \longrightarrow H_3N \longrightarrow AlCl_3$$

(iv) Aluminium chloride reacts with reducing agents such as hydrides to form complex aluminium hydrides.

$$AlCl_3 + 4LiH \xrightarrow{\text{Ether}} LiAlH_4 + 3LiCl$$

(v) Aluminium chloride is hydrolysed by water.

$$AlCl_3 + H_2O \longrightarrow Al_2Cl_6 . 12H_2O \longrightarrow Al_2O_3 + 6HCl + 3H_2O$$

Structure

Measurement of vapour density of aluminium chloride indicates that $AlCl_3$ is a dimer. Aluminium is tetrahedrally bonded to four chlorine atoms. One chlorine atom of an $AlCl_3$ molecule establishes coordinate bond with aluminium atom of the other aluminium chloride molecule (See Figure 12.8).

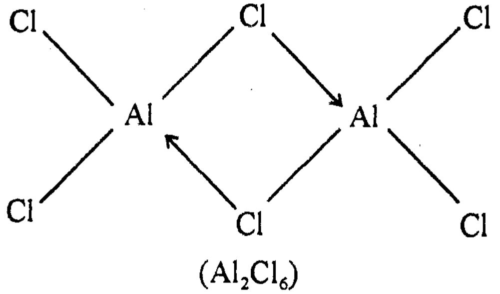


Fig.12.8. Molecular structure of aluminium chloride.

2. **Aluminium Compounds Containing Giant Molecules:**

Aluminium, like Be and B, forms a number of binary compounds which have high melting points. The bonding in these compounds shows both ionic and covalent character. The oxides, carbides, nitride and sulphide of aluminium are examples of such type.

Aluminium Oxide (Alumina), Al_2O_3: Alumina occurs in nature as corundum. ***Bauxite*** also contains large amounts of Al_2O_3. ***Emery*** contains Al_2O_3 and Fe_2O_3. Ruby consists of Al_2O_3. Other precious stones also contain alumina as one of the constituents. In these days, jewels used in watches and other instruments are artificially prepared.

Finally divided Al_2O_3 is called ***activated alumina***. Pure Al_2O_3 is prepared by igniting alum, $Al_2(SO_4)_3$ or $Al(OH)_3$.

$$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_3$$

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

Alumina is unreactive but aluminium oxide behaves as amphoteric substance (possesses both acidic and basic properties).

$$\underset{\text{(basic)}}{Al_2O_3 + 6H_3O^+} \rightleftharpoons 2Al^{3+} + 9H_2O$$

$$\underset{\text{(acidic)}}{Al_2O_3 + 2OH^- + 3H_2O} \rightleftharpoons 2Al(OH)_4^-$$

Freshly prepared alumina reacts slowly with water to form AlO . OH.

$$Al_2O_3 + H_2O \longrightarrow 2AlO\ .\ OH$$

3. Complex Compounds: The '*d*' orbitals in the valency shell ($n = 3$) of aluminium atom are responsible for the octahedral valence state and complex formation. Both non-chelating and chelating ligands are able to form such compounds with aluminium. The non-chelate complex ions are $[AlH_4]^-$, $[AlF_6]^{-3}$, $[Al(NH_3)_6]^{3+}$ etc. Among these $LiAlH_4$ is an important compound and is prepared by the action of $AlCl_3$ with LiH suspended in ether.

$$12LiH + 3AlCl_3 \longrightarrow 3LiAlH_4 + 9LiCl$$

The solution of lithium aluminohydride is a good reducing agent and reduces aldehydes and ketones to alcohols, NO_2 group to NH_2 group.

Chelating agents such as acetylacetone, acetoacetic ester and oxalate ions form cyclic derivatives which are stable and insoluble in water. The bonding in aluminium acetylacetonate is shown in Figure 12.9.

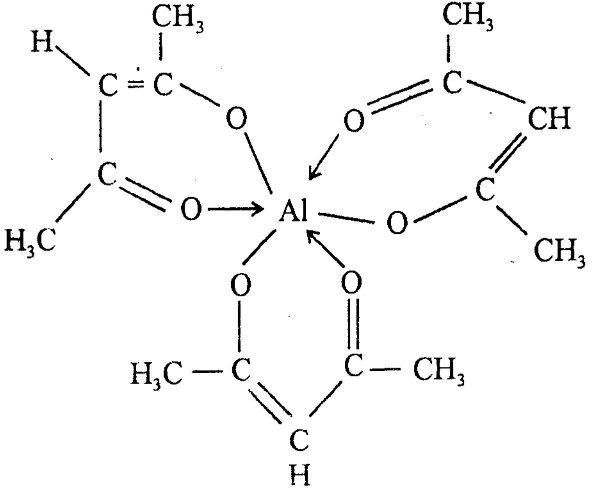


Fig. 12.9. Structure of aluminium acetylacetonate.

The formation and structure of aluminium oxalate is shown in Figure 12.10.

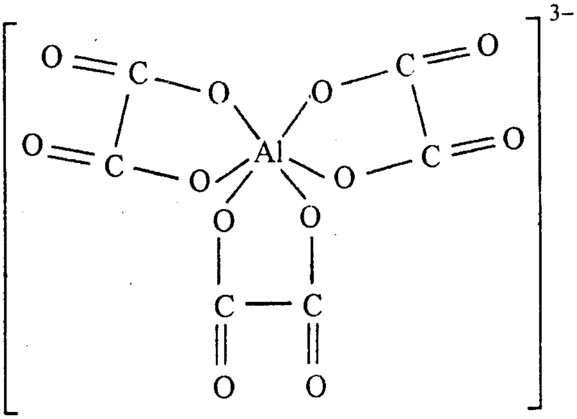


Fig. 12.10. Structure of aluminium oxalate.

ALUMINIUM SULPHATE AND ALUMS:

Aluminium sulphate is obtained by treating bauxite or clay with H_2SO_4. The solution on crystallisation gives $Al_2(SO_4)_3 . 18H_2O$.

$$Al_2Si_2O_5(OH)_4 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 5H_2O + 2SiO_2$$

Alums are double sulphates of Al and some other metals with mostly $24H_2O$. The common alum is $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$. It is prepared from $Al_2(SO_4)_3$ or by one of the following methods:

(a) **From Bauxite:** Bauxite is treated with H_2SO_4 and solution evaporated in presence of K_2SO_4.

$$\text{Bauxite} + H_2SO_4 \xrightarrow[\text{Filtered}]{\text{Boiled}} \text{solution} + K_2SO_4$$

$$\downarrow \text{evaporated}$$

$$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$$

alum crystals

(b) **From Alum Stone:** The alum stone is calcined and the mass is treated with H_2SO_4. The solution is evaporated in presence of K_2SO_4 to get alum.

$$(K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3 \xrightarrow{\text{Calcined}} \text{dry mass} \xrightarrow{H_2SO_4} \text{solution} + K_2SO_4$$

$$\text{Filtered} \downarrow \text{evaporated}$$

$$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$$

(alum crystals)

The K_2SO_4 unit may be replaced by other alkali metals, silver and ammonium and $Al_2(SO_4)_3$ by sulphates of trivalent metals, such as Cr, Fe, etc. Thus chrome alum is $K_2SO_4 \cdot Cr_2(SO_4)_3 24H_2O$ and ferric alum is K_2SO_4 $Fe_2(SO_4)_3 \cdot 24H_2O$.

Alums are soluble in water and form beautiful octahedral crystals. On heating they form porous mass. The solutions gives tests of the corresponding ions present in the alum.

Uses

Alums are mostly used in:

(i) Water purification
(ii) Dyeing of fabrics
(iii) Water proofing
(iv) Sizing of paper
(v) Tanning of hides

General Trends in Group IIIA:

- In addition to the variation in physical and some of the chemical properties mentioned above, the following points regarding the gradation of properties in elements of Group IIIA are noteworthy:

(a) Boron is a typical non-metal (m.p. 600°C). So much so that crystal structure of *boron* is different from that of aluminium. Aluminium, gallium, indium and thallium are all metals and metallic character increases with increase in atomic number. These metals are increasingly soft and malleable from Al to Tl but gallium is a liquid (m.p. 29°C).

(b) The oxides and hydroxide of boron are acidic. $Al(OH)_3$ and $Ga(OH)_3$ are amphoteric but In and Tl hydroxides are basic. Thus the basic nature of their hydroxides increases from top to bottom in this group.

(c) ***Boron*** is extracted from B_2O_3 by reduction with metals. ***Aluminium*** can only be obtained through electrolysis of fused Al_2O_3. The other metals are obtained by reduction of their oxides with hydrogen.

(d) ***Boron*** forms ***covalent*** compounds only. ***Aluminium*** gives mostly ***covalent*** compounds but in some it shows *ionic* character. In and Tl show variable valencies.

(e) Boron gives a green-edged flame. Aluminium does not give any colour. Gallium gives violet colour, indium, a dark blue and thallium, a green coloured flame on heating.

Questions

1. Discuss the diagonal relationship between boron and carbon.
2. What are the general trends in the properties of elements of Group IIIA?
3. Describe the chemistry of following:
   (a) Aluminium chloride (b) Borax (c) Alums
4. Compare the chemistry of boron and silicon. What are the main points of resemblance in these metals?
5. What happens when BF_3 is: (i) passed through ether, (ii) treated with acetylacetone, (iii) treated with metal hydrides, (iv) treated with hydrofluoric acid?
6. Discuss the reactions of boron trihalides (other than BF_3) with special emphasis on substitution reactions.
7. Describe some compounds of boron in which it is in the trigonal valence state.
8. Name any compound of boron in which it is tetrahedrally hybridised. Discuss its characteristics and usefulness.
9. What type of compounds are formed by aluminium? Discuss a compound containing giant molecules.
10. Write notes on the following:
    (a) Chelate complexes of boron and aluminium
    (b) Covalent compounds of aluminium
11. Discuss the general characteristics of members of Group IIIA. Give reactions in which they behave as electron deficient elements.
12. What are the sources of aluminium? Describe the process used to extract Al from bauxite. How is aluminium purified?
13. How is bauxite purified for getting Al? Describe electrolytic process for the extraction and refining of aluminium.
14. Discuss the extraction and refining of aluminium.
15. Give an account of the metallurgy of aluminium.
16. **Write short answers to the following questions:**
    (i) Name and give electronic configuration of elements of Group IIIA.
    (ii) Give the characteristic features of Boron as the first element of Group IIIA.
    (iii) How will you draw comparison between Boron and Silicon?
    (iv) What are the dissimilarities between Boron and Aluminium?

(v) How is Boron isolated in pure form?

(vi) Give in brief the chemical characteristics of Boron.

(vii) Draw the orbital model showing hybridized orbitals in BF_3.

(viii) How is BF_3 generally prepared?

(ix) Give reactions of boron trihalides in which they behave as Lewis acids.

(x) Draw molecular structure of boric acid.

(xi) How is boric acid generally prepared? Give its general characteristics.

(xii) How is sodium borohydride prepared? Give salient features of its reactivity.

(xiii) Describe some chelate compounds of boron.

(xiv) What are the major ores of aluminium?

(xv) How is aluminium extracted from bauxite?

(xvi) How is aluminium extracted from alumina?

(xvii) Describe some important covalent compounds of aluminium.

(xviii) Draw structure of aluminium chloride.

(xix) What are alums? How are they generally prepared?

(xx) Describe two typical complex compounds of aluminium.

17. **Give the correct answer:**

(i) The formula of corundum is:

(a) $Al_2O_3 . 2H_2O$ (b) Al_2O_3

(c) $Al_2O_3 . H_2O$ (d) $Al_2O_3 . SiO_2 . 2H_2O$

(**Ans:** b)

(ii) The formula of bauxite is:

(a) $Al_2O_3 . 2H_2O$ (b) Al_2O_3

(c) $Al_2O_3 . 2SiO_2 . 2H_2O$ (d) $Al_2O_3 . H_2O$

(**Ans:** a)

(iii) Electronic configuration of B is:

(a) $1s^2 2s^2 2p^1$ (b) $1s^2 2s^2 2p^3$

(c) $1s^2 2s^2 2p^2$ (d) $1s^2 2s^2 2p^4$

(**Ans:** a)

(iv) Boric acid resembles silic acid because both are:

(a) weak acids (b) strong acids

(c) Lewis acids (d) Soft acids

(**Ans:** a)

(v) B_2O_3 is:

(a) acidic (b) basic

(c) neutral (d) amphoteric

(**Ans:** a)

(vi) $Al(OH)_3$ is:
(a) acidic
(b) basic
(c) amphoteric
(d) neutral

(Ans: b)

(vii) Boron reacts with H_2SO_4 to produce:
(a) B_2O_3
(b) $B_2(SO_4)_3$
(c) $B(OH)_3$
(d) $B_2O_3 . H_2O$

(Ans: c)

(viii) BF_3 reacts with phosphine to give:
(a) $BF_3 . PF_3$
(b) $BF_3 . P_2O_5$
(c) $BF_3 . PH_3$
(d) $BF_3 . 2PH_3$

(Ans: c)

(ix) BCl_3 reacts with NH_4Cl to give:
(a) $B_3N_3Cl_3$
(b) $BCl_3 . NCl_3$
(c) $BCl_3 . NH_3$
(d) $BCl_3 . NH_4Cl$

(Ans: a)

(x) Acetylacetone (acac) reacts with BF_3 to give:
(a) BF_3 . 4 acac
(b) BF_3 3 acac
(c) BF_3 . 2 acac
(d) BF_3 . acac

(Ans: d)

(xi) Al_2O_3 reacts with NaOH to give:
(a) $NaAlO_2$
(b) $NaAlO_3$
(c) $NaAl_2O_3$
(d) $NaAl_2O_6$

(Ans: a)

(xii) $AlCl_3$ is:
(a) Lewis acid
(b) Lewis base
(c) Hard base
(d) Amphoteric

(Ans: a)

(xiii) Structure of $AlCl_3$ is dimeric because it is
(a) volatile
(b) an acid
(c) salt
(d) electron deficient

(Ans: d)

(xiv) The halide of aluminium which sublimes on heating is:
(a) AlF_3
(b) $AlBr_3$
(c) $AlCl_3$
(d) AlI_3

(Ans: c)

(xv) Next to diamond, the hardest substance is:
(a) AlN
(b) B_4C_3
(c) BN
(d) B_4C

(xvi) Which one of the following statements about Group IIIA elements is incorrect?

(a) All exhibit oxidation state of +3.
(b) All form oxides of the formula M_2O_3.
(c) All form trihalides, MX_3.
(d) All form amphoteric hydroxides, $M(OH)_3$.

(Ans: d)

(xvii) Inorganic benzene, $B_3N_3H_6$, borazole.

(a) resembles C_6H_6 in boiling point
(b) is iso-electronic with benzene
(c) has a cyclic structure
(d) all of these

(Ans: c)

(xviii) The formula of borax is:

(a) $Na_2B_4O_7 . 10H_2O$ (b) $Na_2B_2O_7$
(c) $Na_2B_4O_7 . 5H_2O$ (d) $Na_2B_2O_{10}$

(Ans: a)

(xix) Alum stone is:

(a) $K_2SO_4 . Al_2(SO_4)_2 . 24H_2O$
(b) $K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3$
(c) $K_2SO_4 . Al_2(SO_4)_3 . 12H_2O$
(d) $K_2SO_4 . Al_2(SO_4)_3 . CaCO_3$

(Ans: b)

(xx) Boron forms:

(a) Covalent and ionic compounds
(b) Covalent compounds only
(c) Ionic compounds only
(d) Coordinate covalent compounds only

(Ans: a)

❀ ❀ **12** ❀ ❀

13

CARBON AND SILICON (GROUP IVA)

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are members of Group IVA and have s^2p^2 configurationgeir valency shells. Their electronic configurations are shown in Table 13.1.

TABLE 13.1

Element	Shell Orbital	1	2		3			4				5			6	
		s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
C		2	2	2												
Si		2	2	6	2	2										
Ge		2	2	6	2	6	10	2	2							
Sn		2	2	6	2	6	10	2	6	10		2	2			
Pb		2	2	6	2	6	10	2	6	10	14	2	6	10	2	2

The group IVA elements occupy the middle position in the Periodic Table and bridges the metals and non-metals on both sides of the Periodic Table. The ns^2np^2 configuration indicates bivalent states of these metals because only *p* orbitals would be involved in bond formation. Promotion of one of the *ns* electrons to the *p* orbitals in the excited state gives the atom an electronic configuration $ns^1\ np_x^1\ np_y^1\ np_z^1$. The *s* and all the three *p* orbitals would be involved in hybridization to form sp^3 hybrid orbitals arranged along the corners of a regular tetrahedron. These four hybrid orbitals overlap with orbitals of reacting species to form four covalent bonds and attain stable inert gas configuration. The tendency of 4 covalency is the major characteristic of the chemistry of carbon, which forms four electron-pair bonds with hydrogen, halogens, nitrogen, oxygen, sulphur and with other carbon atoms. The tetravalent compounds of carbon are incapable of attack by means of an electron donating mechanism. Thus these compounds of carbon are stable and would not hydrolyse. On the other hand, the tetravalent compounds of Si, Ge and Sn, especially tetrahalides undergo hydrolysis and other reactions involving expansion of valence shell. Thus they can have covalencies more than four due to the involvement of *d* orbitals

The chemistry of carbon differs from other members of the group mainly due to its ability to form C — C linkage (catenation). This ability is suddenly reduced in other members of the group so much so that Pb does not possess such type of linkage. The reason for catenation in carbon is its inability to attain a covalene greater than four and greater carbon to carbon bond energy (82 kJ/mole per mole). Although silicon-silicon bond is less stable than C — C bond but silicon forms fairly strong bonds with halogens, oxygen and hydrogen as indicated by their bond energy values shown in Table 13.2. From these bond energies one can appreciate that the chemistry of silicon is almost entirely of oxides, fluorides, chlorides and hydrides which indicates a close resemblance in the chemistry of silicon and boron.

TABLE 13.2

Bond Energies

C – C	355 kJ/mole	Si – Si	269 kJ/mole	Si – I	221 kJ/mole
C – Cl	338 kJ/mole	Si – S	251 kJ/mole	Si – Br	305 kJ/mole
C – H	414 kJ/mole	Si – H	338 kJ/mole	Si – Cl	376 kJ/mole
C – O	359 kJ/mole	Si – O	443 kJ/mole	Si – F	569 kJ/mole

General Group Trends

The general characteristics of elements are summarised in the following points:

(i) All members, except carbon and silicon, are metals.

(ii) Carbon and silicon are abundantly present in earth's crust. Carbon is mainly present in the form of compounds containing C — C bonds and minerals consist primarily compounds containing Si — O bonds. Other members of the group are less common.

(iii) Elementary Si, Ge and Sn have crystal structures quite analogous to carbon in the form of diamond having crystal coordination number 4. However, the covalent bonding decreases with increase in atomic number and is more metallic in Sn or Pb. The change from covalent to metallic is reflected in the sharp decrease in M.Pt. from 3600°C for C to about 327.5°C for Pb. The decrease in melting point is also attributed to the increase in size of the atoms resulting in the decrease of electrostatic attraction.

(iv) Allotropic forms are manifested by these elements, especially carbon and tin.

(v) Carbon has the remarkable property of forming chain and ring structures through C — C bonds. Silicon forms a three dimensional network of Si — O linkages. Other elements do not form such type of macromolecular structures.

(vi) Carbon mostly forms compounds having four covalency only. The tendency of change from 4-covalency increases with increase in atomic number. As the atomic radius increases the two *s* electrons of the valency shell become inert pair because of their stable state and would not take part in chemical bonding. Thus only, the other two electrons present in '*p*' orbitals (ns^2np^2) take part in bond formation and divalent states become more and more stable, *e.g.*, Sn^{2+} and Pb^{2+}.

(vii) No cations M^{4+} are found in these elements due to high ionization potential values. Thus the bond in such cases is always covalent, *e.g.*, CCl_4, $SnCl_4$, $PbCl_4$ etc.

Physical Properties:

Some of the most important physical properties of these elements are shown in Table 13.3.

TABLE 13.3

Physical Properties of Group IVA Element

	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Electronic configuration	[He] $2s^2\ 2p^2$	[Ne] $3s^2\ 3p^2$	[Ar] $3d^{10}\ 4s^2\ 4p^2$	[Kr] $4d^{10}\ 5s^2\ 5p^2$	[Xe] $5d^{10}\ 6s^2\ 6p^2$
Atomic weight	40.08	28.08	72.59	118.69	207.19
M.P. °C	3600	1410	937	231.9	327.5
B.P. °C	4827	2355	2830	2260	1744
Density g/cm^3 (sublimes)	3.50 2.25	2.33	5.36	7.31	11.34
Ionization Potential (1st) kJ/mole	47	34	32	30	31
Covalent radius (pm)	77	117	122	140	144

Comparison between Carbon and Silicon

There are some interesting aspects in the chemistry of carbon and silicon which would be observed in the subsequent discussion in this chapter. Let us note some of the important points of comparison in **Carbon and Silicon** mentioned below:

1. Both carbon and silicon have ns^2np^2 electronic configuration. The difference in behaviour arises due to the differences in atomic and ionic radii.
2. Carbon is abundantly available in nature in animals and vegetables as well as in minerals mostly as carbonates and in the free state.
   Silicon is abundantly found in silicate minerals and in the form of silica, $(SiO_2)_n$.

3. The C — C bonds give rise to a large number of carbon compounds. However, Si — O bonds produce a large number of silicate minerals.
4. Carbon and silicon form similar type of hydrides and halides which show covalencies, *e.g.*, CCl_4 and $SiCl_4$; CH_4 and SiH_4 etc.
5. The common oxides of carbon and silicon are CO_2 and SiO_2. Carbon dioxide is a gas but silicon dioxide is a solid due to its polymeric state formed by Si — O linkages.
6. Both CO_2 and SiO_2 react with water to produce acids H_2CO_3 and H_2SiO_3, respectively.
7. Carbon compounds show isomerism fairly commonly but this property is not well marked in silicon compounds.
8. Carbon can attain a maximum covalency of 4 whereas silicon can expand its 6 covalent bonds due to the availability of *d* orbitals in case of Si.
9. In general, carbon compounds are more stable than those of silicon. The silicates and polymers are, however, fairly stable.
10. Carbon is unaffected by alkalies but silicon reacts with both aqueous and fused alkalies

CARBON

Carbon is well known since times immemorial in the form of coal, charcoal, and diamond. In 1800, Mackenzies showed graphite to be in the form of carbon which was formerly supposed to be molybdenum sulphide.

Occurrence

Carbon occurs in nature both in the free and the combined states. In the combined states, it occurs as:

(i) **Carbon dioxide** constitutes about 0.03 percent of air.

(ii) **Carbonates** occur in the form of chalk, limestone and marble ($CaCO_3$); dolomite ($CaCO_3 . MgCO_3$) etc

(iii) **Hydrocarbons** in petroleum and natural gas

(iv) **Complex organic compounds** present in plants and animals.

Allotropy of Carbon

Many elementary substances exist in two or more crystalline forms differing in spatial arrangement of molecules, atoms or ions constituting them.

The existence of a substance in more than one crystal form is known as allotropy (allotropia, meaning variety). Different crystalline forms of the same substance are called **allotropes**. The allotropic forms differ in physical properties but possess the same chemical properties as expected for the substance manifesting allotropy. The allotropic forms have different stabilities and unstable variety changes into the stable allotrope. This change may be brought about by varying temperature. The temperature at which allotropic form, changes into other is called **transition temperature** and has fixed value for each pair of allotropes.

Carbon exists in following allotropic forms:

1. Diamond
2. Graphite
3. Fullerenes or Bucky Balls
4. Polyynes or polyacetylens
5. Amorphous Carbon

1. Diamond

Diamond is found mainly in South Africa, Australia and Brazil. The diamonds from South Africa clay mines are obtained by washing with water to remove lighter clay particles. The heavier residue is then washed over a layer of grease, to which the diamonds stick and are separated.

Diamonds have also been prepared artificially by the crystallization of molten carbon under great pressure. Moissan (1893) succeeded in preparing small diamonds artificially. Pure sugar charcoal was heated to a temperature of 3,500°C in an electric furnace in presence of iron. On cooling, carbon separates as crystals, and since iron containing carbon expands on solidifying, the interior portions were subjected to an enormous pressure. Iron was dissolved away to leave behind some graphite and diamonds (black and colourless).

Properties:

It is the hardest substance known. Among various forms of carbon, diamond is the purest and densest. Diamonds are found to vary in size and colour.

Diamond has the highest refractive index, 2.45. This property is responsible for its value as gems. Koh-i-Noor (mountain of light) is a famous diamond of large size which had the original weight of 186 carats(1 gram = 5 carats) but had to be cut down to 106 carats later on.

The diamond is a nonconductor of electricity because of the complete utilization of valence electrons for the formation of covalent bonds. The density is 3.5 g/cm^3.

The melting point of diamond is quite high, 3600°C. Diamond does not ignite in oxygen below 800°C. It is attacked by sulphur at 1000°C.

Structure:

Diamond contains carbon atoms linked together in a tetrahedral manner. Each carbon atom is surrounded by other carbon atoms (coordination number 4) in a three dimensional network. Each carbon would utilise sp^3 hybrid orbitals in the process of bond formation with other carbon atoms.

The crystal structure of diamond was studied by X-ray diffraction in 1913 by Bragg. The C — C bond distances were found to be 154 pm. Diamond crystal is a giant molecule showing cubic symmetry. The diamond structure is shown in Figure 13.1 which imparts great hardness and permits the four well-defined cleavages.

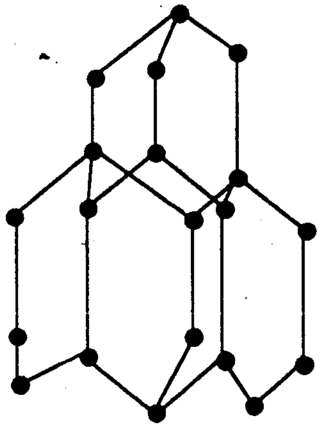


Fig.13.1 Diamond Structure.

Uses:

(i) Diamonds are both colourless and coloured. They are mostly used as jewels and gems in ornaments.

(ii) Black diamonds are known as *Carbonado* because of their great hardness. Thus they are used for glass cutting, rock drilling and for cutting and polishing colourless diamonds.

2. Graphite (Black Lead or Plumbago)

Graphite occurs in large amounts in Siberia, Ceylon, Kashmir and many other places.

Large quantities of graphite are now manufactured by *Achesen Process*. By this process, powdered anthracite or petroleum-coke is heated in an electric furnace in presence of a little sand. Sand acts as a catalyst in the transformation of amorphous carbon into graphite. A powerful alternating current is passed through the mass of amorphous carbon for 24-30 hours. Silicon carbide is first formed which decomposes at very high temperature (3,500°C) to form graphite. Silicon volatilizes off at this temperature.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

$$SiC \longrightarrow Si + C \text{ (graphite)}$$

Properties:

Graphite is very soft and greasy to touch. It has a grey-black colour with metallic lustre.

It is a good conductor of heat and electricity. The electrical conductivity of graphite is due to the presence of an electron remained after sp^2 hybridization This single electron forms π-bond and π-electrons are mobile rendering graphite a conductor of electricity.

The density of graphite is 2.2 g/cm^3. Graphite is quite stable and inert even at 2000°C and high pressure. However, it is more reactive than diamond. The following reactions are noteworthy:

(i) **Fluorine** reacts with graphite at high temperatures to form mainly $(CF)_n$.

$$nC + nF \longrightarrow (CF)_n$$

(ii) **Potassium** is absorbed by graphite to form KC_8 type species.

(iii) **Oxidation of graphite** with strong H_2SO_4, HNO_3, $HClO_4$ and H_3PO_4 results in the separation of layers and acid groups enter to form salt-like compounds.

$$C(\text{Graphite}) + HNO_3 \longrightarrow C_{11}H_4O_5 \text{ (graphitic acid)}$$

$$\text{Graphite}) + H_2SO_4 \longrightarrow (C_{24})^+ (HSO_4)^- . 2H_2SO_4$$

The composition of the product depends upon the concentration of acid and thus the extent of oxidation. The graphite salts are decomposed by water, with the regeneration of graphite.

(iv) **Iron (III) chloride** is taken up by graphite to give a substance of approximate formula $C_6(FeCl_3)$. The magnetic moment value of iron remains unchanged after the formation of the product which indicates that no iron-carbon bond is produced.

(v) **Bromine** vapours are absorbed to form a solid with composition C_8Br Bromine absorption by graphite increases the layer spacing from 3.4 to 7.05A°.

(vi) **Graphitic oxide** is formed when a mixture of concentrated H_2SO_4, HNO_3 and solid $KClO_3$ are kept for several days. The composition of graphitic oxide is found to be (C_xO_y). Complete oxidation of graphite gives mellitic acid, $C_6(COOH)_6$.

Structure

Graphite has a *layer-lattice* structure. The carbon atoms are bonded to only three other carbons in hexagonal rings arranged in layers as shown in Figure 13.2. The carbon atoms are covalently bonded and have C — C bond length 142 pm. However, the *distance between layers* is 340 pm.

The layers are held together by weak binding forces, called 'Van der Waals' forces, which allow the layers to slide over one another. This accounts for the softness and lubricating properties of graphite.

Each carbon atom within each layer is surrounded by only three other carbon atoms forming three σ-bonds located at the corners of an imaginary equilateral triangles.

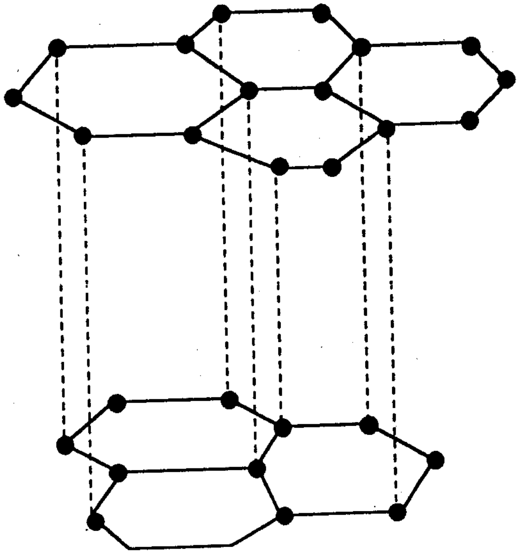


Fig. 13.2.

In this way, 3 out of 4 electrons of each carbon are involved in σ-bond formation and the fourth electron is involved in a π-bond.

Uses:

(i) Graphite is extensively used in the manufacture of 'lead' pencils. For this purpose a variable composition of graphite and fine clay is used. The proportion of clay to graphite in a pencil determines the hardness of a pencil.

(ii) Graphite is also widely used as a lubricant in hot parts of the machinery where oil cannot be used. *Aquadag* is a colloidal solution of graphite in water with little tannic acid and much used as *lubricant.*

(iii) It is also used as electrodes for various electrolytic processes.

(iv) It is also useful in making crucible to withstand high temperatures.

3. Fullerenes (Bucky Balls)

Carbon exists in many structural forms or allotropes. Three of the allotropic forms of carbon are crystalline, *i.e.*, diamond, graphite and recently discovered fullerene. Whereas coke and carbon black are amorphous forms of carbon.

Fullerene was first characterized in 1991 and contains 60 sp^2-hybridized carbon atoms with 12 pentagonal and 20 hexagonal faces that are joined into the spherical shape of a soccer ball (European foot ball). (Fig. 13.3)

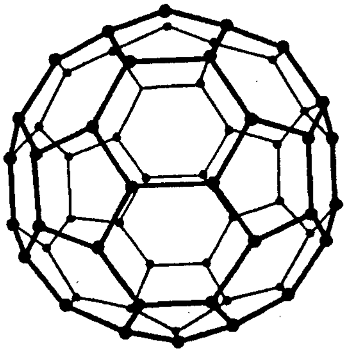


Fig. 13.3.

Richard Smalley, Robert Curl and Harold Kroto in 1996 were awarded Nobel Prize for discovery and production of fullerenes.

Fullerenes can be produced by a simple process. An electric current is passed through graphite rods in a quenching atmosphere of helium inert gas. The graphite rods thus evaporate to produce light, fluffy condensate called, 'fullerene soot'. It is highly soluble in organic solvents like benzene and can be separated by chromatographic technique. The soluble fullerene is composed of 80% C_{60}, 20% C_{70} and 1% higher fullerenes. Upon concentration of solutions, crystals of fullerenes can also be obtained by sublimation under vacuum. Evaporation of graphite by high energy laser also produces fullerenes.

Natural sources of fullerenes are meteorites and regions of lightning strikes. Burning of benzene under specific conditions also produces soot that contains fullerenes.

The fullerene with C_{60} dissolves in toluene to give a purple solution and C_{70} gives an orange-red solution.

A dimer of fullerene, C_{120} (Fig. 13.4) can be synthesized in 18% yield by vigorously vibrating a solid mixture of C_{60} in presence of KCN powder. It has a dumb-bell shape.

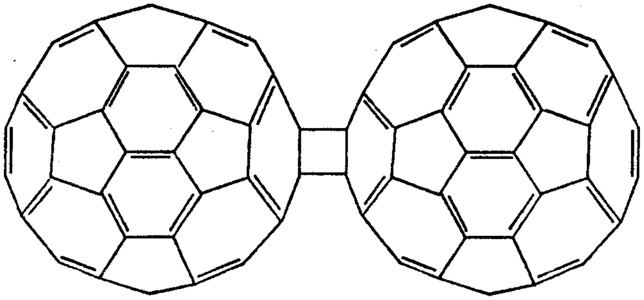


Fig. 13.4.

The fullerene, C_{60} is one of the most strained molecules known so far, but exhibits kinetic stability. It decomposes at 750°C which is faster in presence of oxygen. The fullerene, C_{70} is slightly more stable than C_{60}.

An interesting group of carbon materials are the carbon nanotubes or bucky tubes prepared by evaporation of graphite. They are needle-like cylindrical tubes of graphite carbon capped by fullerene-like hemisphere. The nanotubes are metallic and semiconducting materials which may be used as microelectronic devices.

4. Polyynes or Polyacetylenes

Another crystalline allotropic form of carbon is polyyne form. It was reported by Richard Lagow (1995). The polyyne allotrope consists of linear chains of upto 500 *sp*-hybridized carbons joined by alternate single and triple bonds.

$$\{C \equiv C - C \equiv C - C \equiv C\}_n$$

Polyyne allotrope of carbon

Polyynes can be prepared by laser-induced vaporization of graphite in the presence of trifluoromethyl radicals (CF_3) to 'cap' the ends of long acetylinic chains so as to stabilize the molecules.

Polyyne carbon is soluble in organic solvents like toluene. It appears to be electrically conducting along its long axis, to function as a 'molecular wire'. It can be coated on to other substrates.

5. Amorphous Carbon

Amorphous form of carbon is obtained by heating wood, starch, sugar and other organic substances rich in carbon in absence of air. There are many varieties of amorphous carbon known and the important among them will now be described.

(a) Charcoal

The *residue left* after heating organic substances in absence of air is called *charcoal*. The most important form is *wood charcoal* which is manufactured by heating up a pile of wood in such a way that only a limited supply of air is allowed. The wood is allowed to burn slowly.

Another form of charcoal is called *animal charcoal* (bone-black) which is obtained by destructive distillation of bones. The distillate is liquid and consists of

(i) an oily bone oil, and

(ii) an alkaline aqueous layer.

The residue is called *animal charcoal* and consists of 10 per cent of finely-divided carbon. It is a porous black mass and has a remarkable power of adsorbing colouring matter. Animal charcoal is thus employed for decolouring sugar and certain other organic matter.

Sugar charcoal is the purest form of carbon. It is obtained by heating sugar in absence of air.

(b) Coal

Coal is found in large quantities in nature. It is produced by decomposition of wood and other vegetable matter in limited supply of air. The coal contains varying quantities of hydrogen, oxygen, nitrogen and sulphur along with carbon.

There are different varieties of coal which represent various stages of the transformation of vegetable matter. *Peat* is a light variety of charcoal and represents the first stage of transformation. The product of second stage is called *Lignite* or 'brown coal' and contains about 60 per cent of carbon. Both peat and lignite are used as cheap fuels. The third stage of transformation is commonly called *Bituminous coal*. It contains about 80 per cent of carbon and burns with a smoky flame. It is mainly used to produce *coal gas*.

The last stage in the formation of coal is called Anthracite, which is hard, black and brittle. It contains more than 90 per cent coal and burns without smoke. producing lot of heat.

(c) Coke and gas carbon

Both are obtained by dry distillation of coal. Gas carbon is evolved leaving behind a residue of coke. Gas carbon is obtained as hard, black deposit on the roofs and sides of the retort. It is the pure form of carbon. It is a good conductor of electricity, and is mostly used for making carbon electrodes.

(d) Lampblack

It is prepared by burning tar, petroleum and turpentine oil etc., in limited supply of air. The smoke is passed through coarse blankets on which lampblack is deposited and subsequently removed. Lampblack contains up to 20 per cent of oily impurities and is widely used for making printer's ink, other fast inks and black paint.

Comparison in allotropes of carbon

The comparison in physical properties of the three allotropic forms of carbon are given in Table 13.4.

TABLE 13.4

Property	Diamond	Graphite	Amorphous Carbon
1. Appearance.	Colourless and transparent crystals with shining surface.	Grey, opaque, crystalline solid with metallic lustre.	Black amorphous.
2. Hardness.	The hardest substance known.	Extremely soft.	Varies-mostly soft.
3. Density.	3.5	2.2	1.0 to 1.5
4. Electrical conductivity.	Bad conductor.	Good conductor.	Bad conductor except *gas carbon* which is good conductor.
5. Thermal conductivity.	Good conductor.	Good conductor.	Varies.
6. Behaviour at high temperature.	On strong heating in electric arc, it transforms into graphite.	Fairly stable at high temperature.	Changes to graphite in presence of sand.

Chemical Properties of Carbon

The typical reactions of carbon are given below:

(i) Reaction with Air or Oxygen

Carbon remains unaffected by air or oxygen at ordinary temperature. On strong heating, carbon is converted to CO and CO_2.

$$2C + O_2 \xrightarrow{\Delta} 2CO$$

$$2C + 2O_2 \xrightarrow{\Delta} 2CO_2$$

$$C + CO_2 \xrightarrow{\Delta} 2CO$$

(ii) Reaction with Water

Water has no action on carbon but steam reacts when passed over red-hot carbon to form water gas (CO and H_2).

$$C + H_2O \longrightarrow CO + H_2$$

(iii) Reaction with Halogens

Direct reactions of halogens with carbon at high temperature to form halides of general formula CX.

(iv) Reaction with Hydrogen

When hydrogen is passed through carbon heated at the temperature of electric arc, acetylene is formed.

$$2C + H_2 \xrightarrow{\Delta} C_2H_2$$

(v) Reaction with Sulphur

Carbon reacts with sulphur at a high temperature to form CS_2.

$$C + 2S \xrightarrow{\Delta} CS_2$$

(vi) Formation of Carbides

When carbon (coke) is heated in presence of CaO, silicon and aluminium, calcium carbide is obtained. On heating elements directly, carbides my be formed.

$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$

$$2Be + C \xrightarrow{\Delta} Be_2C$$

(vii) Reducing Action

Carbon has strong affinity for oxygen and possesses therefore, a strong reducing property. It is used on large scale to produce metals from their oxides.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$As_2O_3 + 3C \longrightarrow 2As + 3CO$$

(viii) Reaction with Acids

The oxidising acids such as HNO_3 and H_2SO_4 react with carbon on heating and oxidise it to CO_2.

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(ix) Reaction with Alkalies

Carbon remains unaffected by alkalies.

(x) Reaction with Sodamide

On heating carbon at 500 — 600°C in presence of sodamide, NaCN is obtained.

$$NaNH_2 + C \xrightarrow{500 -- 600^\circ} NaCN + H_2$$

OXIDES OF CARBON

Carbon forms five stable oxides namely, carbon monoxide (CO), carbon dioxide (CO_2), C_3O_2, C_5O_2 and $C_{12}O_9$. C_3O_2 is considered to be anhydride of malonic acid, $CH_2(COOH)_2$.

(a) Carbon Monoxide, CO

Carbon monoxide is present in gases obtained from the blast furnace and other commercial processes. Charcoal flame contains mainly carbon monoxide gas. The following reactions take place during the burning action of coal.

$$C + O_2 \longrightarrow CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

PREPARATION

Carbon monoxide is prepared in the laboratory by the following methods:

(i) From Oxalic Acid

Carbon monoxide is obtained along with carbon dioxide by heating oxalic acid crystals with concentrated H_2SO_4. The mixture of gases is passed through caustic soda solution to remove carbon dioxide.

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$$

(ii) From Formic Acid

Formic acid is added to concentrated H_2SO_4 at 100°C. Sulphuric acid acts as dehydrating agent and produces pure CO.

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

(iii) From Potassium Ferrocyanide

The convenient method to prepare CO is by heating potassium ferrocyanide with concentrated H_2SO_4 (dilute acid should not be used at all because it evolves HCN which is very poisonous).

$$K_4[Fe(CN)_6] + 6H_2O + 6H_2SO_4 \longrightarrow FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 5CO$$

(iv) From Carbon Dioxide

Dry carbon dioxide is passed through a layer of charcoal heated to redness in an iron tube.

$$CO_2 + C \longrightarrow 2CO$$

(v) From Carbon

It can also be prepared by heating a carbonate with reducing metal.

$$MgCO_3 + Zn \xrightarrow{700-750^\circ} ZnO + MgO + CO$$

Physical Characteristics

Carbon monoxide is a colourless gas, with faint odour. It is a poisonous gas and only very slightly soluble in water.

Chemical Reactions

Carbon monoxide is an unsaturated compound and reacts in the following manner:

(i) Combination with Hydrogen

Carbon monoxide reacts with hydrogen in presence of a mixture of ZnO and Cr_2O_3 as catalyst heated at 400°C.

$$CO + 2H_2 \longrightarrow CH_3OH$$

(ii) Combination with Oxygen

Carbon monoxide burns in air or oxygen with a blue flame to produce CO_2.

$$2CO + O_2 \longrightarrow 2CO_2$$

(iii) Reducing Action

Carbon monoxide is a powerful reducing agent and can be easily oxidised to CO_2. The metal oxides can be reduced to free metals.

$$PbO + CO \longrightarrow Pb + CO_2$$

$$CuO + CO \longrightarrow Cu + CO_2$$

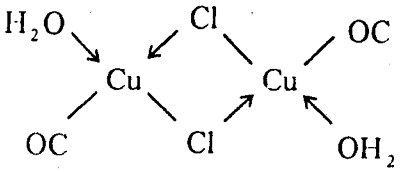
(iv) Combination with Chlorine

Carbon monoxide reacts with chlorine in presence of sunlight producing *phosgene* or carbonyl chloride, which is a very poisonous gas used in chemical warfare.

$$CO + Cl_2 \longrightarrow COCl_2$$

(v) Reaction with Cuprous Chloride

An addition product, CuCl.CO with H_2O is formed by passing CO through a solution of cuprous chloride in ammonia or concentrated HCl. It is dimeric compound having formula:



(vi) Reaction with Alkalies

Carbon monoxide is neutral to the action of litmus and is not affected by alkalies under ordinary conditions. Solid sodium hydroxide reacts with CO under pressure to form *sodium formate.*

$$NaOH + CO \longrightarrow HCOONa$$

(vii) Reaction with metals:

Transition metals react with carbon monoxide under pressure and at high temperatures to form carbonyl compounds. Nickel carbonyl is formed easily by passing carbon monoxide over nickel metal at 60 – 70°C as volatile liquid.

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

Carbonyls of transition metals have been isolated mostly by indirect methods. They are very important compounds from synthetic viewpoint and also act as catalysts in certain industrially important reactions.

The bonding in carbonyl derivatives involves the dative overlap of filled carbon orbitals and back bonding ability of *filled dπ or hybrid dpπ* metal orbitals with empty *anti-bonding* orbitals of carbon monoxide. This type of bonding is called *synergic*. Carbon monoxide is thus bonded to metals through carbon atoms and the overall effect of such type of bonding is no net shift of charge density on to or from metal atoms. Thus metals remain in the zero valent state even after reacting with carbon monoxide. The proof for such type of bonding is obtained through spectroscopic means and by X-ray crystallographic studies. On heating these carbonyls, metal can be obtained in the zero valent state as is evident from the decomposition of $Ni(CO)_4$ to Ni metal. This decomposition reaction is used to produce pure nickel by Mond process.

$$Ni(CO)_4 \longrightarrow Ni + 4CO$$

(viii) Combination with Haemoglobin

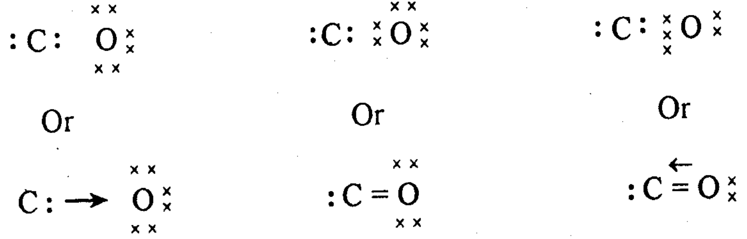
Carbon monoxide combines with haemoglobin, the red matter of the blood to form a very stable, bright red carboxy-haemoglobin. This reaction is based on the fact that haemoglobin contains iron which established linkage with CO molecule. The blood would lose its power to absorb oxygen in presence of carbon monoxide. Thus small amounts of carbon monoxide produce headache and large quantities may cause unconciousness and ultimately death due to the formation of carboxy haemoglobin which stops the normal functioning of blood. Hence, *it is always dangerous to have coal fire in the room* without any ventilation. In cases of carbon monoxide poisoning, the best method is to administer a mixture of 95 per cent oxygen and 5 per cent carbon monoxide.

Structure

The molecule of carbon monoxide, CO has carbon and oxygen covalently linked. The electronic configuration of carbon and oxygen are:

$$\text{Carbon } (C_6) = 1s^2 \quad 2s^2\ 2p^2$$
$$\text{Oxygen } (O_8) = 1s^2 \quad 2s^2\ 2p^4$$

The carbon has 4 electrons in the valency shell and oxygen has 6 electrons in the 2nd orbit. There are three possible ways in which carbon and oxygen atoms may be linked such as:



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These three resonance structures contribute towards the actual structure of CO.

The formation of σ and π bonds in CO is indicated in Figure 13.5. The bonding σ orbitals are formed by the overlap of carbon *sp* hybrid orbitals and *p* orbital of oxygen. Lateral overlap of remaining 2*p* orbitals (each having one electron) results in the formation of two π-type molecular orbitals.

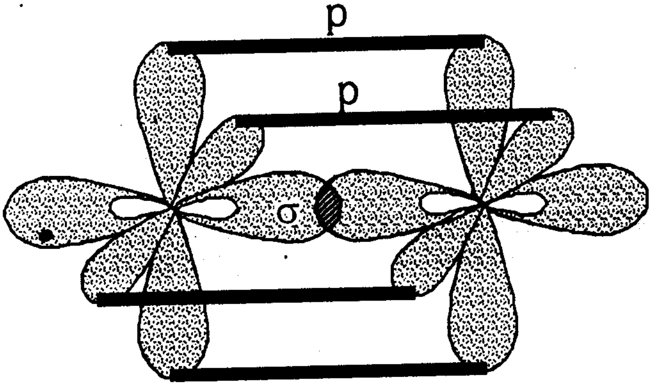


Fig.13.5 Formation of CO molecule.

(b) Carbon Dioxide, CO_2

It is the most stable oxide of carbon. It is present in the atmosphere and can be obtained from carbonates and from fine gases and lime kilns.

Carbon dioxide is freely soluble in water and forms carbonic acid, pH of concentrated solution being 3.7 at 1 atmosphere pressure.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The molecule of carbon dioxide is linear with C — O bond distances of 115pm.

Green House Effect:

Normally 47 % of infrared and visible energy from sun reaches earth. Infrared radiations have the warming effect which are responsible for maintaining temperature on earth's surface. If this radiation is lost the temperature on earth would be decrease to – 20° to – 40°C.

Due to anthroprogenic activities, vehicles exhaust and industrial activities, there is a regular increase of CO_2 in the atmosphere which is approximately 0.7 ppm increase every year. Increase in CO_2 around earth would cause increase in temperature because infrared radiations reflecting back are liable to be stopped by CO_2 blanket which is thickening every year. This global warming is referred to as Greenhouse Effect.

At higher altitudes CO_2 undergoes photochemical decomposition which causes less warming effect there.

$$CO_2 + h\upsilon \xrightarrow{uv} CO + O$$

Carbides:

Binary compounds of carbon with metals and also certain non-metals (*e.g.*, silicon and boron) are called *carbides*. The carbides can be divided into four main groups (a) salt-like carbides, (b) interstitial carbides, (c) iron-type carbides, and (d) covalent carbides.

(a) Salt-like Carbides

Typical examples of such carbides are Be_2C and Al_4C_3. They can be prepared by the direct combination of boron or aluminium with carbon at high temperature

$$2Be + C \xrightarrow{1000^\circ C} Be_2C$$

$$4Al + 3C \xrightarrow{2000^\circ C} Al_4C_3$$

Reduction of metal oxides by carbon or CO may also be utilised for their preparation.

These carbides are easily hydrolysed and liberate hydrocarbons. They are rather classified in accordance with the aliphatic hydrocarbons they give.

The **acetylides** are those salt-like carbides which liberate acetylene on hydrolysis. Thus CaC_2, CrC_2, MgC_2 belong to this group of carbides.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

The **methanides**, such as Al_4C_3 and Be_2C, liberate methane on hydrolysis. They are harder than acetylides.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

Magnesium carbide, Mg_2C_3 liberates allylene on hydrolysis and is formed by heating MgC_2.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3 - C = CH$$

(b) Interstitial Carbides

They are usually carbides of transition metals only and are formed by the direct combination of metals and carbon or by the reduction of the oxide with carbon at 2000°C. Carbon is present in the interstices of the metal lattices.

They are very hard and refractory, good conductors of electricity, brittle, high melting and chemically inert carbides. They are used as hard facings for tools and dies.

(c) Iron-type Carbides

Iron, chromium and manganese form carbides with properties intermediate between those of salt-like and interstitial carbides. These metals have atomic radii less than 130 pm, iron (116 pm), chromium (117 pm) and manganese (117 pm). They liberate a mixture of hydrogen and hydrocarbons on hydrolysis.

(d) Covalent Carbides

Most of these are gases or volatile liquids. Most of them are thermally stable but some of these carbides (silicon and boron carbides) are stable, hard and chemically inert solids. Silicon and boron carbides are made by reducing their oxides with carbon in an electric furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Silicon and boron carbides are employed as abrasive and are useful as refractory materials.

SILICON

Silicon is the next member of this group and shows 4 covalency like carbon.

Occurrence

Silicon constitutes about 25 per cent of the earth's crust and is next to oxygen in order of abundance. Silicon is always found in nature as SiO_2 owing to its strong tendency to combine with oxygen. It is commonly found as silicates which are chief constituents of rocks and clay, the most abundant among them are aluminium containing silicate minerals.

Preparation

Silicon can be prepared in the laboratory by heating a mixture of finely divided silica and magnesium.

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

On industrial scale, silicon is usually formed by heating a mixture of coke and silica in electric furnace.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Characteristics

Silicon is a dark brown, hard substance and can easily scratch glass. The following properties are commonly shown by silicon:

(i) Reaction with Air or Oxygen

Silicon burns in oxygen on heating to form SiO_2.

$$Si + O_2 \longrightarrow SiO_2$$

(ii) Reaction with SiO_2

Si reacts with SiO_2 at high temperature to form silicon monoxide.

$$Si + SiO_2 \longrightarrow 2SiO$$

(iii) Reaction with Alkalies

Silicon gets dissolved in alkalies liberating hydrogen.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

(iv) Combination with Magnesium

It reacts with magnesium in electric furnace to form magnesium silicide which is useful compound to prepare silicon hydrides

$$Si + 2Mg \xrightarrow{\Delta} Mg_2Si$$

(v) Combination with Carbon

Silicon and carbon mixture is heated in electric furnace, silicon carbide is formed

$$Si + C \longrightarrow SiC$$

(vi) Reaction with Water

Silicon does not react with water at ordinary temperatures but reacts with steam to give oxide.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

(vii) Reaction with Halogens

Silicon reacts only with fluorine directly. Chlorine, bromine and iodine do not directly react with it.

$$Si + 2F_2 \longrightarrow SiF_4$$

Uses

Silicon is used in the preparation of hard type of alloys, called silicon-bronze. When a mixture of iron oxide, silica and carbon is heated in electric furnace a useful alloy of iron and silicon is formed called ferro-silicon.

PRODUCTION OF PURE SILICON FOR SOLAR ENERGY CELLS AND SILICON CHIPS

Elemental silicon is produced commercially by the high temperature reduction of silica (silicon dioxide) obtained from sand with coke. Reduction process is carried out in an electric arc furnace by heating mixture of silica, rock and coke. An excess of silica prevents the formation of silicon carbide.

$$SiO_2(\text{excess}) + 2C \xrightarrow{\Delta} Si + 2CO$$

Elemental silicon is used as a source of silicon in silicon polymers. Reduction of a mixture of silicon and iron oxides with coke produces ferrosilicon alloy which is used in the production of acid resistant steel. Aluminium alloys are strengthened for use in aircraft with silicon.

Pure silicon used in transistors and solar energy cells is best prepared by reducing silicon tetrahalides in vapour phase with an active metal such as sodium or magnesium. The tetrahalide is first obtained in pure state by distilling silicon tetrahalide (say tetrachloride) to remove impurities of boron, aluminium and arsenic halides.

$$SiCl_4 + 4Na \longrightarrow 4NaCl + Si$$

Sodium chloride is dissolved in water leaving behind pure silicon which is melted and cast into bars. In order to purify further with less than one part per billion impurity, silicon is purified by zone refining. In this method an induction heater surrounds a bar of the impure solid and passes slowly from one end to another. On repeated passing through the zone, silicon bar of high purity is obtained leaving behind impurities in the zone.

Silicon has become an important semi-conductor in the preparation of micro-electronic devices commonly known as 'microchips'. A single minute chip in a pocket calculator might contain over 30,000 transistors connected in a single integrated circuit.

HALIDES OF SILICON

Silicon forms tetrahalides of general formula SiX_4. Some mixed halides of the type $SiCl_2F_2$ are also known. Halides Si_2X_6, Si_3Br_8 and Si_6Cl_{14}, have also been detected. However, the tetrahalides would be discussed over here.

Tetrahalides of Silicon, SiX_4

Silicon tetrafluoride can be obtained by reactions such as:

$$Si + 2F_2 \xrightarrow{\Delta} SiF_4$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

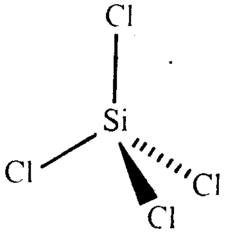
$$CaSiO_3 + 6HF \longrightarrow CaF_2 + SiF_4 + 3H_2O$$

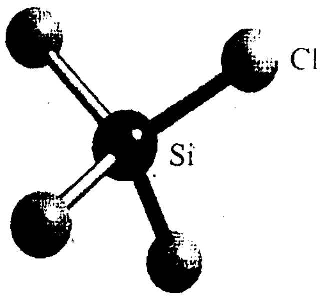
Silicon tetrachloride is obtained either from Si or SiO_2 with chlorine.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

SiF_4 is a gas but $SiCl_4$ is colourless liquid (b.p. 59°C). Other halides of silicon are similar to silicon tetrachloride.





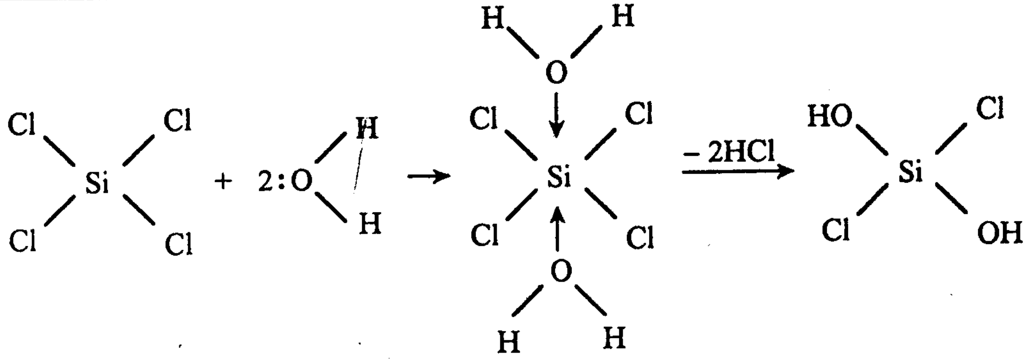
Silicon (IV) chloride

The halides can be easily hydrolysed to give silicic acid.

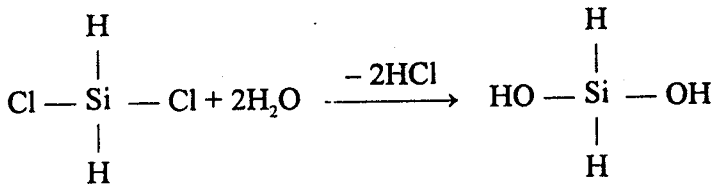
$$3SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2SiF_6$$

$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$$

The hydrolysis of silicon halides is very important and is a key step in the preparation of silicone polymers. The alkyl and aryl derivatives of silicon halides produce silicones. The hydrolysis of silicon halides or their alkyl or aryl substituted derivatives proceed as follows:

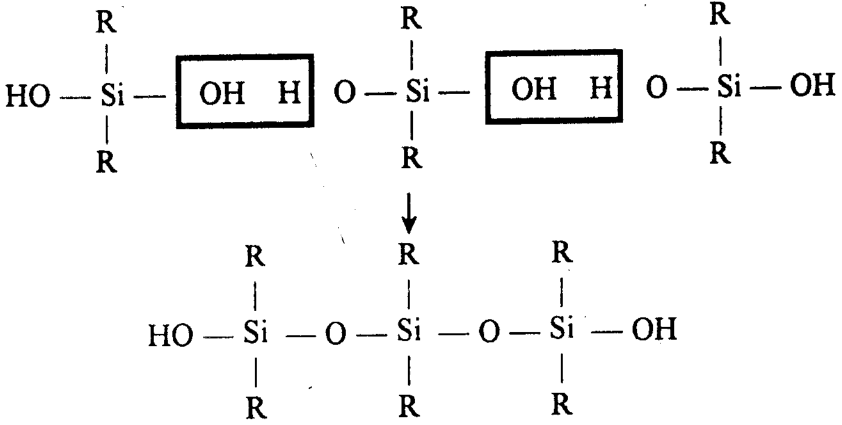


If the starting material is R_2SiCl_2, the product of hydrolysis is $R_2Si(OH)_2$ which polymerises to form silicone structure.



$$\mathrm{Cl-\overset{H}{\underset{H}{Si}}-Cl+2H_2O\xrightarrow{-2HCl}HO-\overset{H}{\underset{H}{Si}}-OH}$$

The polymerisation process occurs due to the removal of water molecules from adjacent positions.



$$\mathrm{HO-\overset{R}{\underset{R}{Si}}-\boxed{OH\quad H}\,O-\overset{R}{\underset{R}{Si}}-\boxed{OH\quad H}\,O-\overset{R}{\underset{R}{Si}}-OH}$$

$$\downarrow$$

$$\mathrm{HO-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH}$$

The process continues and polymer structure is obtained. The number and position of alkyl groups determine the polymer type and extent of polymerisation.

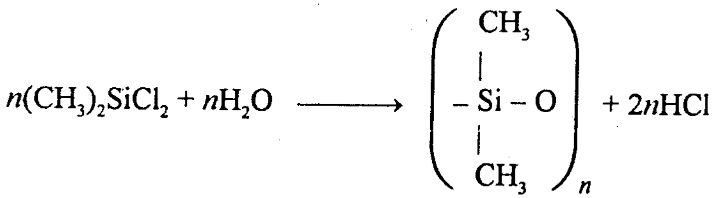
SILICONES

These are important class of silicon compounds. They are polymeric substances with Si – O – Si linkages. These are obtained from silicon dioxide, SiO_2. Silicon dioxide is first reduced to silicon using carbon as a reducing agent. Silicon is then treated with chloromethane in presence of copper catalyst to get dichlorodimethylsilane.

$$SiO_2 + 2C \xrightarrow{3000^{\circ}C} Si + 2CO$$

$$Si + 2CH_3Cl \xrightarrow[\text{Cu Catalyst}]{300^\circ C} (CH_3)_2\,SiCl_2$$

The dichlorodimethylsilane thus obtained polymerizes on treating with water.



$$n(CH_3)_2SiCl_2 + nH_2O \longrightarrow \left(\begin{array}{c} CH_3 \\ | \\ -\,Si - O \\ | \\ CH_3 \end{array} \right)_n + 2nHCl$$

The silicone polymer contains siloxane chain (– Si – O – Si – O – Si –) with two alkyl (or other organic) groups on each silicon atom. This strong backbone of silicone polymer makes it stable to heat and is stable to decomposition. Silicone polymers of different molecular weights can be obtained which give different physical properties to them. Silicone oils are good lubricants and heat transfer fluids. Silicone rubbers are not attacked by ozone and remain flexible at low temperatures. Silicones are also used as lubricants water proof films and refrigerator gaskits.

Silicones have remarkable heat resistance and high electrical insulating properties. So they are used as heat resistant varnishes, and insulating liquids in electrical transformers. Silicones are highly water-repelling and may be used to impregnate cotton or concrete masonry, which prevent water to enter the pores. Silicones are powerful anti-foam agents.

Silicone oils, silicone rubbers and silicone polymers are extensively used in industry where (i) high temperature conditions are to be maintained, (ii) electrical insulation is required, (iii) water repellant properties are to be maintained.

Silicon Dioxide, SiO_2

Silica occurs in nature as sand and quartz. There are three well-defined forms of silica:

$$\alpha\text{-quartz} \xrightleftharpoons{573^\circ} \beta\text{-quartz} \xrightleftharpoons{870^\circ} \text{tridymite} \xrightleftharpoons{1500^\circ} \text{crystobalite}$$

All varieties begin to soften above 1600°C and melt at 1710°C to give a viscous liquid. On cooling, this liquid does not crystallise but forms a glass.

Many varieties of quartz possess beautiful colours, due to the presence of small amounts of impurities, and are used as gems.

Sandstone possesses sand grains cemented together with iron oxide. *Flints* are a mixture of quartz and amorphous silica.

Keiselguler is a siliceous earth left by the remains of minute sea and other organisms. It is used as adsorbent for nitroglycerine, as wood filler etc.

Silica is also found in plants and animals. The stems and coating of straw, bamboo and similar plants contain considerable amounts of silica. Similarly, claws of animals, nails and the quills of feathers also contain silica.

Properties

Silica is a hard, refractory brittle, rough and colourless solid. Molten silica solidifies to glass and is used in the preparation of glassware.

Silica is quite unreactive. Thus it does not react with Cl_2, Br_2, H_2 and most acids as well as metals. But it is attacked by fluorine, HF and alkalies.

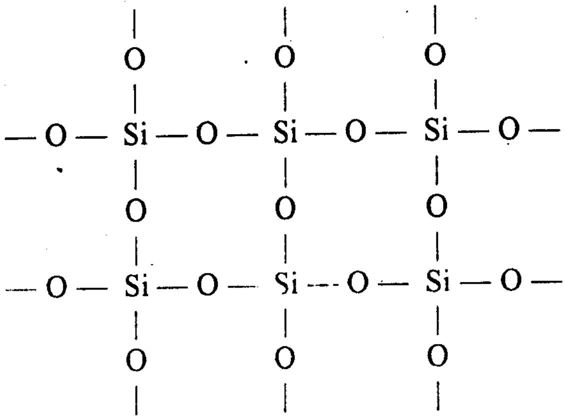
$$SiO_2 + 4HF \longrightarrow SiF_4 + 4H_2O$$

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2$$

Structure

The difference in physical properties of SiO_3 and CO_2 is due to the fact that the former consists of polymer structure $(SiO_2)_x$, whereas CO_2 exists in monomeric state. The structure of $(SiO_2)_x$ can be represented as:



Each silicon atom is in the centre of a tetrahedron with oxygen atoms lying on the corners. Each of the oxygen atoms is in its turn connected to two atoms of silicon. The hardness of quartz is due to the strong bonds between silicon and oxygen. Many crystal modifications of $(SiO_2)_x$ exist but the most well-known is quartz. In each case the structure consists of a regular three dimensional arrangement of SiO_4 tetrahedral units, joined at the corners as shown in Figure 13.6.

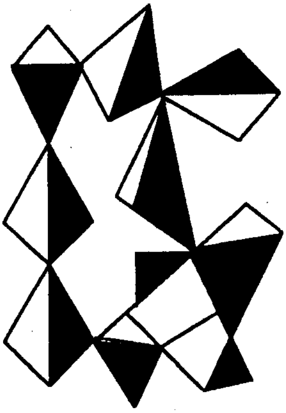


Fig. 13.6. Three dimensional crystal arrangement for silica containing SiO_4 tetrahedra.

Uses

(i) It is used in the preparation of transparent varieties of glass used in the manufacture of spectacle lenses, and optical instruments.

(ii) The quartz glass used in delicate parts of electrical instruments can be prepared from silica.

(iii) Silica is used in the manufacture of ordinary glass, porcelain, sand-paper, cement, concrete and mortar.

(iv) Silica bricks are used as refractory materials in the furnace used to withstand high temperatures.

Sodium Silicate (Water glass)

It is prepared by fusing sand with sodium carbonate.

$$Na_2CO_3 + SiO_2 \xrightarrow{1200^\circ C} \underset{\text{(Sodium silicate)}}{Na_2SiO_3} + CO_2$$

The product is used to prepare soft glass or soda glass which is a mixture of sodium silicate, calcium silicate and free silica. Soft glass or soda glass is manufactured by mixing soda ash, limestone and sand. It involves the above reaction along with the following:

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

Water glass is soluble in water and solution has alkaline nature due to hydrolysis.

$$Na_2SiO_3 + 3H_2O \longrightarrow 2NaOH + H_4SiO_4$$

SILICATES

The salts of silicic acid are called *silicates*. The soluble silicates, *e.g.*, sodium and potassium silicates, are known as *soluble glass*. The aqueous solutions of soluble glass are known as *water glass*.

A large number of salts of H_2SiO_3 ($SiO_2.H_2O$), H_4SiO_4 ($SiO_2 . 2H_2O$) etc. are known. The composition of silicic acids may be expressed by the general formula $m\text{SiO}_2 . n\text{H}_2\text{O}$. Acids in which $m > 1$ (more than one) are called **poly-silicic acids.** Basically, three acids are found to exits, namely: ***Orthosilicic acid***, H_4SiO_4; ***metasilicic acid***, H_2SiO_3 or $(H_2SiO_3)_n$ and ***dimetasilicic acid***, $(H_2Si_2O_5)_x$. The salts of these acids are well-known.

Orthosilicic acid precipitates in the form of jelly and if most of the water is removed from it, a solid white mass is left with tiny pores of high adsorption power. This product is known as **silica gel**.

NATURAL SILICATES

The silicate minerals occurring in nature having varied chemical compositions and structures are called *natural silicates*. The silicate minerals containing aluminium are called alumino silicates and their important types are **feldspars**. Some of the alumino silicates have ability to split into thin flexible flakes or sheets and are called **micas**.

The formulas of some of the important natural silicates are:

Silicates	**Composition**		**Formula**
Kaolin	$Al_2O_3 . 2SiO_2 . 2H_2O$	or	$H_4Al_2Si_2O_9$
Mica	$K_2O . 3Al_2O_3 . 6SiO_2 . 2H_2O_2$	or	$H_4K_2Al_6Si_6O_{24}$
Asbestos	$CaO . 3MgO . 4SiO_2$	or	$CaMg_3Si_4O_{12}$

Silicate Structures

A systematic study of the silicate structures has been made and it is found that the basic unit in all types of silicates is SiO_4 tetrahedron. The SiO_4 tetrahedra are joined together in different manners to give different silicate structures.

The SiO_4 unit consists of **one** Si atom at the centre with **Four** oxygen atoms arranged in a tetrahedral manner around it (Figure 13.7).

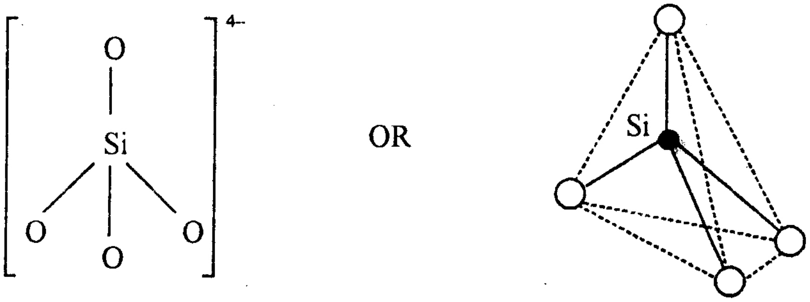


Fig. 13.7. $(SiO_4)^{4-}$ structure.

Let us now discuss the structures of various types of silicates.

1. Orthosilicates

Some of the silicates have crystal structures in which SiO_4^{4-} tetrahedra are independent groups. The SiO_4^{4-} anions are arranged in such a way that interstices (holes) created by them are occupied by cations. Thus, olivine, Mg_2SiO_4, zircon, $ZrSiO_4$ and phenacite, Be_2SiO_4 have individual tetrahedra joined together by Mg^{2+}, Zr^{4+} and Be^{2+} cations, respectively. The structure of the basic unit SiO_4^{4-} is diagrametically indicated in such a way that hollow circles (○) represent the positions of oxygen atoms and dots (◉) indicate the central silicon atoms as shown in Figure 13.8.

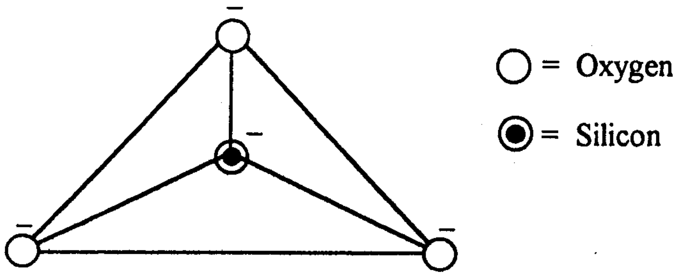


Fig. 13.8. Representation of $(SiO_4)^{4-}$.

2. Pyrosilicates

Two SiO_4^{4-} units may share one corner (or oxygen) to form $Si_2O_7^{6-}$ group, called pyrosilicate or disilicate.

This ion occurs in thortveitite, $Sc_2Si_2O_7$ and hemimorphite, $Zn_4(OH)_2\ Si_2O_7$. It may be noted that Si — O — Si angle in pyrosilicates varies between 131° to 180°. The sharing of an oxygen atom between two SiO_4 tetrahedra to form pyrosilicate or disilicate $[O_3Si — O — SiO_3]^{6-}$ is shown in figure 13.9.

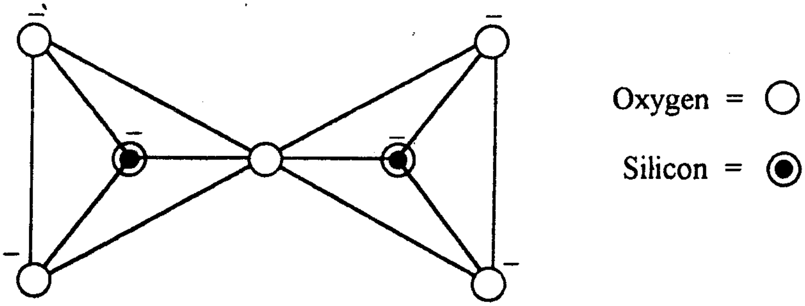


Fig. 13.9. $(Si_2O_7)^{6-}$ ion.

3. Cyclic Silicate Anions

Three or six SiO_4 tetrahedra may join corners and form closed rings or cyclic structures. Only two such cyclic silicate anions have been noticed, $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$. (Each oxygen carries – 2 charge and each silicon + 4 charge). The structures of these silicate anions are shown in Figure 13.10.

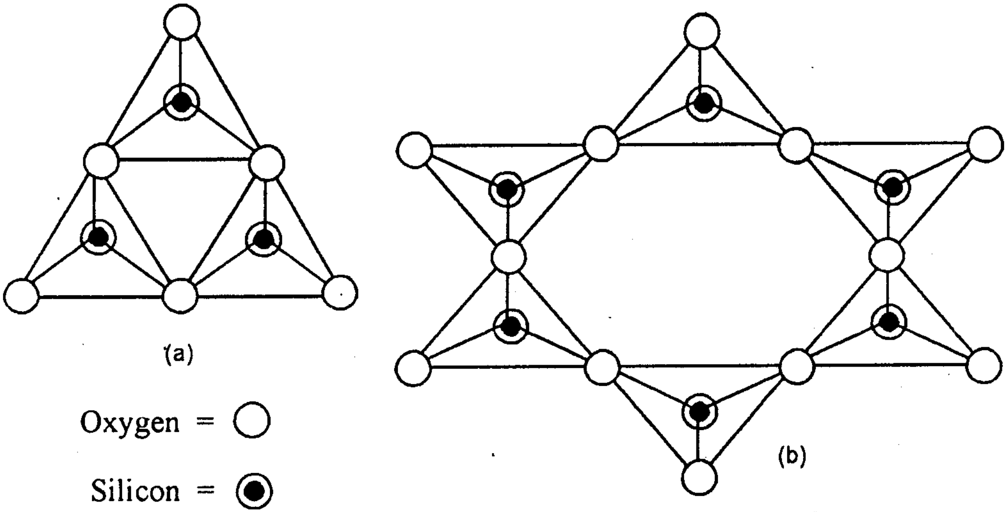
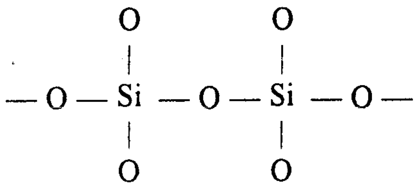


Fig. 13.10. (a) $Si_3O_9^{6-}$ anion, (b) $Si_6O_{18}^{12-}$ anion.

The general formula for such cyclic silicate anions is $Si_nO_{3n}^{2n-}$. The anion $Si_3O_9^{6-}$ occurs in **benitoite, $BaTiSi_3O_9$**. The well-known silicate, **beryl, $Be_3Al_2Si_6O_{18}$** consists of $Si_6O_{18}^{12-}$ anions. It contains a ring of six tetrahedra, Figure 13.10 (b).

4. Metasilicates (containing infinite chain anions)

The anions $(SiO_3^{2-})_n$ and $(Si_4O_{11}^{6-})_n$ represent the metasilicates. *Pyroxenes* contain $(SiO_3^{2-})_n$ anions and have single-strand chains (Fig. 13.11).



$$\begin{array}{ccccc} & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \\ -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- \\ & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \end{array}$$

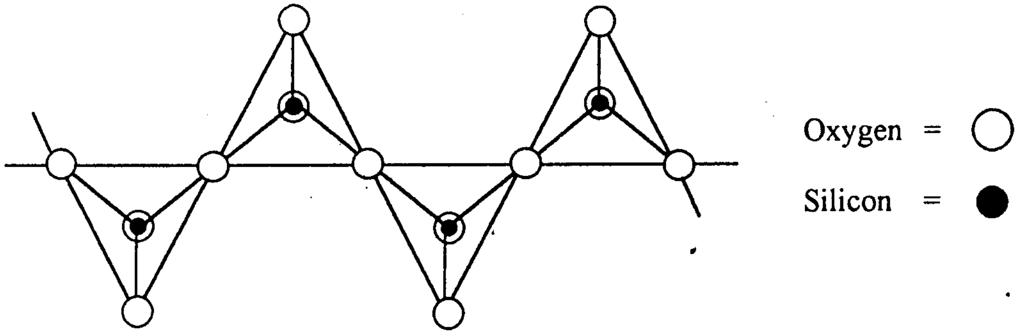


Fig. 13.11. $(SiO_3^{2-})_n$ anion structure.

Examples of pyroxenes are:

Enstatite	$MgSiO_3$

Diopside	$CaMg(SiO_3)_2$
Spodumene	$LiAl(SiO_3)_2$

$(Si_4O_{11}^{6-})_n$ anions have double Si — O chains with cross linking. The anionic units consist of four silicon atoms and nine oxygen atoms present within the unit with other oxygen atoms sharing the neighbouring units as shown in Figure 13.12.

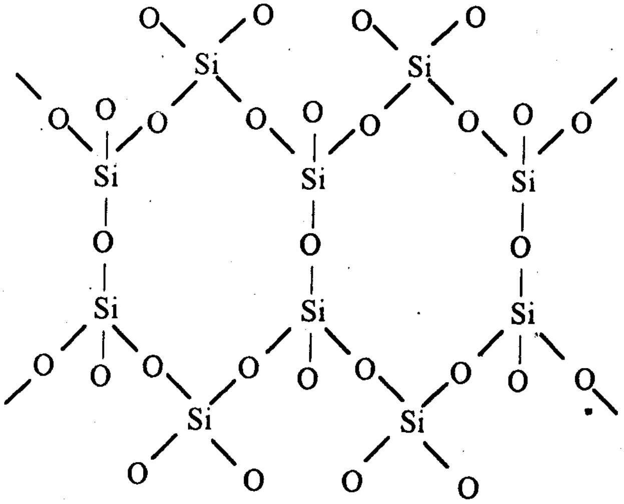


Fig. 13.12 (a).

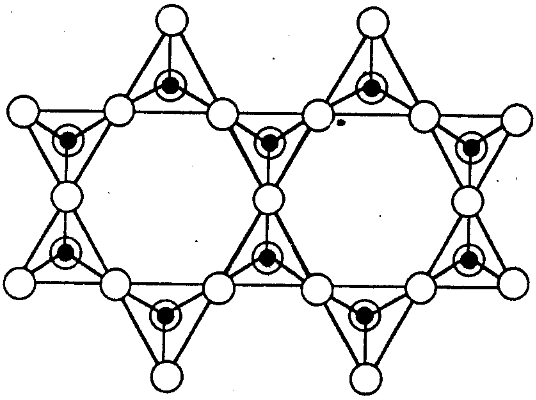


Fig. 13.12 (b). $(Si_4O_{11}^{6-})_n$ chains.

$(Si_4O_{11}^{6-})_n$ anions are found in silicates called **amphiboles**. A typical amphibole mineral is fibrous **tremolite**, $Ca_2Mg_5(Si_4O_{11})_2\,(OH)_2$. Asbestos belongs to amphibole silicates. Because of the strength of $(Si_4O_{11}^{6-})_n$ chains and presence of weak forces between layers, these silicate minerals cleave parallel to the chains.

5. Infinite Sheet Structures

These structures contain $(Si_2O_5^{2-})_n$ anions in which SiO_4 tetrahedra are linked into infinite two dimensional network (Figure 13.13). These sheet structures are held together by metal ions which lie between them. Therefore, they cleave readily into thin sheets.

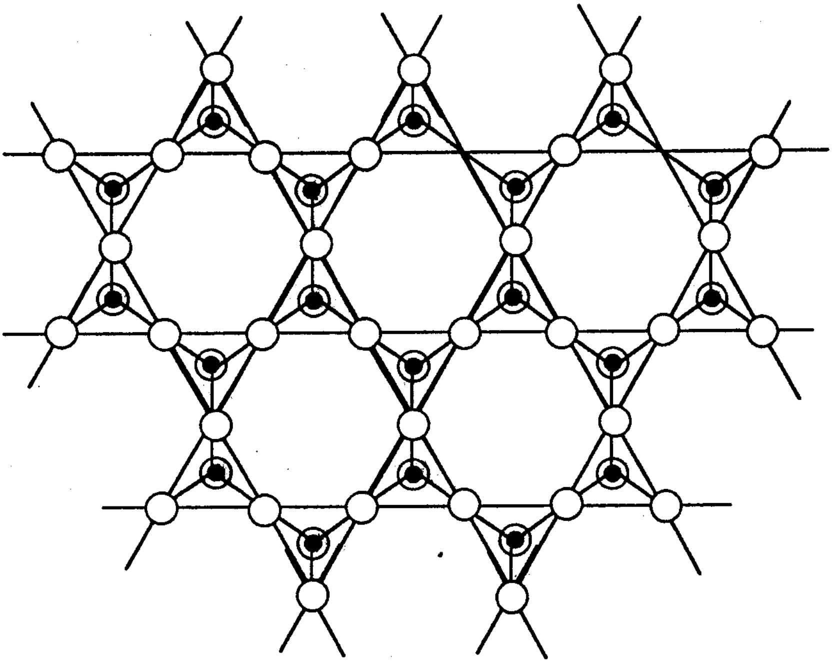


Fig. 13.13 (a).

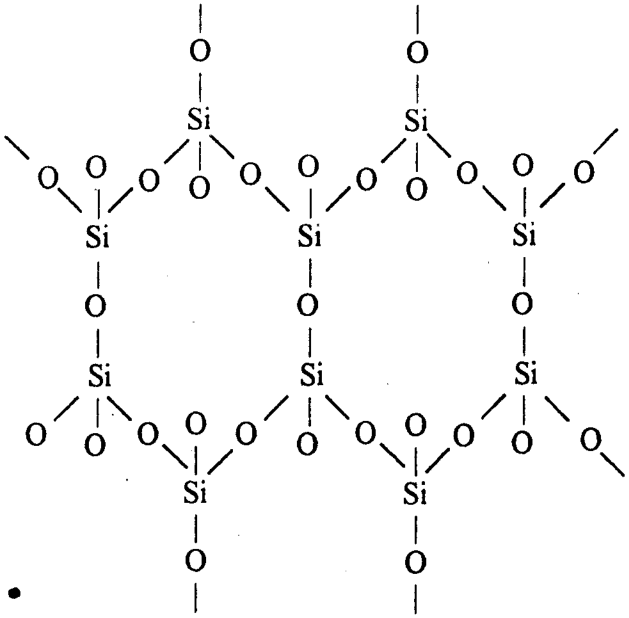
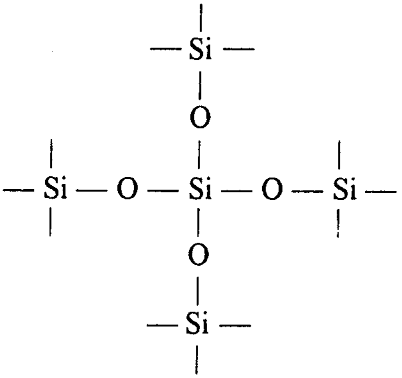


Fig. 13.13 (b). Arrangement of $(Si_2O_5^{2-})_n$ Silicate anions.

There is no simple silicate based upon $(Si_2O_5^{2-})_n$ anion structure. However, it is part of the complex silicate structures of **kaolin**, **talc** and **micas**.

6. Silicates with Three-Dimensional Network

A three-dimensional network of SiO_4 tetrahedra results in the formation of $(SiO_2)_n$ in which a neutral basic unit (SiO_2) is formed. This network is, in fact, the structure of silica (Figure 13.14).



$$\begin{array}{ccccccccc} & & & & | & & & & \\ & & & — & Si & — & & & \\ & & & & | & & & & \\ & & & & O & & & & \\ & | & & & | & & & | & \\ — & Si & — O — & & Si & & — O — & Si & — \\ & | & & & | & & & | & \\ & & & & O & & & & \\ & & & & | & & & & \\ & & & — & Si & — & & & \\ & & & & | & & & & \end{array}$$

Fig. 13.14. $(SiO_2)_n$ Framework.

If one silicon atom is replaced by one aluminium, one negative charge shall be created over the molecule. This is because Si^{4+} carries 4+ve charges which balances the four –ve charges provided by 2 O and replacement of Si^{4+} by Al^{3+} would provide +3 positive charge, one less than required to neutralize – 4 charge on 2 O. But Al^{3+} replaces Si^{4+} due to almost same ionic size.

$$(Si^{+4}O_2^{-4}) \quad (Al^{+3}O_2^{-4})$$

Aluminosilicate structures always carry negative charge which is counterbalanced by some cation. Thus, zeolites contain Na^+ or K^+ ions which counterbalance the charge on aluminosilicate anions. Na^+ or K^+ ions can be replaced by Ca^{2+} without changing the basic structure of silicates. **Zeolite,** therefore, acts as a base exchanger and is used in water purification where Ca^{2+} and Mg^{2+} cations are removed by zeolite through exchange reactions.

Zeolites are used as ion-exchange materials and have been widely used for such purpose. They are also largely employed as adsorbents for gases and liquids (molecular sieves). Zeolites can act as catalysts or catalyst-support materials for a variety of heterogeneous reactions. The zeolites used for such purpose are usually synthetic.

INDUSTRIAL APPLICATIONS OF SILICATES

Clays, silica gel, glass etc., are examples of silicate structures. Clays are called earthenware, porcelain or china, according to the composition and properties. Clays are used for making cement, ceramics, bricks, flowerpots and for decolorising oils.

Thin Layer Chromatography

In thin layer chromatography, finely divided adsorbent is supported on a glass plate. A thin layer of adsorbent is prepared by spreading an aqueous slurry of the finely ground adsorbent over the surface of a glass plate or microscope slide. The plate is then allowed to dry or may be heated in oven.

Thin layer chromatography was first used by Izmailex and Shraiber. The technique was further developed by many other workers such as Kircher, Miller, Stahl etc.

The following basic operations are involved in TLC:

(1) Formation of thin layers on plates.
(2) Application of samples on thin layer plates.
(3) Choice of solvent.
(4) Developing reagent.

(1) Formation of Thin Layer on Plates

Thin layers can be formed by spreading, pouring, spraying or dipping the plate in slurry of adsorbents.

The samples are applied to the plates with the help of capillaries, micropipettes or micro syringes. The common adsorbents used are silica, alumina or aluminium oxide, kieselgular or diatomaceous earth, cellulose etc. Polar and non-polar organic solvents may be used in TLC. A typical solvent mixture is n-hexane-diethylether-acetic acid in the ratio of 9.0 : 10 : 1. The most common solvents used in TLC are petroleum ether, CCl_4, C_6H_6, $CHCl_3$, $C_2H_5OC_2H_5$, CH_3COCH_3, C_2H_5OH, CH_3OH, H_2O.

Advantages of TLC

(1) TLC is a simple method of separation for solid-solid and liquid-liquid systems.
(2) TLC can be performed on analytical and preparative scale.
(3) It is a rapid technique and can be used in laboratory and on industrial scale for checking the path of reaction.
(4) TLC can be used to check adulteration in food.
(5) Trace elements in narcotics, air pollutants, pesticides, dry metabolites can be detected with high sensitivity.
(6) TLC is of great help in determining chromatographic patterns of tissue extracts.
(7) TLC can be used in the separation of serum proteins.
(8) The technique can be used to study biological changes, urine and blood analysis.

TLC is a low cost, simple, speedy and sensitive technique. The only limitation of this technique is its use at small scale.

GLASS INDUSTRY

DEFINITION

Glass may be defined physically as a rigid super cooled inorganic liquid having no definite melting point and a sufficiently high viscosity to prevent crystallisation. Chemically it is a mixture of alkali and alkaline earth silicates containing silicates and borates of other metals also, having random structure.

Composition. Glass is not only one single compound. It is a highly complex mixture which cannot be assigned any particular chemical formula. The approximate formula may be given as:

$$x\, R_2O.\, y\, MO.\, 6SiO_2$$

where R is atom of an alkali metal; M is atom of a bivalent metal and x and y are the number of molecules.

Raw Materials

90% of the glass is made from sand, soda ash and lime.

(i) **Sand:** The sand used in the manufacture of glass should be almost pure quartz. Iron content beyond 0.045% makes the sand unfit for tableware glass. It imparts to the glass an objectionable green or brown colour.

(ii) **Soda Ash:** Soda in the form of carbonate, salt cake, Na_2SO_4 or nitrate may be used for this purpose. Nitrate is useful in oxidising the iron and accelerating melting points and are more resistant to chemical reagents.

(iii) **Lime:** Calcium oxide or limestone, may be used as an essential ingredient of the commercial soft window glass.

(iv) **Feldspar** or other alumino compounds serve to lower the melting point of glass and retard divitrification.

(v) **Borax:** It is used as a major ingredient for making window or plate glass. Borax glass has lower dispersion value and higher refractive index and hence it is used as optical glass.

(vi) **Arseneous Oxide:** It may be added to facilitate removal of bubbles.

(vii) **Cullet:** It consists of broken pieces of glass and facilitates melting. Thus waste glass may be utilized, which helps in making the glass cheaper. The quantity of cullet added varies from 10 – 50% of the total charge depending on its availability.

Manufacture of Glass

A mixture of sodium carbonate, calcium carbonate and quartz or sand in calculated quantities (as determined by the formula Na_2O . CaO. $6SiO_2$) after being finely powdered in grinding machines and intimately mixed is fused in a tank furnace heated by a producer gas as shown in Figure 13.15.

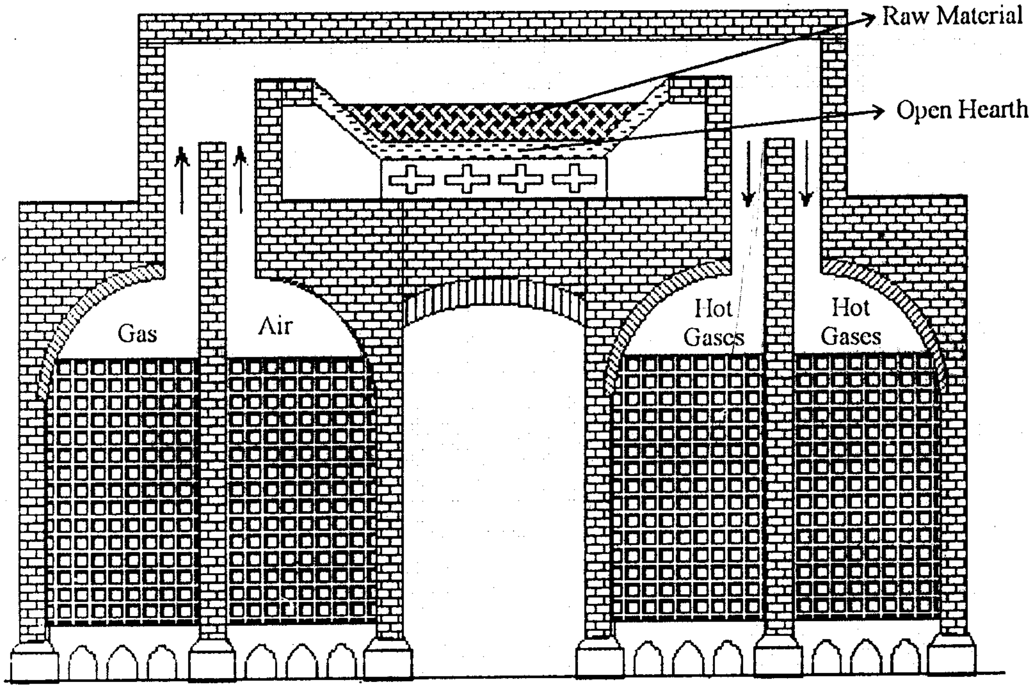


Fig. 13.15. ***Manufacture of Glass.***

It works on the regenerative system of heat economy. The silica and sodium carbonate react with the evolution of carbon dioxide.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2\uparrow$$

The following materials are employed in the manufacture of different varieties of glass:

Soda glass:	Chalk, sodium carbonate and clean sand.
Bohemian glass:	Chalk, potassium carbonate and sand.
Flint glass:	Pb_3O_4 or PbO, potassium carbonate and sand.
Bottle glass:	Chalk, sodium sulphate, coke and ordinary sand.

Heating is continued until the evolution of carbon dioxide ceases. By then, the mass would have melted down to a clear liquid. It is allowed to cool down to a definite temperature so that it attains the required degree of plasticity to work and then used to prepare different articles. It is given the desired shape by blowing, by casting in moulds or by pressing between rollers as the case may be.

Cullet or pieces of broken glass are invariably added to the raw material to increase the fusibility of the glass produced. It is almost impossible to obtain the raw materials free from iron compounds. Ferrous oxide imparts green colour to glass, while ferric oxide imparts a light yellow tinge. In order to obtain colourless glass, oxidizing agents like manganese dioxide or potassium nitrate in the case of ordinary glass, and red lead in the case of flint glass are added as decolouriser.

Annealing of Glass

Articles made of glass are always allowed to cool gradually before being put into the market. The process of slow and homogeneous cooling is known as annealing. If allowed to cool quickly, the superficial layer cools down first, leaving the inner portion in a state of strain. Consequently, such articles develop a crack or break to pages under very slight disturbances.

Process of Colouration

Coloured glass is prepared by adding metallic oxides, finely divided metals, salts of metals and non-metals such as carbon, sulphur etc., to fuse glass during its manufacture. Variations in colour are produced by different substances and different shades are obtained by adding varying quantities of the same substance. The colours obtained on adding various chemical compounds are represented in Table 13.5.

TABLE 13.5

Colouring of Glass

Compounds Added	Colours Obtained
CoO and CuO	Blue
Cr_2O_3 and Fe_3O_4	Green
MnO_2	Violet
Cu_2O, and metallic gold, Se	Ruby
SnO_2, $Ca_3(PO_4)_2$ and CaF_2	Milk or Opaque white
Sb_2S_3	Yellow or Brown
Uranium oxide	Fluorescent
Se or Te compounds	Pink
Large excess of MnO_2, Fe_2O_3, CuO, CoO or Cr_2O_3	Black

Finishing Operations

These operations are cleaning, grinding, polishing, cutting, enamelling and grading etc.

Varieties of Glass

The different types of glass usually met with may be classified as follows:

1. Fused Silicates or Vitreous Silica

It is made by high temperature pyrolysis of $SiCl_4$. It is thermally and chemically resistant.

2. Alkali Silicates or Water Glass or Soluble Glass

It is a thick syrupy liquid used as adhesive in paper manufacture, fire proofing and egg preservation.

3. Soda Lime Glass, Soda Glass or Soft Glass

It is a mixture of sodium and calcium silicates having the approximate formula Na_2O. CaO. $6SiO_2$. It is readily fusible and hence known as soft glass. Articles made of soft glass may be blown and welded with a simple source of heat. It is usually obtained in a colourless state and is comparatively cheaper. Soda glass is used in the preparation of laboratory apparatus, tubes, plates etc.

4. Potash Lime Glass

It is also known as **Hard glass** or **Bohemian glass.** It consists chiefly of a mixture of potassium and calcium silicates having the composition K_2O. CaO. $6SiO_2$. It melts with difficulty and is very hard, hence the name Hard Glass. It is hardly acted upon by water and other solvents and fuses at very high temperature. It is used extensively in the construction of apparatus which have to stand very high temperatures during use.

5. Flint Glass or Potash Lead Glass

It is composed of a mixture of potassium and lead silicates having the formula K_2O. PbO. $6SiO_2$. It has a high specific gravity, brighter lustre and greater refractive index (1.70–1.78) than any other variety of glass. It fuses very easily and hence can be worked with ease. During heating it is not allowed to come in contact with the reducing gases of the furnace since lead silicate is reduced to metallic lead which would turn the glass black and opaque. Flint glass is used in the manufacture of artificial gems, lenses, prisms, electric bulbs, etc.

6. Bottle Glass or Common Glass

It is a mixture of sodium, calcium and iron silicates Na_2O. CaO. Fe_2O_3. SiO_2. It is obtained from cheap raw materials and is yellow or brown in colour. It is fairly tough, fuses with difficulty and is more readily attacked by acids. It is used in the production of ordinary bottles of different designs.

7. Pyrex Glass or Jena Glass

It is a special brand of high class hard glass consisting of mixtures of borosilicates and alumino silicates of potassium, calcium and lime. It is prepared by fusing calculated amounts of boric anhydride and silica along with carbonates or oxides of the metals concerned. This type of glass possesses low coefficient of expansion which renders it much less liable to crack under sudden temperature changes. It is used for the preparation of scientific apparatus.

8. Quartz glass

In preparing quartz glass, silica is melted in an electric furnace and then made into crucibles, dishes, tubes, etc. It is hardly attacked by chemical reagents and can stand a temperature shock of 1000°C. It can be heated to white heat and plunged into water without breaking.

9. Special Glasses

(a) **Coloured Glasses.** They are made by incorporating coloured inorganic oxides or precipitated colloidal particles as given in Table 13.5.

(b) **Transluscent Glasses.** Clear when molten but opalescent when shaped.

(c) **Safety Glasses**. Laminated two layers of glass with a sticky plastic layer in between or heat tempered.

(d) **Optical Glasses.** For lenses etc., glass contains B_2O_3 in place of some SiO_2. BaO in place of CaO.

(e) **Fibre Glasses.** The fibres may be as fine as 0.0005 inch. It can be spun into yarn gathered into a mat and made into an insulation tape or air filter, etc.

Position of Glass Industry in Pakistan

In Pakistan, many small units approximately more than 25 units with the production of 80,000 tons per year are running. Small articles, table ware, bangles and articles of decoration are being manufactured. One of the defects in Pakistani glass is that it gives greenish tinge because the traces of iron are found in the sand used in making the glass. This defect, however, can be removed by introducing other coloured compounds such as V_2O_5 or shaping them in coloured items. Recently, Toyo-Nasic glass factory has been set up at Sheikhupura near Lahore.

CEMENT INDUSTRY

In 1842, an English man Joseph Aspdin prepared an artificial cement made by the calcination of clay containing limestone. He named it Portland cement because concrete obtained from it had resemblance with the famous building stone obtained from the Islands of Portland near England. Hence the name Portland Cement.

Cement may be defined as the material obtained by burning an intimate mixture of calcarious (lime bearing) and argillaceous (clayey) material at a sufficiently high temperature to produce clinker by incipient fusion and subsequently grinding the resulting clinker to a fine powder.

Average Composition of Cement:

Cement is actually a mixture of so many compounds, each one of these having its own individual properties. Hence variation in composition, the rate of heating, the maximum temperature to which it is heated, along with the fineness of the product, should have an effect on the final properties of the cement. An average composition of the Portland Cement is as follows:

CaO	61.5%
SiO_2	22.5%
Al_2O_3	7.5%
MgO	2%
Fe_2O_3	2%
SO_3	1%
Na_2O	1.5%
K_2O	1.5%

Portland Cement consists of essentially a mixture of various aluminates and silicates of calcium *i.e.*, $3CaO.\ SiO_2$ (tricalcium silicate) and $Ca_2Al_2O_4$ (dicalcium aluminate).

Raw Materials

The raw materials used in the manufacture of cement are

(a) Limestone, marble, chalk, marine shells, etc., which are source of CaO components.

(b) Clay, shale, slate, blast furnace slag which provide the argillaceous fractions *i.e.*, acidic component (aluminates or silicate radicals).

(c) Other raw materials being used are gypsum, water and fuel.

A normal batch for cement manufacture consists of 75% limestone, 20–25% clay and 3–4% gypsum. Furnace oil is used as a fuel in most of the cement kilns in Pakistan.

Manufacture of Cement

The manufacturing process consists of the following steps:

(a) Grinding and mixing of the raw materials.

(b) Burning of the mixture at specified temperature for a correct duration.

(c) Grinding the burnt product called (clinker) along with gypsum.

There are two methods available for the manufacture of cement:

(i) Wet Process (ii) Dry Process

The choice between the wet and dry processes depends on certain factors:

(a) Physical conditions of the raw materials.

(b) The price of the fuel.

(c) The local climatic conditions of the factory

In Pakistan, both Wet and Dry processes are being used for the cement. Dry process although cheaper needs excessive **fine grinding**. It is more suited for the hard material (Fig. 3.16).

Wet process, on the other hand, is free from the dust, grinding is easier and the composition of the cement can easily be controlled.

(1) Wet Process

The specific feature of the wet process is that the raw materials are prepared in water whereas in the dry process the materials are ground and mixed dry.

The flow sheet diagram of the wet process for manufacturing Portland cement is given in the Figure 13.17.

The limestone is disintegrated in crushers. The crushed limestone is fed to tube mill, where the limestone and the clay, introduced as a slurry from a clay mixer, are simultaneously subjected to fine grinding. From the mill, the raw material slurry is fed to a reinforced concrete reservoir, where it is stirred with agitators.

The kilns are heated using coal dust, gaseous fuel or fuel oil. The raw material slurry is fed to the kiln from a horizontal slurry basin and inside moves through it counter-current to the hot, gaseous combustion products. Their interaction results in the successive processes of water evaporation, mineral dehydration, limestone dissociation and chemical reaction between the basic oxides, CaO, and the components of the clay – SiO_2, Al_2O_3, Fe_2O_3.

Within the kiln, the process of making the clinker is accomplished in four Zones, *i.e.*, dehydration calcination, clinkering and cooling (Fig. 13.18).

DRY PROCESS

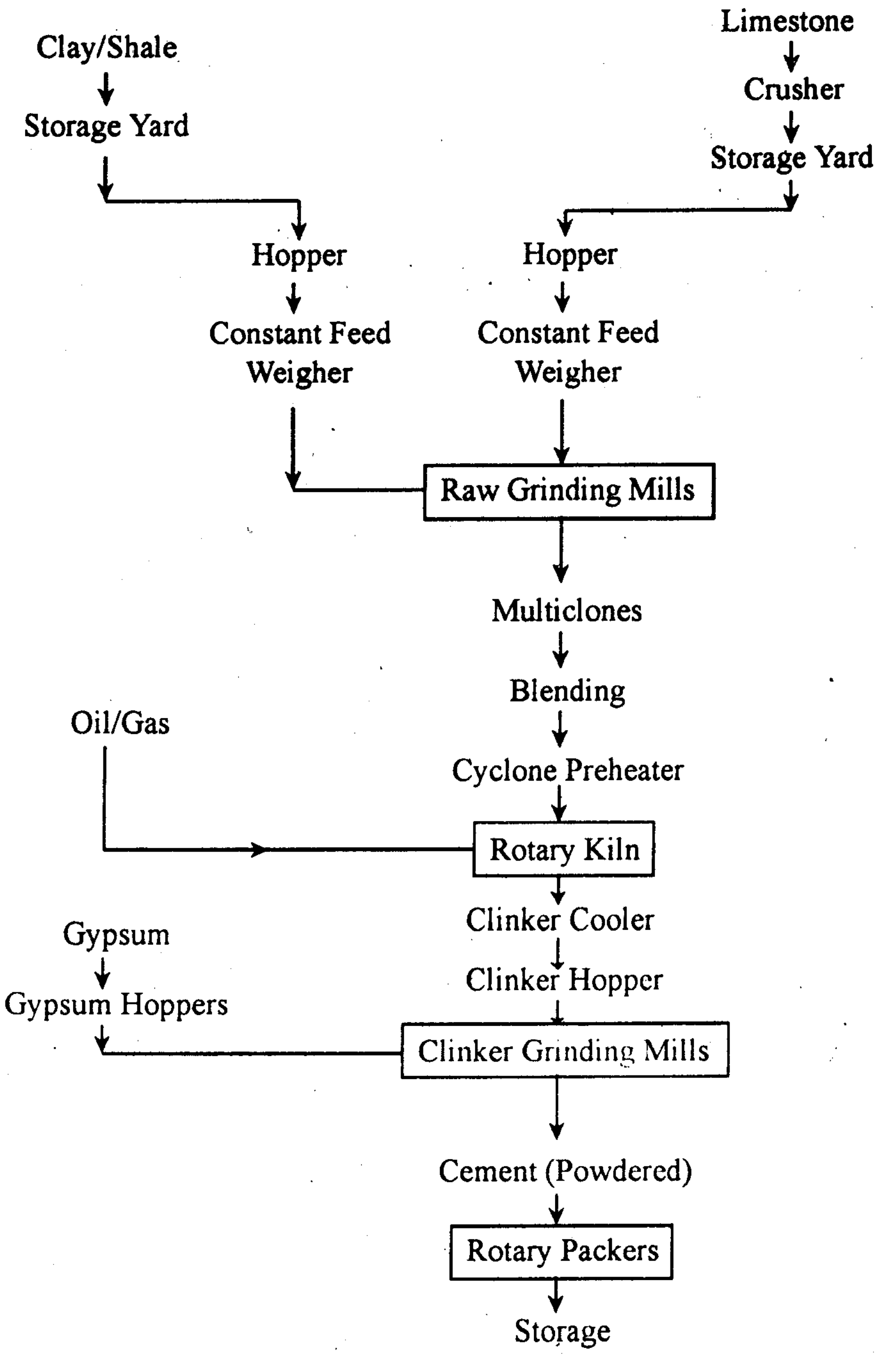


Fig. 13.16. Flow Sheet Diagram of the Dry Process for manufacturing Portland Cement.

WET PROCESS

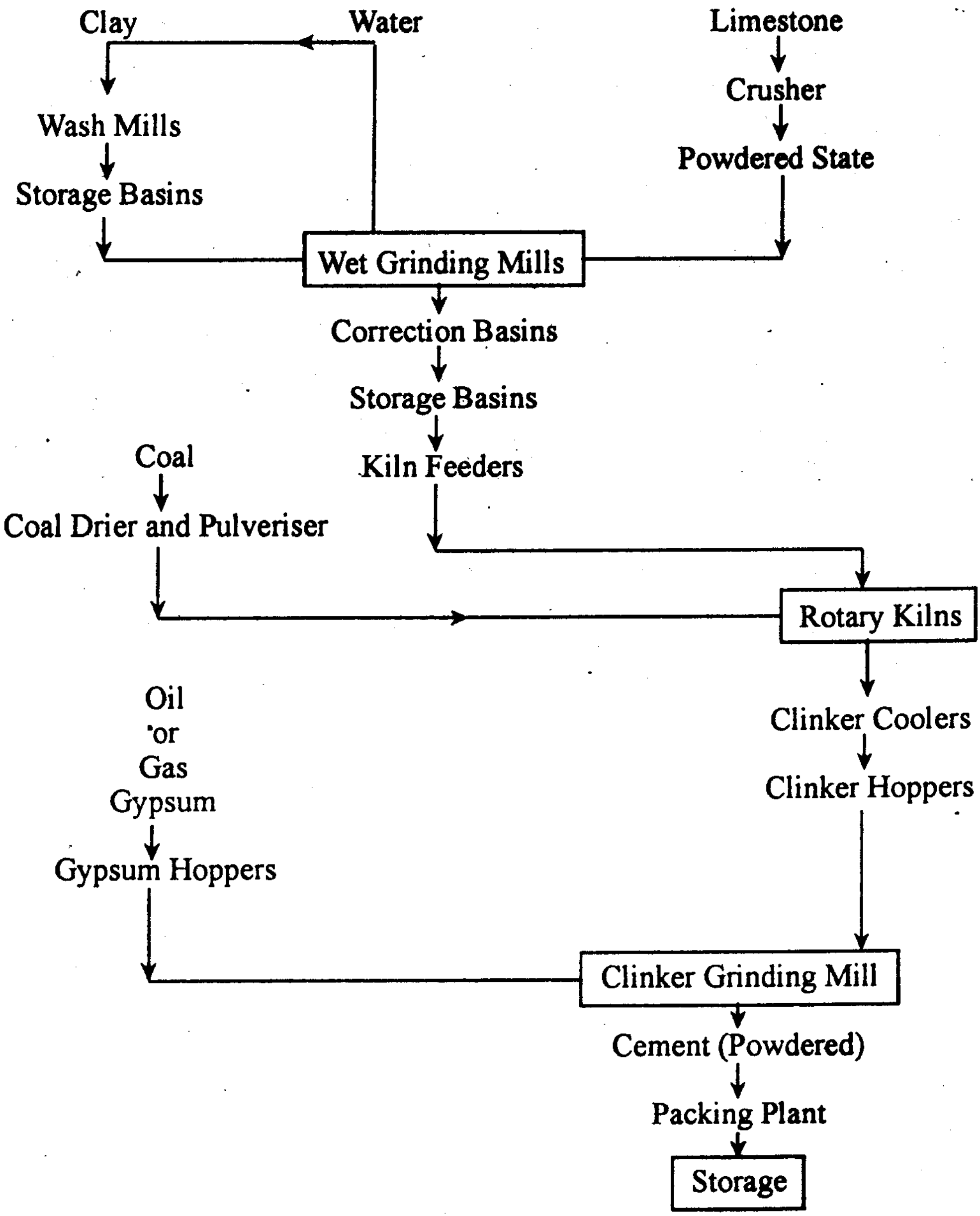


Fig. 13.17. Flow Sheet Diagram of the Wet Process for manufacturing Portland Cement.

1. Dehydration Zone

In this Zone (100°C – 500°C) the evaporation of free water from the fuel and evolution of combined water from the clay takes place (500 – 1000°C).

2. Calcination Zone

In this Zone evolution of CO_2 from the carbonates takes place.

3. Burning Zone

In the Burning Zone the lime-rich mixture containing silica, alumina and ferric oxide with small percentage of other oxides is heated up to the sintering temperature. Burning of the calcined mass is completed at about 1450°C.

4. Cooling Zone

The process of clinker formation is completed in this Zone. Cooling of the clinker starts a few feet short of the discharge end of kiln and is completed when it passes through the cooler and its temperature is approximately 150 – 200°C.

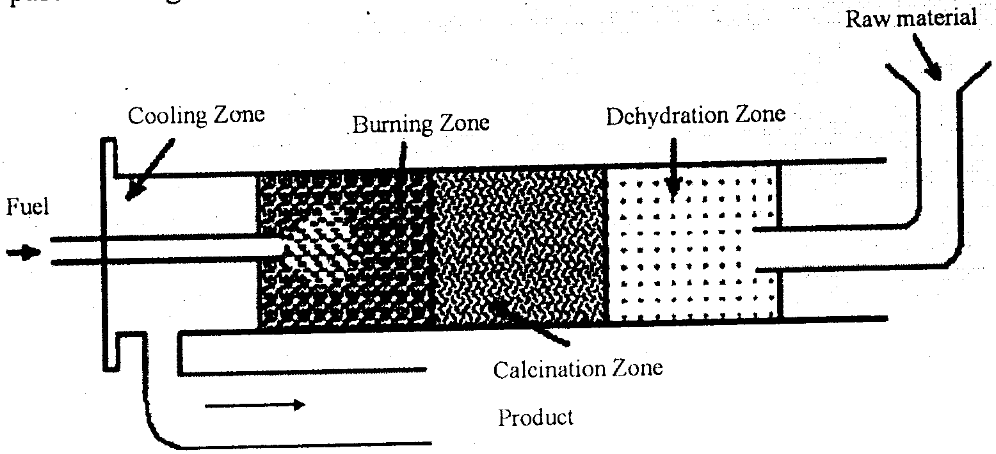


Fig. 13.18.

Clinker is finely ground in ball mills. The cement is stored in reinforced concrete reservoirs with bottoms containing air nozzles through which air is forced when the cement is being discharged. Cement is delivered to consumers in automobiles and railway cement tanks in bulk, or in paper multilayer bags Fig. (13.18).

(2) DRY PROCESS

The dry process for manufacture of cement is preferred only in places where hard crystalline limestones and shales are available. The only advantage of this process is that the fuel consumption is low. The raw materials are first crushed together in the dry state in a multi-chamber tube mill of a fairly large diameter. The drying unit consists of a grade firing with induced draught fan. The grinding and drying operations are carried out simultaneously. This dry powdered mixture from the grinding mill is homogenized by means of compressed air. The dry material is next burnt in a rotary kiln as explained in the Wet Process.

Setting of Cement

Cement has unique property by the virtue of which it combines with water; the resulting mass becoming hard and very resistant to pressure. This process is known as *"Setting of Cement"*. The cause of setting of cement is chiefly a hydration process, followed by the decomposition of calcium silicate and calcium aluminate and formation of new compounds. There are two theories put forward to explain the setting of cement:

(a) According to the first theory, calcium hydroxide and other products of decomposition of water separate in the colloidal form. The strength of the cement is due to the fact that the gel soon dries up, thereby hardening and binding the grains together.

(b) Among the constituents of cement the only one which has the property of quick setting is $3CaO.\ SiO_2$. It combines with water, setting in a few hours to a strong mass of hydrated silicate, containing a certain quantity of calcium hydroxide. The remaining constituents of cement *e.g.*, $2CaO.SiO_2$ and $3CaO_2.\ Al_2O_3$ soon get hydrated, the former sets very slowly and hence it is of little service for the first few weeks while the latter sets quickly. The compounds produced separate in a crystalline form. The strength of the cement is chiefly due to the interlocking of minute crystals deposited from a supersaturated solution.

Physical Testing of Cement

In order to test the suitability of cement for certain purpose a number of tests are carried out, some of them being:

Setting time: A known quantity of cement is mixed with a fixed quantity of water and a stop-watch is started.

The cement is made into a paste by a standard procedure. The paste is then placed on a glass slab in a cylindrical ring and Vicat needle allowed to drop under its own weight. At first the needle can pierce the cement and touch the glass slab, but as the time passes it fails to do so. Note the time when that happens. This interval of time since the start, is called the *initial setting* time. If the experiment is allowed to continue, a time would reach when the cement sets and the needle cannot even pierce it, under its own weight. This is called the *final setting* time.

For a good type of cement initial setting time should not be less than 40–45 minutes and the final setting time not more than 9–10 hours. Gypsum (2%) retards setting, but excessive amount may hasten it. Other tests which can be carried out for the determination of quality of the cement are:

1. Compression strength.
2. Tensile strength.
3. Specific gravity.

Concrete

It mixture of cement with sand and crushed stone, gravel, blast furnace slag, etc, all made up to paste with water. It sets into a very hard solid mass and is extensively used in the construction of buildings and roads. Ferro-concrete contains twisted rods of iron or wire embedded in concrete.

Position of Cement in Pakistan

At the time of partition in 1947, there were four plants in West Pakistan which produced cement about 3,30,000 tons. However, in 1953-54, the roduction of cement went up to 6,60,000 tons. In 1956, PIDC set up cement actories at Daud Khel and Hyderabad. But even then the production of cement as not enough to meet the day-to-day increasing demand for the construction purposes. For a developing country like Pakistan, there is always increasing need of cement for development projects The efforts were and have been made to install more factories. An up-to-date position is detailed below along with the apacity of production shown against each factory.

CEMENT INDUSTRIES

(a) Govt. Sector with Production Capacity in Tons

Factory	*Capacity (000)*	*Process*
Zeal Pak	1,080	Wet
A.C. Wah	450	Wet
A.C. Rohri	270	Wet
Gharibwal	540	Wet
Maple Leaf	300	Wet
National Karachi	160	Wet
National Dandot	50	Wet
White Cement	30	Wet
Mustehkum	660	Dry & Semi-Wet
Javedan	600	Dry
Kohat	330	Dry
Dandot	330	Dry
Thatta	330	Dry
Pak Cement	171	Dry
(b) Private Sector		
Pakland	300	Wet
Cherat	300	Dry
Dadabhoy	300	Dry
Sasella	75	Dry
Fauji	600	Dry
Attock	600	Dry

Questions

1. Compare the properties of carbon and silicon based upon their electronic configurations. Why silicon can accommodate more than eight electrons in its valence shell but carbon does not?
2. Describe the different allotropic forms of carbon. How is charcoal converted into diamond?
3. How is graphite artificially prepared? Discuss its important properties and uses.
4. What is the difference between coal and coke? Give the products of the reaction of red hot coke on (a) air, and (b) steam.
5. What is charcoal? How is it made on large scale? Describe the difference between peat, bituminous coal, anthracite and graphite.
6. (a) How diamond and graphite differ in their structures? Give some of their applications.
   (b) Explain why?
      (i) diamond is hard,
      (ii) diamond is denser than graphite,
      (iii) graphite is soft and good lubricant,
      (iv) graphite is a good conductor of electricity.
7. Write notes on:
   (a) Calcium carbide
   (b) Calcium cyanamide
8. Discuss the general group trends of Group IV. Compare the behaviour of carbon and silicon.
9. What type of oxides are formed by carbon? Discuss their chemistry and structures.
10. What are carbides? Discuss them after classifying into different types.
11. Why does CO_2 differ from SiO_2? Describe the general characteristics and structure of SiO_2.
12. What are silicones? How are they obtained from silicon halides?
13. What are silicates? Discuss the structures of various silicate.
14. How would you explain the fibrous property of asbestos and sheet quality of mica?
15. (a) Show that the composition of the amphibole chain may be expressed as $(Si_4O_{11})_n^{-6n}$.
   (b) Consider a sheet formed by SiO_4 tetrahedra, when each shares three of four oxygen atoms with the neighbouring tetrahedra. Show the composition of such a sheet is $(Si_2O_5)_n^{-2n}$.

16. Explain what is meant by the statement 'carbon monoxide is isoelectronic with nitrogen'.
17. Write down the valence structure of the following molecules and give their geometry:
    (a) CO (b) CF_4 (c) SiH_3Cl
18. Describe the raw material or the manufacture of glass. How is it manufactured on industrial scale?
19. How are the glasses coloured? Discuss the different types and uses of glasses. What are the prospects of glass industry in Pakistan?
20. Describe the composition of Portland cement. Discuss the wet process for the manufacture of cement.
21. What do you understand by the term "setting of cement"? How is the physical testing of cement conducted? Discuss the future of cement industry in Pakistan.
22. **Give short answers to the following questions:**
    (i) Draw electronic configuration elements of Group IVA with atomic numbers given in brackets: C(6), Si(14), Ge(32), Sn(50), Pb(82).
    (ii) Give comparison in characteristic features of carbon and silicon.
    (iii) What are the general group trends of carbon family?
    (iv) Discuss diamond as allotropic form of carbon.
    (v) What is graphite or black lead? What is its structural pattern?
    (vi) What is amorphous carbon? Describe some of its varieties.
    (vii) Discuss salient features of bucky balls.
    (viii) How is CO formed? Draw the orbital structure of CO.
    (ix) What are carbides? Give in brief the types of carbides.
    (x) How is pure silicon produced for solar energy cells and silicon chips?
    (xi) Discuss the characteristic properties of $SiCl_4$.
    (xii) What are silicons? How are these formed?
    (xiii) What is water glass? How is it prepared?
    (xiv) What are silicates? Draw structures of various types of silicates.
    (xv) What are the industrial applications of silicates?
    (xvi) What is glass? How is it manufactured?
    (xvii) What do you understand by the term annealing of glass? How are coloured glasses prepared?
    (xviii) Describe various types of glasses.
    (xix) What are special glasses? Discuss the position of glass industry in Pakistan.

(xx) What is cement? How is it manufactured by wet process?
(xxi) What are the raw materials of cement? How is cement prepared by dry process?
(xxii) How is physical testing of cement carried out?
(xxiii) What is setting of cement?
(xxiv) What is the position of cement industry in Pakistan?
(xxv) How is calcium carbide prepared?

23. **Give the correct answer:**

(i) Silicon has electronic configuration
(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ (b) $1s^2\ 2s^2\ 2p^4$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ (d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
(Ans: a)

(ii) Melting point (°C) of carbon is:
(a) 3600 (b) 4827
(c) 937 (d) 1410
(Ans: a)

(iii) First ionization potential of Sn is:
(a) less than Pb (b) more than C
(c) more than Pb (d) more than Si
(Ans: a)

(iv) Diamond has one of the following structures:
(a) rhomohedral (b) monoclinic
(c) cubic (d) tetrahedral
(Ans: d)

(v) Diamond is:
(a) good conductor of electricity
(b) bad conductor of electricity
(c) bad conductor on heating
(d) good conductor on heating
(Ans: b)

(vi) Carbon monoxide is a poisonous gas because it:
(a) replaces oxygen from lungs
(b) forms carboxy haemoglobin
(c) forms carbon dioxide with oxygen
(d) has a sweet smell
(Ans: b)

(vii) SiO_2 can be reduced with:
(a) Al (b) C
(c) H_2 (d) B
(Ans: b)

(viii) Water glass is:
(a) Na_2SiO_2 (b) Na_2SiO_3
(c) Na_2SiO_4 (d) $NaSiO_2$
(Ans: b)

(ix) Addition of MnO_2 to glass imparts:
(a) blue colour to glass (b) green colour to glass
(c) violet colour to glass (d) pink colour to glass
(Ans: c)

(x) Optical glasses for lenses contain:
(a) Al_2O_3 (b) CuO
(c) CoO (d) B_2O_3
(Ans: d)

(xi) $p\pi$-$d\pi$ bonding exists in:
(a) diamond (b) graphite
(c) trisilylamine (d) none
(Ans: c)

(xii) Water gas is a mixture of:
(a) $H_2O + CO_2$ (b) $CO + H_2$
(c) $CO + CO_2$ (d) $CO + H_2O$
(Ans: d)

(xiii) Glass is a:
(a) liquid (b) solid
(c) polymer (d) supercooled liquid
(Ans: d)

(xiv) The maximum coordination number of carbon is 4 but that of silicon is 6. This is due to:
(a) large size of silicon
(b) availability of low lying *d*-orbitals in silicon
(c) more electropositive nature of silicon
(d) formation of silicates
(Ans: b)

(xv) Silicon is an important constituent of:
(a) haemoglobin (b) chlorophyll
(c) amalgums (d) rocks
(Ans: d)

(xvi) Which of the following metals shows allotropy?
(a) Sn (b) Ca
(c) Mg (d) Pb
(Ans: a)

(xvii) The oxide which cannot act as reducing agent:

(a) SO_2
(b) NO_2
(c) CO_2
(d) ClO_2

(Ans: c)

(xviii) Which of the following is amphoterric:

(a) BeO
(b) CO_2
(c) Ag_2O
(d) SnO_2

(Ans: a)

(xix) Artificial carborundum is:

(a) silicon carbide
(b) boron nitride
(c) quartz
(d) calcium carbide

(Ans: a)

(xx) In lead pencil, which of the following is used?

(a) lead
(b) carbon
(c) silicon
(d) graphite

(Ans: d)

(xxi) Carbon atoms in diamond are bonded to each other in a configuration which is:

(a) planar
(b) linear
(c) tetrahedral
(d) octahedral

(Ans: c)

(xxii) When CO_2 is bubbled through an aqueous solution of Na_2CO_3, we get:

(a) NaOH
(b) $NaHCO_3$
(c) glass
(d) sodalime

(Ans: b)

(xxiii) Water gas is prepared by passing:

(a) steam over HCl
(b) steam over red hot coke
(c) air over red hot coke
(d) steam over CO_2

(Ans: b)

(xxiv) Charring of sugar is due to:

(a) oxidation
(b) reduction
(c) dehydration
(d) hydration

(Ans: c)

(xxv) The function of sand in mortar is:
(a) to decrease the hardness
(b) to make the mass compact
(c) to decrease the plasticity of the mass
(d) to prevent excessive shrinkage which might result in cracks.
(Ans: b)

(xxvi) Cement strength is due to:
(a) tricalcium silicate (b) dicalciam silicate
(c) tricalcium aluminate (d) dicalcium aluminate.
(Ans: a)

(xxvii) Rate of setting of cement can be increased by adding:
(a) NaCl (b) KCl
(c) $CaCl_2$ (d) $AlCl_3$
(Ans: c)

(xxviii) Types of glass used in making lenses and prisms is:
(a) flint glass (b) soft glass
(c) pyrex glass (d) jena glass
(Ans: a)

(xxix) The total number of electrons in one molecule of CO_2 is:
(a) 22 (b) 44
(c) 66 (d) 88
(Ans: b)

(xxx) The components present in producer gas are:
(a) $CO + CH_4$ (b) $CO + H_2$
(c) $CO_2 + H_2$ (d) $CO + CO_2$
(Ans: b)

(xxxi) The shape of $PbCl_6^{2-}$ is:
(a) square planar (b) octahedral
(c) square pyramid (d) irregular octahedral
(Ans: b)

(xxxii) The formula of corundum is:
(a) $Al_2O_3 . 2H_2O$ (b) Al_2O_3
(c) $Al_2O_3 . H_2O$ (d) $Al_2O_3 . 2SiO_2 . 2H_2O$
(Ans: b)

(xxxiii) Silicones are polymeric substances with linkage of:
(a) Si – S – Si (b) $Si(CH_3)_4$
(c) Si – O – Si (d) O = Si = O
(Ans: c)

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14

NITROGEN AND PHOSPHORUS (GROUP VA)

The elements of Group VA are nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). These elements are classified as non-transition members of this group. However, the relative metallic character within this group increases with the increase in atomic number.

ELECTRONIC CONFIGURATION

All the members of this group possess 5 electrons in their valency shells. The characteristic configuration in their valency shell is $ns^2\ np^3$ (Table 14.1). Thus, out of five electrons present in the valency shell, two are present in the *s* orbitals and the rest three electrons remain unpaired and occupy the three *p* orbitals. The *s* orbital electrons may remain inert and the three unpaired electrons in the *p* orbital would form three covalent or electron pair bonds. In this way, they attain the next inert gas configuration ($ns^2\ np^6$).

TABLE 14.1

Electronic Configurations of Group VA Elements

Element	1	2		3			4				5			6	
	s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
N	2	2	3												
P	2	2	6	2	3										
As	2	2	6	2	6	10	2	3							
Sb	2	2	6	2	6	10	2	6	10		2	3			
Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3

The electronic configuration of nitrogen involves only *s* and *p* orbitals. The *ns* orbitals remain inert and are not promoted to *np* orbitals because they are already half-filled. Thus nitrogen will form compounds in which three 3*p* electrons form three covalent bonds. Nitrogen does not involve any *d* orbitals because of their non-availability.

Although phosphorus has electronic configuration $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$, one of the *s* electrons can be promoted to a vacant 3*d* orbital, producing five unpaired electrons in the valency shell (Table 14.2). The five unpaired electrons may be used to form five covalent (electron pair) bonds. Therefore, phosphorus would be able to form compounds in pentavalent state, *e.g.*, PCl_5, P_2O_5 etc. Similarly, five covalent states will be shown by As, Sb and Bi due to the involvement of *d* orbitals of the valency shell.

TABLE 14.2

	1	2		3		
	s	*s*	*p*	*s*	*p*	*d*
N	2	2	1, 1, 1			
P	2	2	2, 2, 2	2	1, 1, 1	
P*	2	2	2, 2, 2	1	1, 1, 1	1

The valency shell of nitrogen cannot accommodate more than eight electrons. Therefore, maximum covalency of nitrogen is four. But phosphorus can accommodate more than eight electrons by utilising its *d* orbitals in addition to their *s* and *p* orbitals and thus gives maximum covalency more than four.

The inability of nitrogen to unpair and promote its 2*s* electrons results in the formation of three covalency which should be more stable than any 5-covalent possible state. The nitrogen compounds in oxidation state (V) should be easily reduced to trivalent state. Thus nitric acid (containing nitrogen in +5 oxidation state) should be able to be reduced and, therefore, acts as an oxidising agent. On the other hand, pentavalent phosphorus is more stable than trivalent phosphorus. Consequently, phosphoric acid (phosphorus in the +5 oxidation state) does not exhibit any oxidising property.

The elements of this group can also attain inert gas configuration by gaining three electrons to form tri-negative ions. But the energy involved in the formation of such ions is extremely large, becoming larger with increase in atomic size. Only nitrogen is found to give such ions, N^{3-}.

None of these elements form simple cations, except bismuth which gives Bi^{3+} cations. Even Bi^{3+} compounds are readily hydrolysed.

The physical properties of the elements of this group are given in Table 14.3.

TABLE 14.3
Physical Properties of the Elements

	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic weight	14.00	30.97	74.92	121.75	209.00
m.p. °C	−210	44(white)	817(36 atoms)	630	271
b.p. °C	−196	280	–	1440	1420
Covalent radius (pm)	74	110	121	141	152
Ionic radius(pm)	11	34	69	90	120
Ionization potential (kJ/mole)	1398	1061	964	829	771
Density	0.8042 (at b.p.)	1.82 (white) 2.20 (red)	1.97 (yellow) 5.73 (grey)	6.67	9.80

NITROGEN

Nitrogen is an essential element for plant and animal life. In the free state it forms about four-fifth by volume of the air.

Chief Sources

(1) Air—about 78% by volume in the atmosphere.
(2) Sodium nitrate or chile saltpetre.
(3) Other nitrates mainly saltpetre, KNO_3.
(4) Ammonium salts present in the soil.
(5) Animal and vegetable matter, *e.g.*, proteins.

Preparation

From Air

Nitrogen can easily be separated from air. For this purpose either of the following procedures is adopted:

(a) By fractional distillation of liquid air.

(b) **From ammonium nitrite:** Ammonium nitrite liberates nitrogen on heating.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

(c) **From ammonium dichromate:** When solid ammonium dichromate is heated, it decomposes to liberate nitrogen.

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

(d) **From ammonia:** Nitrogen can be obtained from ammonia by passing it over red hot cupric oxide.

$$2NH_3 + 3CuO \longrightarrow 3H_2O + 3Cu + N_2$$

Chemical Properties

Nitrogen is very slightly soluble in water. Under ordinary conditions, it is an inert element. It is neutral in character and is neither combustible nor a supporter of combustion.

The chemical inertness of nitrogen may be attributed to a large dissociation value, 941 kJ/mole. The triple bond in nitrogen is different from other triple bonds because it does not undergo addition reaction. The following are the typical reactions of nitrogen:

(i) Combination with Hydrogen

Nitrogen reacts with H_2 at about 600°C under pressure in presence of a catalyst (Haber process for NH_3).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 141 \text{ kJ/mole}$$

(ii) Combination with Calcium Carbide

When calcium carbide is heated at about 1000°C in presence of N_2, calcium cyanamide is formed.

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

(iii) Combination with Oxygen

Nitrogen reacts with oxygen only in presence of electric spark. Reaction of nitrogen and oxygen also takes place in the atmosphere at the time of lightning produced by charged clouds.

$$N_2 + O_2 \rightleftharpoons 2NO - 180 \text{ kJ/mole}$$

(iv) Reaction with Metals

Metals, such as Li, Mg, Ca, Al, etc., react with nitrogen to form nitrides.

$$N_2 + 3Mg \longrightarrow Mg_3N_2$$

$$N_2 + 2Al \longrightarrow 2AlN$$

$$N_2 + 6Li \longrightarrow 2Li_3N$$

(v) Reaction with Al_2O_3 and C

Al_2O_3 and C react with nitrogen at high temperatures to form nitride.

$$N_2 + Al_2O_3 + 3C \longrightarrow 2AlN + 3CO$$

(vi) Reaction with Na_2CO_3 and C

Sodium cyanide is obtained by heating Na_2CO_3 and C in presence of nitrogen.

$$N_2 + Na_2CO_3 + 4C \longrightarrow 2NaCN + 3CO$$

Use of Nitrogen

(i) Nitrogen is used in its fixation to ammonia, nitrates, nitric acid, fertilizers etc.

(ii) High temperature thermometers are filled with nitrogen to stand temperatures up to 500°C.

(iii) Ammonia is synthesised from nitrogen by Haber process.

(iv) For preservation of food in tin cans which are filled with nitrogen.

(v) For the manufacture of alumina by Serpek's process.

(vi) Nitrogen is also used to produce calcium cyanamide, commonly used as fertilizer and for the preparation of ammonia and cyanides.

(vii) Nitrogen gas is used to provide inert atmosphere. Thus, it is used to fill electric light bulbs and to run chemical reactions in absence of air.

NITROGEN CYCLE

Nitrogen present in the atmosphere is the source of various nitrogen containing substances indispensable to animal and vegetable life. Neither animals nor the ordinary plants can assimilate free nitrogen. Animals obtain the nitrogen supply from compounds present in plants, while plants secure the required nitrogen from nitrates present in the soil or from fertilizers. The nitrogenous compounds taken up by plants are converted into **proteins** in presence of light. Proteins are essential for animal life. Thus, plants form a useful link between animals and minerals or soil substances.

The source of combined nitrogen, whether present in living matter or soil is atmospheric nitrogen. The nitrogen matter in the soil (obtained from plants and dead animals, etc.) putrifies by **denitrifying bacteria,** liberating free nitrogen. The atmospheric nitrogen is brought back to the soil in two ways:

(a) By Electric Discharge

In presence of electric discharge nitrogen reacts with atmospheric oxygen to form water soluble oxides and oxyacids (or their salts) of nitrogen which are washed down by rain into the soil.

(b) By Symbiotic Bacteria

The leguminous plants (peas, grams, beans, etc.) live in partnership or **symbiosis** (living with) with certain class of bacteria present in the nodules on their roots. These bacteria get food from the plant and convert atmospheric nitrogen into nitrogenous compounds which are assimilated by plants for their growth.

Nitrogen undergoes a never ending cycle in nature which involves continuous life and death of animals and growth, and decay of plants. The schematic diagram shown in Figure 14.1 represents the nitrogen cycle.

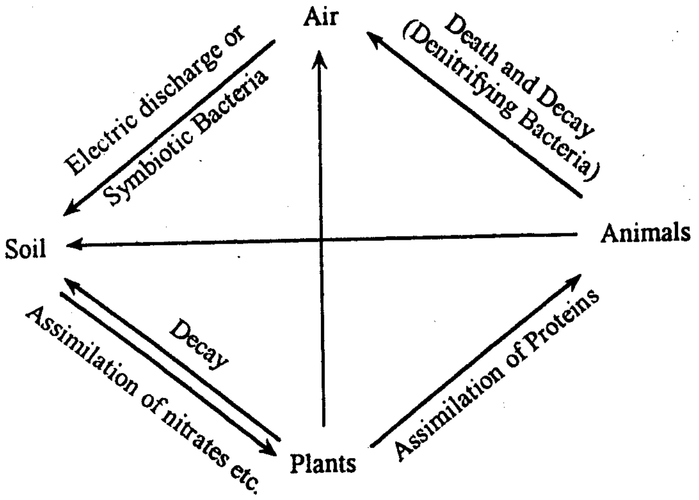


Fig. 14.1. Nitrogen Cycle.

COMPOUNDS OF NITROGEN

Nitrogen forms a very large number of compounds in which the atom is diagonally or trigonally hybridised or may undergo tetrahedral hybridisation.

The compounds formed by diagonal or trigonal hybridisation include *oxides and oxyacids of nitrogen, azides, cyanides and cyanates*. The nitrogen is linked to other atoms by π-bonds as well as σ-bonds.

The compounds in which nitrogen atom undergoes tetrahedral hybridisation are NH_3, ammonium salts and their derivatives. The tetrahedrally hybridised nitrogen compounds of the type NH_3 possess one hybrid orbital (out of four) which is occupied by a lone pair of electrons.

Compounds Containing N Atom in Diagonal Or Triagonal Valence State

The oxides and oxyacids of nitrogen will be selected for discussion under this class.

Oxides of Nitrogen

Among the oxides of nitrogen, we shall discuss nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), dinitrogen pentoxide (N_2O_5) and nitroso group.

(1) Nitrous Oxides, N_2O

Nitrous oxide is prepared by any one of the following methods:

(i) **From Ammonium Nitrate:** On heating crystals of ammonium nitrate, N_2O is obtained.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(ii) **From Hydroxylamine:** Nitrous oxide can be prepared by adding $NaNO_2$ to a warm solution of hydroxylamine hydrochloride or sulphate. It can also be prepared by oxidation of hydroxylamine with $FeCl_3$, HNO_2, etc.

$$NH_2OH\,.\,HCl + NaNO_2 \longrightarrow N_2O + NaCl + 2H_2O$$

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$$

(iii) **From Sulphamic Acid:** When nitric acid is added to sulphamic acid, nitrous oxide is evolved.

$$HSO_3NH_2 + HNO_3 \longrightarrow N_2O + H_2SO_4 + H_2O$$

(iv) **From Zinc and NHO_3:** Zinc reacts with dilute HNO_3 to evolve nitrous oxide.

$$4Zn + 10HNO_3 \longrightarrow 4Zn\,(NO_3)_2 + N_2O + 5H_2O$$

(v) **From Potassium Nitroso Hydroxylamine Sulphonate:** Acidifying the solution of potassium nitroso hydroxylamine sulphonate liberates N_2O.

$$K_2SO_3NONO + 2HCl \longrightarrow N_2O + H_2SO_4 + 2KCl.$$

Properties

Nitrous oxide is a colourless gas with a faint, sweet smell. If inhaled in large amounts, it causes hysterical laughter and is thus called *laughing gas*.

Reactions

(i) N_2O decomposes only when heated above 560°C.

$$2N_2O \xrightarrow{\Delta} 2N_2 + O_2$$

(ii) N_2O is oxidised to NO by strong oxidising agents only.

$$N_2O + [O] \xrightarrow{KMnO_4} 2NO$$

(iii) Nitrous oxide is a supporter of combustion due to its decomposition to N_2 and O_2.

(iv) It is a neutral oxide and would not react with alkalies and acids. On strong heating with alkalies nitrites are formed.

(v) N_2O reacts with metals on heating and liberates N_2.

$$N_2O + Cu \longrightarrow CuO + N_2$$

(vi) N_2O burns in presence of combustible substances such as S and P to form compounds.

$$S + 2N_2O \longrightarrow SO_2 + 2N_2$$

Structure

The molecule is linear as shown by (i) its absorption spectrum, (ii) X-ray analysis in solid and liquid state. The infrared spectrum has shown the molecule to be unsymmetrical.

The crystal lattice of N_2O is similar to CO_2 and both oxides are, therefore, found to dissolve in solid solution.

The N_2O molecule consists of two nitrogen atoms joined together by multiple bonds having O atom in the terminal position. The electronic structure of the molecule is represented by a resonance hybrid consisting of two contributing forms I and II.

$$:\mathrm{N}:::\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{N}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}: \quad \longleftrightarrow \quad :\overset{\cdot\cdot}{\mathrm{N}}::\mathrm{N}::\overset{\cdot\cdot}{\mathrm{O}}:$$

(I) (II)

The values of bond lengths (N – N = 112 pm ; N – O = 119 pm) favour the triple bond character over all the three atoms. Both nitrogen and oxygen are considered to utilise *sp* hybrid orbitals and N_2O structure can be explained on the basis of two σ and two pairs of π-bonds spread over N – N – O molecule (Figure 14.2). The higher orbitals are characterised by bonding in N – N and weak anti-bonding in N – O bonds. Each bond in the molecule would show triple bond character which is more pronounced in N – N bond.

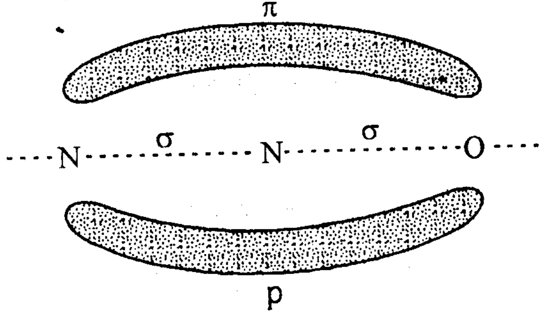


Fig. 14.2. Delocalised π-orbitals in N_2O.

Nitric Oxide, NO

Nitric oxide is a colourless gas but takes up O_2 from the air to form a brown-red gas, NO_2.

It can be prepared by any one of the following methods:

(i) From Cu and HNO_3

On heating Cu turnings with dil. HNO_3, NO is evolved.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(ii) By Direct Combination of N_2 and O_2

N_2 and O_2 combine in presence of electric arc and platinum to form nitric oxide.

$$N_2 + O_2 \longrightarrow 2NO$$

(iii) By Oxidation of Ammonia

Nitric oxide also prepared by oxidising ammonia with air in presence of platinum at 500°C.

$$4NH_3 + 5O_2 \xrightarrow{Pt,\ 500^\circ C} 4NO + 6H_2O$$

(iv) From Potassium Nitrate

Nitric oxide can be prepared by heating KNO_3 in presence of $FeSO_4$ or Hg and H_2SO_4.

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 \longrightarrow 2Fe_2(SO_4)_3 + K_2SO_4 + 2NO + 4H_2O$$

$$2KNO_3 + 4H_2SO_4 + 6Hg \longrightarrow 3Hg_2SO_4 + K_2SO_4 + 2NO + 4H_2O$$

(v) From Nitrites

When a mixture of nitrite and mercury is treated with concentrated H_2SO_4, NO is evolved.

$$2KNO_2 + 2Hg + 2H_2SO_4 \longrightarrow K_2SO_4 + Hg_2SO_4 + 2NO + 2H_2O$$

Properties

The following are the typical reactions of nitric oxide:

(i) Combination with O_2

NO readily combines with O_2 of the air to form NO_2 gas.

$$2NO + O_2 \longrightarrow 2NO_2$$

(ii) Reduction with $LiAlH_4$

Nitric oxide is reduced by $LiAlH_4$ to hyponitrous acid, $H_2N_2O_2$ which can be obtained as silver salt.

$$2NO + 2H \xrightarrow{LiAlH_4} H_2N_2O_2$$

(iii) Reaction with Halogens

F_2, Cl_2 and Br_2 react with nitric oxide, NO.

$$2NO + X_2 \longrightarrow 2NOX\ (X = F, Cl, Br)$$

(iv) Reaction with Hydrogen

Nitric oxide reacts with hydrogen to form N_2 and NH_3.

$$2NO + 2H_2 \xrightarrow{\text{without catalyst}} N_2 + 2H_2O$$

$$2NO + 5H_2 \xrightarrow{\text{Pt black}} 2NH_3 + 2H_2O$$

(v) Formation of Nitrosyl Compounds

The carbonyls of transition metals (Fe, Ru, Ni) react with nitric oxide to form nitrosyl derivatives (NO behaves as three electron donor in nitrosyl derivatives).

$$Fe_2(CO)_9 + 4NO \longrightarrow 2Fe(NO)_2(CO)_2 + 5CO$$

(vi) Reaction with FeI_2

NO reacts with transition metal halides such as FeI_2 to form nitrosyl iodide.

$$2FeI_2 + 4NO \longrightarrow 2Fe(NO)_2I + I_2$$

(vii) Reaction with I_2

When NO is passed through iodine solution, nitric acid is formed.

$$2NO + 3I_2 + 4H_2O \longrightarrow 2HNO_3 + 6HI$$

(viii) Reaction with Reducing Agent

NO is reduced to N_2O with H_2SO_3. Stannous chloride reduces it to hydroxylamine.

$$H_2SO_3 + 2NO \longrightarrow N_2O + H_2SO_4$$

(ix) Reaction with Oxidising Agent

NO can be oxidised to HNO_3 by oxidising agents such as $KMnO_4$.

$$6KMnO_4 + 10NO + 12H_2SO_4 \longrightarrow 6KHSO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$$

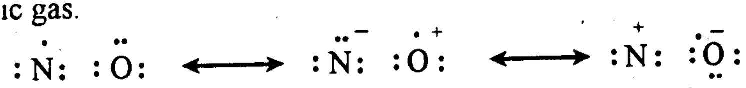
(x) Reaction with Alkalies

NO reacts with concentrated aqueous alkalies to give nitrites.

$$2KOH + 4NO \longrightarrow N_2O + 2KNO_2 + H_2O$$

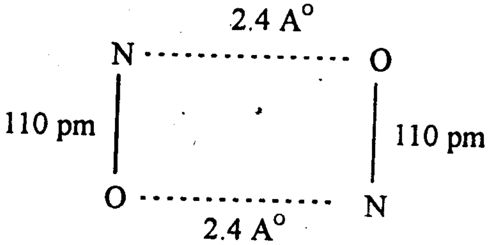
Structure

The following three resonating forms contribute to the structure of NO. It is considered to be an odd molecule containing odd number of electrons in the valency shell as shown by magnetic susceptibility measurements. It is a paramagnetic gas.



(I) (II) (III)

Nitric oxide solidifies to monoclinic crystals. The values of magnetic susceptibility, heat of sublimation and residual energy indicate that crystals consist of dimeric molecules.



The paramagnetic behaviour of NO can be well explained by molecular orbital theory and molecular orbital diagram of nitric oxide molecule is shown in Figure 14.3.

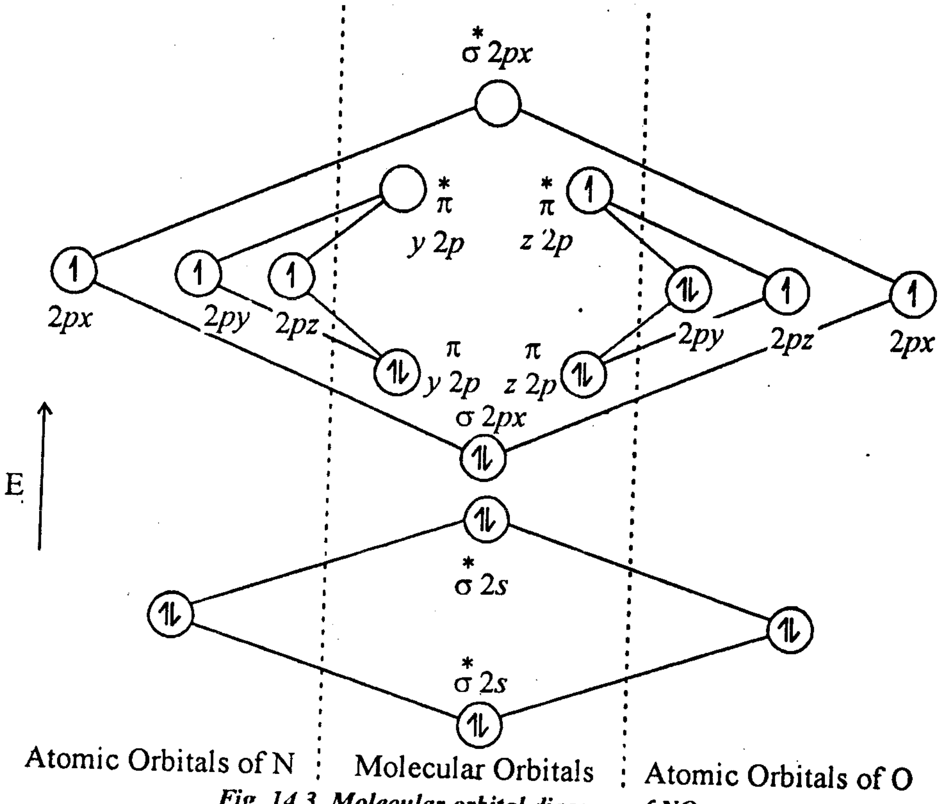


Fig. 14.3. Molecular orbital diagram of NO

Dinitrogen Trioxide, N_2O_3

On cooling a mixture of one part of NO with one part by volume of NO_2, a blue liquid of composition N_2O_3 is obtained at – 21°C which freezes to a blue solid.

$$NO + NO_2 \xrightarrow{-21^\circ C} N_2O_3$$

On warming an equilibrium of the following type is set up.

$$N_2O_3 \rightleftharpoons NO + NO_2$$

It is also obtained by treating arsenious oxide with nitric acid.

$$As_2O_3 + 2HNO_3 \longrightarrow As_2O_5 + N_2O_3 + H_2O$$

Absorption of N_2O_3 with dry alkalies results in the formation of nitrites.

$$N_2O_3 + 2KOH \longrightarrow 2KNO_2 + H_2O$$

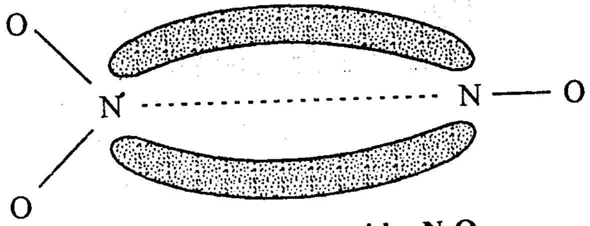
Reaction with H_2SO_4

Results in the disappearance of the blue colour of N_2O_3 with the formation of nitrosonium hydrogen sulphate.

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2NO^+ (HSO_4^-) + H_2O$$

Structure

The structure of N_2O_3 is ambiguous but Mason (1959) has shown the following:



Nitrogen peroxide, NO_2 and nitrogen tetroxide, N_2O_4 (Nitrogen (IV) oxides)

Both gases remain in equilibrium in the gaseous and liquid states.

$$N_2O_4 \rightleftharpoons 2NO_2$$

(Diamagnetic) (Paramagnetic)

Dinitrogen tetroxide is colourless and diamagnetic and can be obtained pure only in the solid state (m.p. – 9.3°C). In the liquid state (b.p. 21.3°C) it contains 1% brown, paramagnetic monomer, NO_2. The dimer, N_2O_4 changes into monomer, NO_2 and contains 90% of NO_2.

Preparation

(i) NO_2 is prepared by heating lead nitrate.

$$2\,Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

(ii) Concentrated hot HNO_3 reacts with copper to liberate NO_2.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O.$$

(iii) It is easily obtained on exposing NO to air or oxygen.

$$2NO + O_2 \longrightarrow 2NO_2$$

Reactions of NO_2

The monomer, NO_2 is an odd-electron molecule and has many characteristics of free radicals such as:

(a) it associates with other radicals,
(b) abstracts hydrogen from saturated hydrocarbons,
(c) adds to unsaturated hydrocarbons.

The typical reactions of nitrogen peroxide are:

(i) Reaction with Water and Alkalies

It is absorbed by water and alkalies to produce a mixture of nitrites and nitrates.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

(ii) Reaction with Transition Metals

NO_2 vapours react with transition metals to form oxides.

$$2Cu + NO_2 \longrightarrow Cu_2O + NO$$

(iii) Oxidising Action

NO_2 is a good oxidising agent and reacts with various inorganic compounds which are readily oxidised.

$$CO + NO_2 \longrightarrow CO_2 + NO$$
$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$
$$NOCl + NO_2 \longrightarrow NO_2Cl + NO$$

(iv) Reaction with Halogens

Only Cl_2 and Br_2 react with NO_2 when mixture is passed through a hot tube.

$$Cl_2 + 2NO_2 \xrightarrow{\Delta} 2ClNO_2$$
$$Br_2 + 2NO_2 \longrightarrow 2BrNO_2$$

(v) Reaction with Oxidising Agents

Powerful oxidising agents react with NO_2 and oxidise it to pentavalent state.

$$O_3 + 2NO_2 \xrightarrow{250°C} O_2 + N_2O_5$$
$$H_2O_2 + 2NO_2 \longrightarrow 2HNO_3$$
$$NO_3 + NO_2 \longrightarrow N_2O_5$$
$$NO_2Cl + 2NO_2 \longrightarrow NOCl + N_2O_5$$

(vi) Nitration of Paraffins

It reacts with paraffins in the vapour state to form nitro derivatives.

$$2C_2H_6 + 4NO_2 \longrightarrow 2C_2H_5NO_4 + N_2O_3 + H_2O.$$

(vii) Addition to Unsaturated Hydrocarbons

NO_2 adds up to the unsaturated hydrocarbons with ethylene the product is $C_2H_4.2NO_2$.

$$C_2H_4 + 2NO_2 \longrightarrow C_2H_4.2NO_2$$

(viii) Decomposition

On heating NO_2 decomposes to give NO.

$$2NO_2 \xrightarrow{\Delta} 2NO + O_2$$

(ix) Combination with NO

It combines with NO at low temperatures to form dinitrogen trioxide.

$$NO_2 + NO \longrightarrow N_2O_3.$$

Reaction of N_2O_4:

The following reactions can take place in liquid N_2O_4.

(i) Reaction with Metals

N_2O_4 reacts with group I metals at −10°C to form nitrates.

$$Na + N_2O_4 \longrightarrow NaNO_3 + NO$$

$$Ag + N_2O_4 \longrightarrow AgNO_3 + NO$$

$$Cu + 2N_2O_4 \longrightarrow Cu(NO_3)_2 + 2NO$$

(ii) Reaction with Anhydrous Oxides and Hydroxides

N_2O_4 reacts with basic oxides and hydroxides to form nitrates, indicating its acidic nature.

$$CaO + 2N_2O_4 \longrightarrow Cu\,(NO_3)_2 + N_2O_3$$

$$NaOH + N_2O_4 \longrightarrow NaNO_3 + HNO_2$$

(iii) Reaction with Water

N_2O_4 reacts with water to form a mixture of HNO_3 and HNO_2 like NO_2.

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2.$$

(iv) Reaction with H_2SO_4

N_2O_4 reacts with H_2SO_4 to give nitrosyl derivative.

$$H_2SO_4 + N_2O_4 \longrightarrow NO\,.\,HSO_4 + HNO_3$$

(v) Reaction with Metal Salts:

N_2O_4 reacts with various salts to produce nitrates as shown by the following reactions:

(a) $N_2O_4 + KCl \longrightarrow KNO_3 + NOCl$

(b) $2N_2O_4 + 2KI \longrightarrow 2KNO_3 + 2NO + I_2$

(KBr gives similar reaction)

(c) $N_2O_4 + NaClO_3 \longrightarrow NaNO_3 + NO_2 + ClO_2$

(d) $KN_3 + N_2O_4 \longrightarrow KNO_3 + N_2 + N_2O$

(e) $Zn(NO_3)_2 + \frac{1}{2}N_2O_4 \longrightarrow (NO_2)[Zn(NO_3)_2]$

(f) $Na_2CO_3 + 2N_2O_4 \longrightarrow 2NaNO_3 + CO_2 + N_2O_3$.

(vi) Reaction with Amines and Alcohols

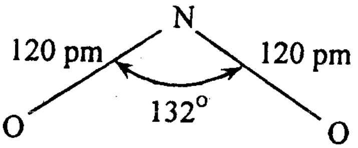
Nitro derivatives are obtained.

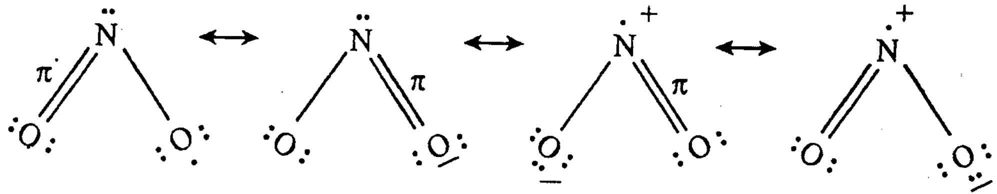
$$N_2O_4 + 2ROH \longrightarrow RONO + HNO_3\ (ROH_2^+ + NO_3^-)$$

$$N_2O_4 + 2R_2NH \longrightarrow R_2N\,.\,NO + HNO_3\ (R_2NH_2^+ + NO_3^-)$$

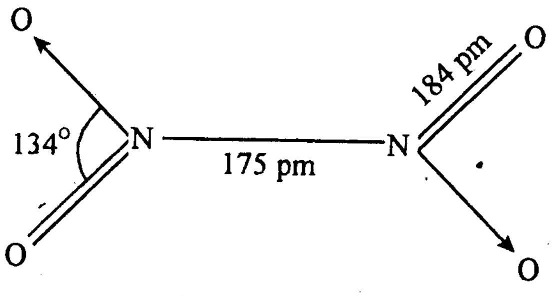
Structures

NO_2 has angular structure which is resonance hybrid of the resonance structures.

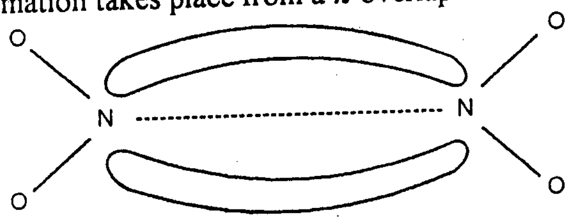




The structure of N_2O_4 is represented as:



Coulson and Duchsen (1957) assigned the following planar structure in which the bond formation takes place from a π-overlap.



Dinitrogen pentoxide or nitrogen (V) oxide, N_2O_5.

Preparation

(i) It is prepared by dehydration of HNO_3 by P_2O_5.

$$P_2O_5 + 2HNO_3 \longrightarrow N_2O_5 + 2HPO_3.$$

(ii) It can also be obtained by passing Cl_2 over heated $AgNO_3$ at about 100°C.

$$2Cl_2 + 4AgNO_3 \longrightarrow 4AgCl + 2N_2O_5 + O_2.$$

Properties

(i) It is stable as colourless crystals (m.p. 41°C) below 8° and decomposes on exposure to sunlight.

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

(ii) **Reaction with water:** It reacts with water exothermally to form nitric acid.

$$N_2O_5 + H_2O \longrightarrow 2HNO_3\ .$$

(iii) **Reaction with halogens:** Dinitrogen pentoxide does not react with Cl_2 and Br_2 but reacts with iodine to form iodine pentoxide.

$$I_2 + N_2O_5 \longrightarrow I_2O_5 + N_2$$

(iv) **Reaction with S and P:**

Sulphur and phosphorus burn in liquid N_2O_5.

$$2S + 5N_2O_5 \longrightarrow (NO)_2S_2O_7 + 8NO_2$$

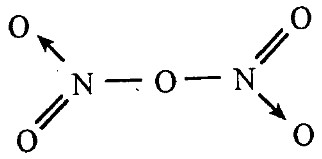
(v) **Reaction with acids:**

N_2O_5 reacts with H_2SO_4, HNO_3 or H_3PO_4 to produce NO_2^+ ions.

$$N_2O_5 + 2H_2SO_4 \longrightarrow 2NO_2^+\,HSO_4^- + H_2O$$

Structure

The structure of N_2O_5 in vapour phase is considered to be:



Nitrogen trioxide (Nitrogen (VI) oxide), NO_3 or N_2O_6

It is very unstable gas and is detected only by the absorption spectrum.

It is prepared by treating vapours of N_2O_5 with 7 – 8 % of ozone.

$$N_2O_5 + O_3 \longrightarrow N_2O_6 + O_2$$

It is reported by Lowry to be a blue gas which decomposes with luminescence at 100°C. The solution in water has oxidising properties due to — O — O — link.

The structure is $O_2N — O — O — NO_2$.

Role of Oxides and Oxyacids of Nitrogen in Environmental Pollution

Air normally contains major amounts of nitrogen (78%) oxygen (21%) and argon (0.9%). In addition to that carbon monoxide, carbon dioxide, nitrogen dioxide, sulphur dioxide and ozone are also present to small extent. The latter gases if present in excessive amounts act as air pollutants. Pollutants are chemicals that are present in excessive concentrations in the atmosphere.

Continuous addition of pollutants causes air pollution. The automobiles are the major polluters of this age. Approximately 60% of the air contaminants are released by motor vehicles and rest by industries and other human activities. The five most important air pollutants which enter the atmosphere are carbon monoxide, sulphur dioxide, nitrogen oxides, hydrocarbons and smoke. Large amounts of carbon dioxide in atmosphere are also injurious.

Carbon monoxide is entirely man-made air pollutant. It is added into the air by incomplete combustion. A motor vehicle on the average exhausts 10g per km of unburnt hydrocarbons.

The reaction of N_2 and O_2 under ordinary conditions takes place to a limited extent but at high temperatures encountered in internal combustion engines. NO is formed, NO is readily oxidised to NO_2 which under *uv* radiations dissociates to NO and O. O_2 combines with O to form ozone, O_3 in the atmosphere.

$$NO_2 \xrightarrow{uv} NO + [O]$$

$$O + O_2 \longrightarrow O_3$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Air contaminants exhausted by motor vehicles also include nitrogen dioxides. Air pollution of this type results in 'smog' which causes reduced visibility and irritation. Temperature beyond certain distance in the atmosphere decreases at higher altitutes. Thus temperature inversions take place. These temperature inversions cause an inversion layer of air above which acts as a lid on the smog and air below

PHOTOCHEMICAL SMOG (SMOKE + FOG)

Photochemical smog is characterised by brown, hazy fumes, which irritate eyes, lungs, leads to cracking of rubber and causes damage to vegetation.

The following steps are involved in photochemical smog:

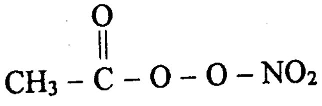
(1) Emission of NO_x and hydrocarbons by vehicles and industry in the atmosphere.

(2) Absorption of sunlight causing photodissociation of NO_x.

(3) Consumption of NO_x and simultaneous build up of the oxidants such as O_3, O, $\dot{O}_2$ and peroxides.

(4) Oxidation of hydrocarbons to produce a vide variety of products – aerosols.

(5) Atmospheric oxidants include H_2O_2, organic peroxides (ROOR), organic hydroperoxides (ROOH) and peroxyacyl nitrate or PAN.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-NO_2$$

PAN

Olefines and NO_x damage plants, leaves and causes bronzing of surfaces.

PAN Damages Vegetation

The following reactions are involved in photochemical SMOG formation:

(1) Primary photochemical reaction

$$NO_2 \xrightarrow{h\upsilon} NO + O$$

(2) Reaction involving oxygen species

$$O_2 + O + M \longrightarrow O_3 + M$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

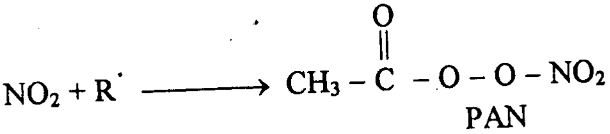
(3) Production of organic free radicals from hydrocarbons

$$O + RH \longrightarrow R^{\cdot} + \text{other products}$$

$$O_3 + RH \longrightarrow R^{\cdot} + \text{other products}$$

(4) Chain propagation, branching and termination

$$NO + R^{\cdot} + O \longrightarrow NO_2 + R$$



$$NO_2 + R^{\cdot} \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-NO_2$$

PAN

A variety of sulphur compounds are also released into the atmosphere from both natural and anthroprogenic sources. The most important of these are the sulphur oxides and hydrogen sulphides.

Among natural sources volcanoes provide 67 % of the oxides of sulphur.

Sunlight plays an important role in smog formation. Hence this type of smog is referred to as photochemical smog. The eye irritation caused by smog is due to the formation of formaldehyde and acrolein from hydrocarbons.

Industrial smog consists primarily of ash and smoke, oxides of nitrogen, SO_2, oil and H_2SO_4 mist and is referred to as 'acid rain'. Industrial operations such as coke refineries, smelters, etc., result in the liberation of SO_2 in atmosphere. Sulphur dioxide can undergo oxidation to SO_3 caused by air or NO_2. Sulphur trioxide reacts with water vapours to produce H_2SO_4 mist. The control of industrial smog can be made by passing SO_2 through scrubbers containing line or MgO when 83 – 85% SO_2 can be removed.

$$Ca(OH_2) + SO_2 \longrightarrow CaSO_3 + H_2O$$

$$MgO + SO_2 \longrightarrow MgSO_3$$

Areas in vicinity to industries contain oxides of sulphur and nitrogen hanging in air. With increase in humidity in air these compounds result in the formation of sulphuric acid and nitric acid in the atmosphere by the following reactions causing acid rain or acid deposition.

$$H_2S + O \longrightarrow HS + OH \xrightarrow{O_2} SO_2 + H_2O$$

$$H_2S + O_3 \longrightarrow SO_2 + H_2O$$

$$SO_2 + O + M \longrightarrow SO_3 + M$$

$$SO_2 + \tfrac{1}{2}O_2 \xrightarrow{h\upsilon} SO_3$$

$$SO_2 + O_3 \xrightarrow{h\upsilon} SO_3 + O_2$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + \tfrac{1}{2}O_2 \longrightarrow H_2SO_4$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O_2 \longrightarrow NO_3 + O$$

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

WATER POLLUTION

Since water is a good solvent, it rarely occurs on the earth in absolutely pure state. Various parameters that determine the quality of water are colour, taste, turbidity, odour, hardness, pH and conductivity. The presence of microorganisms in water is determined by measuring its biological oxygen demand (BOD). The free oxygen present in water is determined and expressed in mg dm^{-3}. BOD level is usually considered as a measure of pollution level of water. If BOD is less than 30 mg dm^{-3} of water, no pollution is noted. BOD values between 30 — 80 mg dm^{-3} indicate mild pollution and over 80 mg dm^{-3} would mean severe water pollution. Water pollution means degradation of the quality of water for human consumption by the introduction of chemicals and biological materials into water. The impurities which make the water unusable are called water pollutants. Certain trace elements in water, such as iron, sodium, zinc, copper, iodine, etc., are essential nutrients. Mercury, lead, arsenic, cadmium, nickel, etc., are considered toxic elements if present beyond permissible limits in water. Lead chromate as indoor paint (although banned in certain countries) poses health hazard, especially to children. Cadmium used in metal plating, causes high blood pressure and damages red blood and kidneys. Cadmium contamination is also found to be responsible for 'ouch ouch' or 'ita itai' disease, which involves painful bone fractures. Increasing amounts of nitrates in drinking water are liable to cause cancer.

Oil may be discharged in river or ocean water during normal shipment and tanker operations or through oil spills. It damages the aquatic life. Certain pollutants, called oxygen-demanding wastes, reduce the amount of oxygen to levels that are dangerous to life. These oxygen demanding wastes include sewage, wastes from food and paper industry. Radioactive pollutants also pose danger to life.

A large number of organic compounds are potential water pollutants. Pesticides, insecticides and weedicides, are used to kill insects, weeds, worms, etc. They find their way into water supply. Most of the pesticides are chlorinated hydrocarbons which are harmful living organism. Dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCB) are typical chemically stable and non-biodegradable insecticides which have harmful effects, especially cause infertility in birds.

The sewage and fertilizer carrying elements contain fairly large amounts of nitrates and phosphates. Blue green algae can flourish due to over-fertilization. These are harmful for fish, because they consume more oxygen than is produced in water which leads to high BOD. The microorganisms responsible for decomposition of dead animals and plants increase in BOD producing more nitrates and phosphates.

International Labour Organization (ILO) in a report has indicated that 70% of the world population, especially in developing countries does not drink safe water. According to World Health Organization (WHO), 80% sickness and diseases such as typhoid, malaria, leprosy, etc., are water borne.

OXYACIDS OF NITROGEN

Typical oxyacids of nitrogen are:

(1)	Hyponitrous acid, HNO or $H_2N_2O_2$	(oxidation state of N: +1)
(2)	Nitrous acid, HNO_2	(oxidation state of N: +3)
(3)	Nitric acid, HNO_3	(oxidation state of N: +5)

In addition to these nitroxylic acid, H_2NO_2 and hyponitric acid, $H_2N_2O_3$ are also known.

1. Hyponitrous Acid, $H_2N_2O_2$

It can be prepared by any one of the following methods:

(i) From nitrous acid

Nitrous acid reacts with hydroxylamine to form hyponitrous acid.

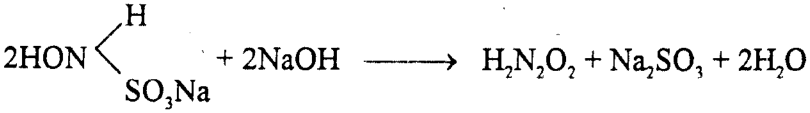
$$HON\boxed{O + H_2}NOH \longrightarrow HO-N=N-OH + H_2O$$

(ii) By Oxidation of hydroxylamine

Hydroxylamine can be oxidised to hyponitrous acid by CuO, Ag_2O or HgO.

$$2H_2NOH + 2Ag_2O \longrightarrow H_2N_2O_2 + 2Ag + 2H_2O$$

(iii) Hyponitrous acid can also be obtained from sodium hydroxylamine N — sulphonate and NaOH.



$$2HON\begin{cases}H\\SO_3Na\end{cases} + 2NaOH \longrightarrow H_2N_2O_2 + Na_2SO_3 + 2H_2O$$

$$H_2N_2O_2 + 2NaOH \longrightarrow Na_2N_2O_2 + 2H_2O$$

(iv) The reaction of $NaNO_3$ or $NaNO_2$ with sodium amalgam results in the deposition of $Na_2N_2O_2$.

$$2NaNO_3 + 8H \xrightarrow{Na/Hg} Na_2N_2O_2 + 4H_2O$$

Ag-salt is precipitated from $Na_2N_2O_2$ by adding $AgNO_3$ to it. Silver hyponitrite reacts with HCl gas in ether to give $H_2N_2O_2$ which remains soluble in ether. Evaporation of ether solution gives crystals of $H_2N_2O_2$.

$$Na_2N_2O_2 + 2AgNO_3 \longrightarrow Ag_2N_2O_2 + 2NaNO_3$$

$$Ag_2N_2O_2 + 2HCl \xrightarrow{Ether} H_2N_2O_2 + 2AgCl$$

Properties

(i) Crystalline hyponitrous acid is explosive in dry state. In addition it decomposes to liberate N_2O.

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$

Sodium hyponitrite (dry) decomposes explosively at 260°.

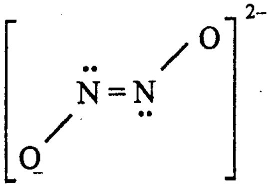
$$3Na_2N_2O_2 \longrightarrow 2NaNO_2 + 2Na_2O + 2N_2$$

(ii) Hyponitrites are reducing agents. Oxidising agents such as $KMnO_4$ react with it to form HNO_3 and alkaline solutions gives nitrites.

$$H_2N_2O_2 + 2O_2 \longrightarrow 2HNO_3$$

Structure

Infrared spectra of Ag, Na and Hg hyponitrites favour the following structure of anion:



2. Nitrous Acid, HNO_2

Preparation

Pure nitrous acid has not been isolated because it is unstable and readily decomposes. It is generally prepared by the following methods:

(i) From Barium Nitrite

After adding H_2SO_4 to a solution of barium nitrite the precipitated $BaSO_4$ is filtered leaving nitrous acid in solution.

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HNO_2$$

(ii) From N_2O_3

A mixture of NO and NO_2 is dissolved in ice cold water to get nitrous acid solution.

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

Properties

Nitrous acid behaves as a weak acid in solution. It decomposes easily in water.

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

(i) Action of Oxidising Agents

HNO_2 acts as a reducing agent and would reduce oxidising agents, *e.g.*, $KMnO_4$, H_2O, $AgBrO_3$, etc., which will in turn oxidise HNO_2 to HNO_3. For example,

$$2KMnO_4 + 3H_2SO_4 + 5NaNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5NaNO_3$$

$$H_2O_2 + NaNO_2 \longrightarrow NaNO_3 + H_2O$$

$$Br_2 + NaNO_2 + H_2O \longrightarrow NaNO_3 + 2HBr$$

$$AgBrO_3 + 3HNO_2 \longrightarrow AgBr + 3HNO_3$$

(ii) As Oxidising Agent

HNO_2 also acts as an oxidising agent and oxidises Fe (II) to Fe (III), Sn (II) to Sn (IV), etc. and itself is reduced to mainly NO but sometimes to N_2O and N_2.

(a) Reactions in which HNO_2 is reduced to NO:

$$FeSO_4 + 2NaNO_2 \longrightarrow Fe(NO_2)_2 + Na_2SO_4$$

$$6Fe(NO_2)_2 \longrightarrow 2Fe_2O_3 + Fe_2O_3 + N_2O_5 + 10NO$$

$$K_4Fe(CN)_6 + HNO_3 + CH_3COOH \longrightarrow K_3[Fe(CN)_6] + CH_3COOK + NO + H_2O$$

$$2KI + 2HNO_3 + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2NO + 2H_2O$$

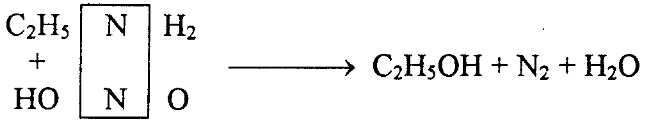
$$H_3AsO_3 + 2HNO_2 \longrightarrow H_3AsO_4 + 2NO + H_2O$$

(b) Reactions in which HNO_2 is reduced to N_2O and N_2:

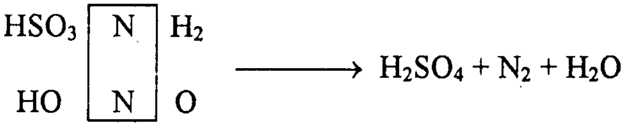
$$2SnCl_2 + 2HNO_2 + 4HCl \longrightarrow 2SnCl_4 + N_2O + 3H_2O$$

$$N_3H + HNO_2 \longrightarrow N_2O + N_2 + H_2O$$

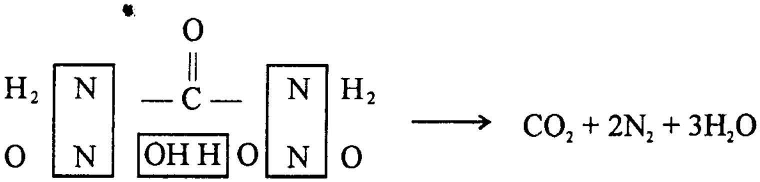
(iii) Reaction with Compounds Containing Amino Groups:



$$\begin{array}{c|c|c} C_2H_5 & N & H_2 \\ + & & \\ HO & N & O \end{array} \longrightarrow C_2H_5OH + N_2 + H_2O$$



$$\begin{array}{c|c|c} HSO_3 & N & H_2 \\ & & \\ HO & N & O \end{array} \longrightarrow H_2SO_4 + N_2 + H_2O$$



$$\begin{array}{ccccc} H_2 & \boxed{N} & -\overset{\overset{O}{\|}}{C}- & \boxed{N} & H_2 \\ O & \boxed{N} & \boxed{OH\,H}\,O & \boxed{N} & O \end{array} \longrightarrow CO_2 + 2N_2 + 3H_2O$$

(iv) Reaction with Sulphides

Sulphides are oxidised to free sulphur.

$$H_2S + 2NaNO_2 + H_2SO_4 \longrightarrow S + 2NO + Na_2SO_4 + 2H_2O$$

(Sodium nitrite is produced from $NaNO_3$ by heating with Pb):

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

(v) Formation of Alkyl Nitrites

Alkyl nitrites are obtained by the action of alcohols on acidified solutions of sodium nitrite.

$$ROH + HNO_2 \longrightarrow RNO_2 + H_2O$$

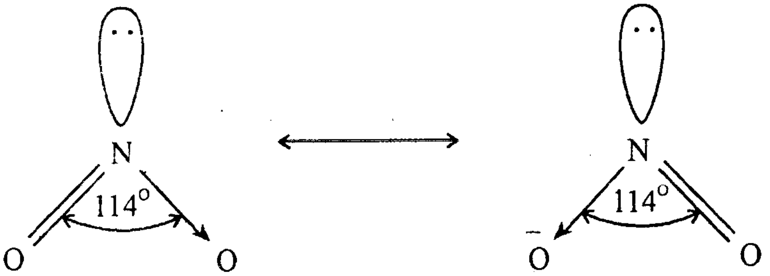
Structure

HNO_2 has the structure:

$$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad \text{or} \qquad HO-N=O$$

The presence of a lone pair of electrons imparts basic and reducing properties to HNO_2. The N = O double bond is responsible for acidic and oxidising properties. NO_2^- ion is a coordinating agent and forms coordinating compounds of the type, $Na_3[CO\,(NO_2)_6]$.

The structure of NO_2^- ion is considered to be resonance hybrid of the following two canonical forms



3. Nitric Acid, HNO_3

Nitric acid is one of the important chemicals of industrial importance.

Generally, the following methods are used for large-scale production of HNO_3.

Preparation

(i) From Nitrates

HNO_3 can be prepared on commercial scale by heating a mixture of $NaNO_3$ and concentrated H_2SO_4 in iron retorts at 200°C and HNO_3 is distilled off.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3.$$

The yellow colour of HNO_3 is due to the presence of NO_2 in it which can be removed by distillation in vacuum.

(ii) From Air (Arc Process)

Air (a mixture of mainly N_2 and O_2) is passed through high tension electric discharge or an electric arc at 3000°C. N_2 and O_2 combine to give NO. This is the most important arc process and called **Birkland-Eyde Process.**

$$N_2 + O_2 \longrightarrow 2NO - 180\ \text{kJ/mole}$$

Only 5% conversion take place at 3000°C. On cooling NO combines with atmospheric oxygen to form NO_2.

$$2NO + O_2 \longrightarrow 2NO_2$$

The brown fumes of NO_2 are passed through water on counter current principle *i.e.*, the vapours going upwards and water trickling downwards in quartz vessel. HNO_3 is obtained in this way.

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

The escaping gases may contain some unused NO and NO_2 which are absorbed in alkali solutions to produce nitrites.

$$NO + NO_2 + Na_2CO_3 \longrightarrow 2NaNO_2 + CO_2$$

(iii) From ammonia (Ostwald's Process)

This process consists of oxidising ammonia to NO and NO is converted to NO_2 which reacts with water to give HNO_3.

Ammonia is mixed with 10 times its volume of air and heated to 600°C in presence of Pt gauze catalyst NH_3 is oxidised to NO.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O + 899\ \text{kJ/mole}$$

The exothermic reaction proceeds without supply of heat except the initial heating. About 90% NH_3 is converted to NO under these conditions.

NO is converted to NO_2 in presence of air or oxygen and passed through the absorption tower as mentioned above in arc process.

$$2NO + O_2 \longrightarrow 2NO_2 + 116\ \text{kJ/mole}$$

$$2NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Pure HNO_3 is prepared by distillation of the crude product under reduced pressure and passing ozone through the distillate.

Properties

HNO_3 is a fuming liquid and freezes to a snow white solid at – 46°C. It is freely miscible with water.

It is available in the market as:

(a) **Fuming nitric acid** – a red liquid made by bubbling NO_2 gas through concentrated HNO_3.

(b) **Concentrated nitric acid** – of density 1.5, containing 98% HNO_3.

(c) **Ordinary strong nitric acid** – of density 1.4, containing about 65% HNO_3.

Reactions

HNO_3 exhibits three types of reactions: (a) as an acid, (b) as an oxidising agent, and (c) as a nitrating agent.

(a) Acid Reaction of HNO_3

It is ionised in aqueous medium to H^+ and NO_3^- which indicates its acidic behaviour. Thus, it reacts with bases such as metal oxides, carbonates and hydroxides to give nitrates.

(i) With Metal Oxides

Oxides are converted to nitrates.

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

$$ZnO + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O$$

(ii) With Carbonates

Carbonates are also converted to nitrates with evolution of CO_2.

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2.$$

(iii) With Hydroxides

HNO_3 neutralises the hydroxides to give nitrates.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

$$6Fe(OH)_2 + 20HNO_3 \longrightarrow 6Fe(NO_3)_3 + 2NO + 16H_2O$$

$$Ca(OH)_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + 2H_2O$$

(iv) With Sulphides

It reacts with sulphides to liberate H_2S.

$$MnS + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2S$$

(b) Oxidising Action of HNO_3

Nitric acid is a strong oxidising agent. It oxidises other substances but is itself reduced to NO_2 or NO.

$$\underset{\text{(Concentrated)}}{2X + 2HNO_3} \longrightarrow 2NO_2 + 2XO + H_2$$

$$\underset{\text{(Dilute)}}{3X + 2HNO_3} \longrightarrow 2NO + 3XO + H_2O$$

The oxidising power of nitric acid depends upon concentration of the acid, nature of the reducing agents (its position in electrochemical series and the temperature of the reaction).

The oxidising actions of HNO_3 may be classified according to the nature of the reducing agent, such as:

1. Action of HNO_3 on Metals

The reaction of HNO_3 with metals is governed mainly by the concentration of the acid and temperature of the reactions.

Thus,

- very dilute acid reacts to give N_2O (oxidation state of N changes from + 5 in HNO_3 to + 1).
- moderately dilute acid solutions give NO (Oxidation state of N changes from + 5 in HNO_3 to + 2).
- concentrated HNO_3 in hot state gives NO_2 (change of oxidation state of N from + 5 in HNO_3 to + 4).
- vapours of HNO_3 when passed over red-hot metal gives N_2 (change of oxidation state of N from + 5 to 0).

For Example

(i) Zinc reacts with very dilute HNO_3 in cold to give N_2O.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(ii) Zn, Fe and Sn, etc., react with extremely dilute HNO_3 in cold and liberates NH_3 which combines with unreacted HNO_3 to form NH_4NO_3.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(iii) Moderately dilute HNO_3 always reacts with metals to liberate NO_2.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$$

(iv) Concentrated and hot HNO_3 reacts with metals to liberate NO_2.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Fe + 6HNO_3 \longrightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

(v) When vapours of HNO_3 are passed over heated Cu, nitrogen gas is evolved.

$$5Cu + 12HNO_3 \longrightarrow 5Cu(NO_3)_2 + 6H_2O + N_2$$

$$5Cu(NO_3)_2 \longrightarrow 5CuO + 10NO_2 + 2.5\ O_2$$

2. Action of HNO_3 on Non-Metals

Concentrated nitric acid reacts with non-metals in hot state to liberate NO_2 and forms oxides or oxyacids of corresponding non-metals.

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$S + 4HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 10NO_2 + H_2O$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

3. Oxidizing Action of HNO_3 on Various Compounds

Nitric acid reacts with various compounds in aqueous solution to liberate NO.

$$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$$

$$3Fe^{2+} + 2HNO_3 + 3H^+ \longrightarrow 3Fe^{3+} + NO + 2H_2O$$

Hot and concentrated HNO_3 reacts with reducing agents to liberate NO_2 gas.

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

$$PbS + 8HNO_3 \longrightarrow PbSO_4 + 8NO_2 + 4H_2O$$

$$CuS + 8HNO_3 \longrightarrow CuSO_4 + 8NO_2 + 4H_2O$$

Some metals and their compounds cannot be oxidised by concentrated hot HNO_3. **A mixture of HNO_3 and HCl in the ratio of 1 : 3 by volume is called aqua regia** and can oxidise such compounds and metals like Au, Pt and Pd. HNO_3 oxidises HCl to form Cl_2 and NOCl (nitrosyl chloride). The activity of aqua regia is due to the chlorine liberated according to the reaction:

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$

The liberated chlorine reacts with metals and compounds to form soluble chlorides or chloro complexes.

$$Au + 3HCl + HNO_3 \longrightarrow AuCl_3 + NO + 2H_2O$$

(c) Action of HNO_3 on Organic Compounds

It oxidises many organic compounds to CO_2. Sometimes the reaction proceeds with explosive violence. Concentrated HNO_3 gives nitro derivatives of organic compounds.

$$C_3H_5(OH)_3 + 3HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3H_2O$$

(Trinitroglycerin)

Trinitrotoluene (TNT) is also formed by nitrating toluene in presence of concentrated H_2SO_4.

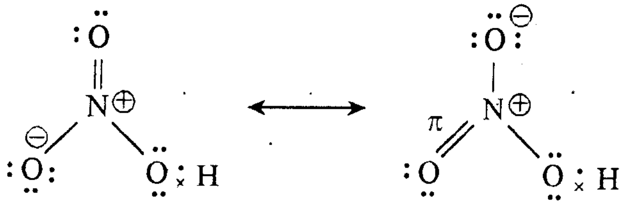
$$C_6H_5CH_3 + 3HNO_3 \longrightarrow (NO_2)_2\, C_6H_2CH_3$$

HNO_3 reacts with benzene in presence of concentrated H_2SO_4 to form nitrobenzene in the following manner:

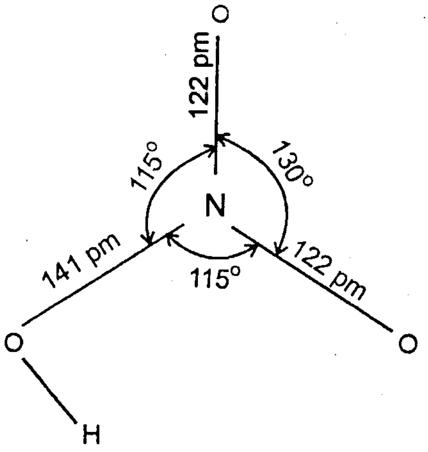
$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$$

Structure

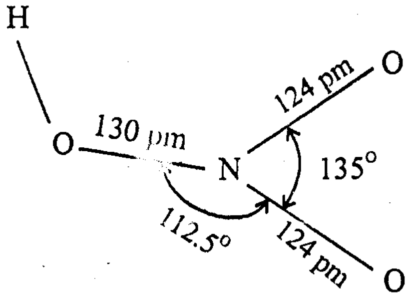
Nitric acid can be written in two equivalent resonance forms:



Electron diffraction measurements have shown the following structure for HNO_3 in vapour phase.



The X-ray measurements of crystals of HNO_3 at − 42° have shown the following structure:



Compounds in which Nitrogen Atom is Tetrahedrally Hybridized

Ammonia, hydrazine and hydroxylamine are the compounds of nitrogen in which nitrogen atom is tetrahedrally hybridised. These are considered to be the hydrides of nitrogen Ammonia molecule contains tetrahedrally hybridised nitrogen atom which consists of three σ bonds and one hybrid orbital occupied by a lone pair.

We shall now discuss individually the chemistry of only NH_3, N_2H_4 and NH_2OH.

1. Ammonia, NH_3:

Ammonia usually exists as a colourles gas but may be preserved as a colourles liquid or ice-like solid. It can be obtained by either of the following methods:

(i) Laboratory Method

In laboratory, NH_3 gas can be prepared by heating an ammonium salt with lime or alkalies.

$$2NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3 + H_2O$$

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

Ammonia can also be obtained by hydrolysis of metal nitrides.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

(ii) From Coal

Destructive distillation of coal evolves NH_3 along with coal gas and other volatile matter. The gases are passed through water and aqueous solution treated with lime to get ammonia. It may be preserved by passing through water or acid solutions usually dilute H_2SO_4.

(iii) Haber Process

Most of the commercial ammonia is now prepared by fixing atmospheric nitrogen. A mixture of 1 volume of nitrogen and 3 volumes of hydrogen is compressed to 200 – 500 atmospheric pressure and passed over catalyst consisting of a mixture of Fe with little Mo (molybdenum) at 500°C. The gases coming out of the catalyst chambers contain 12 per cent ammonia and are passed through refrigerated brine to liquify ammonia. The residual gases are recycled. The sketch of Haber process is shown in Figure 14.4.

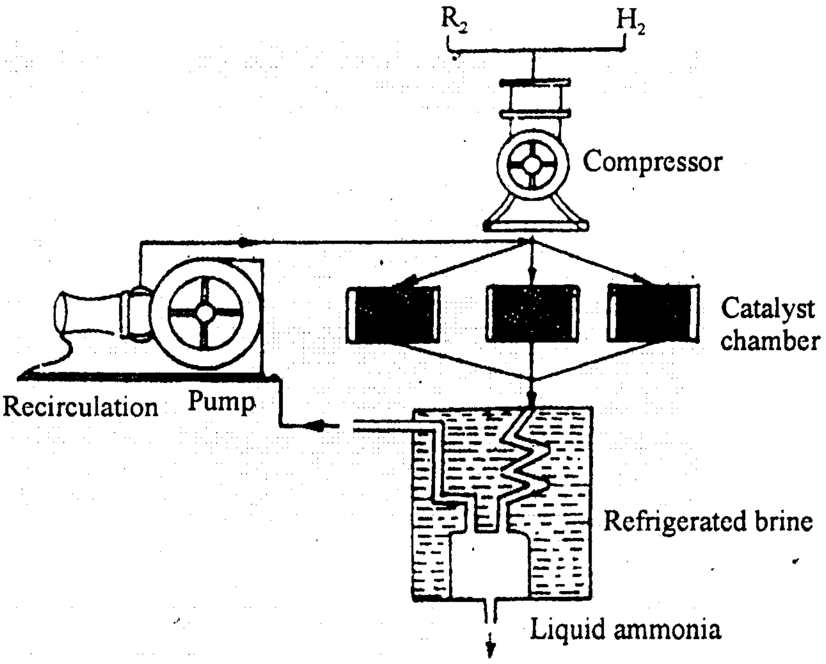


Fig. 14.4. Haber Process for the manufacture of ammonia.

Haber process is the cheapest method for the manufacture of ammonia and is one of the important methods of fixing atmospheric nitrogen.

The reaction between nitrogen and hydrogen is exothermic and reversible process and is accompanied by decrease in volume.

$$N_2 + 3H_2 \rightleftharpoons NH_3 + 100 \text{ kJ/mole}$$

According to Le Chatelier's principle, the most favourable conditions of the reaction are:

(a) High pressure due to decrease in volume of the product.

(b) The temperature must be kept as low as possible. In presence of catalyst the optimum temperature is 500°C.

(iv) Cyanamide Process

Large quantities of ammonia are also obtained by hydrolysis of calcium cyanamide with steam under pressure.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Calcium cyanamide itself is prepared by heating CaO with C in electric furnace in presence of N_2 at 1100°C.

(v) **Serpeks' Process**

Ammonia is also obtained as a byproduct in the purification of bauxite (See metallurgy of aluminium).

Properties

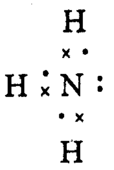
Ammonia is a colourless gas with irritating odour. It is lighter than air and freely soluble in water, ether and alcohol. On heating aqueous solutions gas is removed.

NH_3 can be liquefied and liquid ammonia boils at –33.35°C. It can be solidified as white crystals.

Chemical Reactions

(i) Ammonia as a Base

The basic character is manifested by ammonia due to the presence of lone pair of electrons. The Lewis structure is :

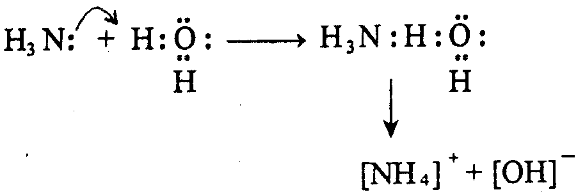


$$\begin{array}{c} H \\ \times\bullet \\ H \overset{\bullet}{\times} N : \\ \bullet\times \\ H \end{array}$$

The following reactions indicate its basic properties:

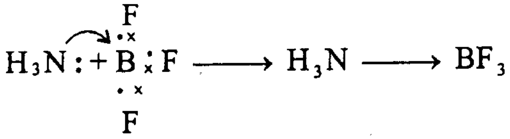
(a) $H^+ + :NH_3 \longrightarrow [H^+ \longleftarrow NH_3]$ or NH_4^+

(b)



$$H_3N: + H:\underset{\underset{H}{\cdot\cdot}}{\ddot{O}}: \longrightarrow H_3N:H:\underset{\underset{H}{\cdot\cdot}}{\ddot{O}}: \longrightarrow [NH_4]^+ + [OH]^-$$

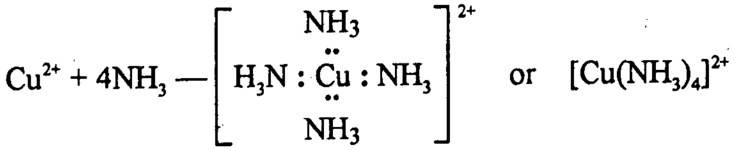
(c)



$$H_3N: + \underset{F}{\overset{F}{B}}\,\overset{\bullet}{\times}F \longrightarrow H_3N \longrightarrow BF_3$$

(d) Ammonia reacts with transition metal ions. The reaction takes place by the donation of lone pair of electrons from: NH_3 to '*d*' orbitals of metal ions.

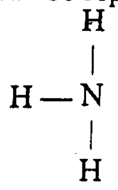
$$Ag^+ + 2NH_3 \longrightarrow [H_3N : Ag\ : NH_3]^+ \text{ or } [Ag(NH_3)_2]^+$$



$$Cu^{2+} + 4NH_3 — \left[\begin{array}{c} NH_3 \\ \cdot\cdot \\ H_3N : Cu : NH_3 \\ \cdot\cdot \\ NH_3 \end{array}\right]^{2+} \text{ or } [Cu(NH_3)_4]^{2+}$$

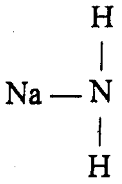
(ii) Ammonia as a Weak Acid

NH_3 can also show weak acidic properties. Thus the hydrogen atoms of ammonia can be replaced by metals.



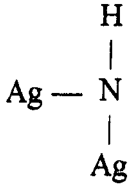
NH_3

Ammonia



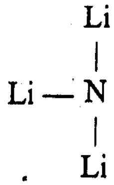
$NaNH_2$

Sodium amide



$NHAg_2$

Silver amide



Li_3N

Lithium nitride

(iii) Non-Ionic Reactions

(a) Decomposition: Ammonia in decomposed into elements by the action of electric sparks or when strongly heated.

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(b) Oxidation: Ammonia may be oxidised by oxygen or oxides of metals (Cu, Fe, etc.) to N_2.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

(c) Action of chlorine and iodine: When Cl_2 is passed through concentrated solution of ammonia, nitrogen is liberated.

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

If excess of chlorine is passed through this solution, **nitrogen trichloride** is obtained.

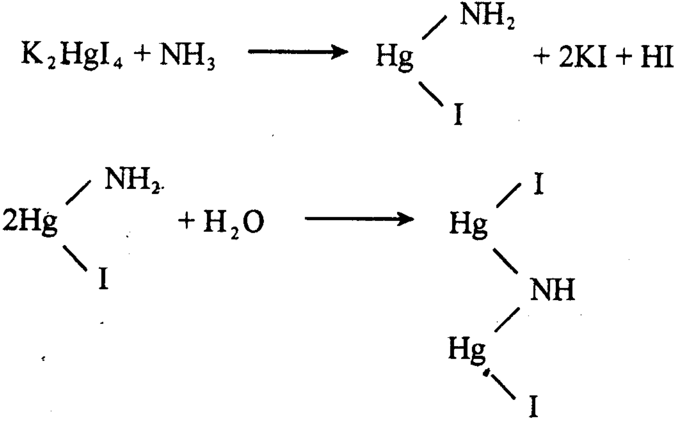
$$NH_4Cl + 3Cl_2 \longrightarrow NCl_3 + 4HCl$$

Iodine reacts with a concentrated ammonia to form $NI_2 . NH_3$.

(d) Reaction with mercurous chloride: Ammonia reacts with Hg_2Cl_2 to liberate free mercury.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg + Hg\,(NH_2)Cl + NH_4Cl$$

(e) Reaction with Nessler's reagent: Nessler's reagent, K_2HgI_4, reacts with ammonia to give a brown precipitate.



$$K_2HgI_4 + NH_3 \longrightarrow Hg(NH_2)I + 2KI + HI$$

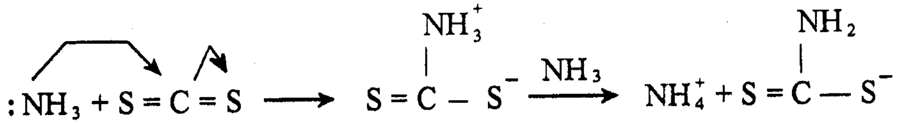
$$2Hg(NH_2)I + H_2O \longrightarrow IHg{-}NH{-}HgI$$

Iodide of Millon's base.

(f) **Formation of Halogen derivatives of NH_3:** Ammonia reacts with hypochlorous acid to form nitrogen trichloride.

$$NH_3 + 3HOCl \longrightarrow NCl_3 + 3H_2O$$

(g) **Reaction with CS_2:** Ammonia reacts with CS_2 with attack on the double bond.



$$:NH_3 + S=C=S \longrightarrow S=\overset{NH_3^+}{\overset{|}{C}}-S^- \xrightarrow{NH_3} NH_4^+ + S=\overset{NH_2}{\overset{|}{C}}-S^-$$

Liquid Ammonia

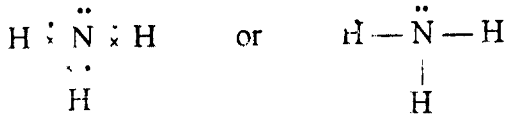
Liquid ammonia acts as a very good non-aqueous solvent. But the property of NH_3 as an associated solvent is less generalised than H_2O as a solvent. However, the action of liquid ammonia and water is quite similar as indicated by the following ionizations:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

H_3O^+ ions in water would show acidic behaviour and OH^- ions would give basic properties. Similarly, NH_4^+ ions in liquid ammonia would act as acids and NH_2^- ions as bases.

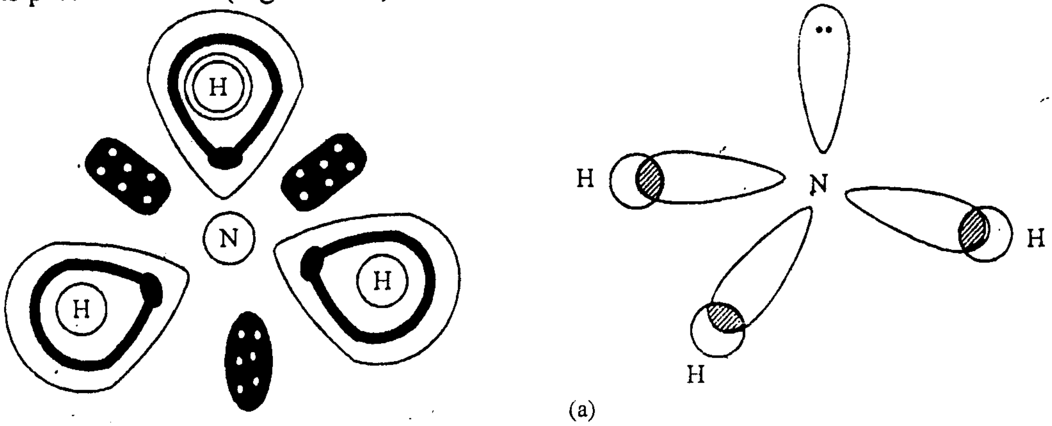
Structure

The octet of electrons around the nitrogen is derived from five electrons of nitrogen itself and one electron from each of the three hydrogen atoms.



$$H\,\overset{\cdot\cdot}{\underset{\underset{\textstyle H}{\times\cdot}}{\vdots N\times}}\,H \quad \text{or} \quad H-\overset{\cdot\cdot}{\underset{\underset{\textstyle H}{|}}{N}}-H$$

The molecule of NH_3 is obtained by sp^3 hybridization and pyramid structure is predicted for it (Figure 14.5).



(a)

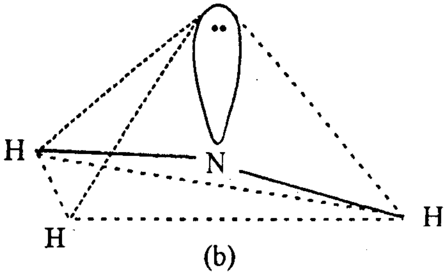


Fig. 14.5. Structure of NH_3 (a) sp^3 hybridized orbitals of N (b) Pyramidal structure.

Uses

Ammonia is used —

(i) in the manufacture of HNO_3, Na_2CO_3, and ammonium salts,

(ii) in fertilizers and explosives,

(iii) as a reagent in the laboratory,

(iv) for ice-making.

2. Hydrazine, N_2H_4

Hydrazine is a poisonous and colourless gas. It is prepared by any one of the following methods:

Preparation

(i) By Oxidation of NH_3

In Raschig's methods sodium hypochlorite is used as an oxidising agent.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

$$NH_2Cl + NH_3 \longrightarrow NH_2 - NH_2 + HCl$$

Any traces of Fe^{3+} and Cu^{2+} ions should be absent because they reduce the yield due to the following reaction:

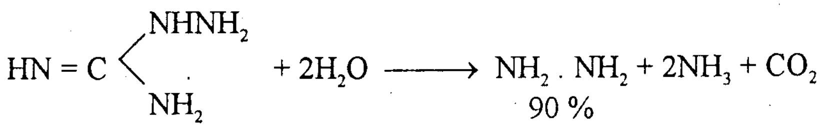
$$2NH_2Cl + NH_2NH_2 \longrightarrow 2NH_4Cl + N_2$$

(ii) From Urea:

A mixture of NaOCl and urea solution is heated to 100°C to get hydrazine

$$2NaOH + O = C(NH_2)_2 + NaOCl \xrightarrow{100^\circ} N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

(iii) By Alkaline Hydrolysis of Amino Guanidine



$$HN = C\begin{cases} NHNH_2 \\ NH_2 \end{cases} + 2H_2O \longrightarrow \underset{90\ \%}{NH_2 . NH_2} + 2NH_3 + CO_2$$

(aminoguanidine)

(iv) From Nitric Oxide

Nitric oxide can be reduced by sodium amalgam in presence of saturated solution of K_2SO_3.

$$2NO + 6H \longrightarrow N_2H_4 . H_2O$$

Anhydrous hydrazine can be prepared by any one of the following reactions:

(a) $N_2H_4 . HCl + CH_3ONa \longrightarrow N_2H_4 + CH_3OH + NaCl$

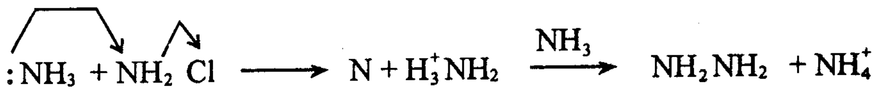
(b) $N_2H_4 . H_2O + Na_2B_4O_7 . 10H_2O \xrightarrow{200^\circ} N_2H_4$

(c) $C_6H_{11}NH_2 + N_2H_4HCl \longrightarrow C_6H_{11}NH_3Cl + N_2H_4$

(Hexahydraniline)

(d) $N_2H_5^+ HSO_4^- \xrightarrow[\text{alkalies}]{\text{Distil with}} N_2H_4 + H_2SO_4$

(e)



$:NH_3 + NH_2\ Cl \longrightarrow N + H_3^+NH_2 \xrightarrow{NH_3} NH_2NH_2 + NH_4^+$

Properties

Anhydrous hydrazine freezes at 1.8°C and boils at 113.5°C. It is thermally stable but highly reactive.

Reactions

The following are the typical reactions of hydrazine:

(i) Action of Heat

Hydrazine decomposes to N_2 and NH_3 on heating.

$$3N_2H_4 \longrightarrow N_2 + 4NH_3$$

(ii) Reaction with Air or Oxygen

N_2H_4 burns in air to liberate N_2.

$$3N_2H_4 \longrightarrow N_2 + 4NH_3$$

(iii) Reaction with Halogens

The reaction of hydrazine with halogens is quite vigorous.

$$N_2H_4 + 2Cl_2 \longrightarrow ClHN-NHCl + 2HCl$$

$$ClH\ \boxed{N-N}\ HCl \longrightarrow N_2 + 2HCl$$

$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$$

(iv) Reaction with H_2O_2

Liquid hydrazine undergoes exothermic reaction with liquid H_2O_2 to give gaseous N_2 and steam. The reaction is also accompanied with tremendous increase in volume and thus it finds its use as rocket fuel.

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

(v) Basic Action of Hydrazine

Aqueous hydrazine is weakly basic as is shown by the following reactions:

$$N_2H_4 + HCl \longrightarrow N_2H_4 \,.\, HCl \text{ or } N_2H_5^+Cl^-$$

$$Zn^{2+} + 4NH_2NH_2 \longrightarrow [Zn(NH_2NH_2)_4]^{2+}$$

(vi) Nucleophilic Displacement on Carbon

$$CH_3Br + NH_2NH_2 \longrightarrow CH_3NHNH_2 + HBr$$

(Methyl hydrazine)

(vii) Condensation Products with Aldehydes and Ketones

Aldehydes and ketones undergo condensation reactions with hydrazine to give **hydrazones and azines.**

$$CH_3CH\boxed{O + H_2}N - NH_2 \longrightarrow CH_3CH = N - NH_2$$

(Hydrazone)

$$CH_3CH\boxed{O + H_2}\,N - N\boxed{H_2 + O}\,HCCH_3 \longrightarrow CH_3CH = N - N = CHCH_3$$

(Azine)

Structure

The structure of hydrazine is similar to H_2O_2 and it bears the same relation to ammonia as H_2O_2 to water. In the solid state (m.p. 1.8°C), the molecules of hydrazine are arranged in zig-zag chains. The structure of hydrazine is represented as shown in Figure 14.6.

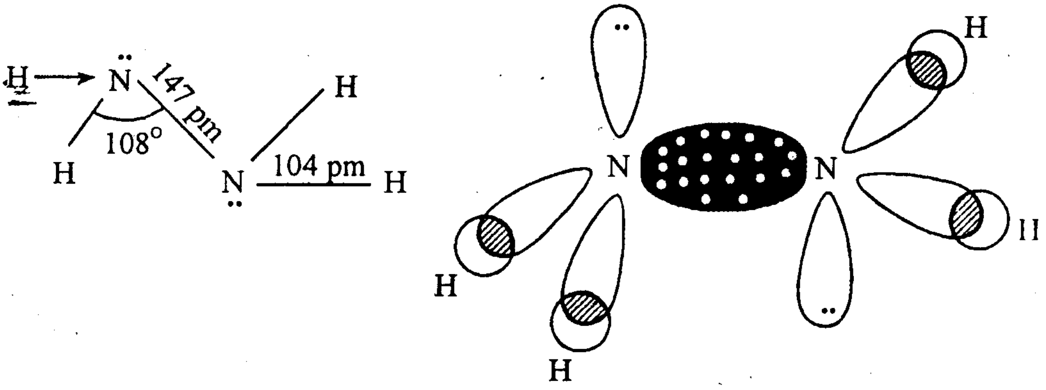


Fig. 14.6. Structure of hydrazine (a) Valence structure (b) Orbital overlap.

HYDROGEN AZIDE AND HYDRAZOIC ACID

Hydrazine and some of its derivatives burn in air with evolution of tremendous amount of heat and are used as rocket fuels.

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -622KJ$$

Since the reaction is highly exothermic, hydrazine is also used in fuel cell. Dissolved oxygen from boiler water is also removed with hydrazine as products of reaction are in gaseous state.

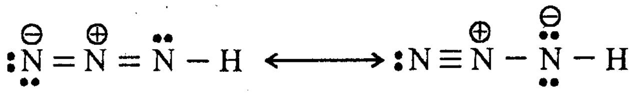
The oxidation of hydrazine in acidic solution by nitrite ion produces hydrogen azide, HN_3.

$$N_2H_4 + H^+ + NO_2^- \longrightarrow HN_3 + 2H_2O$$

Pure hydrogen azide is a colourless liquid (b.p. 37°C). It is very unstable and detonates when subjected to shock.

The aqueous solution of HN_3 is a weak acid and is called hydrazoic acid. The salts of hydrazoic acid are called azides. Azides resemble chlorides. Silver azide, AgN_3 is insoluble in water like AgCl and behaves as a pseudohalide. Pb, Hg and Ba azides explode when struck and are used in detonation.

The structure of HN_3 is :



$$:\overset{\ominus}{\underset{\cdot\cdot}{N}} = \overset{\oplus}{N} = \overset{\cdot\cdot}{N} - H \longleftrightarrow :N \equiv \overset{\oplus}{N} - \overset{\ominus}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}} - H$$

Sodium salt is prepared from sodamide as follows:

$$3NaNH_2 + NaNO_3 \xrightarrow{\Delta} NaN_3 + 3NaOH + NH_3$$

$$2NaNH_2 + N_2O(g) \xrightarrow{\Delta} NaN_3 + NaOH + NH_3$$

Sodium azide is not explosive and decomposes on heating to 300°C.

$$2NaN_3(s) \xrightarrow{\Delta} 2Na + 3N_2$$

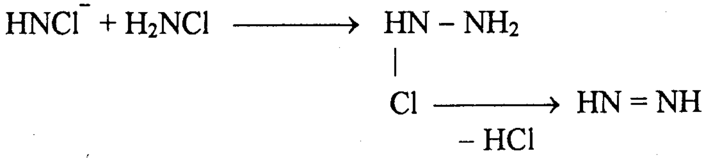
Diamine:

The parent compound, HN = NH cannot be isolated easily. It is usually obtained by oxidation of hydrazine with oxidizing agents *e.g.*, oxygen, peroxides, chloramines – T etc.

$$N_2H_4 \longrightarrow N_2H_2$$

It is also formed by reaction of alkali with chloramine – T

$$H_2NCl \xrightarrow{OH^-} HNCl^-$$



$$HNCl^- + H_2NCl \longrightarrow \underset{\displaystyle Cl}{\underset{|}{HN}} - NH_2 \xrightarrow[-HCl]{} HN = NH$$

Diamine decomposes to give N_2 and H_2 or N_2 and hydrazine.

$$H_2N_2 \longrightarrow N_2 + H_2$$

or

$$2H_2N_2 \longrightarrow N_2 + N_2H_4$$

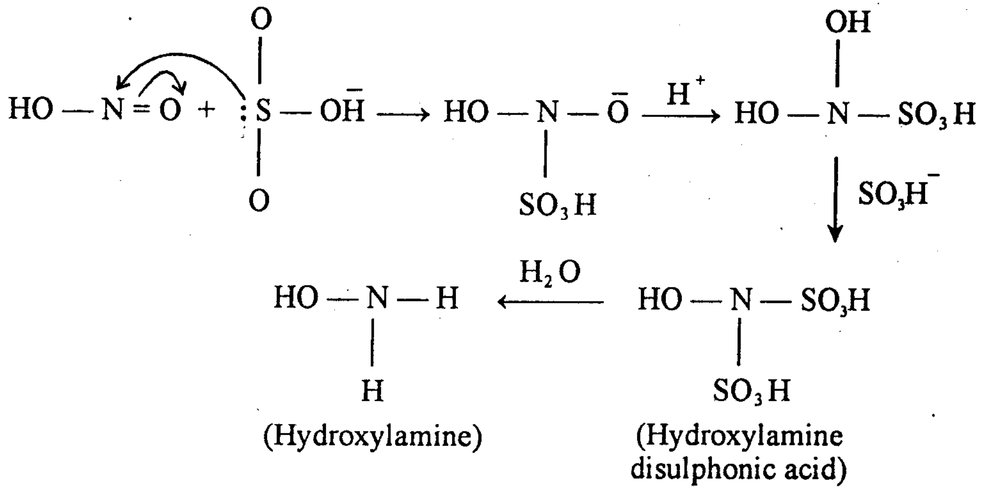
3. Hydroxylamine, NH_2OH

It may be regarded as derivative of ammonia and is prepared by any one of the following methods.

Preparation

(i) By Reduction of HNO_2

Nitrous acid can be reduced by H_2SO_3. The reaction proceeds by formation and breakage of covalent bonds. The probable course of this reaction is:



(ii) By Electrolytic Reduction of HNO_3

Electrolytic reduction of HNO_3 at the cathode gives HNO_2 first which is further reduced to hydroxylamine.

$$HNO_3 + 2H \longrightarrow HNO_2 + H_2O$$

$$HNO_2 + 4H \longrightarrow NH_2OH + H_2O$$

(iii) From NO

NO may be reduced to NH_2OH by Sn and concentrated HCl.

$$NO + 3H \xrightarrow{Sn/HCl} NH_2OH$$

(iv) From Ethyl Nitrate

Ethyl nitrate is reduced to NH_2OH by tin and HCl.

$$C_2H_5NO_3 + 6H \longrightarrow NH_2OH + C_2H_5OH + H_2O$$

Anhydrous hydroxylamine can be prepared by the following methods:

(i) Hydroxylamine hydrochloride can be treated with sodium methioxide.

$$NH_2OH \cdot HCl + CH_3ONa \longrightarrow NH_2OH + CH_3OH + NaCl$$

Hydroxylamine is soluble in methyl alcohol and is thus separated from sodium chloride. NH_2OH is made pure by removing CH_3OH by distillation under reduced pressure.

(ii) When Hydroxylamine phosphate is heated, NH_2OH is obtained.

$$(NH_2OH)_3 \cdot H_3PO_4 \longrightarrow 3NH_2OH + H_3PO_4$$

Properties

Hydroxylamine is a white solid which in the pure state exists as needles which melt at 33°C. It is soluble in water and ether. It is thermally unstable.

Reactions

(i) Hydroxylamine forms salts with HCl and H_2SO_4 and is also available in these forms.

$$NH_2OH \cdot HCl \text{ and } NH_2OH \cdot H_2SO_4$$

(ii) It is a good reducing agent and reacts readily with powerful oxidising agents.

$$2NH_2OH + 2Cl_2 \longrightarrow N_2O + H_2O + 4HCl$$

$$2NH_2OH + 4FeCl_3 \longrightarrow 4FeCl_2 + N_2O + 4HCl$$

(iii) **Reducing action in alkaline solution:** Hydroxylamine precipitates metallic gold from auric chloride, cuprous oxide from Fehling's solution, and metallic silver from ammoniacal solution of silver nitrate.

$$2NH_2OH + 4CuO \longrightarrow N_2O + 2Cu_2O + 3H_2O$$

Hydroxylamine reduces nitrous acid to N_2O.

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$$

Hydroxylamine reduces mercuric chloride first to mercurous chloride and then to mercury. Iodine is reduced to iodide ion in presence of $NaHCO_3$ or sodium acetate. Br_2 and Cl_2 are attacked readily.

$$4NaHCO_3 + 2I_2 + 2NH_2OH \longrightarrow N_2O + 4NaI + 4CO_2 + 5H_2O$$

(iv) **Reaction with H_2O_2:** H_2O_2 and NH_2OH undergo mutual reduction.

$$HONH_2 + H_2O_2 \longrightarrow NH_3 + O_2 + H_2O$$

(v) **Reducing action of hydroxylamine in acid solution:** Hydroxylamine hydrochloride reduces HNO_3 to NO.

$$NH_2OH \,.\, HCl + HNO_3 \longrightarrow 2NO + 2H_2O + HCl$$

(vi) **Oxidising action:** Hydroxylamine oxidises $Fe(OH)_2$ to ferric hydroxide quantitatively.

$$2Fe(OH)_2 + NH_2OH + H_2O \longrightarrow 2Fe(OH)_3 + NH_3$$

$$NH_2OH + Na_3AsO_3 \longrightarrow Na_3AsO_4 + NH_3$$

Sodium arsenite is oxidised to sodium arsenate.

Hydroxlamine hydrochloride oxidises

HI to I_2, $SnCl_2$ to $SnCl_4$ and SO_2 to $(NH_4)_2SO_4$

$$NH_2OH + 2HI \longrightarrow NH_3 + H_2O + I_2$$

PHOSPHORUS

Phosphorus is the second element of the V group. It resembles nitrogen in many respects but possesses some distinct differences as well.

Occurrence

Phosphorus is too reactive to exist in the free state. In fact phosphorus is the only element of Group V which does not occur in the free state. It is widely distributed in the form of phosphates. The important phosphate minerals are:

Phosphorite	$Ca_3(PO_4)_2$
Chlorapatite	$3Ca_3(PO_4)_2 \,.\, CaCl_2$
Florapatite	$3Ca_3(PO_4)_2 .\, CaF_2$

Phosphorus is an essential constituent of all living matter – animals and vegetables. Bones, teeth and muscle tissues contain phosphorus Plants take up *Phosphorus* from soil as soluble phosphates. Foods, such as eggs, beans, milk, peas, etc., contain phosphorus.

Preparation

White phosphorus is obtained from bone ash or a mineral phosphate.

(i) **From Bone Ash:**

Bones are boiled with water to remove gelatine and then treated with CS_2 to remove fats. The degreased bones are distilled under reduced pressure and the residue is burnt to get bone charcoal Bone charcoal is heated to high temperature when $Ca_3(PO_4)_2$ is obtained. Calcium phosphate is then treated with concentrated

H_2SO_4 and then heated with coke to get **white phosphorus**. The flow sheet for this procedure is shown as:

$$\text{Degreased bones} \xrightarrow[\text{and burnt}]{\text{Distilled}} \text{bone charcoal} \xrightarrow[\text{high temp.}]{\text{Heated to}} Ca_3(PO_4)_2 \text{ (bone ash)}$$

$$\xrightarrow{H_2SO_4} H_3PO_4 \xrightarrow{\Delta} HPO_3 \xrightarrow[\text{with coke}]{\text{Heated}} \textbf{White phosphorus}$$

(ii) From Phosphate Rock:

Phosphorus is obtained on commercial scale from phosphate rocks, $Ca_3(PO_4)_2$. Calcium phosphate is heated with carbon and silica in electric furnace at about 1500°C to get phosphorus:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$$

The phosphorus is distilled off and collected in the solid state after cooling.

At 1150°C, P_2O_5 is formed which gets converted to **Phosphorus** at 1500°C.

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10C \longrightarrow P_4 + 10CO$$

Crude phosphorus is purified by melting it under water and treated with oxidising agent ($Na_2Cr_2O_7$) in presence of an acid. Pure phosphorus thus obtained is filtered through canvas bags in the hot state and preserved as sticks under water.

ALLOTROPIC FORMS OF PHOSPHORUS:

Phosphorus exists in a number of allotropic forms but two varieties are common.

(i) White phosphorus, and (ii) Red phosphorus

(i) White Phosphorus:

It is the ordinary form of phosphorus and is also called **yellow phosphorus**. It is white when pure and gets yellow after exposure to light. It glows at night.

White phosphorus is insoluble in water but soluble in CS_2, ether and petroleum ether.

It has garlic odour and highly poisonous. Workers in match factories suffer from disease called **Phossy jaws** in which bones of jaw and teeth decay.

(ii) Red Phosphorus:

Red phosphorus is obtained by gradual conversion of the unstable white phosphorus. *The rate of conversion of white phosphorus to red phosphorus can be accelerated by rise of temperature or by exposure to light or in presence of iodine.* Conversion of white phosphorus takes place easily between 230°C and 250°C. In presence of little iodine the change occurs at 200°C.

Red phosphorus is manufactured by heating white phosphorus in an iron pot heated between 240°C to 250°C. It is ground to powdered state under water and boiled with the alkaline solution to remove excess white phosphorus and finally washed and dried.

The conversion of yellow to red phosphorus is an exothermic change.

Red phosphorus has a violet-red colour with density 2.1. It volatilises without melting when heated to 290°C. It is insoluble in CS_2 and does not glow in dark.

Comparison of White and Red Phosphorus

The physical and chemical properties of white and red phosphorus are:

TABLE 14.4

Property	White Phosphorus	Red Phosphorus
1. Colour	White changes to yellow on exposure to light.	Violet Red.
2. Odour	Garlic-like.	Odourless.
3. Hardness	Soft, can be cut with knife.	Brittle powder.
4. Specific gravity	1.80	2.7
5. Melting point	44°C	620 °C
6. Solubility	Soluble in CS_2.	Insoluble in CS_2.
7. Phosphorescence	Shows phosphorescence in dark.	Does not show phosphorescence.
8. Physiological action	Poisonous.	Non-poisonous.
9. Action of Cl_2	Burns spontaneously in Cl_2.	Reacts only when heated.
10. Action of hot NaOH	Phosphine is evolved.	No action.

Let us now consider the other two forms of phosphorus also.. **Black phosphorus** is grey solid with metallic lustre and conductor of heat and electricity. In this respect it resembles graphite. It consists of polymeric layers of phosphorus atoms held together by P — P covalent bonds. The layers are joined together by weak Van der Waals' type forces. This form shows metallic characteristics and is often called 'metallic phosphorus'. The layers are not in one plane as shown in Figure 14.7.

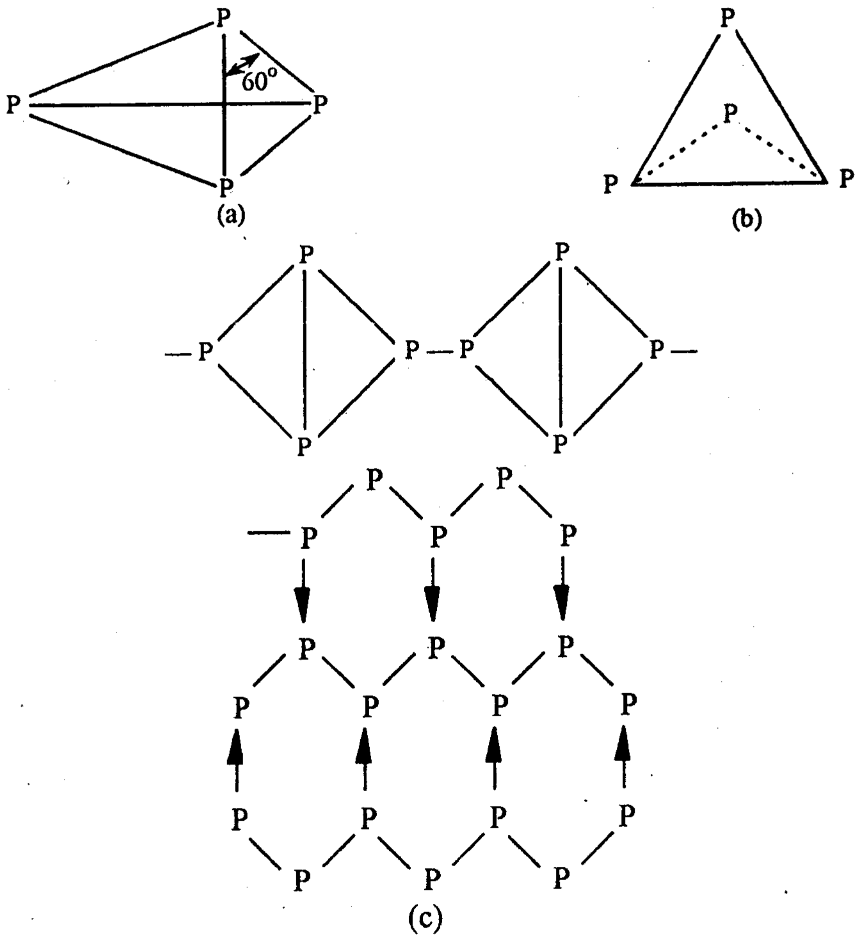


Fig. 14.7. Structures of the allotropes of phosphorus.
(a) White or yellow phosphorus (b) Red phosphorus
(c) Black phosphorus

Another variety is called **Brown phosphorus**. It is stable only at −196°C and is prepared by rapidly condensing the vapours of phosphorus. The reactivity of phosphorus with other reacting species decreases in the order brown > white > red > black. (Fig. 14.8)

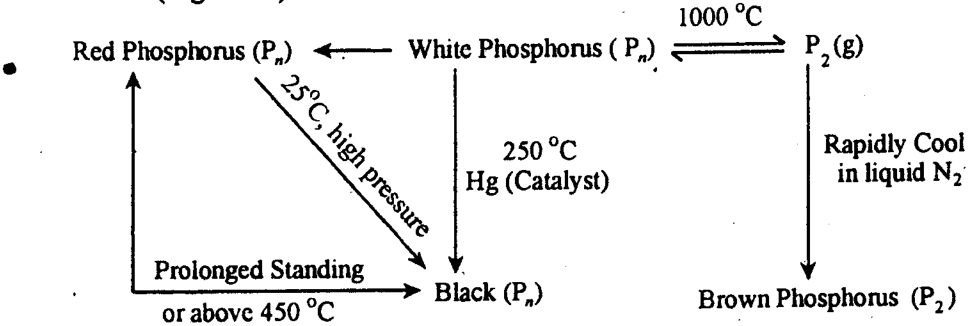


Fig. 14.8.

All these allotropic forms of phosphorus are interconvertible as shown in Figure 14.8.

Chemical Reactions

The electronic configuration of phosphorus atom is: $1s^1\ 2s^2\ 2p^6\ 3s^2\ 3p_x^{\ 1}\ 3p_y^{\ 1}\ 3p_z^{\ 1}$. Phosphorus atom shows +5 oxidation state in most of its compounds. The phosphorus atom, unlike nitrogen atom, does not form molecules containing lone pair of electrons. The chemistry of phosphorus is different from nitrogen in many respects. The following reactions are more common:

(i) Reaction with Oxygen

White phosphorus ignites with glare at 35° — 45°C in presence of oxygen but red phosphorus does not react with oxygen below 240°C.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

(ii) Reaction with Hydrogen

Phosphorus does not react with H_2 in the elementary state.

(iii) Reaction with Halogens

Phosphorus reacts with halogens to form PX_3. F_2 reacts more vigorously.

$$P_4 + 6F_2 \longrightarrow 6PF_3 \text{ (Colourless gas)}$$

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3 \text{ (Colourless liquid)}$$

$$P_4 + 6Br_2 \longrightarrow 4PBr_3 \text{ (Colourless liquid)}$$

$$P_4 + 6I_2 \longrightarrow 4PI_3 \text{ (Orange solid)}$$

PCl_5 and PBr_5 are also formed.

(iv) Phosphorus combines with sulphur with explosive violence to form mixture of phosphorus sulphides. The products depend on the ratios of components and the reaction conditions.

$$P + S \longrightarrow P_4S_3 + P_4S_7 + P_4S_{10} \text{ etc.}$$

(v) Reaction with Alkali and Alkaline Earth Metals

These metals combine with phosphorus on heating to give phosphides.

$$3Na + P \longrightarrow Na_3P$$

$$3Ca + 2P \longrightarrow Ca_3P_2$$

Aluminium (Group III) also reacts to give AlP.

(vi) Reaction with Alkalies

Alkalies react with white phosphorus to liberate phosphine gas. Red phosphorus does not react under these conditions.

$$P_4 + 3H_2O + 3NaOH \longrightarrow PH_3 + 3NaH_2PO_2$$

(Sodium hypophosphite)

(vii) Reaction with Acids

Phosphorus is oxidised to H_3PO_4 by concentrated HNO_3

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

It is oxidised with H_2SO_4 to phosphorus acids.

$$2P + 3H_2SO_4 \longrightarrow 2H_3PO_3 + 3SO_2$$

(viii) Reaction with Metal Oxides

Phosphorus is oxidised by metal oxides to P_2O_5 and sometimes to phosphates.

$$2P + 5Fe_3O_4 \longrightarrow P_2O_5 + 15FeO$$

$$8P + 5Fe_3O_4 \longrightarrow 4P_2O_5 + 15Fe$$

$$P_2O_5 + 3FeO \longrightarrow Fe_3(PO_4)_2$$

$$Fe_3(PO_4)_2 + 11Fe \longrightarrow 2Fe_3P + 8FeO$$

CaO reacts with phosphorus at low redness to give pyrophosphate.

$$14P + 14CaO \longrightarrow 5Ca_3P_2 + 2Ca_2P_2O_7$$

(ix) Reaction with $CuSO_4$

$CuSO_4$ solution reacts in cold to form phosphoric acid and copper is deposited.

$$2P + 5CuSO_4 + 8H_2O \longrightarrow 5Cu + 2H_3PO_4 + 5H_2SO_4$$

In the hot state copper phosphide is formed.

$$3P + 3CuSO_4 + 6H_2O \longrightarrow Cu_3P + 2H_3PO_3 + 3H_2SO_4$$

Uses

(i) Phosphorus is used in making alloys. Thus **phosphor bronze** containing 0.2 to 4% of phosphorus is a hard and tenacious alloy which does not get corroded with water.

(ii) Phosphorus is employed in making bombs and for producing smoke-screens.

(iii) White phosphorus is used as a poison for rats when mixed with flour and grease.

(iv) The main use of phosphorus is in the manufacture of **matches**. Both **lucifer and friction matches** as well as **safety matches** utilise phosphorus.

A friction match is made by dipping it in melted paraffin or sulphur and then in $KClO_3$ or red lead in glue. Finally match is dipped in a mixture of P_4S_3, glass and glue. Friction matches are always a source of fire danger and are replaced by safety matches.

Safety matches contain a mixture of:

(i) Antimony sulphide (combustible substance).

(ii) $KClO_3$, red lead (Pb_3O_4) or $K_2Cr_2O_7$ (oxidising agent).

(iii) Powdered glass and glue.

The match boxes have a mixture of red phosphorus, ground glass and glue pasted along their sides.

Compounds of Phosphorus

Although phosphorus forms a variety of compounds we shall discuss only its hydrides, halides, oxides and oxyacids.

Hydrides of Phosphorus

The hydrides of phosphorus include PH_3, P_2H_4, $P_{12}H_6$, P_5H_2 and P_9H_2. Phosphine is a gas; P_2H_4, a liquid and all other are solids.

Only PH_3 and P_2H_4 are well known and would be considered over here.

Phosphine, PH_3

Phosphine is a colourless and poisonous gas with fishy smell. It is prepared by the action of acids or water on metallic phosphides or by the action of alkalies with P or by thermal decomposition of phosphorus acid containing P – H link or by decomposition of phosphonium compounds or phosphides.

Preparation

(i) From Phosphorus

PH_3 can be prepared by boiling white phosphorus with strong solution of NaOH in an atmosphere of H_2, oil gas or ether vapours.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

(ii) From Calcium Phosphide

When water is dropped on calcium phosphide, it is decomposed, spontaneously liberating phosphine.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3.$$

(iii) From Phosphorus Acids

It is a convenient method of obtaining **Phosphine** and consists of heating a solution of phosphorus acid.

$$4H_3PO_4 \longrightarrow 3H_3PO_4 + PH_3$$

$$2H_3PO_2 \longrightarrow H_3PO_4 + PH_3$$

(iv) From Phosphide and Phosphonium Compounds

Aluminium phosphide reacts with H_2SO_4 to liberate PH_3.

$$2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3$$

When a solution of phosphonium iodide is treated with 30% KOH solution.

$$PH_4I + KOH \longrightarrow PH_3KI + H_2O$$

Reactions

(i) Decomposition

Phosphine is decomposed by electric sparks or by heating it to 440°C.

$$2PH_3 \longrightarrow 2P + 3H_2$$

(ii) PH_3 is oxidised by O_2, N_2O and NO to phosphoric acid.

$$PH_3 + 2O_2 \longrightarrow HPO_3 + H_2O$$

$$PH_3 + 4N_2O \longrightarrow H_3PO_4 + 4N_2$$

(iii) Reaction with Cl_2

PH_3 reacts with chlorine spontaneously.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

(iv) Formation of Metal Phosphides

Phosphine reacts with metal salts to form precipitates of metal phosphides.

$$PH_3 + 3AgNO_3 \longrightarrow Ag_3P + 3HNO_3$$

$$2PH_3 + 3CuSO_4 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

$AgNO_3$ can be reduced to silver metal.

$$PH_3 + 6AgNO_3 \longrightarrow Ag_3P.3AgNO_3 + 3HNO_3$$

$$Ag_3P.3AgNO_3 + 3H_2O \longrightarrow 6Ag + H_3PO_3 + 3HNO_3$$

(v) Reaction with Acids

PH_3 is neutral to litmus but reacts with acids showing feebly basic properties.

$$PH_3 + HI \longrightarrow PH_4I$$

Structure

PH_3 is a tetrahedrally hybridised molecule and resembles NH_3. The H — P — H bond angle is smaller than H — N — H but P — H bond length is larger than N — H. The structure of phosphine is shown in Figure 14.9.

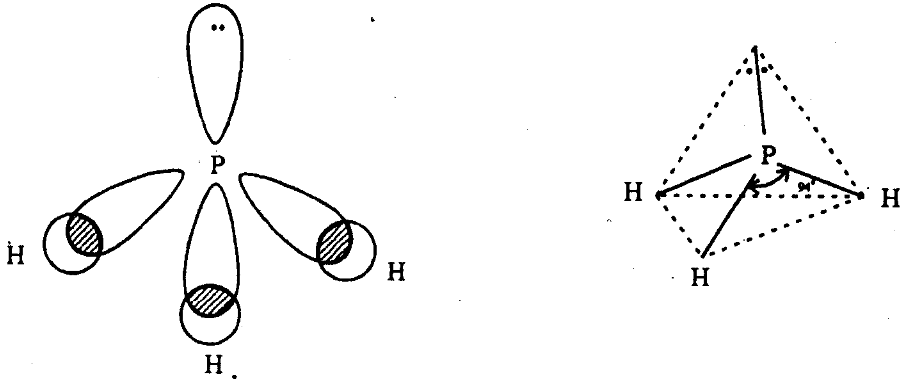


Fig. 14.9. Structure of PH_3

(a) sp^3 hybridised molecule. (b) Pyramidal structure.

Uses

1. PH_3 is used in making **Holme's signals** in sea water. A mixture of calcium phosphide and carbide are placed in drums floating on water. The water enters the tin and liberates a mixture of PH_3 and C_2H_4 which spontaneously catches fire and lights the sea.
2. A curious natural phenomenon called *ignus fatus* or *ghost* is observed in damp soils when phosphorus hydrides present decompose to give PH_3 which catches fire in air.

Phosphorus hydride, P_2H_4

It is a colourless and volatile liquid (b.p. 52°C). P_2H_4 is obtained by the action of Ca_3P_2 and H_2O.

$$Ca_3P_2 + 4H_2O \longrightarrow 2Ca(OH)_2 + P_2H_4$$

The vapours of P_2H_4 are unstable and spontaneously inflammable. The liquid decomposes on exposure to light to give P with the evolution of PH_3.

$$3P_2H_4 \longrightarrow 2P + 4PH_3$$

Structure

The structure of P_2H_4 is shown in Figure 14.10.

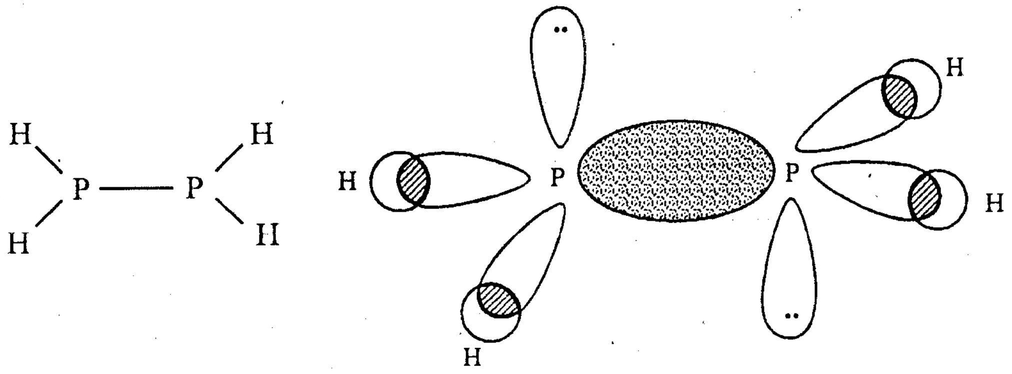


Fig. 14.10. Structure of P_2H_4.

HALIDES OF PHOSPHORUS

Fluorine, chlorine and bromine combine directly with phosphorus to form halides of the type PX_3 and PX_5 (X = F, Cl, Br). Iodine reacts to form PI_3 and P_2I_4.

(a) Phosphorus Trifluoride

It is a colourless gas and is prepared by any one of the following methods:

(i) By action of AsP_3 with PCl_3.

$$PCl_3 + AsF_3 \longrightarrow PF_3 + AsCl_3$$

(ii) By heating copper phosphine with PbF_2

$$2Cu_3P + 3PbF_2 \longrightarrow 2PF_3 + 3Pb + 6Cu$$

(iii) By warming PBr_3 with ZnF_2.

$$2PBr_3 + 3ZnF_2 \longrightarrow 2PF_3 + 3ZnBr_2$$

Reactions

(i) It is readily hydrolysed by water to give phosphorus acid and HF.

$$PF_3 + 3H_2O \longrightarrow H_3PO_3 + 3HF$$

(ii) It decomposes on heating to give phosphorus.

$$5PF_3 \longrightarrow 3PF_5 + 2P$$

(iii) A mixture of PF_3 and oxygen explodes when sparked

$$2PF_3 + O_2 \longrightarrow 2POF_3$$

(b) Phosphorus Trichloride, PCl_3

It is colourless liquid and can be obtained:

By passing gaseous HCl over phosphorus oxide.

$$P_4O_6 + 6HCl \longrightarrow 2H_3PO_3 + 2PCl_3$$

It undergoes reactions in which it acts as reducing agent.

(a) $PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$

(b) $PCl_3 + 2H_2SO_4 \longrightarrow SO_3.HCl + SO_2 + 2HCl + HPO_3$

(c) $3PCl_3 + S_2Cl_2 \longrightarrow PCl_5 + 2PSCl_3$

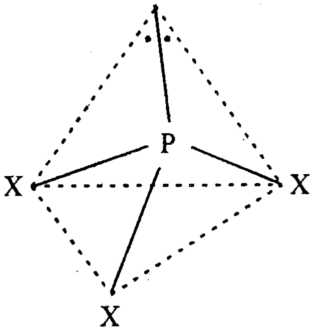
It reacts with NH_3 to form $PCl_3.5NH_3$.

PCl_3 reacts with metal carbonyls to replace CO groups.

$$Ni(CO)_4 + 4PCl_3 \longrightarrow Ni(PCl_3)_4 + 4CO$$

Structure

The structures of PX_3 (X = halogen atom) type molecules are similar to PH_3 except that X — P — X bonds are slightly larger.



PX_3(X = halogen atom) molecule.

Other Trihalides

PBr_3 is similar to PCl_3 but PI_3 is a dark red solid and is made by the action of I_2 on white phosphorus in CS_2 or by the action of KI on PCl_3.

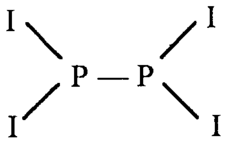
$$2P + 3I_2 \longrightarrow 2PI_3$$

$$PCl_3 + 3KI \longrightarrow PI_3 + 3KCl$$

Diphosphorus tetraiodide is an orange solid and is prepared by the action of I_2 on PCl_3 in warm glacial acetic acid solution.

$$2PCl_3 + 5I_2 \longrightarrow P_2I_4 + 6ICl$$

The structure of P_2I_4 is:



Phosphorus Pentahalides

PF_5 and PCl_5 are the representative halides of PX_5 type in which phosphorus utilises all its orbitals for bond formation with halogens.

PF_3 is prepared by any one of the following methods:

(i) $6P_2O_5 + 5CaF_2 \longrightarrow 2PF_5 + 5Ca(PO_2)_2$

(ii) $3PCl_5 + 5AsF_3 \longrightarrow 3PF_5 + 5AsCl_3$

(iii) $PF_3 + F_2 \longrightarrow PF_5$

PCl_5 is obtained:

(i) by oxidising PCl_3 with Cl_2:

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

(ii) by the action of sulphuryl chloride with phosphorus or PCl_3.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

$$PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$$

PCl_5 is a straw coloured solid and dissociates reversibly but can also be sublimed.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

PCl_5 is readily hydrolysed as:

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

In presence of excess water, phosphoric acid is obtained.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_3 + 5HCl$$

PCl_5 is a good chlorinating agent and is itself reduced by metals such as Zn, Al and Pt.

$$PCl_5 + Zn \longrightarrow PCl_3 + ZnCl_2$$

Structure

Phosphorus has 3*d* orbitals available for bond formation because their energy is not much different from 3*s* and 3*p* orbitals. This enables phosphorus to expand its valence shell beyond 8 electrons and to form many compounds with coordination number more than 4 (Nitrogen cannot form such compounds due to the non-availability of *d* orbitals for bond formation).

The structure of PF_5 is trigonal bipyramidal and is shown in Figure 14.11.

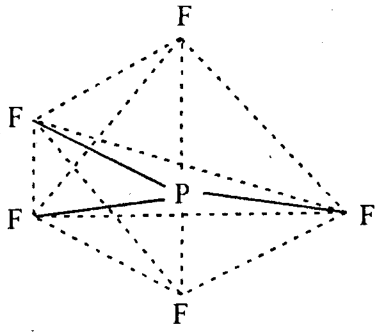


Fig. 14.11. Structure of PF_5.

Solid phosphorus pentachloride is ionic. Its crystal lattice contains positive tetrahedral PCl_4^+ ions and negative octahedral PCl_6^- ions as shown in Figure 14.12.

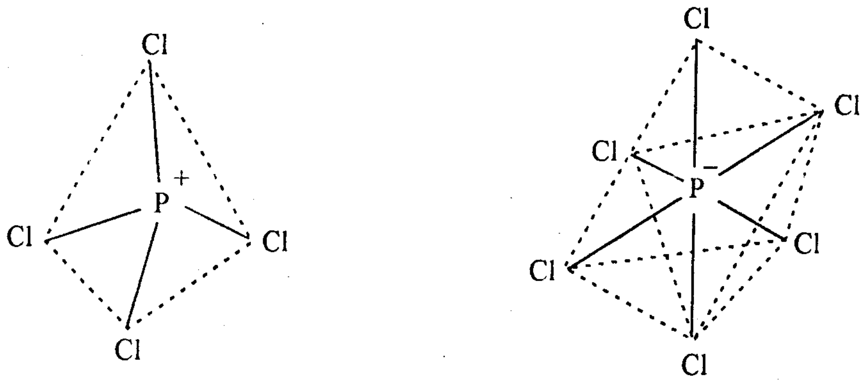


Fig. 14.12. Structure of PCl_5 in solid state containing PCl_4^+ and PCl_6^- units.

OXIDES OF PHOSPHORUS

There are four oxides of phosphorus; P_4O_6, P_4O_{10}, P_3O_6 and $(PO_5)_n$. Only P_4O_6 and P_4O_{10} are well defined and would be taken up for discussion.

(a) Phosphorus (III) oxide, P_4O_6

This compound is often called phosphorus trioxide. It is a white crystalline solid (m.p. 22.5°C).

It is prepared by passing oxygen-enriched air through white phosphorus under reduced pressure.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

P_4O_6 is readily hydrolysed to phosphorus acid.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

On heating P_4O_6 in a sealed tube 440°C, polymeric oxide, $(PO_2)_n$ is obtained

$$nP_4O_6 \longrightarrow 3(PO_2)_n + nP$$

Structure

The molecular weight determination of phosphorus oxide in benzene corresponds to formula, P_4O_6 (Fig. 14.13a). Six oxygen atoms are inserted within P_4 atoms containing P — P bonds which are changed to P — O — P bridges. The electron diffraction experiments have shown the structure as in Figure 14.13 (b).

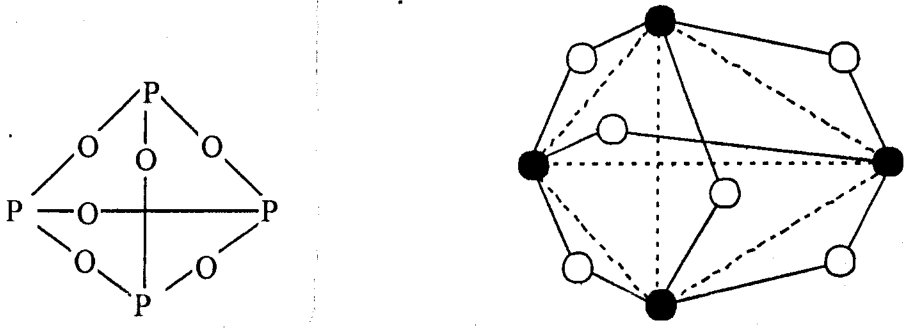


Fig. 14.13. (a) Structure of P_4O_6 in relation to P_4, (b) Structure of P_4O_6 obtained from electron diffraction studies.

(b) Phosphoric (V) Oxide

It is a white solid which is stable even at high temperature.

It is prepared by burning white or red phosphorus in excess of air or oxygen. P_4O_6 formed along with it is removed by sublimation in a current of ozonised oxygen.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

Reactions

(i) It is an anhydride of phosphoric acid and, therefore, hydrolyses to give metaphosphoric, pyrophosphoric and orthophosphoric acids, respectively.

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$$

(Metaphosphoric acid)

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

(Orthophosphoric acid)

$$P_4O_{10} + 2H_2O \longrightarrow 2H_4P_2O_7$$

(Pyrophosphoric acid)

(ii) **As drying agent:** This most important property of P_4O_{10} is due to its large affinity for water. It is considered to be very efficient as drying and dessicating agent below 100°C.

It is also employed in dehydrating acids to get their anhydrides or oxides.

$$H_2SO_4 - H_2O \xrightarrow{P_4O_{10}} SO_3$$

$$2HNO_3 - H_2O \xrightarrow{P_4O_{10}} N_2O_5$$

$$2HClO_4 - H_2O \xrightarrow{P_4O_{10}} Cl_2O_7$$

(iii) **Reaction with alcohols:** P_4O_{10} reacts with alcohols to give esters of phosphoric acids. With ethyl alcohol,

$$P_4O_{10} + 6C_2H_5OH \longrightarrow 2(C_2H_5O)_2\,PO.\,OH + 2C_2H_5OP(OH)_2$$

Structure

P_4O_{10} molecule has structure containing P — O — P bridges like P_4O_6 but also contains oxygen atoms attached to phosphorus atoms at terminal positions as shown in Figure 14.14.

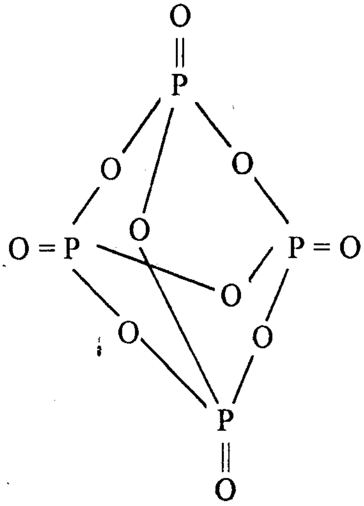


Fig. 14.14. Structure of P_4O_{10}.

OXYACIDS OF PHOSPHORUS

Phosphorus forms a number of oxyacids which can be classified into two groups:

(a) Oxyacids of phosphorus (III)
(b) Oxyacids of phosphorus (V)

(a) Oxyacids of Phosphorus (III)

The well known oxyacids of phosphorus in +3 oxidation state are:

(1) Orthophosphorous acid, H_3PO_3
(2) Hypophosphorous acid, H_3PO_2
(3) Pyrophosphorous acid, $H_4P_2O_5$
(4) Metaphosphorous acid, $(HPO_2)_n$

(1) Orthophosphorous acid H_3PO_3 (Phosphorous acid):

It is a white, deliquescent crystalline solid (m.p. 73.6°C).

Preparation

(i) It is prepared by the hydrolysis of PCl_3 or other trihalides of P with water or oxalic acid solution.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$PCl_3 + 3(COOH)_2 \longrightarrow H_3PO_3 + 3CO + 3CO_2 + 3HCl$$

(ii) It can also be obtained by hydrolysis of P_4O_6.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

Only the first two methods are important and shall be taken up for further discussion.

Properties

It is freely soluble in water.

(i) Although H_3PO_3 contains three hydrogen atoms, it is only a dibasic acid because only two hydrogen atoms are linked through oxygen and hence ionizable. The third hydrogen atom is bonded directly to central P atom. The two ionization reactions of H_3PO_3 with K_1 and K_2 values are:

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \quad K_1 = 2 \times 10^{-2} \text{ mole/l}$$

$$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-} \quad K_2 = 2 \times 10^{7} \text{ mole/l}$$

HPO_3^{2-} ion does not ionize further. Hence PO_3^{3-} ions do not exist in solution.

(ii) **Decomposition:** It decomposes at 200°C undergoing auto-oxidation-reduction reaction to give PH_3 on the one hand and H_3PO_4 on the other hand.

$$4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$$

(iii) **As reducing agent:** It is a mild reducing agent and would precipitate heavy metals from the solutions of their salts.

$$2AgNO_3 + H_3PO_3 \longrightarrow Ag_2HPO_3 + 2HNO_3$$

$$Ag_2HPO_3 + H_2O \longrightarrow 2Ag + H_3PO_4$$

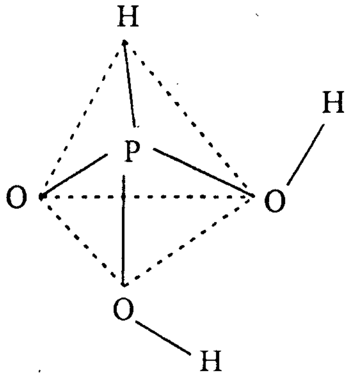
$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow Hg_2Cl_2 + 2HCl + H_3PO_4$$

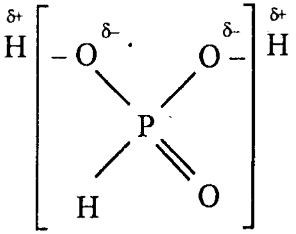
Phosphorous acid reduces SO_2 to free sulphur.

$$SO_2 + 2H_3PO_3 \longrightarrow 2H_3PO_4 + S$$

Structure

The dibasic nature of phosphorous acid and its reducing properties indicate the following structure for it.





(2) Hypophosphorous acid, H_3PO_2

It is a solid (m.p. 27°C) and is formed by the following methods:

(i) By the Oxidation of Phosphine with I_2

Iodine reacts quantitatively with PH_3 to form hypophosphorous acid.

$$PH_3 + 2I_2 + 2H_2O \longrightarrow H_3PO_2 + 4HI$$

(ii) From $Ba(OH)_2$ and White Phosphorus

$Ba(OH)_2$ reacts with white phosphorus to form salt of hypophosphorous acid. It gives H_3PO_2 on treatment with H_2SO_4.

$$2P_4 + 3Ba(OH)_2 + 6H_2O \longrightarrow 3Ba(H_2PO_2)_2 + 2PH_3$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow 2H_3PO_2 + BaSO_4$$

Reactions

(i) Hypophosphorous acid disproportionates at 130°C.

$$3H_3PO_2 \longrightarrow 2H_3PO_3 + PH_3$$

(ii) **Action of Zn and H_2SO_4:** H_3PO_2 can be reduced to PH_3 by Zn and H_2SO_4.

$$H_3PO_2 + 2H_2 \longrightarrow PH_3 + 2H_2O$$

(iii) **Reducing action:** It reduces the salts of heavy metals such as Au, Ag, Pt, Hg, etc., to metallic state or to hydrides.

$$2CuSO_4 + 3H_3PO_2 + 3H_2O \longrightarrow 2CuH + 3H_3PO_3 + 2H_2SO_4$$

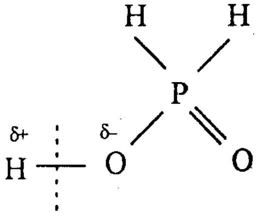
$$2CuH \longrightarrow 2Cu + H_2$$

(iv) **Reaction with diazonium compounds:** H_3PO_2 reduces diazonium compounds to aromatic hydrocarbons.

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + H_3PO_3 + N_2 + HCl$$

Structure

The acid is monobasic which indicates that only one hydrogen atom is linked through oxygen to the central phosphorus atom. The results of the crystal structure of its nickel salt, $Ni[H_2PO_2]_2\ 2H_2O$ indicate its tetrahedral arrangement. The structure assigned to H_3PO_2 is:



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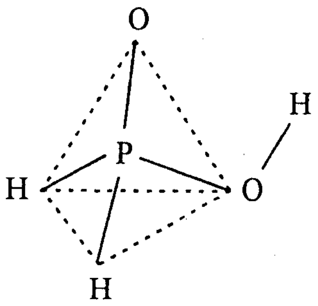


(b) Oxyacids of phosphorous (V)

The well known oxyacids of phosphorus in +5 oxidation state are:

(1) Orthophosphoric acid, H_3PO_4.
(2) Pyrophosphoric acid, $H_4P_2O_7$.
(3) Metaphosphoric acid, $(HPO_3)_n$.

The three acids differ from one another by the amount of water content by P_4O_{10}.

(1) Orthophosphoric acid, H_3PO_4

It exists as colourless, deliquescent, rhombic crystals (m.p. 42°C.)

Preparation

(i) From Bone Ash

Commercial orthophosphoric acid is prepared by treating bone ash (calcium phosphate) with H_2SO_4. After reaction, the precipitate of $CaSO_4$ is filtered and the solution evaporated to get crystals of H_3PO_4.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

(ii) From Red Phosphorus

H_3PO_4 is prepared in the laboratory by dissolving red phosphorus in nitric acid diluted with equal volume of water.

$$P_4 + 10HNO_3 + H_2O \longrightarrow 4H_3PO_4 + 5NO + 5NO_2$$

The solution is kept in a vacuum dessicator over concentrated H_2SO_4. On cooling the dessicator in a freezing mixture, crystals of H_3PO_4 are deposited.

(iii) From P_4O_{10}

When P_4O_{10} is dissolved in water, H_3PO_4 is obtained.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

(iv) From PCl_5

Phosphorus pentachloride hydrolyses to give H_3PO_4.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Properties

(i) Orthophosphoric acid is a tribasic acid because all the three hydrogen atoms in H_3PO_4 are bonded to central phosphorus atom through oxygen atoms. The electronegativity difference between hydrogen and oxygen atoms would allow the liberation of H^+ in solution. The ionization of H_3PO_4 takes place in three steps:

$$H_3PO_4 \longrightarrow H^+ + H_2PO_4^- \qquad K_1 = 9 \times 10^{-3}$$
$$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-} \qquad K_2 = 6 \times 10^{-8}$$
$$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-} \qquad K_3 = 1 \times 10^{-12}$$

(ii) **Reaction with perchloric acid:** H_3PO_4 reacts with perchloric acid, $HClO_4$. H_3PO_4 acts as a base in presence of very strong acid, $HClO_4$,

$$\underset{\text{(base)}}{H_3PO_4} + \underset{\text{(acid)}}{HClO_4} \longrightarrow [P(OH)_4]\,[ClO_4]$$

(iii) With phosphoryl chloride, prophosphoric acid is obtained.

$$POCl_3 + 5H_3PO_4 \longrightarrow 3H_4P_2O_7 + 3HCl$$

(iv) **Formation of salts:** Three series of salts are obtained with orthophosphoric acid. For example, the sodium salts are:

$$NaH_2PO_4,\ Na_2HPO_4 \text{ and } Na_3PO_4$$

The primary salt NaH_2PO_4 crystallises with only one water molecule but other two carry $12H_2O$ as water of crystallisation. All primary salts are soluble in water.

All tertiary salts, excepts those of Ti, Th, Fe(III), Al, Cr are soluble.

Ammonium salts can be decomposed to pyrophosphates.

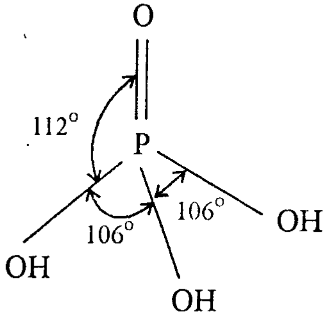
$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{(magnesium pyrophosphate)}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Orthophosphates react with ammonium molybdate in presence of HNO_3 in cold state to give a yellow precipitate of ammonium phosphomolybdate.

$$(NH_4)_2MoO_4 + HNO_3 + PO_4^{3} \longrightarrow (NH_4)_3\,(PMo_{12}O_{40}2HNO_3.H_2O)$$

Structure

The arrangement of oxygen atoms around phosphorus atom is only approximately tetrahedral The angle HO — P — OH is 106° and O = P — OH, 112°.



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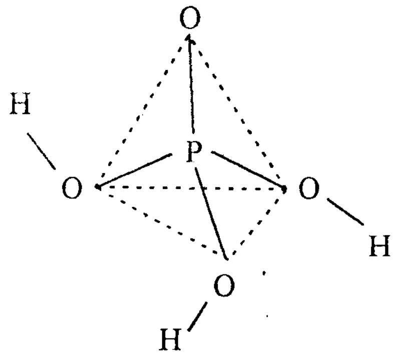


(2) Pyrophosphoric Acid, $H_4P_2O_7$

It exists as white, granular crystals (m.p. 61°C).

Preparation

It is prepared by the following methods:

(i) **From orthophosphoric acid:** By heating orthophosphoric acid at 220°C, pyrophosphoric acid is obtained.

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

(ii) **From sodium orthophosphate:** Sodium orthophosphate is heated above 240°C to give sodium diphosphate or pyrophosphate. It is treated with lead nitrate to give lead pyrophosphate. On passing H_2S through lead pyrophosphate, pyrophosphoric acid is obtained.

$$2Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O$$

$$Na_4P_2O_7 + Pb(NO_3)_2 \longrightarrow Pb_2P_2O_7 + 4NaNO_3$$

$$Pb_2P_2O_7 + 2H_2S \longrightarrow H_4P_2O_7 + 2PbS$$

(iii) **From phosphoryl acids and H_3PO_4:** Heating a mixture of phosphoryl chloride and orthophosphoric acid gives pyrophosphoric acid.

$$POCl_3 + 5H_3PO_4 \longrightarrow 3H_4P_2O_7 + 3HCl$$

Properties

(i) Pyrophosphoric acid is tetrabasic acid. The dissociation constants are:

$$K_1 = 1.4 \times 10^{-1};\ K_2 = 1.1 \times 10^{-2};\ K_3 = 2.9 \times 10^{-7};\ K_4 = 3.6 \times 10^{-9}$$

(ii) If the solution of pyrophosphoric acid is allowed to stand for some time it converts to orthophosphoric acid.

$$H_4P2O_7 + H_2O \longrightarrow 2H_3PO_4$$

(iii) The metal salts of pyrophosphoric acid are fairly stable even at high temperature.

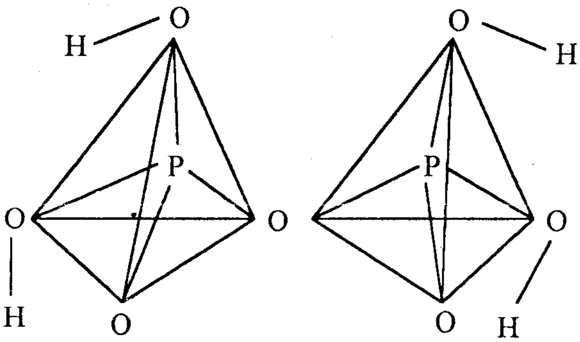
$$2MgNH_4PO_4 \longrightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$

(iv) Alkyl derivatives of pyrophosphoric acid have also been prepared. Thus ethyl pyrophosphate can be prepared from silver pyrophosphate and ethyl iodide.

$$Ag_4P_2O_7 + 4C_2H_5I \longrightarrow (C_2H_5)_4P_2O_7 + 4AgI$$

Structure

Pyrophosphoric acid has oxygen atom which bridges the two phosphorus atoms present in its molecule. The structure is:



(3) Metaphosphoric acid, $(HPO_3)_n$

HPO_3 is obtained by heating ortho or pyrophosphoric acid to red heat.

$$H_3PO_4 \longrightarrow HPO_3 + H_2O$$

$$H_4P_2O_7 \longrightarrow 2HPO_3 + H_2O$$

It can also be obtained by dissolving P_2O_5 in water

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$$

Metaphosphoric acid is a transparent, glassy solid and is commercially known as **glacial phosphoric acid**.

In aqueous solution it slowly changes to orthophosphoric acid.

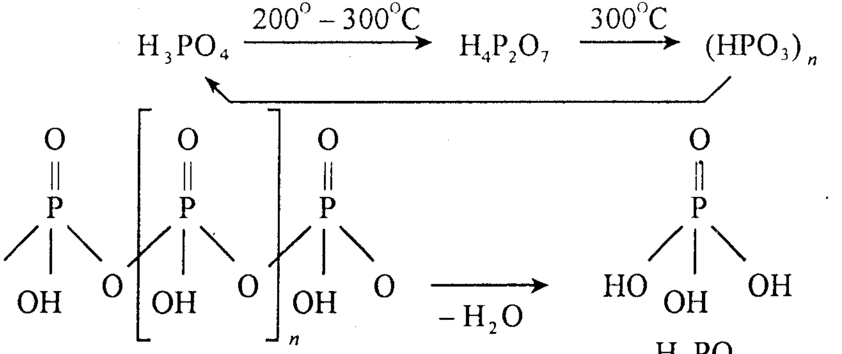
$$HPO_3 + H_2O \longrightarrow H_3PO_4$$

The sodium salt is obtained by heating sodium dihydrogen phosphate, NaH_2PO_4.

$$NaH_2PO_4 \longrightarrow (NaPO_3)_n + H_2O$$

If sodium metaphosphate is heated above 700°C and rapidly cooled it changes to polymetaphosphate, $(NaPO_3)_6$.

Relationship Between Phosphoric Acids



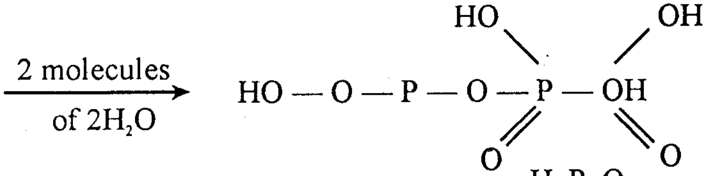
$$H_3PO_4 \xrightarrow{200^{\circ} - 300^{\circ}C} H_4P_2O_7 \xrightarrow{300^{\circ}C} (HPO_3)_n$$

$(HPO_3)_n$

(Metaphosphoric acid)

H_3PO_4

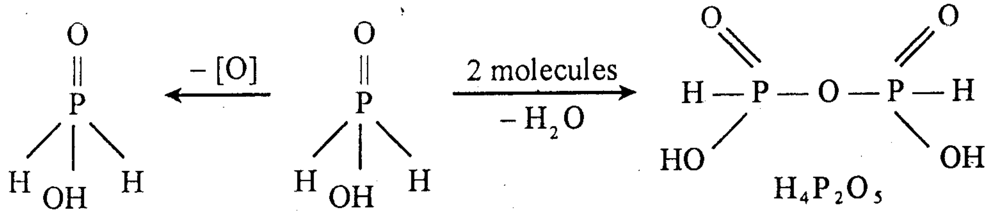
(Orthophosphoric acid)



$H_4P_2O_5$

(Pyrophosphoric acid)

Relationship Between Phosphorous Acids



H_3PO_2 (Hypophosphorous Acid)

H_3PO_3 (Orthophosphorous Acid)

$H_4P_2O_5$ (Pyrophosphorous Acid)

Distinction Between Ortho, Pyro and Metaphosphoric Acids

Test	Orthophosphoric Acid	Pyrophosphoric Acid	Metaphosphoric Acid
1. Addition of $AgNO_3$ to metal solution.	Yellow precipitate of Ag_3PO_4.	White crystalline precipitate of $Ag_4P_2O_7$ insoluble in excess of phosphate solution.	White gelatinous precipitate of $AgPO_3$ soluble in excess of phosphate solution.
2. Addition of $Ca(NO_3)_2$ to neutral solution.	Violet blue precipitate soluble in acetic acid.	Pink precipitate insoluble in acetic acid.	No precipitate.
3. Addition of $MgSO_4$ in the presence of NH_4Cl and NH_4OH (Magnesia mixture).	White precipitate of $MgNH_4PO_4$ insoluble in excess of the reagent.	White precipitate of $Mg_2P_2O_7$ soluble in excess of the reagent.	No precipitate.

FERTILIZERS

Fertilizers are the inorganic salts which contain elements essential for plant growth and which are introduced into the soil to obtain increased amount of crops regularly. Nitrogen, Phosphorus and Potassium containing minerals are especially important for normal plant life.

Need for Fertilizers

These elements stimulate processes of metabolism in the plant cells, growth of the plant and specially its fruits, increase the content of such valuable plant components as the starch of potatoes, sugars of beets, fruits and berries, proteins of grains and increase resistance to frost, draught and diseases. By consuming these minerals, the soil becomes exhaustive and to make up the deficiency of such minerals, artificial fertilizers containing elements of nitrogen, phosphorus and potassium are needed to replenish and in order to avoid plant starvation. The need for fertilizers is threefold.

(a) To supplement what has been eaten up by the plants.

(b) To give an additional supply of tonic and good food, so that they may grow more healthy and produce a better yield. In other words, the soil has to be fertilized.

(c) Fertilizers help to maintain the pH of the soil in the vicinity, of 7 to 8 and thereby facilitate optimum growth and health. This value of pH is near neutrality or slight alkalinity, and forms the most favourable condition for the microbes. Any soil above pH 10 and below pH 3 may be said to be sterile. Factors contributing towards increase in acidity (Too much of humus resulting in its decay into some organic acids) lowers neutrality or the alkalinity of the soil and hence hinders the growth of plants. During the cultivation of soil, calcium, magnesium and base forming materials are removed by the crops, which results in decrease of pH value. The microbes are highly sensitive to acids and an imbalance in the pH value of the soil will naturally hinder their activity and thus the soil becomes unfertile. The increase in the acidity of soil is easily corrected by a small addition of bases like lime whereby the acids get neutralized and thus facilitates the growth and activity of soil microorganisms. If the soils have a pH value of less than 3, no cultivation is possible.

Classification of Fertilizers

Fertilizers can be classified according to their mode of operation in the soil:

(1) Direct Fertilizers

These fertilizers which are directly assimilated by the plants are called Direct Fertilizers. For example, superphosphates, nitrates and ammonium compounds. These contain nutrient elements in the form of mineral salts which can be absorbed directly.

(2) Indirect Fertilizers

These are the substances which are introduced into the soil mainly to improve its mechanical, chemical or biological properties. Ground dolomite and limestone used to reduce soil acidity, and gypsum used to improve the properties of soils with a high salt content are the examples of indirect fertilizers.

(3) Complete Fertilizers

These contain all the principal ingredients for the growth of plants in the combined form, so that an additional fertilizer is not necessary. These fertilizers are classified as double or triple containing two or three ingredients, respectively. Complete fertilizers contain nitrogen, phosphorus, potassium and mineral salts thus supplying all the requirements. Guano is an example of complete fertilizers. These fertilizers are being manufactured artificially.

(4) Incomplete Fertilizers

These fertilizers contain only one or two needed elements such as ammonium phosphate or potassium nitrate. They supply only a part of the requirements.

(5) Mixed Fertilizers

Fertilizers containing several ingredients and obtained by mechanical mixing of various fertilizers are known as mixed fertilizers.

(6) Micro Fertilizers

These contain the elements boron, manganese, zinc and copper needed in very small amounts to stimulate the plant growth

(7) According to their **solubility** in the moisture or in the soil, fertilizer can be classified as water soluble or soluble in soil acid. For example, all nitrogenous, phosphate and potash fertilizer, are soluble in water. These are readily assimilated by plants, but are retained in the soil much longer. However, the phosphate fertilizers dissolve much slower in water.

(8) According to their **physiological effect** on the soil to which they are introduced, fertilizers are classified as physiologically acid, physiologically alkaline or physiologically neutral. According to their form (physical properties), fertilizers are subdivided into powder form and granular ones. Granulated fertilizers are less hygroscopic, they do not care during storage, are not subjected to weathering after being introduced into the soil and are retained by the soil for a longer time *i.e.*, are not washed out quickly by rains.

(9) Natural Fertilizers

These can be classified as:

(a) **Natural organic fertilizers:** Examples are plant matter, farm yard manures, animal matter, etc.

(b) **Artificial organic fertilizers:** Important example being waste materials such as waste obtained from animal excretion. Meat obtained from slaughter houses consisting of scrap meat, black dry blood, hoofs etc., containing 5–10% nitrogen, phosphorus fertilizers, urea, etc.

(c) **The natural inorganic fertilizers:** Example being chile saltpetre, rock phosphates, potassium salts, etc.

(d) **Artificial inorganic fertilizers:** Examples are nitrates and other ammonium salts, such as calcium nitrate, ammonium sulphate, ammonium nitrate, ammonium chloride, calcium cyanamide, super phosphates, etc.

The fertilizers manufactured on the large scale using industrial methods are Nitrogen and Phosphate fertilizers as are discussed below.

Nitrogenous Fertilizers

Most of the Nitrogenous fertilizers are synthetic products obtained by neutralizing acids with alkalies. The nitrogen is contained in the fertilizers either as NH^{4+} cations *i.e.*, in the ammonium form, as NH_2 (amide) or in NO_3^- anion *i.e.*, in the nitrate form; some fertilizers contain both ammonium and nitrate forms of nitrogen. All nitrogenous fertilizers are soluble in water and are readily available to plants, but they are easily carried away into the deeper layers of the soil if there is an excess of rain or irrigation. The important nitrogenous fertilizers are:

(1) Ammonia (NH_3) (2) Urea (3) Ammonium Nitrate (4) Ammonium Chloride (5) Ammonium Sulphur Nitrate (6) Calcium Ammonium Nitrate (7) Ammonium Sulphate (8) Monoammonium Phosphate (9) Diammonium Phosphate (10) Nitrophosphate.

The importance of these fertilizers are discussed below:

(1) Urea

Urea (carbamide) is a high quality nitrogenous fertilizer with a 46% nitrogen content. Urea is also as a nitrogen containing admixture to animal food.

Synthesis of Urea

Urea is synthesized from ammonia and carbon dioxide. The manufacturing process consists of the following stages:

(i) Chemical reaction between NH_3 and CO_2.

(ii) Distillation of the synthetic products.

(iii) Processing the urea solutions into end products.

Synthesis consists of two steps:

(a) In the first step ammonium carbamate is formed.

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 + 665 \text{ kJ/mole}$$

(b) The second step is dehydration of the carbamate to produce liquid phase urea (melt).

$$NH_4COONH_4 \longrightarrow (NH_2)_2CO + H_2O - 1192 \text{ kJ/mole}$$

A simplified flow diagram of urea-manufacturing plant is given in Figure 14.15.

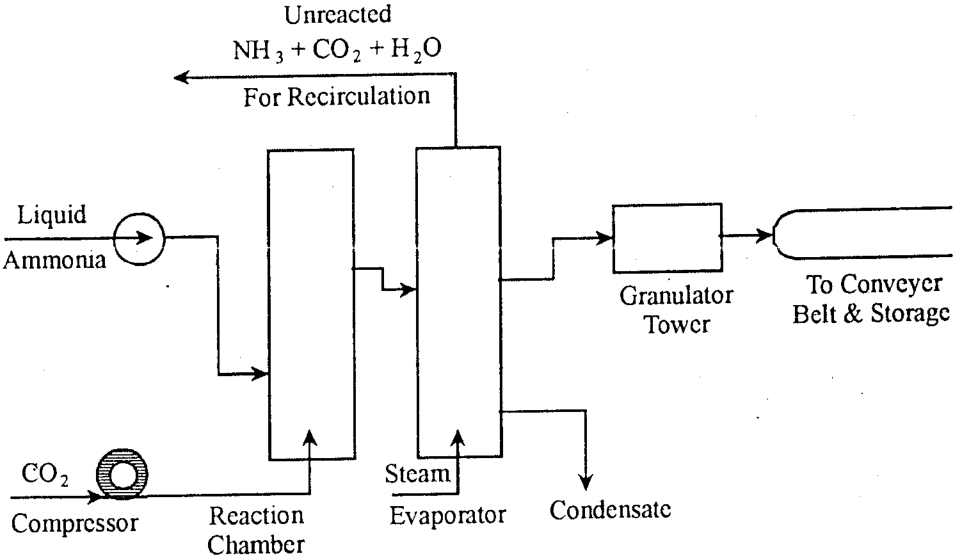


Fig. 14.15.

Synthesis takes place in a tower made of alloy steel, the inner cylinder of the tower serves to protect the walls of high pressure vessel against corrosion by the reaction mixture. Liquid ammonia is fed to the annular space between the tower wall and the inner cylinder by a pump, it flows along the walls protecting from corrosion. The ammonia reacts with CO_2 which is fed to the tower inside the cylinder at the bottom. The molten urea is removed from the upper part of the tower, is throttled to atmospheric pressure and transferred to a distillation tower, where the excess ammonia and products of the decomposition of ammonium carbonate salts are stripped from the urea solution. The solution is concentrated in an evaporator and the urea is produced in the form of either crystals or it is granulated in a prilling tower. The gases discharged from the distillation tower are regenerated.

From Natural Gas

Urea has been obtained from natural gas (Sui gas) and air as follows:

(i) Hydrogen is prepared from natural gas by passing its mixture with steam over heated Nickel.

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

(ii) Air is then mixed to provide the necessary amount of nitrogen in the ratio ($N_2 : H_2$) 1 : 3 to form ammonia.

$$N_2 + 3H_2 \underset{450 - 500^\circ C}{\overset{Fe_2O_3 + Mo}{\rightleftharpoons}} 2NH_3$$

(iii) The ammonia is liquefied and reacted with CO_2 (liquid) under pressure to form ammonium carbamate; which then decomposes to give urea.

$$2NH_3(l) + CO_2(l) \longrightarrow NH_2COONH_4 \longrightarrow NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H_2O$$

(iv) HNO_3 acid can also be prepared by the oxidation of ammonia in the presence of Pt and Rh.

$$4NH_3 + 5O_2 \xrightarrow[800-900^\circ C]{Pt} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

(v) Ammonia is absorbed in Nitric acid to form ammonium nitrate.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

The heat of the reaction is used to concentrate the solution up to 85 % and steam is used to concentrate to about 98 %. The solution then goes to a granulator when it is also mixed with some lime to make it granulated product. About 10 % of organic material is also added to prevent caking and other undesirable chemical reactions.

2. Ammonium Nitrate

It is manufactured by the neutralization reaction between NH_3 and HNO_3 as given above

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 + 621\ kJ/mole$$

The following flow diagram (Figure 14.16) illustrates the process of the manufacture of ammonium nitrate. The solution is partially concentrated by evaporation. The apparatus consists of a cylindrical vessel made of stainless steel with a second cylinder inside it. Gaseous ammonia and the nitric acid are continuously fed to the cylinder; the nitric acid is introduced through a sprayer nozzle. The annular space between the inner and the outer cylinders serves as evaporator. The solution of ammonium nitrate formed flows over the upper rim of the cylinder into the evaporator part, where water is evaporated. The ammonium nitrate solution (60 to 80% NH_4NO_3) depending on the concentration of the nitric acid used flows to a vessel with an agitator through a hydraulic seal and then to a multistage vacuum evaporation unit. Two or three stages of evaporation are used and the concentration is brought to 98 – 99 % NH_4NO_3. Granulation is accomplished by spraying the molten mass down a hollow reinforced concrete tower. While flowing from the tower, the drops of the molten mass solidify into granules, when they are cooled by the air forced up through the tower counter current to the drops by fans. The granules drop into a conveyer belt, which transports the product to the drying and packing sections.

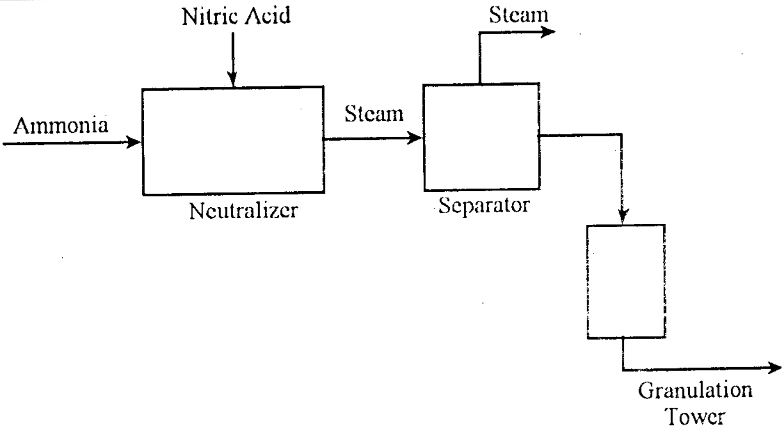


Fig. 14.16. Flow Sheet Diagram for the Manufacture of Ammonium Nitrate.

Some plants produce ammonium nitrate in the form of crystalline aggregates (flakes) instead of granules, by crystallizing the melt on the surface of a rotary drum cooled from the inside with water as shown in Figure 14.17. In this plant, the manufacture of ammonium nitrate is based on a rapid reaction under a pressure of 4 atmosphere between ammonia and 60 % nitric acid, preheated in inter changers. The vapour-liquid emulsion leaving the reactor is separated into its composite parts in a separate and the 97 – 98 % NH_4NO_3 melt is transferred to a granulator.

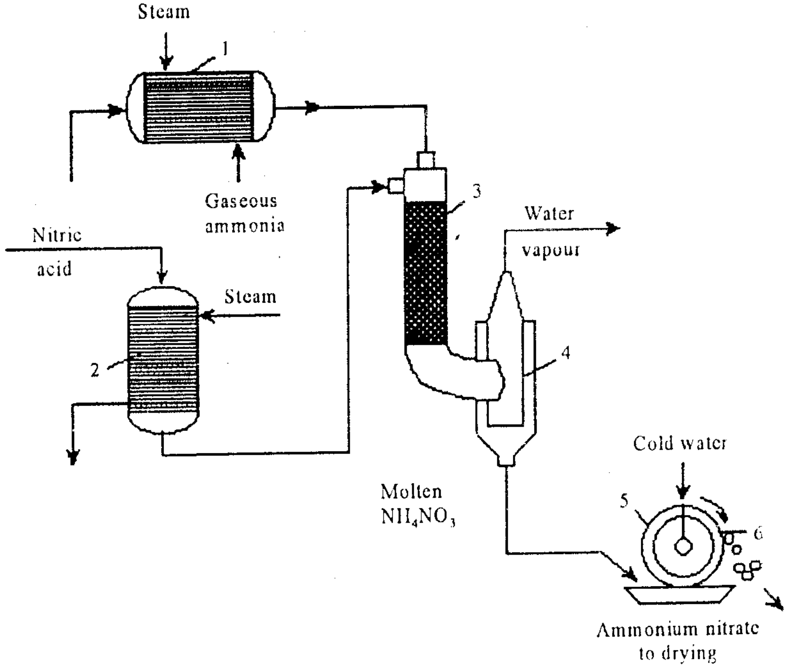


Fig. 14.17. 1. Ammonia heater, 2. Nitric acid heaters, 3. Reactor, 4. Separator, 5. Draw crystallizer, 6. Knife.

3. Ammonium Sulphate, $(NH_4)_2SO_4$

It is prepared from ammoniacal liquor which is a product of the dry distillation of coal. It contains various ammonium salts like $(NH_4)_2CO_3$, $(NH_4)_2S$, NH_4HS, NH_4CN, $(NH_4)_2SO_3$, $(NH_4)_2SO_4$ and NH_4Cl. The total ammonia in combination is 17 gm per litre.

The liquor is heated in stills, first by steam and then with calcium hydroxide to decompose the volatile as well as the fixed salts.

$$NH_4HS \underset{}{\overset{\text{Heat}}{\rightleftharpoons}} NH_3 + H_2S$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The mixture of ammonia and steam is passed through a lead lined tank containing 60 % H_2SO_4.

The ammonia gas may also be absorbed in suspended calcium sulphate (calcined gypsum) and CO_2 passed. The precipitated $CaCO_3$ is filtered off.

$$CaSO_4 + 2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

The synthetic ammonia is also converted into ammonium sulphate by absorbing it in sulphuric acid.

4. Ammonium Sulphur Nitrate

It may be prepared by mixing $(NH_4)_2SO_4$ and NH_4NO_3. The fertilizer is acidic in nature and is more suited to alkaline soils.

5. Ammonium Chloride

It is prepared from ammonium sulphate by boiling its solution with sodium chloride or by liberating ammonia from ammonium sulphate and absorbing it in hydrochloric acid. It is also made by neutralizing the ammoniacal liquor of the gas works with hydrochloric acid, evaporating the solution and crystallising.

PHOSPHATIC FERTILIZERS

The various phosphatic fertilizers depending on their composition, have different solubles in soil solutions and are, therefore, assimilated by plants differently. According to their solubility they are classified as water soluble, available and insoluble.

Simple and double or triple superphosphates are the examples of the **water soluble group**. Precipitated, calcined phosphate, fused phosphates and basic slag belong to the group of **available fertilizers**. Insoluble fertilizers contain non-readily available phosphorous salts, which are soluble only in strong inorganic acids. Examples of this group are phosphatic flour, apatites, bone flour, etc.

The solubility of phosphoric salts increases with increasing acidity of the salt. The neutral salt $Ca_3(PO_4)_2$ is only soluble in mineral acids. $CaHPO_4$ is soluble in organic soil acids and the most acid salt $Ca(H_2PO_4)_2$ is soluble in water. Naturally, therefore, in manufacturing phosphatic fertilizers it is desirable to convert as large a part of the phosphorus as possible into monocalcium phosphate $Ca(H_2PO_4)_2$. Amongst the artificial fertilizers used to improve the soil, **calcium hydrogen phosphate** or the **superphosphate** is one of the best known.

Calcium Superphosphate

It is prepared from the natural phosphate bearing rocks, the well-known minerals being phosphorite Ca_3PO_4, wavellite $2[2AlPO_4Al(OH)_3]$ 9HO, and apatite $3Ca(PO_4)_2{\cdot}CaF_2$. These minerals are insoluble in water but are decomposed under action of strong sulphuric acid and the calcium dihydrogen phosphate thus produced is soluble in water. This calcium salt is known as "superphosphate". So much heat is produced during the reaction that water is driven off and the product obtained is a solid mass. The reaction are as follows:

(i) In presence of enough water, the reaction is complete in one stage.

$$Ca_3(PO_4) \longrightarrow Ca_3P_2O_8$$

$$Ca_3P_2O_8 + 2H_2SO_4 + 5H_2O \longrightarrow 2[CaSO_42H_2O] + Ca(H_2PO_4)_2 . H_2O$$

(ii) In presence of restricted quantities of water.

$$3Ca_3P_2O_8 + 6H_2SO_4 \longrightarrow 4H_3PO_4 + Ca_3P_2O_8 + 6CaSO_4$$

$$3H_3PO_4 + Ca_3P_2O_8 \longrightarrow 3Ca(H_2PO_4)_2$$

$$3Ca(H_2PO_4)_2 + 3H_2O \longrightarrow 3Ca(H_2PO_4)_2 . H_2O$$

In this reaction the free phosphoric acid combines with tricalcium phosphate to form the water soluble calcium dihydrogen phosphate. The success of the reaction depends on:

(i) The regulated quantity of water, and *(ii) Concentration of sulphuric acid.* The quantity of water should be just sufficient to be utilized by the superphosphate hydrate, by the calcium sulphate hydrate and to allow for the loss of water by the heat of reaction. Too much of water leads to wet sludge and too little would leave free phosphoric acid. The concentration of sulphuric acid depends upon the composition of the rock. There are two processes for the manufacture of superphosphate:

(a) The Old Process.

(b) The Modern Process.

(a) The Old Process

In this process, the sulphuric acid is charged into a brick-lined pit and finely ground mineral phosphate added while the mass is agitated by hand rakes. Since in certain rocky minerals, such as fluorapatite or chlorapatite hydrofluoric or hydrochloric acid gas is evolved during the reaction (besides SO_2 fumes from the action of organic impurities and the acid), the process is very nauseating and is a nuisance to the workers.

Since the use of machinery, the old pit has been displaced by the "dens". The plant used is shown in Fig. 14.18. The well-powdered phosphate rock is introduced in a cylindrical mixer with the calculated quantity of conc. sulphuric acid. The whole is mixed by means of paddles for some time and then dumped mechanically into one of the dens A_1 or A_2 through the valves L_2 or L_1 where it is left for 24 hours. The reaction starts in the mixer, continues in the dens and the temperature usually rises to almost 100°C. Acid fumes are absorbed in water to give hydrofluorocilicic acid, H_2SiF_6.

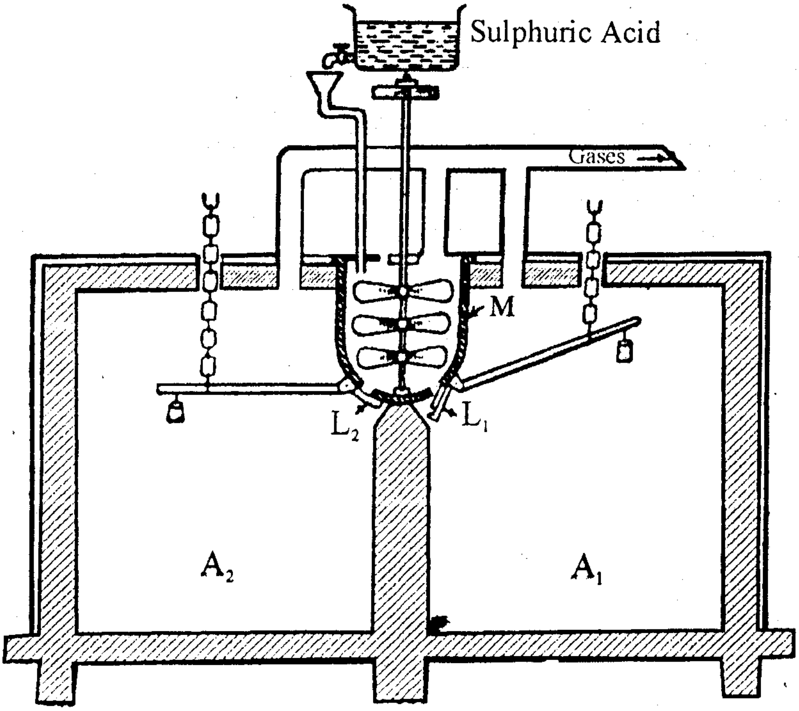


Fig. 14.18.

(b) The Modern Method

The chief feature of this process is the employment of a digester operated under pressure. The reaction as accelerated, but there is no evolution of fumes and no loss of water so that acid remains at the correct concentration. The finished product is also in a granular form, unlike a hard tough mass obtained in the old process.

The digesters are lead-lined autoclaves 21 ft. long and of double cone shape, being 5 ft. 7 inches in diameter at the ends and 6 ft. 7 inches at the centre. These vessels are jacketed for steam under 75 lb. pressure per square inch, and are geared to revolve five times per minute. Internally, they are submitted alternately to pressure and vacuum. They have an accommodation for 6 tons of charge which can be introduced in 1 minute and during the 30 minutes reaction, the internal pressure attained is 95 lbs. per square inch. The gaseous products are withdrawn by suction and the finished superphosphate, discharged in 3 to 4 minutes through a manhole while the vessel is still revolving and is carried by the endless belts.

Diammonium Phosphate, $(NH_4)_2 HPO_4$

This compound of fairly high purity may be prepared by a continuous process that consists of passing anhydrous ammonia gas and relatively pure phosphoric acid into saturated mother liquor kept at 60° – 70°C and pH 5.8 to 6.0. The heat of reaction vaporizes water from the liquor and the crystals of diammonium phosphate developed are withdrawn, centrifuged, washed and dried. This product contains about 75 % plant nutrients and is deemed suitable for use either alone or in mixture with other fertilizers.

Nitrophosphate

A new process for making nitrophosphate fertilizers has been developed in Germany. The novel feature of this process is the use of carbon dioxide to convert corrosively unstable and hygroscopic calcium nitrate into carbonate without separating the nitrate from the mixture. Salts containing magnesium and aluminium have to be incorporated before ammoniation of the nitric acidulated phosphate.

Mixed Fertilizers Without Sulphuric Acid

The recent improvement in this field consists of obtaining complex fertilizers containing proper proportions of essential nitrogen, phosphorus and potash. The process is simple and consists in acidulating the phosphate rock by nitric acid, treating the mass with ammonia and then with carbon dioxide and a stabilizer, such as magnesium sulphate. The total reactions of the process are summarized below:

Acidulation

$$P_2O_5 . 3.5CaO + 6HNO_3 \longrightarrow P_2O_5 . 0.5CaO + 3Ca(NO_3)_2 + 3H_2O$$

Ammoniation Carbonation

$$P_2O_5 . 0.5CaO + 3Ca(NO_3)_2 + 6NH_3 + 1.5CO$$

$$\downarrow$$

$$P_2O_5 . 2CaO + 6NH_4NO_3 + 15CaCO_3$$

Fertilizer Industry in Pakistan

Pakistan is essentially an agricultural country. In order to keep up the production of agricultural commodities and to compensate the potential of land, which gets exhausted by repeated cultivations, the use of fertilizers has gained importance. The Government of Pakistan is trying its utmost to meet the supply and demand of the cultivators in this regard and is setting up new factories located at the places shown in the following chart along with their annual production capacity.

NFC AND PRIVATE FACTORIES

Location	Name of the Factory	Name of Product	Annual Capacity
NFC N.W.F.P. Hazara	Pak-China Fertilizer Ltd. Hazara Phosphate Plant	Urea S.S.P.	95,700 tons 80,000 tons
PUNJAB Faisalabad	Lyallpur Chemicals & Fertilizers Ltd. Fertilizer Research Development Institute Ltd.	S.S.P. $ZnSO_4$ Home Garden Fertilizer	24,000 tons 2,000 tons 60,000 tons
Jaranwala	Lyallpur Chemicals & Fertilizers (Ltd.)	S.S.P.	90,000 tons
Multan	Pak-Arab Fertilizer Ltd.	Urea Nitrophos N.P. Amm. Nitrate	90,000 tons 3,24,000 tons 45,000 tons
Daud Khel	Pak-American Fertilizer Ltd.	Amm. Sulphate Urea Plant (Under construction)	90,000 tons 95,000 tons
PRIVATE Lahore	Dawood Hercules Fertilizer (Ltd.)	Urea	3,45,000 tons
SIND Mirpur	Pak-Saudi Fertilizer (Ltd.)	Urea	6,46,200 tons
Sadiqabad	Fauji Fertilizers Corporation (Ltd.)	Urea	5,57,000 tons
Dharki	Esso Fertilizer Company	Urea	1,73,000 tons

Questions

1. Discuss the comparative chemistry of nitrogen and phosphorus giving emphasis on their compound formation.
2. How would you prepare a specimen of pure nitrogen?

   What is the action of nitrogen on (a) CaC_2 (b) Mg (c) Na_2CO_3 and C?

   Give an outline of the methods used to utilize atmospheric nitrogen.
3. Write an essay on the Nitrogen cycle. Discuss its importance in nature.
4. Discuss the chemistry of compounds containing nitrogen atom in diagonal and trigonal valence state.
5. How are the different oxides of nitrogen obtained? Describe their chemistry and structures.
6. (a) How would you prepare dry ammonia in the laboratory? What are its important reactions and tests?

   (b) 5.35 gm. of NH_4Cl is heated with excess of quicklime. What is the weight of NH_3 obtained? If all ammonia thus liberated is absorbed in 1 litre of water, calculate the normality of the solution.
7. Describe (a) Haber process, and (b) the cyanamide process for the manufacture of ammonia.
8. Discuss the various methods used for the manufacture of nitric acid.
9. Give the reactions of nitrous acid in which it acts as oxidising and reducing agent.
10. Write an essay on compounds of nitrogen in which it is tetrahedrally hybridised.
11. Discuss the structure of ammonia. Give a few examples where ammonia acts as an acid and a base.
12. Describe various methods for the preparation of hydrazine. How it is obtained in anhydrous state? Give some of its typical reactions and structure.
13. Write a short note on the chemistry of NH_2OH.
14. How many allotropic forms of phosphorus have been isolated? How are they interconverted and prepared?
15. How would you distinguish between white and red phosphorus? Discuss some of the typical reactions of white phosphorus.

16. Describe the manufacture of phosphorus on a large scale. How is red phosphorus prepared?

17. How is orthophosphoric acid prepared from (a) bone ash, (b) phosphorus? How is orthophosphoric acid converted into other oxyacids of phosphorus?

18. Complete and balance the following equations:
    (a) $S + HNO_3 \text{ (conc.)} \longrightarrow$
    (b) $NH_4NO_3 \xrightarrow{\Delta}$
    (c) $NH_2OH + HNO_2 \longrightarrow$
    (d) $I_2 + HNO_3 \longrightarrow$
    (e) $P_4 + NaOH \longrightarrow$
    (f) $P_4O_{10} + H_2O \longrightarrow$

19. Discuss the hydrides of phosphorus emphasizing on PH_3. How would you compare it with NH_3?

20. Predict the products of the following reactions:
    (a) Acid solution of KNO_2 and $FeSO_4$.
    (b) BF_3 bubbled through liquid hydroxylamine.
    (c) HCl passed through P_4O_6.
    (d) NO passed through $Fe_2(CO)_9$.
    (e) NO_2 vapours passed over hot Cu.

21. By means of equations, illustrate the behaviour of NH_3 as:
    (a) a base,
    (b) a reductant,
    (c) a complexing agent.

22. If 60 ml. of NH_3 and 60 ml. of O_2 at S.T.P., are reacted according to the equation

$$4NH_{3(g)} + 3O_{2(g)} \longrightarrow 2N_{2(g)} + 6H_2O_{(g)}$$

    (a) What volume of oxygen is left unreacted?
    (b) What volume of nitrogen is produced?
    (c) What is the total change in volume after the reaction?

23. What are Fertilizers? Why are they needed? Discuss the classification of fertilizers and their uses.

24. How are the urea and ammonium nitrate manufactured in Pakistan? Describe in detail the processes used.

25. Discuss in detail the manufacture of calcium superphosphate. Describe the various reactions involved in the process. What are the prospects of fertilizer industry in Pakistan?

26. **Give short answers to the following questions:**

(i) Write the electronic configuration of the following with atomic numbers given in brackets.

(a) N(7) (b) P(15) (c) As(33) (d) Sb(51) (e) Bi(83)

(ii) Discuss nitrogen cycle in atmosphere.

(iii) What is laughing gas? How is it prepared? Draw the delocalised π-orbitals in it.

(iv) Draw the molecular orbital diagram of NO.

(v) Give typical reactions of NO_2.

(vi) Discuss the role of oxides and oxyacids of nitrogen in environmental pollution, especially in acid rain and formation of 'smog'.

(vii) Describe the present status of water pollution.

(viii) Give the reactions of HNO_2 with the following:

(a) H_2O_2 (b) Br_2 (c) KI (d) $FeSO_4$ (e) $SnCl_2$

(ix) How is HNO_3 manufactured?

(x) Write reactions of HNO_3 with the following:

(a) Zn (b) Cu (c) C (d) S (e) P

(xi) How is ammonia manufactured by Haber Process?

(xii) Give reactions of NH_3 with the following:

(a) BF_3 (b) Cu^{2+} (c) Cl_2 (d) K_2HgI_4 (e) CS_2

(xiii) Describe pyramide structure of NH_3 on the basis of sp^3 hybridisation.

(xiv) What is hydrazine? How is it prepared?

(xv) Give reactions of hydrazine with the following:

(a) Cl_2 (b) H_2O_2 (c) HCl (d) CH_3Br (e) CH_3CHO

(xvi) Draw structure of hydrazine.

(xvii) How is hydroxylamine prepared?

(xviii) Write reactions of the following with NH_2OH:

(a) Cl_2 (b) $FeCl_3$ (c) CuO (d) HNO_2 (e) H_2O_2

(xix) How is phosphorus prepared?

(xx) Discuss the allotropic forms of phosphorus.

(xxi) Give reactions of the following with P:

(a) F_2 (b) $NaOH$ (c) H_2SO_4 (d) CaO (e) $CuSO_4$

(xxii) What is phosphine? How is it prepared?

(xxiii) Give reactions of PH_3 with the following:

(a) O_2 (b) N_2O (c) Cl_2 (d) $AgNO_3$ (e) $CuSO_4$

(xxiv) How in phosphorus pentachloride prepared? Draw its structure.

(xxv) How is phosphoric acid, H_3PO_4 prepared?

(xxvi) What is relationship between meta and orthophosphoric acids?

(xxvii) What are fertilizers? How are they classified?

(xxviii) How is urea synthesized? Name major industries in Pakistan which manufacture urea.

(xxix) How is calcium superphosphate synthesised?

27. **Give the correct answer:**

(i) Which of the following oxides is neutral?

(a) N_2O_5 (b) N_2O_3

(c) N_2O_4 (d) N_2O

(ii) Action of conc. HNO_3 on metallic tin produces:

(a) stannous nitrate (b) stannous nitrite

(c) stannic nitrate

(d) stannous oxide (hydrated)

(iii) The starting material in Birkland & Eyde process for the manufacture of HNO_3 is:

(a) NH_3 (b) NO_2

(c) air (d) KNO_3

(iv) Which of the following oxides is brown gas?

(a) NO_2 (b) NO

(c) N_2O (d) N_2O_5

(v) When P_2O_5 is heated with conc. HNO_3, if forms?

(a) NO (b) N_2O

(c) NO_2 (d) N_2O_5

(vi) Ammonia is dried over:

(a) slaked lime (b) quick lime

(c) $CaCl_2$ (d) PCl_5

(vii) Which of the following acids, possesses oxidizing, reducing and complex forming properties?

(a) HCl (b) HNO_2

(c) HNO_3 (d) H_2SO_4

(viii) Which of the following in tetrabasic?

(a) orthophosphoric acid (b) orthophosphorus acid

(c) metaphosphoric acid (d) pyrophosphoric acid

(ix) Phosphine is prepared by the action of:

(a) P and H_2SO_4 (b) P and NaOH

(c) P and H_2S (d) P and HNO_3

(x) Which of the following is the most stable?

(a) PH_3 (b) SbH_3

(c) NH_3 (d) AsH_3

(xi) The strongest acid oxide is:

(a) SO_2 (b) SO_3

(c) P_2O_5 (d) Sb_2O_3

(xii) Nitric acid in the bottle on standing develops brown fumes which are due to:

(a) NO_2^+ (b) NO_2^-

(c) NO_2 (d) NO

(xiii) Which of the following does not exist?

(a) PF_5 (b) AsF_5

(c) SbF_5 (d) BiF_5

(xiv) HNO_3 (dilute) reacts with Zn to produce:

(a) NO (b) NH_4NO_3

(c) NO_2 (d) O_2

(xv) Which element of Group VA gives the most basic compound with hydrogen?

(a) N (b) Bi

(c) As (d) P

(xvi) Ammonium nitrite on heating produces:

(a) N_2O (b) N_2

(c) N_2O_3 (d) N_2O_4

(xvii) Phosphoric acid reacts with NaOH to produce:

(a) Na_3PO_4 (b) NaH_2PO_4

(c) Na_2HPO_4 (d) $NaHPO_3$

(xviii) The structure of PCl_5 is:

(a) octahedral (b) trigonal bipyramidal

(c) tetrahedral (d) pyramidal

(xix) PCl_3 reacts with water to produce:

(a) PH_3 (b) H_3PO_3

(c) $POCl_3$ (d) H_3PO_4

(xx) White phosphorus reacts with caustic soda to produce PH_3 and NaH_2PO_2. The reaction is:

(a) oxidation (b) reduction

(c) reduction and oxidation (d) neutralization

(xxi) The explosive compound of nitrogen is:

(a) N_2O_5 (b) NH_3

(c) NF_3 (d) NCl_3

(xxii) Urea reacts with hydrogen to give:

(a) N_2 (b) H_2

(c) CO (d) $N_2 + H_2$

(xxiii) A mixture of NH_3 and air at about 800°C in presence of Pt gauze forms?

(a) N_2O (b) NO

(c) NH_2OH (d) N_2O_3

(xxiv) Nitric oxide is prepared by the reaction of:

(a) Cu and HNO_3 (b) C and HNO_3

(c) Cu and N_2O (d) Ag and HNO_2

(xxv) Bond order of NO is:

(a) 1.5 (b) 2.0

(c) 2.5 (d) 3.0

(xxvi) Hydrolysis of PCl_3 produces:

(a) H_3PO_3 and HClO (b) H_3PO_3 and HCl

(c) H_3PO_4 and HCl (d) PH_3 and HClO

(xxvii) Which of the following elements does not form stable diatomic molecules?

(a) iodine (b) phosphorus

(c) nitrogen (d) oxygen

(xxviii) Pure N_2 is obtained from:

(a) $NH_3 + NaNO_2$ (b) $NH_4Cl + NaNO_2$

(c) $N_2O + Cu$ (d) $(NH_4)_2Cr_2O_7$

(xxix) Concentrated HNO_3 oxidises sugar to:

(a) CO_2 and H_2O (b) CO and water

(c) CO, CO_2 and H_2O (d) oxalic acid and water

(xxx) Orthophosphoric acid on heating gives:

(a) phosphine (b) P_2O_3

(c) phosphorous acid (d) metaphosphoric acid

(xxxi) Urea is a high quality nitrogenous fertilizer with:

(a) 76 % nitrogen (b) 46 % nitrogen

(c) 66 % nitrogen (d) 26 % nitrogen

❀ ❀ 14 ❀ ❀

15

SULPHUR (GROUP VIA)

The elements of this group are oxygen, sulphur, selenium, tellurium and polonium. Polonium is the disintegration product of radium. The characteristic valency shell configuration for these elements is $ns^2\ np^4$ (See Table 15.1). By gaining 2 electrons the elements attain the next inert gas configuration and form bivalent anions such as: O^{2-}, S^{2-}, Se^{2-} and Te^{2-}.

TABLE 15.1

Electronic Configurations of Group VIA Elements.

Element	1	2		3			4				5			6	
	s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
O	2	2	4												
S	2	2	6	2	4										
Se	2	2	6	2	6	10	2	4							
Te	2	2	6	2	6	10	2	6	10		2	4			
Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4

It is clear from the electronic configuration of the elements, that their atoms contain one pair of *s* electrons and four electrons in *p* orbitals. Two of the *p* electrons are paired and the other two remain unpaired, *e.g.*, np_x^2, np_y^1, np_z^1. In this way, all these elements show a covalency of two. These elements can also gain a pair of electrons by acting as electron-pair acceptors in a dative covalent bond.

Oxygen is found to show 2-covalent, 3-covalent and 4-covalent compounds at the most. However, two and three covalent compounds are more common. An example of 2-covalent compound is H_2O and that of 3-covalent compound is H_3O^+. Sulphur and other elements can promote the electrons from *ns* and *np* orbitals to vacant *d* orbitals. As a result of this six electrons become unpaired and spread over *s*, *p* and *d* orbitals. Sulphur, selenium and tellurium would be able to utilize two, four or all the six electrons in the valency shell and would form 2, 4 and 6-covalent bonds, respectively, *e.g.*, SCl_2, SCl_4 and SF_6.

Oxygen is a colourless, odourless gas present in air. Sulphur is a yellow solid existing in a number of allotropic modifications. Selenium also exists in two solid allotropic forms, grey and red. Tellurium is a brittle, silvery grey, crystalline solid. Some of the physical properties of these elements are shown in Table 15.2.

TABLE 15.2

Physical Properties of Elements of Group VIA

	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic weight	15.9994	32.064	78.96	127.60	approx. 210
Atomic radius (pm)	74	104	117	137	153
Ionic radius (pm)	140	184	198	221	—
Density of solid (g/cm^3)	1.27	2.06	4.50 (grey)	6.24 (metal)	9.51
Melting point (°C)	– 218.9	112.8	217.4	450	254
Boiling point (°C)	– 183	444.6	688	1390	962

GROUP TRENDS

The general trends in physical and chemical properties are quite expected such as:

(i) There is an overall increase in metallic character down the group.

(ii) The stability of the 2 oxidation state decreases down the group.

(iii) The +6 oxidation state decreases in stability down the group, and the stability of +4 state increases down the group.

(iv) The tendency to form compounds containing larger co-ordination numbers increases down the group *e.g.*, TeF_8^{2-}.

(v) The tendency to form condensed acids decreases sharply from sulphur to selenium.

(vi) Catenation decreases from sulphur to selenium.

(vii) The acidity of the oxides decreases down the group.

(viii) The hydrides show decreasing thermal stability and increasing acidity with increase in atomic number in the group.

Comparison of Oxygen and Sulphur

Oxygen differs from sulphur in the following respects:

(i) Oxygen is a colourless gas but sulphur is a yellow solid.

(ii) Oxygen occurs more abundantly in nature than sulphur or other members of the group.

(iii) Oxygen adopts generally the negative oxidation state of –2 much more readily as compared to other elements. But this tendency of adopting –2 oxidation state decreases in the order O > S > Se > Te > Po.

(iv) The tendency to form negative oxidation state is more pronounced in oxygen. Hence it acts as good oxidising agent as compared to other elements of the group.

(v) Oxygen does not lose 6 electrons to 'assume +6 state which is more common for S, Se and Te.

(vi) Oxygen possesses small atomic volume and high ionization potential as compared to other members of the series. This gives special properties to oxygen.

(vii) Oxygen is one of the most electronegative elements except fluorine. This gives special properties to oxygen. Thus heat of formation of H_2O (246.9 KJ/mole) is much more than that of H_2S, H_2Se and H_2Te.

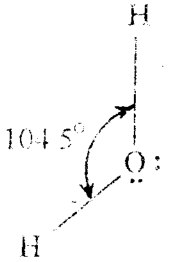
The strength of the acidity and reducing power increases in the order:

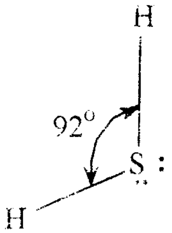
$$H_2O < H_2S < H_2Se < H_2Te < H_2Po$$

(viii) The double bond in O_2 is stronger than in sulphur. Therefore, oxygen can exist as O_2 but S, Se and Te do not exist as separate molecular species. The bond energy in O = O is much more than S = S.

(ix) O_2 molecule shows paramagnetic behaviour which is not so pronounced in other elements of the group.

(x) Although the molecular structures of H_2O and H_2S are similar but due to electronegativity difference and increase in ionic radii the bond length and bond angle would differ.





Points of Resemblance in O_2 and S

(i) O_2 and S do not show photoelectric behaviour.

(ii) Both oxygen and sulphur show the phenomenon of allotropy.

(iii) Both of them exist in [illegible] states.

General Reaction of Sulphur Group

(1) Reaction with Air

S, Se and Te form dioxides when ignited in air. The oxides have acidic character.

(2) Reaction with Water

The members of sulphur group do not react with water under ordinary conditions.

(3) Reaction with Acids

Only oxidizing acids, such as HNO_3, $HClO_4$ etc., react with S, Se and Te.

$$Se + 6HNO_3 \longrightarrow \underset{\text{Selenic acid (White solid)}}{H_2SeO_4} + 6NO_2 + 2H_2O$$

(4) Reaction with Alkalies

Alkali solutions dissolve S, Se and Te to form polycompounds, *i.e.*, polysulphides.

(5) Reaction with Halogens

Variety of halides are obtained with these elements such as MX_2, MX_4, MX_6 etc.

(6) Metal sulphides, selenides and tellurides are stable compounds and occur in nature.

(7) Oxyacids

S, Se and Te form oxyacids which give well defined salts.

(8) Hydrides

Well-known hydrides H_2O, H_2S, H_2Se and H_2Te are obtained by reaction of elements with H_2.

The lithosphere contains about 47% oxygen by weight and oceans about 89%. Ordinary oxygen is found to contain ^{18}O (0.2%) and ^{17}O (0.04%) in addition to ^{16}O. Oxygen is quite reactive and forms atomic oxygen when O_2 is passed through electric discharge or irradiated by ultraviolet light. O_2 forms oxides with metals and non-metals such as:

$$2Ca + O_2 \longrightarrow 2CaO$$

$$Si + O_2 \longrightarrow SiO_2$$

$$4P + 5O_2 \longrightarrow P_4O_{10}$$

Ozone is an allotropic form of O_2. Higher regions of the atmosphere contain some amount of ozone.

Ozone can be prepared,

(i) by subjecting O_2 to electric discharge,

(ii) by the action of F_2 on water,

$$3Fe + 3H_2O \longrightarrow 6HF + O_3$$

(iii) by electrolysing aqueous perchloric acid at –50°C between lead cathode and platinum anode.

Ozone is unstable and acts as powerful oxidizing agent. The oxidation reactions of O_3 are exemplified below:

$$2KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2$$

$$2HCl + O_3 \longrightarrow H_2O + Cl_2 + O_2$$

$$N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$$

$$3SO_2 + O_3 \longrightarrow 3SO_3$$

$$I_2 + H_2O + 5O_3 \longrightarrow 2HIO_3 + 5O_2$$

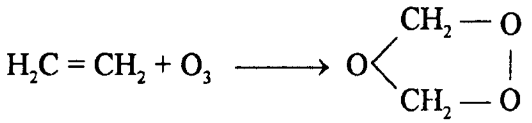
$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

$$3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$$

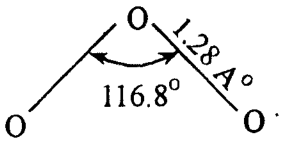
$$2Ag + O_3 \longrightarrow Ag_2O + O_2$$

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$



Structure

Microwave and electron diffraction (ethylene ozonide) studies show the molecule of ozone to be angular.

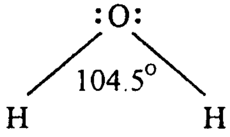


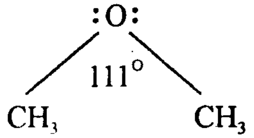
Stereochemistry of Covalent Compounds of Oxygen

Stereochemistry of covalent compounds of oxygen can be described on the following basis:

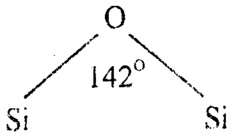
1. Two-Coordinate Oxygen:

Majority of oxygen compounds are two-coordinate. In these compounds, oxygen forms two single bonds to other atoms and has two unshared pairs of electrons in its valence shell. For example, water, oxides, ethers and alcohols.

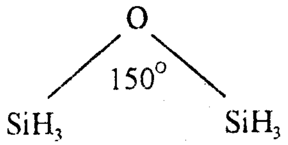




Atoms containing *d*-orbitals can also interact with oxygen to form A–O–A bonds. Such interaction results in shortening of bond and widening of bond angle.



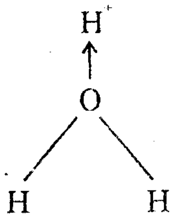
(in Quartz)

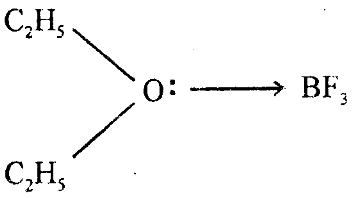


2. Three-Coordinate Oxygen:

Three coordinate bonds form either pyramidal or planar geometries.

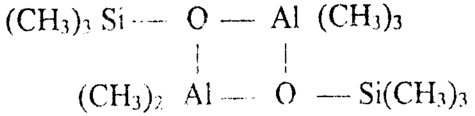
The pyramidal geometries are represented by 'oxonium ions' *e.g.*, H_3O^+, ROH_2^+, R_3O^+ and Lewis acid-base complexes.





When water, alcohol and ether act as ligands for metal ions, pyramidal complexes are formed.

Three bonds to oxygen are coplanar such as:



$$\begin{array}{ccccc} (CH_3)_3\,Si - & O & - & Al & (CH_3)_3 \\ & | & & | & \\ (CH_3)_2\;Al - & O & - & Si(CH_3)_3 & \end{array}$$

3. Four-Coordinate Oxygen:

This coordination number is not common. A few examples of four coordinate oxygen are given below.

$Cu_4OCl_6\,(Ph_3PO)_4$	$Mg_4OBr_6 \,.\, 4C_4H_{10}O$
(Ph_3 = triphenylphosphine)	(C_4H_{10} = butyl group)

4. Unicoordinate, Multiply-bonded Oxygen:

One coordinate compounds of oxygen are known. A typical example is XO group *e.g.*, $\gt\overset{+}{N}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$ Equilibrium exists between two ionic species of XO group

$$\overset{+}{X}\;:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-} \quad \longleftrightarrow \quad \overset{-}{X}::\overset{+}{O}:$$

R_3PO (R = alkyl group), R_3 As O, MnO_4^-, OsO_4, PO_4^{3-}, ClO_4 etc., are examples of such type species.

SULPHUR

Occurrence

Sulphur occurs in nature in free and combined states.

In the free state, it mainly occurs near volcanic regions of the earth. Free sulphur is usually found under the earth's surface at about 700 – 900 feet below.

Sulphur in the combined state is found in nature as:

Iron pyrites	FeS_2
Copper pyrites	$Cu_2S \cdot FeS_2$
Galena	PbS
Cinnabar	HgS
Orpiment	As_2S_3
Gypsum	$(CaSO_4 \cdot 2H_2O)$

Extraction of Sulphur

Sulphur is being extracted by different methods which depend upon the source. The following methods are more common:

1. Frasch Method

This process is used for getting sulphur from the underground. A hole is drilled through which four concentric pipes are passed up to the sulphur-bearing bed. The innermost pipe is used to compress air and the pipe next to it is used to pass steam which melts the sulphur under the earth. Molten sulphur and its emulsion with water flow out of the third pipe (from inside). The outermost pipe allows the unused steam to be removed.

The emulsified sulphur is transferred to large settling tanks where it solidifies on cooling. This process gives about 99% pure sulphur which can directly be used without further purification.

2. Sicilian Process

In Sicily, sulphur is found mixed with gypsum and quartz. The lumps of ore in the form of heap are heated in closed chamber. Sulphur melts and is collected from the base of the chamber.

The sulphur thus obtained is further refined in closed iron retorts and sulphur vapours are collected in large chambers to get **flowers of sulphur**. This is melted to get **roll sulphur** or **brimstone**.

3. From Sulphides and Sulphide Ores

The sulphide ores are usually treated to extract metals, and SO_2 is obtained as a result of roasting during this process. Sometimes it becomes necessary to reduce SO_2 to free sulphur.

$$SO_2 + C \longrightarrow S + CO_2$$

The overall process starting from CaS is:

$$CaS + H_2O + CO_2 \longrightarrow CaCO_3 + H_2S$$

$$2H_2S + O_2 \longrightarrow 2S + 2H_2O$$

4. From Coal Gas

Coal gas contains H_2S which is removed by passing the gas over heated Fe_2O_3 to get Fe_2S_3 and FeS. The mixture is known as **spent oxide**. When Fe_2S_3 and FeS mixture is allowed to remain in contact with water and air to undergo weathering, sulphur is deposited.

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$

$$2Fe_2S_3 + 3O_2 + 2H_2O \longrightarrow 2Fe_2O_3 + 2H_2O + 6S$$

5. By Bacterial Action

Certain bacteria have the remarkable ability to convert sulphates into free sulphur. Artificially prepared strains of bacteria have been used to prepare sulphur from calcium sulphate.

ALLOTROPIC FORMS OF SULPHUR

Sulphur exists in several **allotropic** forms. These allotropic forms exist in the solid, liquid and gaseous states. We shall discuss these various allotropes of sulphur under these three main headings:

1. SOLID SULPHUR

Several crystalline forms of sulphur exist in solid state. The following species are well established:

(a) Cyclo-octasulpur, S_8

This is the most common molecular species which exists in three main allotropes or crystal forms:

(i) Rhombic Sulphur or α-Sulphur: The first allotropic form is called *rhombic sulphur*. It is the most stable form and is composed of S_8 molecules. This is also called *octahedral* or *α-sulphur*. This form consists of S atoms in S_8 molecule giving eight-membered ring. The arrangement is **'puckered'**, *i.e.*, four S atoms lie in one plane and the other four S atoms lie in another plane (Figure 15.1) held together by Van der Waals' forces. Each sulphur atom is linked to the other atom by a single covalent bond.

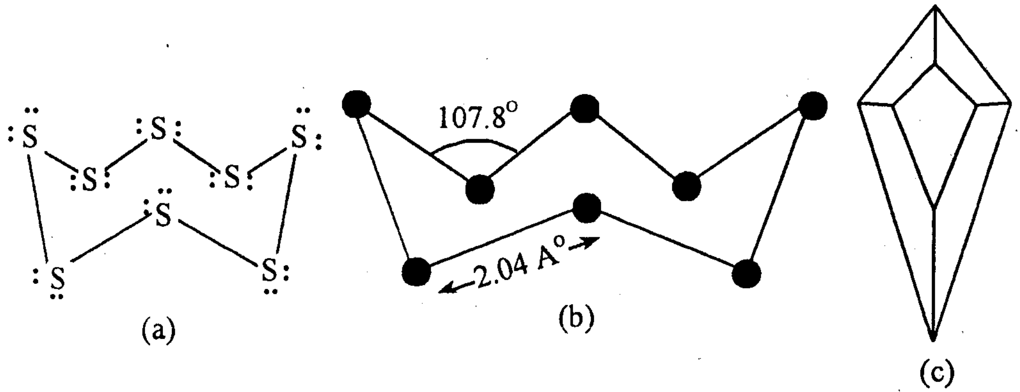


Fig. 15.1. Structure of rhombic form containing S_8 molecule in sulphur.

(a) Electronic arrangement in S_8 molecule.

(b) Puckered arrangement in rhombic sulphur.

(c) Crystals of rhombic sulphur.

Rhombic or α-sulphur (S_α) can be obtained by dissolving ordinary sulphur in CS_2 or benzene and evaporating it to get transparent yellow crystals of shape (Figure 15.1 c). The rod sulphur sold in the market consists of rhombic sulphur having poorly shaped crystals.

Rhombic sulphur has density of 2.07 g/cm^3 and a melting point of 112.8C°. It is insoluble in water but dissolves in CS_2 and benzene.

(ii) Monoclinic Sulphur or β-Sulphur: This crystal form is obtained by melting sulphur and cooling slowly. The sides of the container will be covered on the inside with long, deep yellow, needle-like crystals of **monoclinic** or **prismatic** or **β-sulphur** (S_β). It has density of 1.96 g/cm^3 and melts at 96°C. At ordinary temperatures, the monoclinic sulphur slowly changes into rhombic form. On heating rhombic form below 100°C, it is reconverted to monoclinic sulphur.

Rhombic or α-sulphur $\xrightarrow{95.5^\circ C}$ Monoclinic or β-sulphur. The enthalpy of transition is small.

In laboratory, monoclinic sulphur is prepared by heating roll sulphur (rhombic sulphur) in a china dish on a sand bath. When whole of sulphur has just melted, the dish is allowed to cool until a crust is formed on the surface. Two holes are pierced through the crust and liquid is poured out. Transparent yellow needles of monoclinic sulphur will be sticking to the sides to the dish.

On keeping monoclinic or β-form for a few days the deep yellow crystals become opaque and change to lemon yellow crystals, owing to conversion into rhombic or α-sulphur.

Monoclinic sulphur is insoluble in water but soluble in CS_2. The solution on evaporation yield rhombic sulphur. Crystals shape of monoclinic sulphur is shown in Figure 15.2.

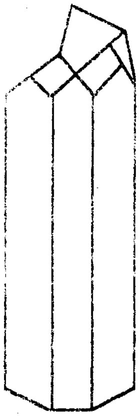


Fig. 15.2. Shape of monoclinic sulphur.

Another form of monoclinic sulphur (Sr; m.p. 106.8°C) is obtained by slow crystallization of sulphur from ethanolic ammonium polysulphide solution.

(b) Cyclohexasulphur, S_6 (S_p)

This is rhombohedral sulphur and is prepared by addition of concentrated HCl to a solution of $Na_2S_2O_3$ at low temperature (–10°C). The precipitate of S is extracted with benzene and crystallized to get orange crystals. They are unstable and decompose in presence of light and impurities.

S_6 or Sp can also be obtained from the following reaction:

$$H_2S + S_4Cl_2 \longrightarrow S_6 + 2HCl$$

(c) Other Cyclosulphur

Thermodynamically unstable allotropes of sulphur are obtained which contain 7–, 9–, 10–, 12– membered rings. The general method of preparation is:

$$(C_5H_5)_2\,TiS_5 + S_nCl_2 \xrightarrow{CS_2} (C_5H_5)_2\,TiCl_2 + S_{5+n}$$

These cyclosulphurs have the following physical properties:

S_7: intense yellow, m.p. 30°C, polymerizes to viscous liquid (45°C)

S_9. intense yellow, more stable than S_7.

S_{10}. intense yellow, polymerizes above 60°C to viscous liquid.

S_{12}. light yellow, m.p. 145°C.

2. LIQUID SULPHUR

If any form of solid sulphur is heated to just above the melting point (119°C), a clear straw coloured liquid is obtained, which again contains S_8 molecules. On raising the temperature beyond 160°C, the S_8 rings are ruptured and liquid sulphur is obtained. Liquid sulphur consists of long open chains of S atoms to form λ-sulphur.

$$-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-\ddot{\underset{\cdot\cdot}{S}}-$$

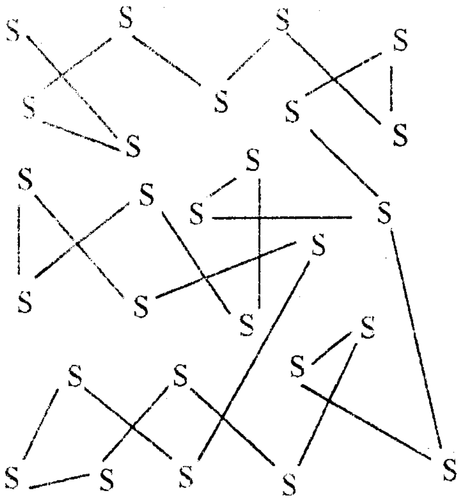


Fig. 15.3. Coiled chains of plastic sulphur.

If yellow liquid sulphur (λ-sulphur) is suddenly poured in ice cold water, a soft, sticky, rubber-like material is formed, called **plastic sulphur**. Plastic sulphur contains long chains of sulphur atoms coiled up as shown in Figure 15.3.

The elasticity of plastic sulphur is due to uncoiling of chains under tension and recoiling of chains when tension is removed. These coiled chains seem to be under tension and rearrange to S_8 ring molecules. This is ascertained by slow change of plastic sulphur to brittle rhombic sulphur.

If the temperature of liquid sulphur is raised further, the yellow liquid gradually darkens. At 160°C it becomes viscous and at about 200°C, gummy, brown semi-solid is obtained. On raising the temperature beyond 200°C, the liquid again becomes less viscous until at boiling point (444.6°C) it is almost black, mobile liquid. The changes in physical properties may be correlated to the formation of several different geometric arrangements.

3. VAPOUR SULPHUR

The liquid sulphur is made up of S_8 molecules at 444.6°C (boiling point). At this temperature, the liquid is in equilibrium with rod sulphur vapours, which contain mostly cyclic S_8 molecules. Above the boiling point, the S_8 molecules dissociate into S_2 molecules and the colour of the vapour changes to yellow.

Above 2,000°C the S_2 molecules partially dissociate into gaseous monoatomic atoms.

$$S_{2(g)} \xrightleftharpoons{2000^\circ C} 2S_{(g)}$$

4. COLLOIDAL SULPHUR

Colloidal sulphur is formed by the interaction of H_2S and SO_2 or by the decomposition of $Na_2S_2O_3$ with H_2SO_4. Colloidal sulphur may be formed by the

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

$$Na_2S_2O_3 + H_2SO_4 \longrightarrow S + Na_2SO_4 + SO_2 + H_2O$$

addition of an electrolyte such as alum solution.

Properties of Sulphur

Elementary sulphur is a non-metallic stable solid and quite reactive. Many metals undergo ready reaction with metals. Thus, rubbing mercury with sulphur would give HgS.

Elementary sulphur is both oxidizing and reducing agent. Sulphur contains $3s^2\ 3p^4$ valence electrons and would take up 2 electrons to get $3s^2\ 3p^6$ (next inert gas configuration) electrons and hence would act as an oxidizing agent and the S is reduced to S^{2-}. The oxidation of S involves loss of electrons and is oxidized to +4 and +6 oxidation states whereby acting as a reducing agent.

The following are the typical reactions of sulphur:

(i) Reaction with H_2

Sulphur combines directly with H_2 to give H_2S.

$$H_2 + S \longrightarrow H_2S$$

The amount of H_2S formed increases with temperature.

(ii) Reaction with non-metals

Sulphur reacts directly with other non-metals, *i.e.*, C, Cl_2, etc.

$$C + 2S \longrightarrow CS_2$$

(iii) Reaction with metals

Sulphur reacts with metals such as Zn, Al and Fe on heating to give sulphides.

$$Zn + S \longrightarrow ZnS$$

$$Fe + S \longrightarrow FeS$$

It represents the oxidizing action of S.

(iv) Reducing agent

When sulphur is treated with oxidizing agents, it acts as a reducing agent as is exemplified by the following reactions:

(a) Reaction with O_2: Sulphur burns in air or oxygen with blue flame to give SO_2 and traces of SO_3 (3 – 4%).

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

If S is exposed to moist air; it may be oxidised to H_2SO_4.

$$2S + 2H_2O + 3O_2 \longrightarrow 2H_2SO_4$$

(b) Reaction with halogens: Halogens combine directly with sulphur to form a series of products.

$$S + F_2 \longrightarrow S_2F_2, SF_4, SF_6, S_2F_{10}$$
$$S + Cl_2 \longrightarrow S_2Cl_2, SCl_2, SCl_2$$
$$S + Br_2 \longrightarrow S_2Br_2$$

(c) Reaction with acids: S reacts with oxidizing acids such as HNO_3 and H_2SO_4 (concentrated and hot) and is oxidised.

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$
$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(v) Reaction with water

S reacts with steam to form H_2S and SO_2. In this reaction sulphur is reduced as well as oxidised.

$$S + 2H_2O \longrightarrow 2H_2S + SO_2$$

(vi) Reaction with alkalies

When S is boiled with alkalies both sulphide and thiosulphate are formed.

$$4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$$

Uses of Sulphur

(i) It is used in the manufacture of an important industrial acid, H_2SO_4.

(ii) S and SO_2 are used for industrial bleaching purpose.

(iii) S is used, for the production of CS_2 which is an industrial solvent.

(iv) Raw rubber is cured or vulcanized by sulphur in order to get elasticity.

(v) Gunpowder and explosive have sulphur as an essential ingredient.

(vi) Matches industry utilizes sulphur as an essential item.

(vii) For the preparation of ultramarine (a blue dye) sulphur is largely used.

COMPOUNDS OF SULPHUR

HYDROGEN SULPHIDE, H_2S

Preparation

Hydrogen sulphide can be prepared in small amounts by passing H_2 through boiling sulphur. The reaction is reversible.

$$H_2 + S \rightleftharpoons H_2S$$

However, the following methods are commonly used.

(i) Laboratory Method

Hydrogen sulphide is generally prepared in the laboratory by the action of HCl or H_2SO_4 on iron sulphide, FeS – in Kipp's apparatus,

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$$

(ii) From Stibnite

Pure H_2S can be obtained by heating antimony sulphide (stibnite) with HCl.

$$Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S.$$

(iii) H_2S can also be obtained by hydrolysis of methyl thiourea.

$$CH_3CSNH_2 + 2H_2O \longrightarrow CH_3COONH_4 + H_2S$$

Physical Characteristics

H_2S is a colourless gas with unpleasant smell of rotten eggs. It is poisonous and readily produces headache.

Chemical Reactions

The most common chemical characteristics of H_2S are:

(i) Thermal Dissociations

On heating H_2S dissociates to H_2 and S. The dissociation starts at 310°C and is complete at 1700°C.

$$H_2S \rightleftharpoons H_2 + S$$

(ii) Reaction with air or oxygen

Hydrogen sulphide burns in air or oxygen with blue flame. In the inner zone of the flame H_2S dissociates to produce H_2 and S. They burn in the outer zone in presence of plenty of oxygen.

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

(iii) Acid properties

H_2S is a weak acid and ionizes in aqueous solution to produce HS^- and S^{2-} ions

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$

It turns blue litmus red and undergoes neutralization reactions with alkalies.

$$H_2S + KOH \longrightarrow KHS + H_2O$$
$$KHS + KOH \longrightarrow K_2S + H_2O$$

All metals except Au and Pt are attacked by H_2S and form corresponding sulphides. Even silver gets black in an atmosphere of H_2S.

$$HS + 2Ag \longrightarrow Ag_2S + H_2$$

$$H_2S + Sn \longrightarrow SnS + H_2$$

Many metals form insoluble sulphides in weakly acid or alkaline solution and identification of metals such as Cu, Cd, Sb, As, Pb, Ag, Hg, Sn, Zn, etc.

(iv) Reducing action

Because of its decomposition to H_2 and S it acts as an active reducing agent and reduces.

(a) **Bromine and iodine:** Br_2 and I_2 are reduced to Br^- ad I^-.

$$4Br_2 + 8H_2S + 4H_2O \longrightarrow 8HBr + 8H_2SO_4$$

(b) **$KMnO_4$ and $K_2Cr_2O_7$:** The reaction occurs in presence of H_2SO_4.

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4) + 3S + 7H_2O$$

(c) **Ferric chloride:** It is reduced to ferrous chloride

$$2FeCl_3 + H_2S \longrightarrow FeCl_2 + S + 2HCl$$

(d) **Nitric acid** is reduced to NO_2

$$H_2S + 2HNO_3 \longrightarrow S + 2NO_2 + 2H_2O$$

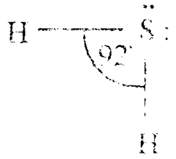
(e) **Sulphur dioxide** is reduced to S

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

(f) **H_2SO_4:** $H_2S + H_2SO_4 \longrightarrow SO_2 + S + 2H_2O$

Structure

The two hydrogen atoms are covalently bonded to sulphur atom with H – S – H bond angle of 92°.



SULPHIDES

Two series of sulphides namely, normal sulphides and hydrosulphides are known. The sulphides are formed by the action of H_2S in solution or by the direct interaction of metals with sulphur.

The soluble ionic sulphides hydrolyse into HS^- and OH^- and in some cases H_2S is obtained.

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$

This equilibrium shows that BaS, Na_2S and K_2S etc. would give alkaline solutions. Sulphides of Al, Fe and Cr cannot be prepared in aqueous solution because they are readily hydrolysed.

Some of the coloured sulphides *i.e.*, FeS_2, CoS, PbS etc., resemble alloys in their properties. This is due to the delocalization of some of the electrons as is found in the structure of metals and graphite.

POLYSULPHIDES

When excess sulphur is boiled with a solution of soluble sulphides, polysulphides are obtained and the solution turns yellow or orange-red. If the solution of polysulphides is acidified, a mixture of hydrogen polysulphides, H_2S_x ($x = 1, 2, 3, 4, 5$) is obtained. The combination of sulphur with S^{2-} ions can be shown as:

$$S + S^{2-} \rightleftharpoons S_2^{2-}$$

$$2S + S^{2-} \rightleftharpoons S_3^{2-}$$

$$3S + S^{2-} \rightleftharpoons S_4^{2-}$$

$$4S + S^{2-} \rightleftharpoons S_5^{2-}$$

The polysulphides are oxidizing agents and oxidise most of the metal sulphides to the thio complexes.

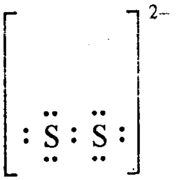
$$As_2S_3 + S^{5-} \rightleftharpoons AsS_3^{3-}$$

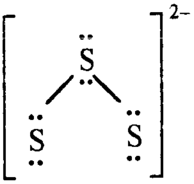
$$Sb_2S_3 + S^{2-} \longrightarrow SbS_3^{3-}$$

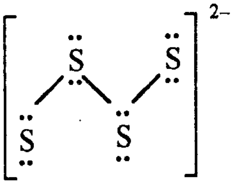
$$SnS_2 + S^{2-} \longrightarrow SnS_3^{2-}$$

Structure

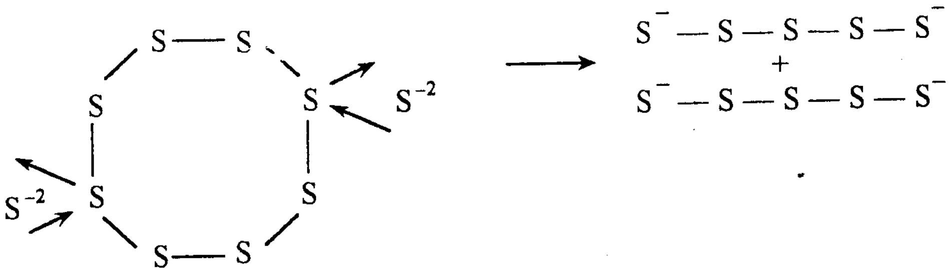
The S atoms in polysulphides are linked through covalent bonds. The high stability of catenation (extensive covalent bond formation) of sulphur atoms is responsible for the formation of polysulphides.







The mechanism for the opening up of S_8 ring in sulphur by S^{2-} ion is suggested as given below:



OXIDES OF SULPHUR

Sulphur combines with oxygen to give numerous oxides, such as:

SO	Sulphur monoxide
S_2O_3	Sulphur sesquioxide
SO_2	sulphur dioxide
SO_3	Sulphur trioxide
S_2O_7	Sulphur heptoxide
SO_4	Sulphur tetroxide

Only SO_2 and SO_3 are well-known and quite stable. Others are unstable and important.

Sulphur dioxide, SO_2

Sulphur dioxide is present in volcanic gases and also in small quantities in the air of towns and industries due to burning of sulphur compounds present in coal.

Preparation

Sulphur dioxide is prepared by any one of the following methods:

(i) By burning sulphur or roasting sulphide ores

Large quantities of sulphur dioxide are obtained by burning sulphur or roasting iron pyrites.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(ii) By the reduction of H_2SO_4

Certain metals and non-metals reduce H_2SO4 to SO_2. Thus Cu, C and S react with concentrated sulphuric acid produce SO_2.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(iii) From Sulphites and Bisulphites

Sulphites and bisulphites react with dilute acids to liberate SO_2.

$$Na_2SO_4 + 2HCl \longrightarrow SO_2 + 2NaCl + H_2O$$

Physical And Chemical Characteristics

Sulphur dioxide is a colourless gas which has pungent suffocating odour of burning sulphur. It is readily soluble in water. The gas can be liquefied. Liquid SO_2 is a good solvent and conduct electricity.

The important chemical reactions of SO_2 are:

(i) Addition reactions

Sulphur dioxide is an unsaturated compound and combines with oxygen, chlorine etc., to form compounds in which sulphur changes from tetrastate to hexavalent state

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(Sulphuryl chloride)

(ii) Bleaching action

SO_2 is a good bleaching agent and shows its bleaching action due to the formation of nascent hydrogen produced in presence of moisture. The colour is restored on exposing the bleached articles to air or oxygen due to oxidation.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

(iii) Reducing action

Sulphur dioxide acts as reducing agent and is itself oxidized to H_2SO_4.

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$$

(iv) Oxidizing agent

It can also act as oxidizing agent. SO_2 oxidizes H_2S and reduces itself to free S.

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

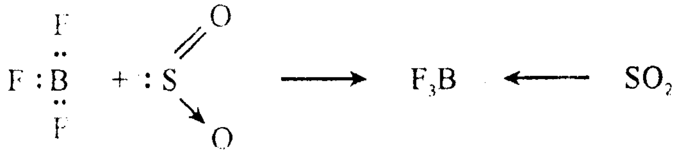
(v) Acid properties

SO_2 dissolves in water to form sulphurous acid. Therefore, the aqueous solutions are acidic to litmus. H_2SO_3 is a weak, dibasic acid and exists only in solution.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

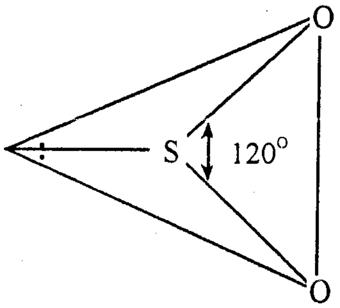
(vi) As Lewis base

Due to the presence of lone pair of electrons on S it acts as a Lewis base (electron pair donor).

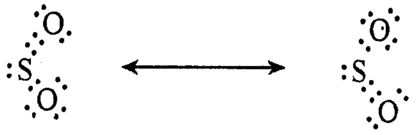


Structure

Sulphur dioxide exists as individual SO_2 molecules in the vapour state. SO_2 molecule has V shape with O – S – O angle 120° which indicates its trigonal planar arrangement.



SO_2 molecule consists of two contributing electronic structures I and II. These structures have one bond between S and each O. In addition to this S forms a resonating π bond and also possesses a lone pair of electrons.



(I) (II)

Role of Sulphur Dioxide in Pollutions

Sulphur Trioxide, SO_3

Sulphur trioxide can be prepared by any one of the following methods:

(i) **From SO_2**

SO_2 reacts with O_2 in presence of platinized asbestos at 400°C.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

(ii) **From H_2SO_4**

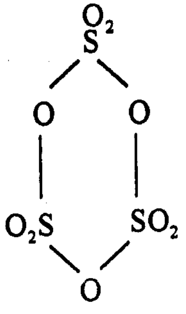
When H_2SO_4 is distilled over phosphorus pentoxide, SO_3 is formed by the removal of H_2O from its molecule.

$$H_2SO_4 + P_2O_5 \longrightarrow SO_3 + 2HPO_3$$

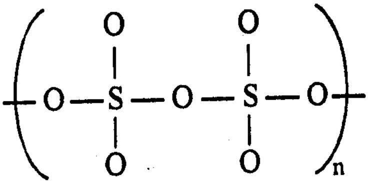
Properties

SO_3 is a gas which freezes at 15°C to give ice-like crystals.

There are three solid forms of SO_3: (1) trimeric $(SO_3)_2$, ice-like, (2) long-chain SO_3 groups, asbestos-like, (3) long chain SO_3 (unstable form) containing groups joined in layers.



$(SO_3)_3$



Chain SO_3

Sulphur trioxide reacts with H_2O to form H_2SO_4. While dissolving the gas produces a loud hissing noise.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

It dissolves in concentrated H_2SO_4 to form fuming sulphuric acid or oleum $H_2S_2O_7$.

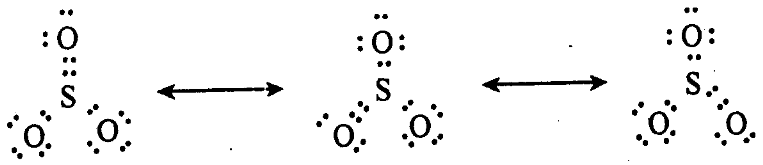
$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

SO_3 combines directly with many metal oxides forming sulphates.

$$BaO + SO_3 \longrightarrow BaSO_4$$

Structure

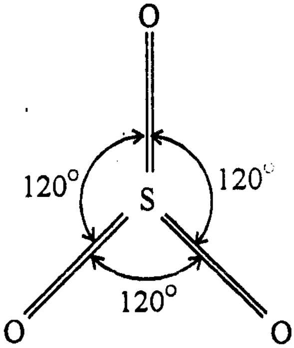
The gaseous SO_3 molecule has a trigonal planar arrangement with O – S – O bond angle 120°. The structure is explained based on three contributing structures (I, II, III). Each S – O bond in SO_3 has one-third of a double bond (α and π) character.



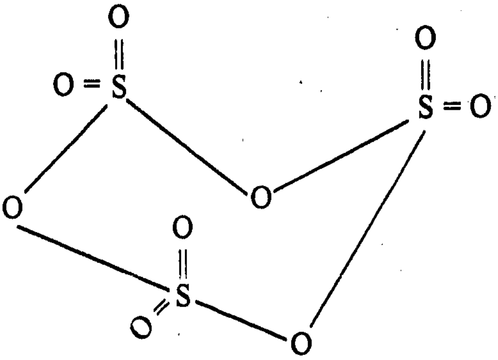
(I) (II) (III)

In the solid state, SO_3 molecules join together through oxygen bridges to form trimers, $(SO_3)_3$ present in the form of puckered rings or polymers containing infinite zig-zag chains, $(SO_3)_n$.

The overall structure of SO_3 can be represented as:



$SO_3(g)$



Oxyacids of Sulphur

A large number of oxyacids of sulphur are known in which S atom is in the oxidation states +2, +3, +4 and +6. They are classified in the following type:

(a) Normal oxyacids

They are well-known and are sulphurous acid, H_2SO_3 and sulphuric acid, H_2SO_4.

(b) Pyroacids

These are formed by the condensation reactions of H_2SO_3 and H_2SO_4.

$$2H_2SO_3 \longrightarrow H_2S_2O_5 + H_2O$$

$$2H_2SO_4 \longrightarrow H_2S_2O_7 + H_2O$$

(c) Thionic acids

They have general formula $H_2S_nO_6$ where $n = 2$ to 6.

(d) Peroxyacids

These acids contain linkage – O – O – and two well-known acids are:

H_2SO_5	$H_2S_2O_3$
Permonosulphuric acid	Perdisulphuric acid

Normal Oxyacids

Under this category we shall discuss the chemistry of H_2SO_3 and H_2SO_4. The manufacture of H_2SO_4 will be taken up in Chapter 21.

Sulphurous Acid, H_2SO_3

Sulphur dioxide dissolves in water to the extent of 10% by weight at 20°C to form H_2SO_3 in solution.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

On cooling crystals of hydrated sulphurous acid, $H_2SO_3 . 6H_2O$ are obtained. Sulphurous acid is slowly oxidized by oxygen of the air to sulphuric acid.

$$2H_2SO_3 + O_2 \longrightarrow 2H_2SO_4$$

Sulphurous acid acts as a good reducing agent and would reduce Cl_2, $KMnO_4$ and $K_2Cr_2O_7$ etc.

$$\overset{+4}{H_2SO_3} + \overset{0}{Cl_2} + H_2O \longrightarrow \overset{+6}{H_2SO_4} + 2\overset{-1}{HCl}$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

Sulphurous acid also acts as an oxidising agent.

$$H_2SO_3 + 2H_2S \longrightarrow 3S + 3H_2O$$

The salts of sulphurous acid are well-known.

$$2NaOH + SO_2 + H_2O \longrightarrow Na_2SO_3 + 2H_2O$$

$$K_2CO_3 + 2SO_2 + 2H_2O \longrightarrow 2KHSO_3 + CO_2 + H_2O$$

$$Ca(OH)_2 + 2SO_2 + H_2O \longrightarrow Ca(HSO_3)_2 + H_2O .$$

Sulphuric Acid, H_2SO_4

The manufacture of H_2SO_4 is described in the last chapter. It is a colourless oily liquid almost twice as heavy as water and solidifies at 10.37°C to colourless crystals.

Chemical Reactions

The majar chemical reactions are:

(a) Ionic Reactions

In presence of water, H_2SO_4 ionizes to give hydrogen ions and sulphate ions.

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

(i) Reaction of Hydrion

An aqueous solution of acid turns blue litmus red, has a sour taste, and neutralizes alkalies to form bisulphates and sulphates.

$$H_2SO_4 + NaOH \longrightarrow \underset{\text{sodium bisulphate}}{NaHSO_4 + H_2O}$$

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

(ii) Reaction of Sulphate Ions

The solutions of Ba^{2+} and Pb^{2+} react with SO_4^{2-} ions to produce insoluble sulphates.

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$$

$$H_2SO_4 + Pb(NO_3)_2 \longrightarrow PbSO_4 + 2HNO_3$$

(b) Dehydrating Reactions

Addition of H_2SO_4 in water produces a lot of heat because the formation of H_3O^+ ions. H_2SO_4 has affinity for water and would act as dehydrating agent. So much so that water can be removed from organic compounds also.

$$C_{22}H_{22}O_{11} + 11H_2SO_4 \longrightarrow 12C + 11(H_2SO_4.\ H_2O)$$

Oxalic acid and formic acid etc., are dehydrated to liberate CO and CO_2.

$$HOOCH \xrightarrow{H_2SO_4} H_2O + CO$$

$$H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO + CO_2$$

$$C_2H_5OH \xrightarrow[(180°C)]{H_2SO_4} C_2H_4 + H_2O$$

Many organic substances such as cotton and wood etc., are carbonized for the same reason.

(c) As Sulphonating Agent

It is an important chemical reaction. Benzene reacts with H_2SO_4 to form benzene sulphonic acid.

$$C_6H_6 + H_2SO_4 \xrightarrow{\Delta} C_6H_5SO_2OH + H_2O$$

(d) Reaction with PCl_5

Sulphuric acid is supposed to possess the formula $SO_2(OH)_2$ and reaction with PCl_5 in the replacement of two OH groups by Cl.

$$SC_2(OH)_2 + PCl_5 \longrightarrow SO_2(OH)Cl + POCl_3 + 2HCl$$

$$SO_2(OH)_2 + PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

(e) Thermal Decomposition

When vapours of H_2SO_4 are passed through red hot silica tube, it decomposes to SO_2, O_2 and H_2O.

$$2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + O_2$$

(f) As Oxidising Agent

Because of its possibility to lose oxygen, hot concentrated H_2SO_4 possesses oxidising properties. The following reactions illustrate the oxidising action of sulphuric acid:

(i) Action on non-metals

Hot concentrated H_2SO_4 reacts with metals such as Cu, Sn, etc., to liberate SO_2.

(ii) Action on metals

Carbon and sulphur are easily oxidised to CO_2 and SO_2, respectively.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(iii) Action on hydrides

Haloacids and H_2S etc., react with sulphuric acid to liberate SO_2.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

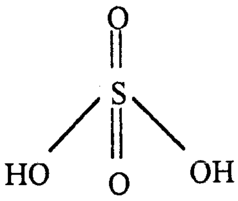
$$H_2S + H_2SO_4 \longrightarrow SO_2 + 2H_2O + S$$

(iv) Oxidation of organic compounds

H_2SO_4 is used on large scale for the oxidation of naphthalene to phthalic acid. It is also used in Kjeldahl method for the estimation of nitrogen, sulphur.

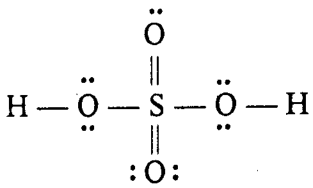
Structure

Sulphur atom is surrounded by four oxygen atoms in a tetrahedral manner.

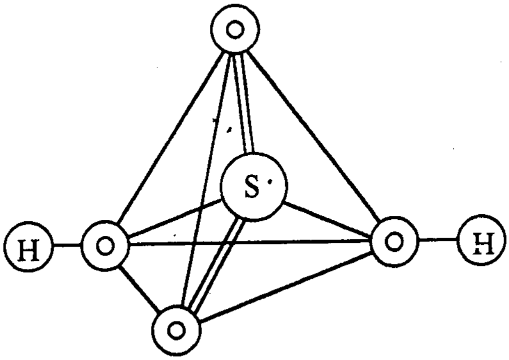


High boiling point of H_2SO_4 is due to extensive hydrogen bonding in its molecules.

The bonding present in sulphuric acid molecule is:



$$\mathrm{H-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-\underset{\underset{:O:}{\|}}{\overset{\overset{\ddot{O}}{\|}}{S}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H}$$



THIONIC ACIDS

The general formula of these acids is $H_2S_nO_6$ (n = 2 to 6). The thionic acids are named after the number of sulphur atoms they contain. Thus the thionic acid containing two sulphur atoms, $H_2S_2O_6$ is called dithionic acid. Similarly, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$ and $H_2S_6O_6$ are called trithionic acid, tetrathionic acid, pentathionic acid and hexathionic acid, respectively.

Dithionic acid, $H_2S_2O_6$

Dithionic acid is obtained from its salts by treatment with dilute H_2SO_4. The salts are obtained by the following reactions:

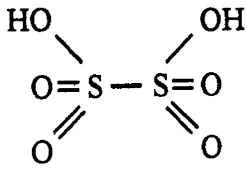
$$2MnO_2 + 2H_2SO_3 \longrightarrow MnSO_4 + MnS_2O_6 + 3H_2O$$

It is unstable and decomposes in neutral or alkaline or acid solutions.

$$2H_2S_2O_6 \longrightarrow SO_2 + H_2SO_4$$

The salts of alkali and alkaline earth metals are stable in boiling aqueous solutions.

The structure of dithionic acid is represented as:



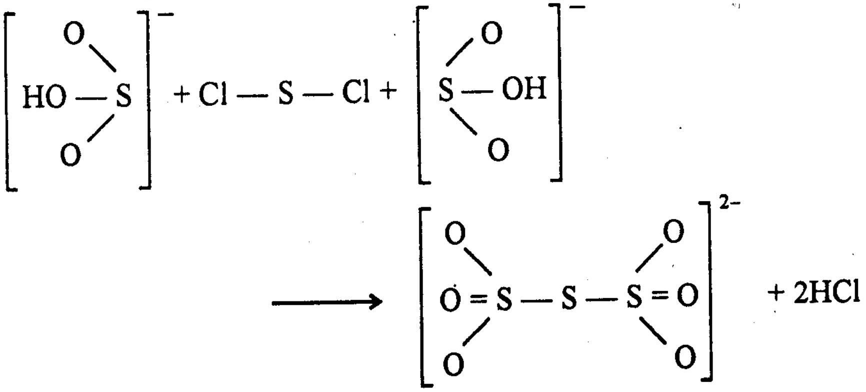
Trithionic acid, HS_3O_6

The salts of trithionic acid are obtained by following methods:

(i) SO_2 reacts with thiosulphates to form trithionates.

$$2K_2S_2O_3 + 3SO_2 \longrightarrow 2K_2S_3O_6 + S$$

(ii) By shaking a concentrated aqueous solution of $KHSO_3$ with sulphur dichloride in petroleum.



(iii) Trithionates are also obtained by treating ice-cold saturated solution of sodium thiosulphate with H_2O_2.

$$2Na_2S_2O_3 + 4H_2O_2 \longrightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

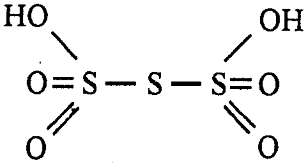
The acid is obtained from its salt by treatment with dilute H_2SO_4.

The aqueous solutions of trithionic acids decompose on concentration or heating.

$$H_2S_3O_6 \longrightarrow H_2SO_4 + SO_2 + S$$

The silver and mercury salts are insoluble in water.

The **structure** of trithionic acid is:



Tetrathionic acid, $H_2S_4O_6$

The tetrathionates can be obtained by the action of iodine on sodium thiosulphate.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

The salts can also be obtained by the anodic oxidation of $NaHS_2O_3$.

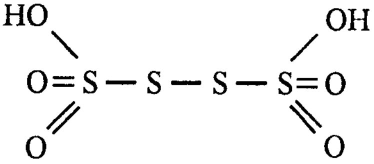
$$2NaHS_2O_3 \xrightarrow[\text{oxidin}]{\text{anodic}} Na_2S_4O_6$$

Thionic acid and its salts are soluble in water and unstable. They are decomposed by alkalies.

The acid decomposes on heating.

$$H_2S_4O_6 \longrightarrow H_2SO_4 + SO_2 + 2S$$

The structure of tetrathionic acid can be represented as:



The oxidation of thiosulphate ion, $S_2O_3^{2-}$ to tetrathionate ion, $S_4O_6^{2-}$ is interesting from structural viewpoint because it involves the formation of S – S between two $S_2O_2^{2-}$ ions (Figure 15.4).

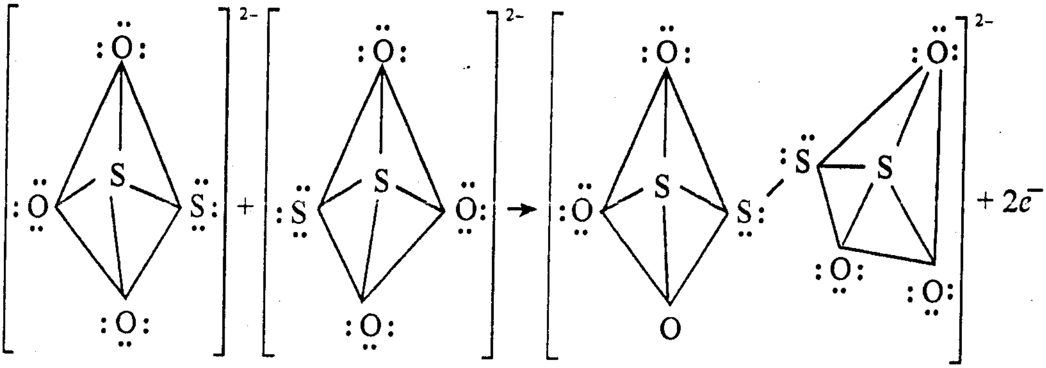


Fig. 15.4. Formation of $S_2O_3^{2-}$ and their structures.

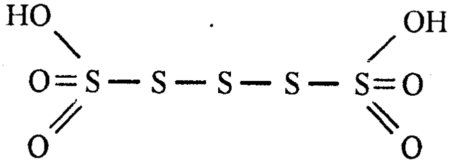
Pentathionic acid, $H_2S_5O_6$

Pentathionic acid is obtained from solution (Wackenroder's solution) obtained by passing H_2S to aqueous solution of SO_2 until all sulphur dioxide is destroyed. Wackenroder's solution contains sulphur, pentathionic and tetrathionic acid. On adding KOH to the solution, rhombic crystals of $H_2S_5O_6 \cdot 1.5\ H_2O$ are obtained.

On concentrating the solution, pentathionic acid decompose to give S.

$$H_2S_5O_6 \longrightarrow H_2SO_4 + SO_2 + 3S$$

The structure of pentathionic acid is:

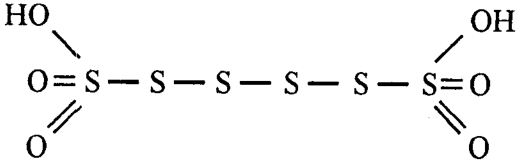


Hexathionic acid, $H_2S_6O_6$

Sodium or potassium hexathionate may be obtained by adding cold concentrated HCl to a solution of sodium or potassium thiosulphate containing a nitrite or arsenite. Potassium salt is easily crystallized.

The hexathionates decompose in solution to give pentathionate and sulphur.

The structure of hexathionic acid is shown below:



The reactions of salts of polythionic acids are shown in Table 15.3.

TABLE 15.3

Reactions of Salts of Polythionic Acids

Reagent	Dithionates	Trithionates	Tetrathionates	Pentathionates	Hexathionates
1. Sulphur	No action.	Tetra-and pethathionates are formed.	Pentathionate is formed.	—	—
2. Sodium amalgam	Forms Na_2SO_3.	Forms Na_2SO_3 and $Na_2S_2O_3$.	Forms $Na_2S_2O_3$.	Forms $Na_2S_4O_6$ and $Na_2S_2O_3$.	—
3. Sodium sulphite	No action.	No action.	Gives $Na_2S_3O_6$ and $Na_2S_2O_3$.	Gives $Na_2S_4O_6$ and $Na_2S_2O_3$.	Gives $Na_2S_5O_6$ and $Na_2S_2O_3$.
4. Sodium sulphide	No action.	$Na_2S_2O_3$ is formed.	$Na_2S_2O_3$ and S are formed.	$Na_2S_2O_3$ and S are obtained.	—
5. Decomposition in concentrated aqueous solution.	Forms Na_2SO_4 and SO_2.	Forms Na_2SO_4, SO_2 and S.	Forms Na_2SO_4, SO_2 and S.	Forms Na_2SO_4, SO_2 and S.	Forms Na_2SO_4, SO_2 and S.

Sodium Thiosulphate, $Na_2S_2O_3$

The acid has not yet been isolated in the free state but salts are well-known as thiosulphates. Sodium thiosulphate is quite commonly used under the name **'hypo'** in photography.

Preparation

It can be prepared by the following methods:

(i) By boiling Na_2SO_3 solution with sulphur powder.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

(ii) By adding I_2 to a mixture of Na_2SO_3 and Na_2S.

$$Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$$

(iii) By the interaction of SO_2 with Na_2S and Na_2CO_3.

$$Na_2CO_3 + 2Na_2S + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2$$

(iv) By the action of SO_2 with Na_2CO_3 solution in presence of sulphur.

$$Na_2CO_3 + H_2O + 2SO_2 \longrightarrow 2NaHSO_3 + CO_2$$

$$Na_2CO_3 + 2NaHSO_3 \longrightarrow Na_2SO_3 + CO_2 + H_2O$$

$$Na_2CO_3 + S \longrightarrow Na_2S_2O_3$$

Properties

Sodium thiosulphate exists as colourless, well-defined crystals, $Na_2S_2O_3.5H_2O$ (hypo). It is commonly used as a reducing agent and used in photographic process called 'fixing' in which excess AgBr is dissolved by 'hypo'.

$$AgBr + Na_2S_2O_3 \longrightarrow NaAg(S_2O_3) + NaBr$$

Iodine reacts with $Na_2S_2O_3$ to give tetrathionate and is reduced to I^-.

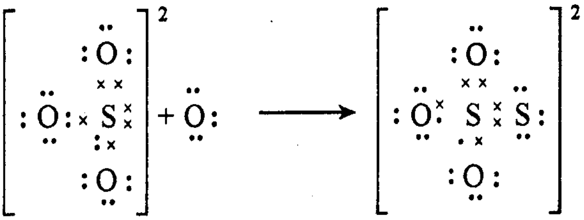
$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The reaction is quantitative and is the basis of iodometry and iodimetry in analysis.

Sodium thiosulphate is also used to remove excess Cl_2 from the bleaching industry under the name **'antichlor'**.

Structure

$S_2O_3^{2-}$ is similar to SO_4^{2-} as is indicated by its mode of preparation.



(Sulphite ion) (Thiosulphate ion)

PEROXYACIDS OF SULPHUR

Two important acids containing peroxide, — O — O link are known. These are:

Permonosulphuric acid (Caro's acid) — H_2SO_5

Perdisulphuric acid (Marshall's acid) — $H_2S_2O_8$

Peroxymonosulphuric acid, H_2SO_5

It can be prepared by any one of the following methods:

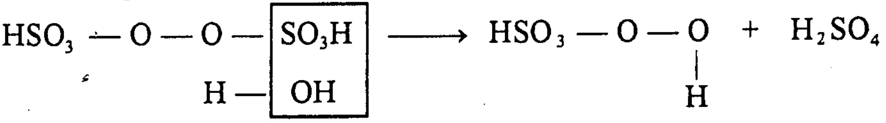
(i) **From Chlorosulphuric acid**

Chlorosulphonic acid reacts with hydrogen peroxide to give peroxymonosulphuric acid.

$$H-O-O-\boxed{H+Cl}\,SO_2\,.\,OH \longrightarrow H_2SO_5 + HCl$$

(ii) **From K or NH_4 Persulphate**

Potassium or ammonium persulphate is converted with ice-cold concentrated sulphuric acid to peroxymonosulphuric acid.



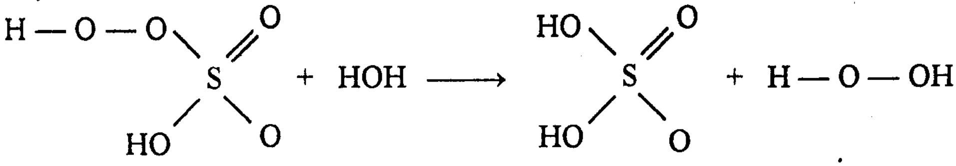
$$\begin{array}{r} HSO_3-O-O- \\ H- \end{array}\boxed{\begin{array}{c} SO_3H \\ OH \end{array}} \longrightarrow HSO_3-O-\underset{H}{\underset{|}{O}} + H_2SO_4$$

(iii) SO_3 reacts with H_2O_2 to form H_2SO_5.

$$SO_3 + H_2O_2 \longrightarrow H_2SO_5$$

Peroxymonosulphuric acid exists as hygroscopic crystals, m.p. 45°C.

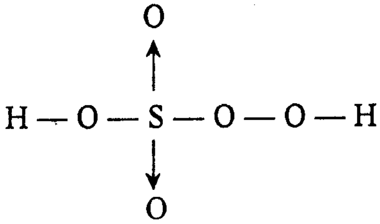
It is soluble in ether, acetic acid, benzene, phenol, etc., and is liable to explore. It behaves as a monobasic acid in aqueous solution and is slowly hydrolysed with water.



(H_2SO_5) (H_2SO_4)

No stable salt of this acid is known.

Structure

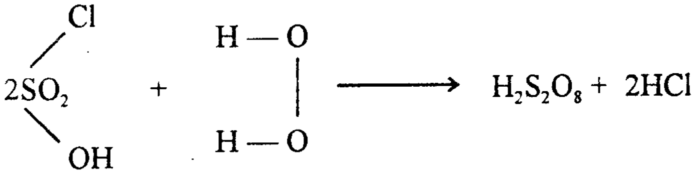


$$\begin{array}{c} O \\ \uparrow \\ H-O-S-O-O-H \\ \downarrow \\ O \end{array}$$

Peroxydisulphuric Acid, $H_2S_2O_8$

It is prepared:

(i) by action of chlorosulphuric acid with H_2O_2.



(ii) By electrolysis of sulphuric acid or ammonium sulphate solution at low temperature and high current density, 1 – 2 amp dcm^{-2}. The cathode used is lead or graphite and anode being platinum.

$$2HSO_4^- - 2e \longrightarrow H_2S_2O_3$$

(iii) SO_2 and O_2 mixture is subjected to electric discharge to get S_2O_7 which reacts with water to give $H_2S_2O_8$.

$$S_2O_7 + H_2O \longrightarrow H_2S_2O_8$$

(iv) By the action of concentrated H_2SO_4 on a concentrated solution of H_2O_2.

$$H_2O_2 + 2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H_2O$$

Properties

Peroxydisulphuric acid is a crystalline solid, m.p. 65°C.

It decomposes with loss of oxygen. It is easily hydrolyed to H_2SO_5 and then gives H_2O_2.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$H_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2H_2SO_4$$

It reacts with organic compounds and explodes with alcohol and ether.

On heating the salts also decompose to give sulphates.

$$2K_2S_2O_8 \xrightarrow{\Delta} 2K_2SO_4 + 2SO_3 + O_2$$

Hot aqueous solutions decompose to liberate O_2,

$$2K_2S_2O_8 + 2H_2O \longrightarrow 4KHSO_4 + O_2$$

$$(NH_4)_2S_2O_8 + 6H_2O \longrightarrow 7(NH_4)_2SO_4 + 2HNO_3 + 9H_2SO_4$$

Ammonium peroxydisulphate oxidises ammonia to liberate N_2. $AgNO_3$ acts as a catalyst.

$$3(NH_4)_2S_2O_8 + 8NH_3 \longrightarrow 6(NH_4)_2SO_4 + N_2$$

Silver nitrate reacts with peroxydisulphates to give Ag_2O.

$$2AgNO_3 + K_2S_2O_8 + 2H_2O \longrightarrow Ag_2O + 2KHSO_4 + HNO_3$$

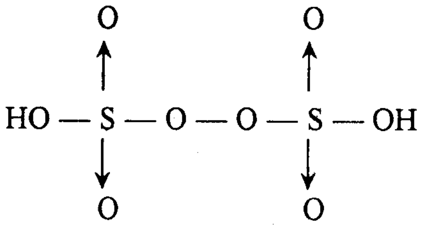
Although $K_2S_2O_8$ does not decolourise $KMnO_4$ but oxidises Fe^{2+} to Fe^{3+} Cr^{2+} to Cr^{3+} and I_2 to IO_3^-.

KI and HI react to liberate I_2

$$2HI + [O] \longrightarrow I_2 + H_2O$$

Aniline reacts form aniline black.

Structure



$$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$$

Compounds in which S is Octahedrally Hybridized

The examples of such compounds are SF_6, S_2F_{10}, SF_5Cl, etc., but SF_6 is the only well-known compound and would be taken up for discussion.

Sulphur Hexafluoride, SF_6

It is a colourless and odourless gas. It is usually prepared by burning sulphur in fluorine.

$$S + 3F_2 \longrightarrow SF_6$$

S_2F_{10} is also formed which decomposes at 400°C to give SF_6.

$$2SF_{10} \longrightarrow 3SF_6 + SF_2$$

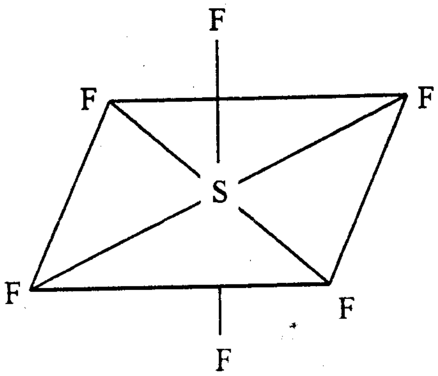
Sulphur hexafluoride condenses to a solid at −63.8°C. It is highly soluble in water and alcohol.

It is chemically inert and can be heated to 800°C without decomposition. It is neither hydrolysed by water nor reacts with acids or bases. It remains unaffected by most of the chemical reagents.

It is decomposed by H_2 at 400°C and attacks S at 400°C.

Structure

SF_6 is an octahedral molecule with S atom sitting in the centre and F atoms arranged along the corners of an octahedron. The inertness of the molecule is probably due to the maximum utilization of valency electrons of S and 'steric hindrance' by 6F atoms from further attack.



The energetics of the formation of SF_6 from S and F_2 are shown in Figure 15.5. The energy set free in the formation of SF_6 is large which also accounts for its stability and inertness.

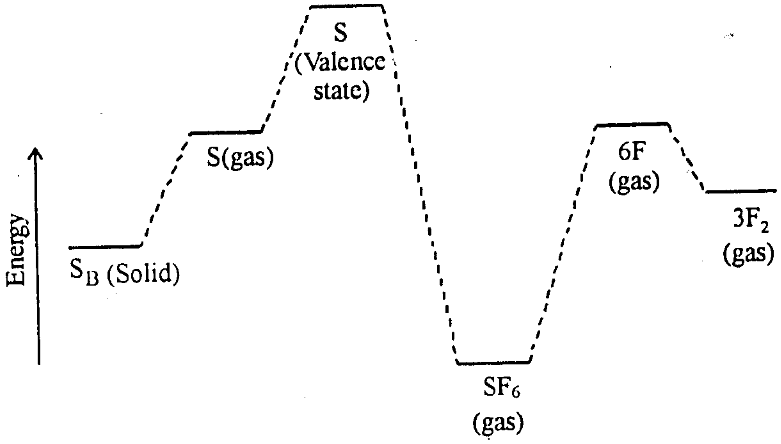


Fig. 15.5. Energetics of the formation of SF_6 from S and F_2.

PHOTOGRAPHY

The light sensitive property of silver halides is applied in photography. A glass plate or film of celluloid is coated with an emulsion of silver bromide (mixed with a little silver iodide) in gelation. The film is placed in the camera and exposed momentarily to the object for getting its image on the film. The silver halide granules in the emulsion are affected by light when minute granules of silver are deposited. The formation of silver granules depends on the intensity of light falling on the film. The part of photographic film (or plate) more exposed to light will become dark due to deposition of more silver. The film is then treated with a reducing agent such as pyrogallol or hydroquinone. This process is called 'developing'. The dark parts of the object appear bright and vice-versa. The image is thus reverse of that of the object and is called 'negative'. The 'negative' is immersed in a solution of a fixer such as sodium thiosulphate commonly called 'hypo'. This step is called 'fixing' and is carried out to remove unwanted silver bromide. The film or plate is then washed with water and dried. A print is then made by laying the 'negative' upon a senitized printing paper. The print gives the same shade as the object. The print on paper is referred to as 'positive'. The paper is finally treated with a solution of sodium thiosulphate to fix the image. The print may be imersed in a solution of gold chloride to get a reddish tone. This process is called 'toning'. The image may be rendered steel-gray by using platinum salts instead of gold and has the same shade as the real object. In this way the true photograph of the object is obtained.

Theory

During the fixing process the undecomposed AgBr (s) left after exposure to light is dissolved and the complexed silver ion is washed away.

$$\mathrm{AgBr\,(s)} + 2\mathrm{S_2O_3}^{2-} \longrightarrow [\mathrm{Ag(S_2O_3)_2}]^{3-} + \mathrm{Br}^-$$

The sensitivity of photographic emulsion is caused by the presence of minute traces (about 1 ppm) of organic sulphur compounds in gelatine. It is proposed that in the process of ripening of the emulsion minute specks of silver sulphide are formed on the surface of the grains of silver bromide. The action of light on silver bromide is known to emit electrons and the number of electrons emitted is proportional to the quanta of light absorbed. The electrons thus emitted are believed to be trapped by the specks of silver sulphide which then attract interstitial silver ions from the body of the grains of silver halide. The rate of reduction (developing) also depends on the number of grains of silver which have been formed by exposure to light as they are known to catalyse the process.

Questions

1. What elements are present in Group VI. Discuss their group tends based upon electronic configurations.
2. Compare the general and chemical characteristics of oxygen and sulphur.
3. What do you understand by the term allotropy? How are the allotropic forms of sulphur prepared and show how can they be converted into one another?
4. How is hydrogen sulphide gas prepared in the laboratory? Discuss its general reactions with special emphasis on its reducing action and acid properties.
5. What are the chief ores of sulphur? How is sulphur extracted and purified? Describe its chemical characteristics.
6. Discuss the general properties of Group VIA based upon their electronic configurations.
7. Name different allotropic forms of sulphur. Discuss the rhombic and plastic sulphur with special reference to their structures.
8. Describe and explain the effect of roll sulphur when heated in a container to boiling point. What different varieties of sulphur exist? Describe their preparation and important properties.
9. 100 ml. of a gas were completely decomposed by hot tin when tin is converted to SnS. The residual gas being hydrogen which on passing over heated copper oxide gave 0.081 grams of water. The vapour density of gas is 17. Deduce the formula of the gas from the above data.
10. Discuss the important oxides of sulphur with special reference to their preparation, properties and structure.
11. Explain the structures of oxides and oxyacids of sulphur.
12. Describe the chemical behaviour of sulphurous and sulphuric acid. Give example of a reaction in which sulphurous acid acts as an oxidising agent.
13. Write equations for the following reactions:
    (i) Action of concentrated H_2SO_4 on (a) carbon, (b) oxalic acid, and (c) HI.
    (ii) Action of H_2SO_3 on (a) Cl_2 (b) O_2.
    (iii) Concentrated H_2SO_4 as dehydrating agent.

14. What are thionic acids? How are they usually prepared? Discuss the structures and stabilities of thionic acids and their salts

15. How is sodium thiosulphate prepared? Discuss its characteristics and structure.

16. What are persulphuric acids? How are they prepared? Discuss the structures of these acids as well.

17. Write note on SF_6.

18. Compare and contrast H_2S with HCl with respect to acidity, stability and redox reactions.

19. Discuss the electronic structure of the following:

$$H_2SO_4\,,\ S_2O_3^{2-}\,,\ SO_3^{2-},\ SO_2$$

20. (a) What property of H_2SO_4 is depicted by the following reactions:

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

(b) The equilibrium constant for the reaction at 800°C.

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3$$

21. Calculate the weight of SO_3 in equilibrium with one mole of SO_2 and $\frac{1}{2}$ mole of oxygen (volume of vessel being one litre).

22. **Write short answers to the following questions:**

(i) Give the electronic configuration of the following elements of Group VIA with atomic numbers given in brackets:

(a) O(8) (b) S(16) (c) Se(34) (d) Te(52)

(ii) What are the group trends of elements of Group VIA?

(iii) Draw comparison in properties of oxygen and sulphur.

(iv) What is ozone? Give the reactions of ozone with the following:

(a) KI (b) HCl (c) I_2 (d) H_2O_2 (e) PbS

(v) How is sulphur extracted?

(vi) How does sulphur occur in nature?

(vii) What are the common allotropic forms of sulphur?

(viii) Write a brief note on rhombic sulphur.

(ix) What is monoclinic sulphur? Draw its shape.

(x) What is the reaction of S with:

(a) C (b) H_2SO_4 (c) HNO_3 (d) NaOH (e) Cl_2

(xi) How is H_2S prepared?

(xii) Write the reducing reactions of H_2S with:

(a) Br_2 (b) $KMnO_4$ (c) $K_2Cr_2O_7$ (d) HNO_3 (e) SO_2

(xiii) Give or brief note on polysulphides.

(xiv) Write reactions of SO_2 with:

(a) $KMnO_4$ (b) $K_2Cr_2O_7$ (c) H_2S (d) Cl_2

(xv) What is the reaction of H_2SO_4 with:

(a) Zn (b) PCl_5 (c) C (d) S (e) H_2S

(xvi) What are thionic acids? Give structure of $S_2O_3^{2-}$.

(xvii) How is sodium thiosulphate prepared?

(xviii) Discuss the chemistry of peroxydisulphuric acid.

(xix) Give the chemistry of photography.

(xx) What is hypo? What is its commercial use?

23. **Give the correct answer:**

(i) What is the geometry and mode of hybridization of SF_6?

(a) d^2sp^3, octahedral (b) dsp^3, pyramidal

(c) $d^2 sp^3$, square planar (d) dsp^2, square planar

(ii) The oxidation state of S in $H_2S_2O_8$ is:

(a) + 2 (b) + 4

(c) + 6 (d) + 8

(iii) Which of the following hydrides is most acidic?

(a) HBr (b) H_2Se

(c) AsH_3 (d) PH_3

(iv) O_2 is a gas because:

(a) it has no *d* orbitals

(b) oxygen atoms do not catenate

(c) oxygen has double bond

(d) oxygen is paramagnetic

(v) Rhombic sulphur is soluble in:

(a) water (b) alcohol

(c) CS_2 (d) acetic acid

(vi) The contact process for manufacture of H_2SO_4 involves:

(a) heterogeneous catalytic oxidation of SO_2 to SO_3

(b) homogeneous catalytic oxidation of SO_2 to SO_3

(c) direct absorption of SO_3 with water

(d) without a catalyst

(vii) Heating $K_4[Fe(CN)_6]$ with 50 % H_2SO_4 produces:

(a) CO (b) CO_2

(c) HCN (d) SO_2

(viii) Heating $KClO_3$ with conc. HCl produces:

(a) Cl_2 (b) ClO_2

(c) $HClO_3$ (d) HClO

(ix) Stock H_2SO_4 (~ 16 M) is transported in:

(a) lead vessels (b) glass vessels

(c) steel vessels (d) earthenware pots

(x) $KMnO_4$ solution is decolorised by passing H_2S through it which produces:

(a) S (b) SO_2

(c) MnS (d) K_2S

(xi) On mixing H_2S with SO_2, the following is produced:

(a) S (b) SO_3

(c) H_2SO_4 (d) H_2SO_3

(xii) On heating $Fe_2(SO_4)_3$, the following is produced:

(a) $SO_2 + SO_3$ (b) $SO_2 + O_2$

(c) SO_2 (d) S

(xiii) SO_2 is produced when:

(a) copper is heated with conc. H_2SO_4

(b) FeS is treated with dilute H_2SO_4

(c) Na_2S is treated with dilute H_2SO_4

(d) Mg reacts with H_2SO_4

(xiv) The molecules with smallest bond angle is:

(a) H_2O (b) H_2S

(c) H_2Se (d) H_2Te

(xv) The greatest acid strength is shown by:

(a) H_2O (b) H_2Se

(c) H_2S (d) H_2Te

(xvi) Bleaching action of SO_2 is due to:

(a) reduction (b) oxidation

(c) hydrolysis (d) catalysis

(xvii) Acid rain is due to:

(a) formation of oxides of sulphur

(b) formation of H_2SO_4 and HNO_3

(c) formation of oxides of nitrogen

(d) formation of HNO_2

(xviii) Which of the following statements is false?

(a) products of photochemical smog include PAN

(b) ozone layer is depleted by chlorofluorocarbons

(c) ozone is an angular molecule

(d) S_2 is diamagnetic

(xix) Hypo is used:

(a) to dissolve unreacted AgBr in photography

(b) to estimate I_2

(c) to remove excess of Cl_2 in bleaching

(d) as an oxidizing agent

(xx) Acid rain is due to oxides of sulphur and nitrogen, and causes damage to buildings and trees. Damage to marble monuments can be cured by:

(a) treating the monuments with lime water

(b) reducing SO_2 to S by H_2S

(c) using catalyst

(d) growing more trees

(xxi) When lead storage battery is discharged:

(a) SO_2 is produced (b) $PbSO_4$ is consumed

(c) Pb is formed (d) H_2SO_4 is consumed

(xxii) Ozone reacts with dry KOH to form:

(a) ozonides (b) peroxides

(c) dioxide (d) superoxide

(xxiii) Which is the false statement for SF_6, SeF_6, TeF_6:

(a) they are gases

(b) they are inert

(c) they have octahedral structure

(d) they cannot be prepared by direct synthesis

(xxiv) Which of the following is not true for H_2O_2:

(a) it is an oxidizing agent

(b) it is a reducing agent

(c) it is a base

(d) it is an acid

(xxv) Which of the following is incorrect for H_2SO_4?

(a) it is an oxidizing agent with copper

(b) it is a dehydrating agent for sugar

(c) it acts as an acid with BaO_2

(d) it acts as reducing agent with Cu_2O.

(xxvi) Which of the following statement is incorrect?

(a) SO_2 is a V-shaped molecule

(b) SO_3^{2-} is triangular planar

(c) SO_4^{2-} is tetrahedral

(d) SO_3^{2-} is pyramidal

(xxvii) Bleaching action of which one is due to reduction:

(a) O_3 (b) Cl_2

(c) SO_2 (d) ClO_2

(xxviii) SO_2 does not:

(a) turn blue litmus red

(b) produce yellow ppt. with H_2S

(c) decolourised $KMnO_4$ solution

(d) turn starch iodide paper blue

(xxix) Industrial use of O_3 includes:

(a) lubricants (b) water treatment

(c) synthesis of pharmaceuticals (d) catalyst

(xxx) HCl and not HNO_3 is used to prepare H_2S from FeS because:

(a) HCl is not oxidizing agent (b) H_2S reduces HNO_3 to S

(c) HNO_3 renders FeS passive

(d) HNO_3 is less reactive than HCl

(xxxi) Free sulphur is usually found under the earth's crust at:

(a) 400 – 500 feet deep (b) 200 – 400 feet deep

(c) 700 – 900 feet deep (d) > 1000 feet deep

(xxxii) Formula of dithionic acid is:

(a) H_2SnO_6 (b) H_2SO_5

(c) $H_2S_2O_3$ (d) H_2SO_4

❀ ❀ 15 ❀ ❀

16

THE HALOGENS (GROUP VIIA)

The elements belonging to this sub-group are called **halogens** (halogen means salt-forming) and include fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Astatine is quite rare and radioactive member of the series. The characteristic valency shell configuration of the elements of this group is ns^2 np^5, which is one short of the octet or next inert gas configuration (Table 16.1). Thus halogens are capable of completing the octet either by accepting an electron to form halide ion X^-, or by sharing one electron with its unpaired *p* electron in the valency shell to form a single covalent bond.

TABLE 16.1

Electronic Configurations of Groups VIIA Elements

Element	1	2		3			4				5			6	
	s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
F	2	2	5												
Cl	2	2	6	2	5										
Br	2	2	6	2	6	10	2	5							
I	2	2	6	2	6	10	2	6	10		2	5			
At	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5

General Chemistry and Group Trends

Halogens exist as diatomic molecules F_2, Cl_2, Br_2 and I_2 because in this way they achieve stability by sharing an electron from each atom forming an **electron pair bond** or **covalent bond.**

$$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{F}}\,\overset{\bullet}{\underset{\times}{\bullet}}\,\overset{\times\times}{\underset{\times\times}{F}}\,\overset{\times}{\underset{\times}{}} \qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\,\overset{\bullet}{\underset{\times}{\bullet}}\,\overset{\times\times}{\underset{\times\times}{Cl}}\,\overset{\times}{\underset{\times}{}} \qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{Br}}\,\overset{\bullet}{\underset{\times}{\bullet}}\,\overset{\times\times}{\underset{\times\times}{Br}}\,\overset{\times}{\underset{\times}{}} \qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{I}}\,\overset{\bullet}{\underset{\times}{\bullet}}\,\overset{\times\times}{\underset{\times\times}{I}}\,\overset{\times}{\underset{\times}{}}$$

The *relative sizes of the halogens* are useful in explaining many of their physical and chemical properties. The difference in the values of atomic and ionic radii is much more in F and Cl than from chlorine onwards. This gives us a clue regarding much difference in physical and chemical properties of F from other halogens.

The *electronegativity* of halogens decreases down the group. Fluorine is the most electronegative element and would be able to form hydrogen bonding in HF which shows associated molecules, $(HF)x$. The ionic character of metal fluorides should be more than other halides and should decrease with decrease in electronegativity of the halogens. Ionic character of silver halides decreases in the order $AgF > AgCl > AgBr > AgI$ Whereas AgF is highly ionic, AgI is covalent in nature.

The *dissociation energy* of halogen molecules X_2 decreases with increase in atomic number $Cl_2 > Br_2 > I_2$ but F_2 has exceptionally low value. The low dissociation energy of F_2 is attributed to greater repulsion between lone-pair of electrons which is always more in smaller atoms. Due to small dissociation energy of F_2 it shows greater reactivity.

The *oxidation potentials* and, therefore, the oxidizing power of halogens decreases with increase in atomic number $F > Cl > Br > I$. Oxidizing power of halogens depends upon (a) heat of dissociation of the molecules, (b) electron affinities of the atoms, (c) hydration energies of the ions, and (d) heats of vapourization (for Br_2 and I_2 only). The oxidizing power of halogens may be seen in terms of rate of reduction of X_2 to X^- ions shows in the following steps:

$$\frac{1}{2}X_{2}(s) \xrightarrow{\text{melts}} \frac{1}{2}X_{2}\text{(liquid)} \xrightarrow{\text{vapourizes}} \frac{1}{2}X_{2}(g) \xrightarrow{\text{dissociation}}$$

$$X^{\circ} \xrightarrow{+e^-} X^- \xrightarrow{\text{hydrates}} X^-\text{ (hydrated)}$$

The *high oxidizing power* for a halogen is favoured by (a) low heat of dissociation of X_2, (b) a high electron affinity of the atom, and (c) a higher hydration energy of the ion. The higher value of the oxidizing power of F_2 is related to its low heat of dissociation and higher hydration energy of the ions formed. The electron affinity of F_2 is comparable to Br_2 and would not be able to show marked difference in oxidizing power of F_2 from other halogens.

The *colours* of halogens arise from the absorption of visible light which is caused by excitation of one or more of the outer electrons to higher energy levels. F_2 requires higher energy to excite the electrons and hence gives a pale yellow colour. I_2, on the other hand, requires less energy for excitation and appears dark violet. The colour of the halides, *i.e.*, silver halides also depends upon polarization. The energy of excitation of electrons in iodides is the least and hence the longest wavelength absorption which gives colour when decomposed.

The *melting and boiling points* of halogens increase with increase in the atomic number or atomic weights. This can be well explained based upon the size of atoms. With increase in size of the atoms, the electron clouds of the halogen molecules increase their area and are susceptible to more distortion or polarization. With greater distortion or polarization the Van der Waals' forces become more and more. Thus, F_2 and Cl_2 are gases but bromine is a liquid and iodine, a solid with some metallic lustre. Astatine is also a solid with some metallic character. These physical states are related to the increasing values of Van der Waals' forces acting between molecules from F_2 to I_2. The small values of Van der Waals' forces in F_2 and Cl_2 render them gases.

The heavier elements of this group show greater tendency to expand their octets than the lighter elements. This trend depends upon the availability of more orbitals with increasing atomic number. Thus, F combines with only one more halogen, chlorine with 3 flourines, bromine with 5 flourines and iodine with 7 flourines to give the following compounds, called **interhalogens**.

$$F—Cl \qquad ClF_3 \qquad BrF_5 \qquad IF_7$$

The predominant *oxidation state* for halogens is −1, but compounds of halogens are known in which they show +1, +5 and +7 oxidation states. A smaller number of compounds are also known to have halogens in +3 oxidation states. Various oxidation states for chlorine and represented by Cl^-, ClO^-, ClO_2^-, ClO_3^- and ClO_4^- ions, having −1, +1, +3, +5 and +7 states, respectively.

Occurrence

Fluorine is found in all natural waters, bones, teeth, blood and plants. Chlorine occurs mainly as rock salt. It has cubic crystal structure known as halite. The major source of bromine is sea-water. Iodine occurs as iodate in Chilean saltpetre and caliche. The main minerals containing halogens are given is Table 16.2.

The important physical properties of halogens are shown in Table 16.2.

TABLE 16.2

Physical Properties of Halogens

Properties	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic weight	18.998	35.453	79.909	126.904	210
Atomic radius (pm)	72	99	114	133	—
Ionic radius (pm)	136	181	195	216	—
Melting point	− 223	− 103	− 7.2	113.5	—
Boiling point	− 188	− 34.5	58.76	184.35	—
Density (liquid) (g cm^{-3})	1.11 (b.p)	1.56(b.p.)	3.12	4.94 (solid)	—
Dissociation energy	37.80	58.00	53.40	51.00	27.70
Electron affinity	3.70	4.00	3.80	3.40	3.20
Oxidation potential (ev)	+ 2.87	+ 1.36	+ 1.08	+ 0.53	—

Summary of the General Trends

(i) The valency shell of halogens contains ns^2np^5 electrons.

(ii) The relative sizes of atoms and ions of halogens play an important role in determining their physical and chemical properties.

(iii) The melting and boiling points of halogens can be explained based upon the values of intermolecular Van der Waals' forces between halogen molecules.

(iv) The colour of the halogens and their compounds are shown due to the absorption of visible light which is shown by the excitation of valency electrons.

(v) The stability of F_2, Cl_2, Br_2 and I_2 molecules and their compounds depends upon the dissociation energy. F_2 has the lowest heat of dissociation. Cl_2 has highest dissociation energy which decreases with increase in atomic number towards Br_2 and I_2.

(vi) Halogens with higher atomic number have greater tendency to form multiple bonds.

(vii) The usual oxidation states of halogens are:
F, –1; Cl, – 1, +1, +2, +3, +5, +7; Br, – 1, +1, +1, +3, +5; and I, – 1, +1, +3, +5, +7.

(viii) Fluorides are more ionic than chlorides, bromides and iodides. Iodides are mostly covalent in nature.

(ix) The halides of larger ionic radii are deeply coloured but others are colourless.

(x) Oxidizing power of halogens decreases with increase in atomic number.

Anomalous Behaviour of Fluorine

Fluorine differs from other halogens in many respects. The following are the major points of difference:

(i) Fluorine does not form oxyacids and oxysalts.

(ii) Fluorine cannot be prepared by the methods used for other halogens.

(iii) The fluorides of Ca, Mg, Ba, Sr, lanthanides and actinides are insoluble in water but other halides of these metals are soluble.

(iv) F forms compounds which exhibit hydrogen bonding.

(v) Flourine can form only one covalent bond.

(vi) The low F – F dissociation energy (bond energy) makes many of the reactions of F_2 highly exothermic. Thus flourination of organic compounds with undiluted fluorine takes place with explosive violence.

The above mentioned anomalies of fluorine with respect to other halogens are due to the following reasons:

- (i) The electronegativity of F(4.0) is the highest and is even greater than O(3.5). Other halogens are less electronegative than oxygen.
- (ii) F has small atomic size.
- (iii) F_2 molecule has low bond energy.
- (iv) F is not capable of expanding its octet.
- (v) The reaction of F with other elements and compounds is exothermic due to high bond energy.
- (vi) High lattice energy values of their crystal structures are responsible for the insolubility of their fluorides.

FLUORINE, F_2

Fluorine could not be prepared pure due to its reactivity for long time till 1886 when Moisson isolated it by electrolysing anhydrous HF.

Occurrence

The two sources of fluorine are:

Fluorspar	CaF_2
Cryolite	Na_3AlF_6

These minerals are mostly found in Mexico, Greenland and other parts of the world.

Industrial Preparation

Fluorine is prepared in the laboratory and on industrial scale by the electrolysis of fused KHF_2 or HF to which KHF_2 is added in order to make it conductor of electricity. Fused KHF_2 or mixture of HF and KHF_2 liberates fluorine at the anode and H_2 at the cathode.

$$\underset{\text{(fused)}}{2KHF_2} \xrightarrow{\text{electrolysed}} 2KF + 2HF$$

$$2KF \longrightarrow 2K^+ + 2F^-$$

$$2HF \longrightarrow 2H^+ + 2F^-$$

$$2K^+ + 2F^- \longrightarrow 2KF$$

$$2F^- - 2e \longrightarrow F_2 \text{ (at anode)}$$

$$2H^+ + 2e \longrightarrow H_2 \text{ (at cathode)}$$

The electrolysis of an aqueous solution of KHF_2 does not produce F_2 but liberates H_2 and O_2 gas. It is due to the fact that H_2O is oxidized to O_2 at a much lower voltage (1.23 volts). But F_2 is liberated at a higher voltage (2.85 volts).

Procedure and Apparatus

Fluorine is prepared by electrolysing fused KHF_2 (m.p. 227°C) or KF. 3HF (m.p. 56°C) in a V-shaped cell made of copper, nickel or monel metal (Figure 16.1).

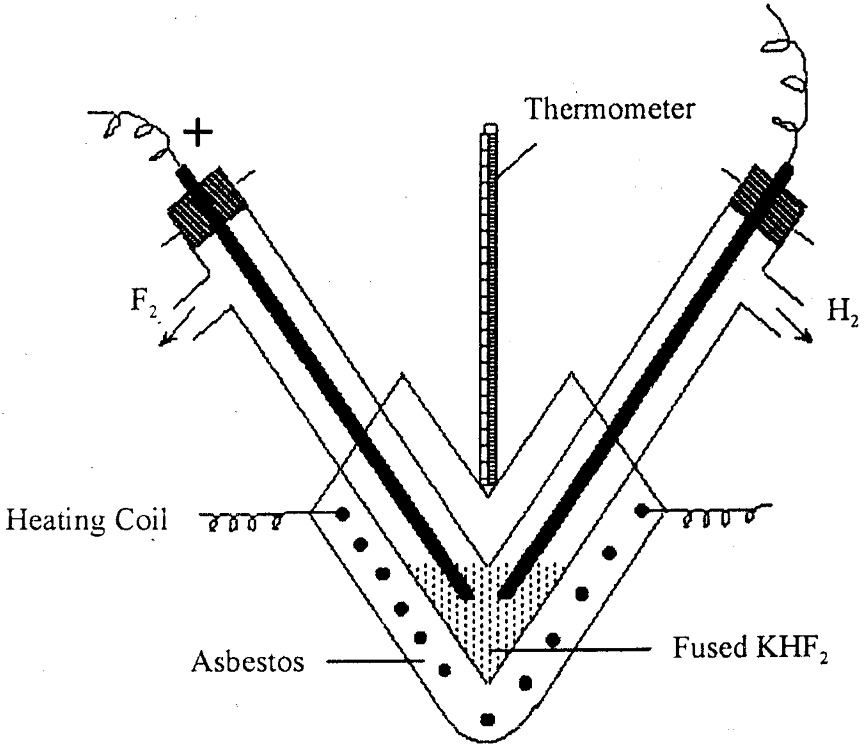


Fig. 16.1. Electrolytic cell for the preparation of F_2.

The anode is made of **graphite**. Therefore, fluorine liberated at the anode also contains small amounts of CF_4 which is removed by passing F_2 gas through liquid oxygen when carbon tetrafluoride is entrapped. The anode is insulated from the vessel by applying a thick paste of calcium fluoride and water glass mixture.

Copper cathode and copper vessel is used because the first coating of CuF_2 formed on the surface of the metal stops further reaction. All traces of moisture must be removed in order to avoid the reaction of F_2 and H_2O. The temperature of the fused electrolyte is maintained between to 100 – 200°C. The fluorine exit tube is also made of copper.

Properties

Fluorine is a pale greenish-yellow gas with pungent odour. Although poisonous but less than HF.

Chemical Reactions

Fluorine is highly electronegative element and very reactive. It combines directly with almost all elements except N_2. The following reactions are quite common:

(i) Combination with H_2

Fluorine combines explosively with hydrogen even at – 252°C and in dark.

$$H_2 + F_2 \longrightarrow 2HF$$

(ii) Combination with Metals

Alkali and alkaline earth metals in an atmosphere of fluorine to form corresponding fluorides. Lead, iron and other metals are also readily attacked. Gold and platinum also react on heating.

$$2Na + F_2 \longrightarrow 2NaF$$

$$2Au + 3F_2 \longrightarrow 2AuF_3$$

(iii) Action with Water

F_2 has strong affinity for water and decomposes with water to give HF.

$$F_2 + H_2O \longrightarrow OF_2 + H_2$$

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

(iv) Displacement of other Halogens

F_2 liberates Cl_2, Br_2 and I_2 from the metal halides.

$$2NaCl + F_2 \longrightarrow 2NaF + Cl_2$$

$$2KI + F_2 \longrightarrow 2KF + I_2$$

(v) Reaction with Halogens

F_2 combines with halogens to form interhalogen compounds.

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3$$

$$Cl_2 + F_2 \longrightarrow 2ClF$$

(vi) Reaction with I_2O_5

Heating fluorine with iodine pentoxide gives nitrogen compound, IF_5 and liberates O_2.

$$2I_2O_5 + 10F_2 \longrightarrow 5O_2 + 4IF_5$$

(vii) Reaction with Hydrocarbons

Fluorine reacts rapidly with a number of hydrocarbons to form fluorocarbon derivatives.

$$CH_3-CH_3+2F_2 \longrightarrow 2CF_4+6HF$$

(viii) Reaction with H_2S

F_2 reacts with H_2S to liberate S.

$$F_2+H_2S \longrightarrow S+2HF$$

Sulphur reacts with F_2 to form SF_6.

$$S+3F_2 \longrightarrow SF_6$$

INDUSTRIAL PREPARATION OF HALOGENS

Now the preparation and sources of chlorine, bromine and iodine would be discussed one by one.

Chlorine, Cl_2

OCCURRENCE

Chlorine is found in the form of chlorides. Sodium chloride, NaCl is the primary source and is found under the name rock-salt or common salt at Khewra Salt Mines in Pakistan.

PREPARATION

(i) Laboratory Preparation

Chlorine can be prepared in the laboratory by oxidation of HCl with oxidizing agents such as $KMnO_4$, MnO_2.

$$MnO_2+4HCl \longrightarrow MnCl_2+Cl_2+2H_2O$$

$$2KMnO_4+16HCl \longrightarrow 2KCl+2MnCl_2+8H_2O+5Cl_2$$

A mixture of NaCl and H_2SO_4 also reacts with MnO_2 to liberate Cl_2 gas.

$$MnO_2+NaCl+3H_2SO_4 \longrightarrow 2NaHSO_4+MnSO_4+2H_2O+Cl_2$$

(ii) Manufacture of Cl_2 (Electrolytic Process)

Chlorine is obtained on large scale by electrolysis of an aqueous solution of sodium chloride. Sodium hydroxide is also obtained at the same time. Various types of electrolytic cells are used for this purpose by Nelson cell (Figure 16.2) is more common.

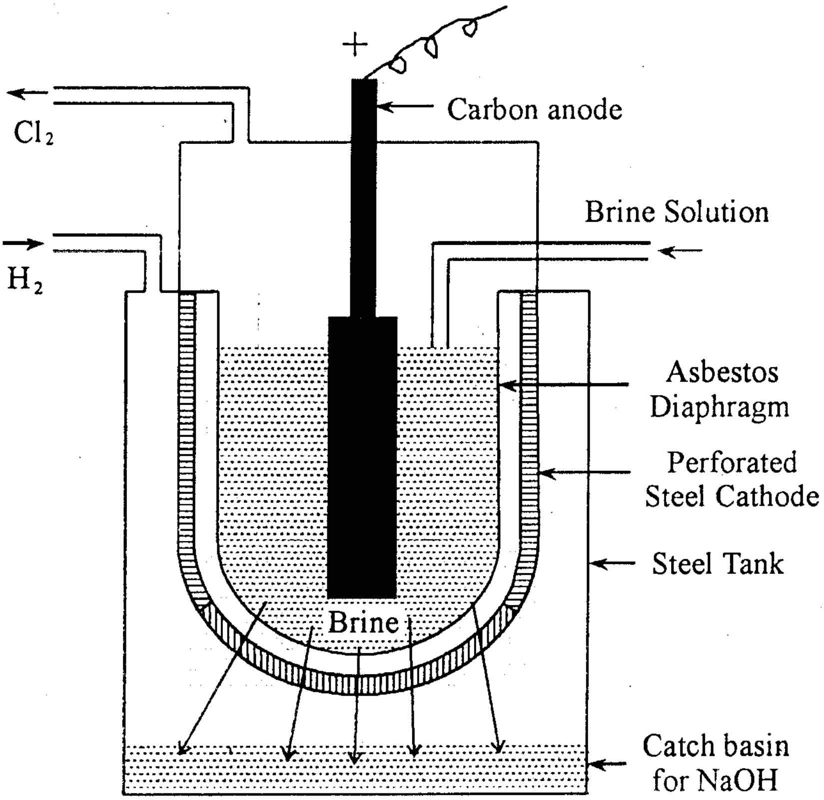


Fig. 16.2. Nelson cell for the manufacture of Cl_2 and NaOH.

Nelson cell consists of U-shaped trough supported by a steel tank. The cathode is steel U-shaped vessel containing an asbestos diaphragm which separates it from carbon anode hanging in the solution of brine. The anode compartment is kept filled with solution (NaCl solution). On passing current Cl_2 is liberated at the anode. Sodium ions collect at the cathode which form sodium. The later reacts with water to form NaOH. Cl_2 is sold in the market in steel cylinders.

$$2Na^+Cl^- + 2H_2O \xrightarrow{\text{Electrolysis}} 2Na^+OH^- + Cl_2 + H_2$$

(iii) Deacon's Process

It involves oxidation of HCl by atmospheric oxygen in presence of $CuCl_2$ as a catalyst.

$$4HCl + O_2 \xrightleftharpoons{CuCl_2} Cl_2 + 2H_2O$$

The function of the catalyst may be shown as follows:

$$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$$

$$Cu_2Cl_2 + O \longrightarrow CuO.CuCl_2$$

$$CuOCuCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

Bromine, Br_2

Occurrence

The chief sources of bromine are:

Sea-water – Containing $MgBr_2$

Carnallite contains 1% $MgBr_2.\ 6H_2O$ (Brom-Carnallite)

PREPARATION

(i) Laboratory Preparation

Bromine can be prepared in the laboratory by heating a mixture of MnO_2, KBr and H_2SO_4 in a retort.

$$MnO_2 + 2KBr + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

(ii) From Carnallite or Sea-water

Cl_2 reacts with $MgBr_2$ present in sea-water or mother liquor left after crystallization of carnallite to liberate Br_2.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2.$$

The hot mother liquor from carnallite or fairly concentrated solution of $MgBr_2$ obtained from sea-water is allowed to flow down the tower filled with earthenware balls so that liquid only percolates through it. This would expose the maximum surface to the action of Cl_2. A current of Cl_2 enters the base of the tower and passes upwards. The liberated bromine vapours along with unreacted Cl_2 pass out of the top of the tower. These vapours are passed through condenser where most of bromine liquefies. The bromine vapours escaping the condenser are caught in the tower filled with iron filings. Bromine reacts with iron to form ferroso-ferric bromide, Fe_3Br_8 ($FeBr_2 . 2FeBr_3$) from which KBr can be obtained.

The spent mother liquor is passed from the bottom of the tower (Figure 16.3) to a container through which steam passed and mixture stirred vigorously by means of shelves. The bromine carried by mother liquor escapes and is collected in condenser.

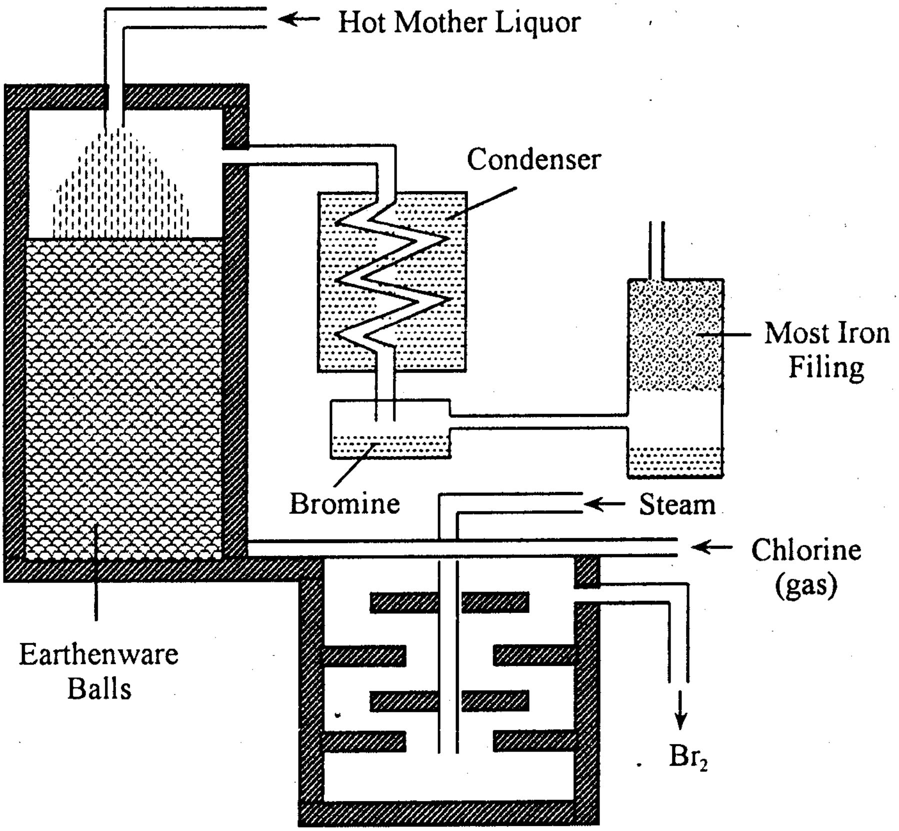


Fig. 16.3. Manufacture of Bromine.

The pH of hot mother liquor is adjusted to 1 – 4 with H_2SO_4 before passing Cl_2.

The liberated Br_2 obtained by the oxidizing action of Cl_2 may be absorbed in sodium carbonate solution. The solution is distilled after acidification to get Br_2.

$$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$$

$$3Br_2 + 3CO_3^{2-} \longrightarrow 5Br^- + BrO_3^- + 3CO_2$$

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Pure bromined is obtained by distilling it over KBr and ZnO which remove chlorine and I_2, respectively.

(iii) Electrolytic Process

The mother liquor from carnallite containing a mixture of NaBr and [illegible] can be electrolysed. Br_2 is liberated at the anode along with Cl_2 and can be easily separated.

Iodine I_2

Occurrence

The chief sources of iodine are:

Seaweeds (kelp) (0.5% in ashes of **Laminalia** a deep seaweed)

Chile saltpetre (Caliche) – contains 2% $NaIO_3$

(i) From Chile Saltpetre

The mother liquor obtained from chile saltpetre left after its purification contains 4 – 5 grams of sodium iodate per litre. Iodine is obtained by reduction process. For reduction purpose calculated amount of $NaHSO_3$ is used. The precipitated iodine is passed, dried and sublimed.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$$

(ii) From Seaweeds

The seaweeds are collected and dried during summer. The dried weeds are burnt in shallow pits. The ash known as kelp, contains over 1% iodine. The kelp is stirred thoroughly with hot water and insoluble matter allowed to settle. The solution is concentrated to crystallizes less soluble salts such as chlorides, sulphates and carbonates of alkali metals. The mother liquor containing more soluble salts, such as iodides, is mixed with MnO_2 and H_2SO_4 and distilled in cast iron retorts (Figure 16.4). The iodine comes out and is collected in stoneware receivers called **aludels**.

The crude iodine obtained by the above two processes is further **purified** by resubliming it over KI, to remove Cl_2 or Br_2 present as impurities.

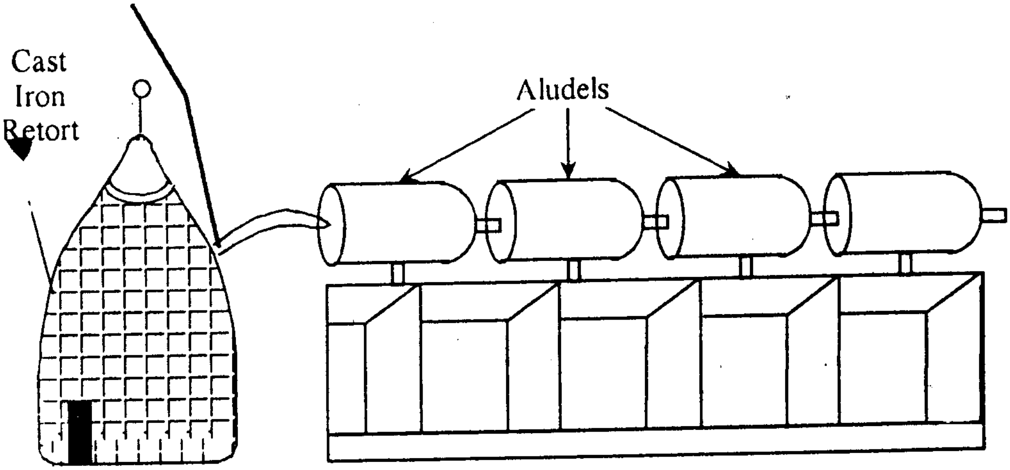


Fig. 16.4. Manufacture of Iodine.

(iii) Laboratory Method

Iodine can be prepared by the action of H_2SO_4 with MnO_2 and KI.

$$MnO_2 + 2KI + 3H_2SO_4 \longrightarrow MnSO_4 + 2KHSO_4 + I_2 + 2H_2O$$

PROPERTIES OF HALOGENS

PHYSICAL

Chlorine is a greenish-yellow gas, with a pungent and characteristic choking odour. It is poisonous gas which has irritating effect on nose, throat and lungs. It is fairly soluble in water.

Bromine is a dark-red liquid, which boils at about 59°C. It is very volatile and the vapour has a strong, irritating effect on eyes and nose. It has corrosive action on skin.

Iodine is a greyish-black solid with metallic lustre. It crystallizes in plates. Even at ordinary temperatures it gives off vapours which have irritating smell. It can be sublimed. It is almost insoluble in water (only 1 part of I_2 dissolves in 3,600 parts of water at a particular degree). It is freely soluble in CS_2, benzene, petroleum ether to give violet solutions. The solutions of iodine in alcohol and ether are brown.

Iodine is soluble in potassium iodide solution owing to the formation of soluble potassium tri-iodide.

$$KI + I_2 \rightleftharpoons KI_3$$

CHEMICAL PROPERTIES OF HALOGENS

The most important reactions of halogens (Cl_2, Br_2, I_2) are:

(a) Reaction with H_2

All halogens reacts with hydrogen under different conditions to give hydrogen halides. The reaction of F_2 is quite vigorous; Cl_2 reacts only in presence of light; bromine reacts readily but iodine shows a sluggish reaction.

$$H_2 + X_2 \longrightarrow 2HX \text{ (X = halogens)}$$

(b) Reaction with Oxygen

Halogens form a number of oxides. Fluorine reacts with oxygen in presence of high voltage electric discharge. Other oxides can be prepared by indirect means.

$$F_2 + O_2 \longrightarrow O_2F_2$$

$$HgO + 2Cl_2 \longrightarrow Cl_2O + HgCl_2$$

(c) Reaction with Other Elements

Halogens react with white and red phosphorus to form corresponding halides. Phosphorus spontaneously catches fire in an atmosphere of Cl_2 and reacts with explosive violence with Br_2.

$$2P + 3Cl_2 \longrightarrow 2PCl_3$$

$$2P + 5Cl_2 \longrightarrow PCl_5$$

Chlorine reacts with antimony and other metals to form halides.

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

Cl_2 + Br_2 react with S to form S_2X_2 (X = Cl, Br).

(d) Reaction with Water

Cl_2 and Br_2 react readily with water to give acidic solutions with the formation of hydrogen halides and hypohalous acids. Thus chlorine will turn blue litmus red in presence of moisture.

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

$$2HClO \longrightarrow 2HCl + O_2$$

$$2Br_2 + 2H_2O \longrightarrow 4HBr + O_2$$

Iodine does not reacts under ordinary conditions.

(e) Reaction with Alkalies

Halogens react with alkalies in cold and hot state to form different salts of oxyacids.

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$$

$$3Cl_2 + 6NaOH \xrightarrow{\Delta} 5NaCl + NaClO_3 + 3H_2O$$

$$Br_2 + 2NaOH \longrightarrow NaBr + NaBrO + H_2O$$

$$3Br_2 + 6NaOH \xrightarrow{\Delta} NaBrO_3 + 5NaBr + 3H_2O$$

$$I_2 + NaOH \longrightarrow NaI + HIO$$

$$3I_2 + 6NaOH \xrightarrow{\Delta} NaIO_3 + 5NaI + 3H_2O$$

If chlorine, bromine, or iodine is dissolved in aqueous alkalies, the colour of halogen disappears with oxidation of halogens. The reaction proceeds as:

(f) Reactions with FeX_2

FeX_2 reacts with corresponding halogens to form FeX_3 (X = halogen).

$$X_2 + 2FeX_2 \longrightarrow 2FeX_3$$

(g) Reaction with H_2S

Halogens oxidise H_2S to liberate free sulphur.

$$X_2 + H_2S \longrightarrow 2HX + S$$

The reaction takes place in the order $Cl_2 > Br_2 > I_2$.

(h) Reaction with Halogens Among Themselves

Halogens react among themselves to form a large number of compounds called **interhalogens.**

$$Br_2 + I_2 \longrightarrow 2IBr$$

(i) Oxidation Reaction of Halogens

Oxidations by halogens are quite common and important reactions. The reaction with F_2, Cl_2, Br_2 and I_2 are called fluorination, chlorination, bromination and iodination, respectively.

The following reactions depict the oxidizing nature of halogens:

$$CS_2 + 3Cl_2 \longrightarrow S_2Cl_2 + CCl_4$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The oxidation of thiosulphate ion to tetrathionate ($S_4O_6^{2-}$) ion is shown to proceed as:

$$Br_2 + SO_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$$

$$Cl_2 + SnCl_2 \longrightarrow SnCl_4$$

$$I_2 + AsO_2^- + 2H_2O \longrightarrow AsO_3^- + 4H^+ + 2I^-$$

(j) Reaction with Organic Compounds

Halogens usually undergo substitution and addition reactions with organic compounds depending upon their nature.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

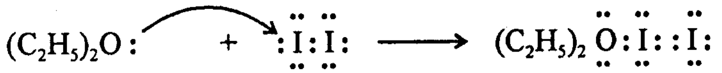
$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

(k) Reaction with Ammonia

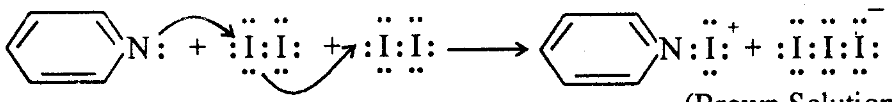
$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

COLOUR OF IODINE SOLUTIONS

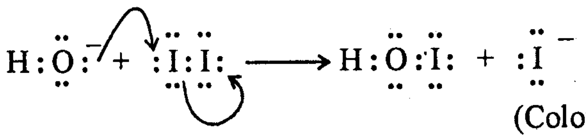
Iodine dissolves in different solvents to give variation in colour of iodine solutions. In completely non-basic solvents, iodine appears violet, the same colour as that of iodine vapours orange or brown. The basicity of solvents makes the electronic excitation responsible for iodine colour more difficult due to the approach of electron rich reagents. In presence of basic solvents, the I – I bond also weakens. Thus in presence of pyridine (an organic base), the I – I bonds are almost broken which are completely disconnected in presence of aqueous alkalies and thus give colourless solutions. The nucleophilic attack on iodine by bases is responsible for colour changes as shown below:

(i) 

(Brown Solution)

(ii) 

(Brown Solution)

(iii) 

(Colourless)

COMPOUNDS OF HALOGENS

Halogens form a variety of compounds but hydrogen halides, oxides, oxyacids of halogens will only be discussed over here.

Hydrogen Halides, HX

All the halogens form binary compounds with hydrogen to form hydrogen halides of the type HX (X = F, Cl, Br, or I). Although H_2 and F_2 react rapidly to form HF but reaction is too vigorous to be adopted as a method of preparation for HF.

Hydrogens Fluoride (Hydrofluoric acid), $(HF)_x$:

PREPARATION

(i) From CaF_2 and H_2SO_4

Aqueous hydrofluoric acid is obtained by heating CaF_2 with H_2SO_4 in a platinum or lead retort. The vapours are dissolved in water.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

(ii) Anhydrous hydrogen fluoride is obtained by heating KHF_2 in a platinum retort and cooling HF vapours in a freezing mixture.

$$KHF_2 \longrightarrow KF + HF$$

Properties

Hydrogen fluoride is a colourless, strongly-fuming liquid (b.p. 19.4°C) having an extremely pungent odour. The vapours of hydrofluoric acid are highly poisonous.

Hydrofluoric acid reacts with glass and silica to form SiF_4, a colourless gas.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

Hydrofluoric acid behaves as a typical acid and reacts with metals, decomposes carbonates, neutralizes alkalies and turns blue litmus red.

$$M + (HF)_x \longrightarrow MF_x + xH$$

$$(HF)_x + Na_2CO_3 \longrightarrow 2NaF + CO_2 + H_2O$$

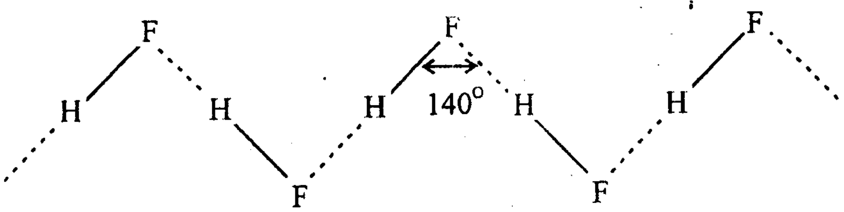
$(x = 2)$

$$Na_2SiO_3 + 6HF \longrightarrow 2NaF + SiF_4 + 3H_2O$$

Hydrofluoric acid does not react with noble metals such as Ag, Au and Pt.

Hydrofluoric acid is mainly used for etching or marking glass.

Structure



$(HF)_x$

OTHER HYDROGEN HALIDES, HX

Cl_2, Br_2 and I_2 form HCl, HBr and HI, respectively.

General Methods of Preparation

(i) By Direct Union of Elements

H_2 and halogens combine to form hydrogen halides.

$$H_2 + X_2 \rightleftharpoons 2HX$$

HCl is obtained by combustion of hydrogen in chlorine. Reaction between H_2 and Br_2 is less vigorous and HBr is obtained by heating the mixture at 200°C in presence of Pt or C as catalyst. Excess of H_2 is used to force the equilibrium to the right hand direction.

HI is not prepared by this method because of decomposition to H_2 and I_2 at equilibrium.

(ii) By the Action of H_2SO_4 or H_3PO_4 on Metallic Halides

This is a convenient method for the preparation of hydrogen halides, especially HF and HCl.

Concentrated H_2SO_4 or concentrated H_3PO_4 and alkali metal halides are used for this purpose.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

Sodium bromide and iodide react with concentrated H_2SO_4 to liberate HBr and HI which react further to liberate Br_2 and I_2, respectively.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

$$8HI + H_2SO_4 \longrightarrow H_2S + 4I_2 + 4H_2O$$

Concentrated H_3PO_4 (non-oxidizing acid) reacts with alkali metal bromides and iodides to form HBr and HI only.

$$NaBr + H_3PO_4 \longrightarrow HBr + NaH_2PO_4$$

$$NaI + H_3PO_4 \longrightarrow HI + NaH_2PO_4$$

(iii) By Hydrolysis of non-metal Halides

The non-metal halides (PBr_3, PI_3, etc.) are hydrolysed with water to give HX.

$$PBr_3 + 3H_2O \longrightarrow H_3PO_3 + 3HBr$$

$$PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$$

(iv) By Reduction of H_2S or H_2SO_3

Br_2 and I_2 reduce H_2S or H_2SO_3 to liberate HBr and HI.

$$Br_2 + H_2S \longrightarrow S + 2HBr$$

$$I_2 + H_2S \longrightarrow S + 2HI$$

$$Br_2 + H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2HBr$$

$$I_2 + H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2HI$$

(v) By Halogenation of Hydrocarbons

F_2, Cl_2 and Br_2 react with hydrocarbons in presence of a catalyst to form halogenated hydrocarbons with the liberation of corresponding hydrogen halides.

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$$

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

GENERAL PROPERTIES

HCl, HBr and HI are all colourless gases which dissolve in water to give corresponding acid solutions. The solubility and acidity of these compounds is due to the following reaction equilibrium:

$$HX + H_2O \rightleftharpoons H_3O^+ + X^- \qquad (X = Cl, Br, I)$$

Metals above H with respect to E.M.F. react with acids to liberate H_2.

$$Zn^\circ + 2HX \longrightarrow ZnX_2 + H_2 \qquad (X = Cl, Br, I)$$

These hydrogen halides react with bases to form salts.

$$NaOH + HX \longrightarrow NaX + H_2O$$

Some of the important properties of hydrogen halides are given in Table 16.3.

TABLE 16.3

Some Properties of Hydrogen Halides

Properties	HCl	HBr	HI
Melting point (°C)	– 114	– 87	– 51
Boiling point (°C)	– 85	– 67	– 35
Solubility in water ($g/100$ g of H_2O)	93 (– 15°C)	221 (0°C)	425 (10°C)
Dielectric constant of liquid	9	6	3
Heat of formation (KJ/mole)	92.0	36.4	24.7

OXIDES OF HALOGENS

Halogens form a number of oxides which depict their oxidation states also. The most common oxides are:

OF_2	Cl_2O	Br_2O	I_2O_4
O_2F_2	ClO_2	Br_3O_8	I_4O_9
	Cl_2O_6	BrO_2	I_2O_5
	Cl_2O_7		

OXYGEN FLUORIDES

Oxygen difluoride, OF_2 is a colourless gas but oxygen monofluoride, O_2F_2 is a red liquid. OF_2 is formed when F_2 reacts with NaOH solution.

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$$

OF_2 dissolves in water but explodes in steams.

$$OF_2 + H_2O \longrightarrow O_2 + 2HF$$

OF_2 liberates halogens from their acids and salts.

$$OF_2 + 4HX \longrightarrow 2X_2 + 2HF + H_2O$$

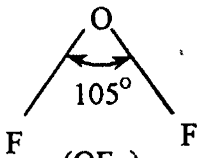
O_2F_2 is prepared by passing the high voltage electric discharge through a mixture of O_2 and F_2.

$$O_2 + F_2 \longrightarrow O_2F_2$$

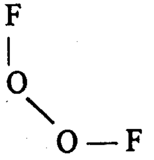
It is a powerful fluorinating and oxidizing agent. It reacts with chlorine to give a purple colour and an intermediate $(O_2ClF_3)_x$ can be isolated.

Another oxygen fluoride detected is O_3F_2, trioxygen difluoride.

The structures of OF_2 and O_2F_2 are given below:



(OF_2)



(O_2F_2)

Oxides of Chlorine, Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7

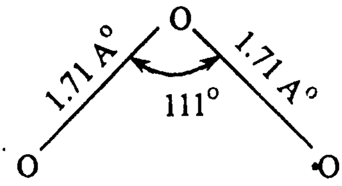
They are strong oxidizing agents and react vigorously, **chlorine monoxide,** Cl_2O is prepared by passing Cl_2 over dry mercury oxide at 0°C.

$$2HgO + 2Cl_2 \longrightarrow Cl_2O + HgCl_2 . HgO$$

Cl_2O is a reddish-yellow gas which reacts with water to give hypochlorous acid and thus may be considered anhydride of this acid.

$$Cl_2O + H_2O \longrightarrow 2HOCl$$

The molecule is V-shaped with O – Cl bond length 1.71A° and Cl – O – Cl angle 111°.



Chlorine dioxide, ClO_2 is a reddish-yellow gas which explodes violently when pure. It is prepared from $KClO_3$ by treating with concentrated H_2SO_4 or oxalic acid.

$$4KClO_3 + 4H_2SO_4 \longrightarrow 4KHSO_4 + 4ClO_2 + O_2 + 2H_2O$$

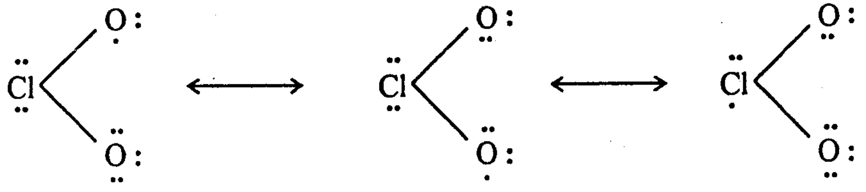
$$2KClO_3 + 3H_2C_2O_4 \longrightarrow 2ClO_2 + 3CO_2 + 2KHC_2O_4 + 2H_2O$$

It can be conveniently prepared from sodium chlorite and Cl_2 diluted with air.

$$Cl_2 + 2NaClO_2 \longrightarrow 2NaCl + 2ClO_2$$

ClO_2 is found to be useful as an antiseptic, for water purification and bleaching of cellulose materials.

The ClO_2 molecule has an odd electron and is resonance hybrid of at least three resonating forms.



Chlorine Hexa-oxide, Cl_2O_6

It can be prepared by u.v. irradiation of ClO_2.

$$8ClO_2 \longrightarrow 2Cl_2O_6 + 2Cl_2O + O_2$$

Ozone reacts with ClO_2 to form chlorine hexa-oxide.

$$2O_3 + 4ClO_2 \longrightarrow 2Cl_2O_6 + O_2$$

Cl_2O_6 is a red oily liquid and decomposes to ClO_2 and O_2 even at its melting point. It is an oxidizing agent.

Chlorine hepta-oxide, Cl_2O_7 is considered to be anhydride of perchloric acid, $HClO_4$ and is thus obtained by the dehydration of $HClO_4$ with P_2O_5 at −10°C, followed by vacuum distillation.

$$2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3$$

It reacts with alkalies to form perchlorate ions.

OXIDES OF BROMINE

Bromine oxides are dark volatile liquids which have recently been identified. They have low thermal stability.

Bromine monoxide, Br_2O is prepared by the action of Br_2 vapour with anhydrous HgO at 50°C.

$$HgO + 2Br_2 \longrightarrow HgBr_2 + Br_2O$$

It can also obtained by reacting Br_2 in CCl_4.

Bromine monoxide is stable in CCl_4 in dark at − 20°C. Bromine monoxide is an oxidizing agent and converts iodide to iodate ion.

Bromine dioxide, BrO_2

Bromine dioxide can be prepared by passing silent electric discharge through a mixture of bromine and oxygen under reduced pressure and low temperature. It decomposes even at 0°C to Br_2 and O_2.

Tribromine octoxide, Br_3O_8 is prepared by treating bromine vapours with ozone at 0°C. It readily dissolves in water and gives oxidizing solutions.

OXIDES OF IODINE

There are three oxides of iodine known, I_2O_5 is the most important.

Oxyacids of Halogens and Their Salts

Oxyacids of fluorine or their salts are unknown. Cl_2, Br_2 and I_2 have strong tendency to form oxyacids but chlorine shows greater tendency to form these acids. The oxyacids formed by halogens are shown in Table 16.4.

TABLE 16.4

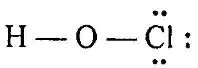
Oxidation States and Oxyacids of Halogen

Oxidation State	Cl_2	Br_2	I_2
+ 1	HClO	HBrO	HIO
+ 3	$HClO_2$	$HBrO_2$	—
+ 5	$HClO_3$	$HBrO_3$	HIO_3
+ 7	HCl_4	—	HIO_4 H_5IO_6

The strength of the oxyacids increases with increasing number of oxygen atoms (more precisely the oxygen atoms which are not combined with oxygen). Thus $HClO_4$ would be more acidic than $HClO_3$ and $HClO_3$ would be more acidic than $HClO_2$ and HClO. In fact, $HClO_4$ is the strongest acid known. The sequence of the acid strength of oxyacids is:

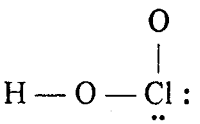
$$HXO_4 > HXO_3 > HXO_2 > HXO$$

The H and halogen atoms are interlinked through oxygen atoms. Thus the structures of oxyacids of chlorine are:



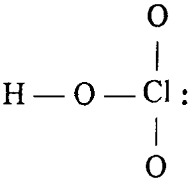
$H-O-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$

(Hypochlorous acid)



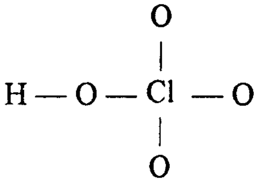
$H-O-\overset{\overset{O}{|}}{\underset{\cdot\cdot}{Cl}}:$

(Chlorous acid)



$H-O-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{Cl}}:$

(Chloric acid)



$H-O-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{Cl}}-O$

(Perchloric acid)

The bonds between H and O have polar nature and are responsible for the formation of H^+ and oxyacid anions on hydrolysis. However, the bonds between O and halogen atoms are covalent and the oxidation states of halogens are depicted by the number of electrons of halogen atoms which are shared with oxygen atoms. For example, HClO, $HClO_2$, $HClO_3$ and $HClO_4$ share 1, 3, 5 and 7 electrons of chlorine with oxygen atoms and hence show oxidation states +1, +3,

+5 and +7, respectively. The greater is the number of oxygen atoms around halogens, the greater would be the stability of oxyacid anions and hence stronger the acid. The large size of the halogen with small electronegativity values result in lowering of stability of anions and hence the acids would be weaker.

The reactivity of oxyacids depend upon the number of oxygen atoms. It decreases with increasing number of oxygen atoms. Thus HXO would be more reactive than HXO_3 or HXO_4. All oxyacids and their salts are good oxidizing agents.

The structures of oxyacid anions are tetrahedral. The symmetry of ClO^-, ClO_2^-, ClO_3^- and ClO_4^- are shown in Figure 16.5.

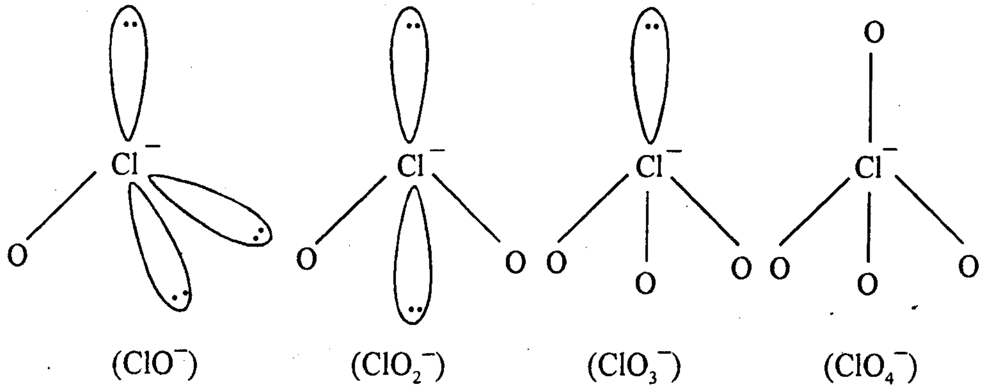


Fig. 16.5. Tetrahedral symmetry of oxyacid anions.

OXYACIDS OF HALOGENS

Hypochlorous acid, HClO

This acid is found only in the solution and has not yet been isolated pure.

It is usually **prepared** by passing chlorine through water.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

Chlorine monoxide also dissolves in water to produce hypochlorous acid.

$$Cl_2O + H_2O \longrightarrow 2HClO$$

Hypochlorous acid can also be prepared by passing chlorine gas through a suspension of mercuric oxide in water.

$$HgO + H_2O + 2Cl_2 \longrightarrow HgCl_2 + 2HClO$$

The precipitated $HgCl_2$ and unreacted HgO are filtered off and solution distilled.

Properties

Hypochlorous acid exists as pale yellow solution and decomposes to liberate chlorine monoxide.

$$2HClO \longrightarrow Cl_2O + H_2O$$

It possesses bleaching, oxidizing and germicidal properties. It decomposes to give oxygen when heated or exposed to light.

$$2HClO \longrightarrow 2HCl + O_2$$

$$2HClO + ClO^- \longrightarrow ClO_3^- + 2HCl$$

Hypochlorous acid reacts with ClO^- to form ClO_3^-.

The salts of hypochlorous acid are called **hypochlorites**. The most important salt is bleaching powder (See Chapter 10).

Calcium hypochlorite, $Ca(ClO)_2$ is obtained by the action of NaClO on $CaCl_2$ and is sold under the name **high-test hypochlorite** (HTH). It is more soluble and more effective than bleaching powder, CaCl(OCl).

$$CaCl_2 + 2NaClO \longrightarrow Ca(ClO)_2 + 2NaCl$$

HBrO and HIO are also known and behave similar to HClO.

HALOUS ACIDS AND HALITES

The only halous acid definitely known is $HClO_2$.

Chlorous acid, $HClO_2$

It is prepared by treating a suspension of barium chlorite with H_2SO_4. The precipitated $BaSO_4$ is filtered off.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$$

Barium chlorite is made by heating ClO_2 solution with H_2O_2 in presence of BaO_2.

$$2ClO_2 + H_2O_2 \longrightarrow 2HClO_2 + O_2$$

$$BaO_2 + 2HClO_2 \longrightarrow Ba(ClO_2)_2 + H_2O_2$$

The chlorites are obtained by the action of caustic alkalies on ClO_2. They are usually associated with ClO_3^-.

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

The reaction of peroxides with ClO_2 also results in the formation of chlorites.

$$Na_2O_2 + 2ClO_2 \longrightarrow 2NaClO_2 + O_2$$

$$Ba_2O_2 + 4ClO_2 \longrightarrow 2Ba(ClO_2)_2 + O_2$$

The metal chlorites decompose on heating:

$$3NaClO_2 \longrightarrow NaCl + 2NaClO_3$$

Chlorous acid and its salts are oxidizing agents and liberate iodine from KI.

$$NaClO_2 + 2H_2O + 4KI \longrightarrow NaCl + 2I_2 + 4KOH$$

Bromous acid, $HBrO_2$ is obtained by the action of $AgNO_3$ with excess of Br_2 water.

$$2Br_2 + 3AgNO_3 + 2H_2O \longrightarrow HBrO_2 + 3AgBr + 3HNO_3$$

HALIC ACIDS AND HALATES

Chloric acid, $HClO_3$ and bromic acid, $HBrO_3$ are only obtained in solution. But iodic acid, HIO_3 can be isolated as colourless crystals soluble in water.

Preparation

(i) All these acids are obtained by the action of H_2SO_4 on barium chlorate, bromate, or iodate.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$$

$$Ba(IO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HIO_3$$

(ii) HIO_3 can also be obtained by oxidizing I_2 with concentrated HNO_3.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 4H_2O + 10NO_2$$

(iii) Cl_2, Br_2 and I_2 react with hot alkalies to produce halates and halides.

$$3X_2 + 6NaOH \longrightarrow NaXO_3 + 5NaX + 3H_2O$$

(X = Cl, Br, I).

Sodium halates are separated from halides by fractional crystallization.

(iv) Cl_2 oxidizes Br_2 and I_2 in aqueous solutions to give $HBrO_3$ and HIO_3.

$$Br_2 + 5Cl_2 + 6H_2O \longrightarrow 2HBrO_3 + 10HCl$$

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

All halic acids are strong acids and good oxidizing agents.

$$3HClO_3 \longrightarrow HClO_4 + 2ClO_2 + H_2O$$

The chloric acid decomposes to liberate chlorine in concentrated solutions.

$$3HClO_3 \longrightarrow HClO_2 + 2O_2 + Cl_2 + H_2O$$

Iodates crystallize with iodic acid to give compounds such as $KIO_3 . HIO_3$, $KIO_3 . 2HIO_3$.

Potassium chlorate is an important salt of chloric acid and can be obtained by the action of Cl_2 on $Ca(OH)_2$.

$$6Ca(OH)_2 + 6Cl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$$

$KClO_3$ decomposes to give potassium perchlorate,

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

but on strong heating KCl is obtained.

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

Perchloric Acid, $HClO_4$

It is colourless mobile liquid, m.p. −112°C. b.p., 19°C. Perchloric acid is obtained by $HClO_3$ or its exposure to light.

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

The acid can also be obtained by the action of $KClO_4$ with H_2SO_4.

$$KClO_4 + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HClO_4$$

The acid can be obtained by treating NH_4ClO_4 with acids.

The sodium and potassium perchlorates are usually formed by prolonged electrolysis of NaCl or KCl solution.

$$\underset{\text{(obtained from } Cl^-)}{ClO_3^- + H_2O} \xrightarrow{\text{electrolysis}} ClO_4^- + 2H^+$$

Perchloric acid forms well defined salts. The acid and its salts are good oxidizing agents but less than chloric acid and chlorates.

Anhydrous perchloric acid is hygroscopic and dissolves in water with a hissing sound to form a series of hydrates ($HClO_4 . H_2O$: $HClO_4 . 2H_2O$: $HClO_4 . 3H_2O$).

Perchloric acid is the strongest of all acids.

The salts of perchloric acid are stable and soluble in water. NH_4ClO_4 on heating decomposes to liberate Na, Cl, and O_2.

$$2NH_4ClO_4 \longrightarrow N_2 + Cl_2 + 2O_2 + 4H_2O$$

Anhydrous $Mg(ClO_4)_2$ is an excellent drying agent. $KClO_4$ is used in match industry and explosives.

Perbromic acid and perbromates have not yet been prepared.

PER-IODIC ACIDS

Per-iodic acid exists in solution as tetrahedral ion, IO_4^- and in several hydrated forms. The normal formula of the acid is H_5IO_6 in contrast to its chlorine analogue, perchloric acid ($HClO_4$). H_5IO_6 is called para per-iodic acid to distinguish it from other forms of per-iodic acids, *i.e.*, HIO_4, (meta per-iodic acid), H_3IO_5 (meso per-iodic acid) and $H_4I_3O_9$ (a mixture of the other two).

META PER-IODIC ACID

(HIO_4) It can be obtained by heating para per-iodic acid at 100°C under vacuum.

$$H_5IO_6 \xrightarrow{100^\circ C} HIO_4 + 2H_2O$$

The sodium and silver salts of meta per-iodic acid are well-known. The hydration of para per-iodic acid to meta per-iodic acid takes place stepwise and forms $H_4I_2O_9$ at 80° under reduced pressure. This indicates that various per-iodic acids are different hydrated forms of I_2O_7.

$$\underset{(I_2O_7.\ 5H_2O)}{2H_5IO_6} \xrightarrow{80^\circ C} \underset{(I_2O_7.\ 2H_2O)}{H_4I_2O_9} \xrightarrow{100^\circ C} \underset{(I_2O_7.\ H_2O)}{2HIO_4}$$

Meso per-iodic acid (H_3IO_5) has not yet been prepared but its silver salt, Ag_3IO_5 is obtained as a black precipitate by reacting sodium para per-iodates with boiling $AgNO_3$ solution.

$$Na_5IO_6 + 3AgNO_3 + H_2O \longrightarrow Ag_3IO_5 + 3NaNO_3 + 2NaOH$$

Para per-iodic acid (H_5IO_6) can be prepared by the action of silver meso per-iodate with Cl_2 or Br_2.

$$4Ag_3IO_5 + 6Cl_2 + 10H_2O \longrightarrow 4H_5IO_6 + 3O_2 + 12AgCl$$

Silver chloride is filtered off and the filtrate deposits crystals of para per-iodic acid on standing.

Barium iodate can be converted to barium para per-iodate first which reacts with H_2SO_4 to give H_5IO_6 (para per-iodic acid).

$$5Ba(IO_3)_2 \longrightarrow Ba_5(IO_6)_2 + 4I_2 + 9O_2$$

$$Ba_5(IO_6)_2 + 5H_2SO_4 \longrightarrow 2H_5IO_6 + 5BaSO_4$$

The alkali metal para per-iodates can be easily prepared from iodates. For example,

$$2Na^+ + IO_3^- + Cl_2 + 3OH^- \longrightarrow Na_2H_3IO_6 + 2Cl^-$$

Or

$$NaIO_3 + Cl_2 + 3NaOH \longrightarrow Na_2H_3IO_6 + 2NaCl$$

$Na_2H_3IO_6$ can also be prepared by passing Cl_2 through a boiling solution of iodine in an excess of NaOH.

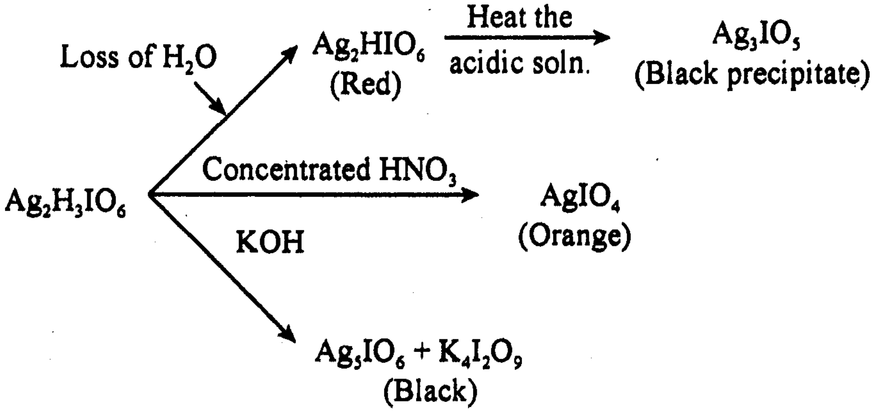
$$I_2 + 7Cl_2 + 18NaOH \longrightarrow 2Na_2H_3IO_6 + 8H_2O + 14NaCl$$

Treatment of $Na_2H_3IO_6$ suspension in water with $AgNO_3$ gives a black precipitate of silver para per-iodate.

$$\underset{}{Na_2H_3IO_6 + 5AgNO_3} \longrightarrow \underset{\text{(black)}}{Ag_5IO_6} + 2NaNO_3 + 3HNO_3$$

$$Na_2H_3IO_6 + 2AgNO_3 \longrightarrow \underset{\text{(greenish-yellow)}}{Ag_2H_3IO_6} + 2NaNO_3$$

Silver para per-iodate can be converted to silver salts of other per-iodic acids which indicates the presence of other per-iodates.



Ag_5IO_6 reacts with chlorine to liberate para per-iodic acid, H_5IO_6.

$$4Ag_5IO_6 + 10Cl_2 + 10H_2O \longrightarrow 4H_5IO_6 + 5O_2 + 20AgCl$$

Aqueous para per-iodic acid is weak but a powerful oxidizing agent.

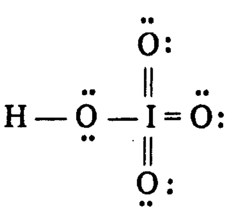
$$H_5IO_6 + 7H^+ + 8e \longrightarrow I^- + 6H_2O$$

Gentle heating of H_5IO_6 gives a white solid, I_2O_5.

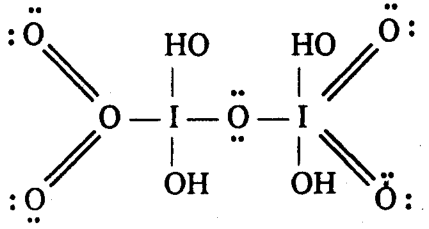
$$2(HO)_5IO \xrightarrow{\Delta} I_2O_5 + O_2 + 5H_2O$$

Structure

Larger iodine atom can accommodate up to six oxygen atoms around it having octahedral arrangement. The structure of various forms of per-iodic acid are:



(HIO_4)



($H_4I_2O_9$)

Para per-iodic acid, H_5IO_6 has central iodine atom surrounded by five OH groups and one oxygen atom in an octahedral manner (Figure 16.6).

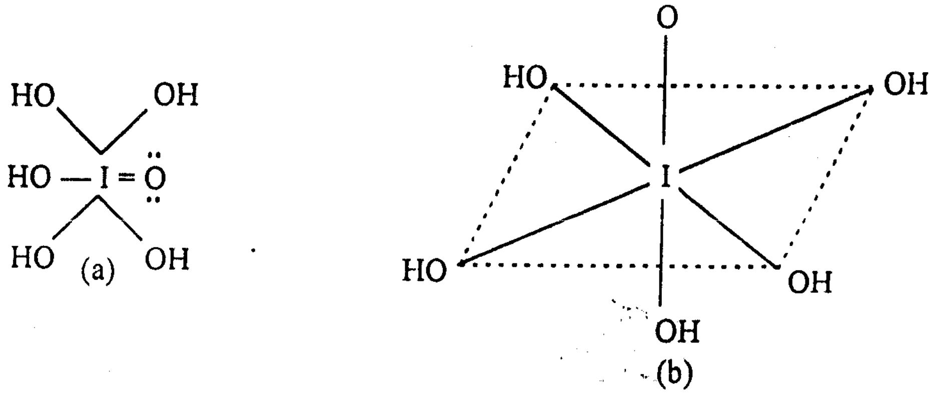


Fig. 16.6. Structure of H_5IO_6 (a) Attachment of OH group and O around I. (b) Arrangement of groups and atoms in octahedral manner.

INTERHALOGEN COMPOUNDS STRUCTURAL AND CHEMICAL ASPECTS

The binary compounds of halogens among themselves are called interhalogen compounds. Four types of such compounds are known, namely XX', XX_3', XX_5' and XX_6'. They are regarded halides of the more electropositive components. Thus, ClF is called chlorine monofluoride and ICl_3, iodine trichloride. The halogen atoms in interhalogen compounds are linked by covalent bonds in exactly the same manner as halogen atoms among themselves to form molecules. As a result of the electronegativity between X and X' halogen atoms the interhalogen compounds show polarity in bonds. Thus ICl, ICl_3 and BrF_3 show certain ionic character in their bonds.

The interhalogens consists of a larger halogen atom (X) surrounded by smaller halogen atoms (X'). Geometrical limitations restrict the formation of certain possible interhalogens. For example, BrF_7 does not exist whereas IF_7 has been isolated.

Let us now discuss the interhalogen compounds under the four general types, *i.e.*, XX', XX_3', XX_5' and XX_7'.

XX' TYPE INTERHALOGENS

Only five interhalogens of this type are known.

Chlorine monofluoride	ClF	(Colourless gas, b.p. — 101°C)
Bromine monofluoride	BrF	(Pale brown gas, b.p. 20°C)
Bromine monochloride	BrCl	

Iodine monochloride	ICl	(α form — red solid, m.p. 27.2°C; β form – brownish-red solid, m.p. 14°C)
Iodine monobromide	IBr	(Grey solid, m.p. 42°C).

Chlorine monofluoride, ClF is a colourless gas which liquefies to a yellow liquid and solidifies to colourless solid with characteristic odour.

It is prepared by the direct combination of Cl_2 and F_2 at room temperature.

$$Cl_2 + F_2 \longrightarrow 2ClF$$

ClF undergoes reactions similar to that of F_2.

Structure

Chlorine monofluoride has linear structure.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

BROMINE MONOFLUORIDE, BrF

It condenses to dark red liquid which freezes to a yellow crystalline solid.

Gaseous bromine reacts with F_2 at 50°C to give BrF.

$$Br_2 + F_2 \longrightarrow 2BrF$$

BrF is reactive and decomposes to BrF_3 and BrF_5 along with free bromine.

$$3BrF \longrightarrow BrF_3 + Br_2$$

$$5BrF \longrightarrow BrF_5 + 2Br_2$$

Iodine monofluoride does not exist.

IODINE MONOCHLORIDE, ICl

It exists as red transparent crystals which melt to brownish-red liquid. The liquid boils at 100°C to red vapour with a choking smell. The vapours cause bad burns on skin.

Preparation

(i) It is prepared by adding iodine to liquid chlorine and keeping the mixture at 35°C for 24 hours.

$$I_2 + Cl_2 \longrightarrow 2ICl$$

(ii) An aqueous solution of potassium iodide and iodate react with HCl to liberate Cl_2.

$$KIO_3 + 5KI + 6HCl \longrightarrow \boxed{3I_2} + 3H_2O + 6KCl$$

$$KIO_3 + 2I_2 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$$

Properties

Iodine monochloride is hydrolysed in aqueous solutions to liberate iodine.

$$5ICl + 3H_2O \longrightarrow HIO_3 + 2I_2 + 5HCl$$

Liquid iodine monochloride is a good solvent and dissociates as:

$$2ICl \longrightarrow I^+ + [ICl_2]^-$$

Heavy alkali metal chlorides dissolve in ICl except LiCl, NaCl to give ionising salts.

$K^+(ICl_2)^-$

$$KCl + ICl \longrightarrow K^+[ICl_2]^-$$

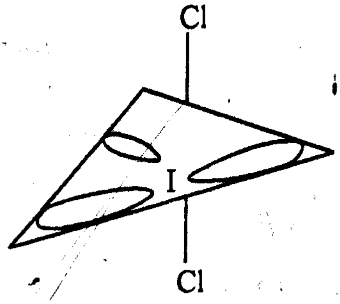
PCl_5, $SbCl_5$, $SnCl_4$, $AlCl_3$ etc., react with ICl to ionising acidic solution.

$$ICl + PCl_5 \longrightarrow I^+[PCl_6]^-$$

HCl reacts with ICl to form a strong acid, $HICl_2$.

$PCl_5, SbCl_3, SnCl_4$

$$HCl + ICl \longrightarrow H[ICl_2]^-$$



Structure

Iodine monobromide, IBr is also obtained by the direct combination of I_2 and Br_2.

$$I_2 + Br_2 \longrightarrow 2IBr$$

$ICl + H_2O \rightarrow HIO_3, I_2, HCl$

XX'_3 Type Interhalogens

Only three interhalogen compounds of XX'_3 type are known:

Chlorine trifluoride	ClF_3	(Colourless gas, b.p. 12°C)
Bromine trifluoride	BrF_3	(Greenish-yellow liquid, b.p. 127.6°C)
Iodine trichloride	ICl_3	(Orange-yellow solid, melts with decomposition at 101°C)

Chloride trifluoride, ClF_3

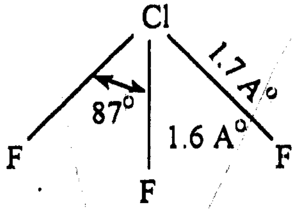
The colourless gas is obtained by direct combination of Cl_2 or ClF and excess F_2 at 250°C in a nickel tube.

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3$$

It reacts with glass and attacks many compounds and most of the elements. It reacts with water giving a loud crack.

Structure

Microwave data have shown a planar structure for ClF_3.



Bromine trifluoride, BrF_3

It is prepared by mixing bromine vapours with excess F_2 in presence of nitrogen

$$Br_2 + 3F_2 \xrightarrow{N_2} 2BrF_3$$

BrF_3 is a good ionizing solvent.

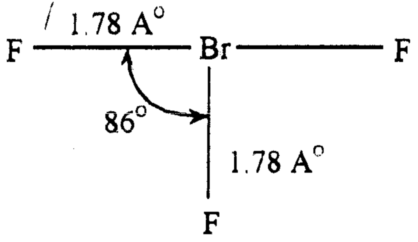
$$2BrF_3 \longrightarrow [BrF_2^+] + [BrF_4^-]$$

It reacts with metals and metal oxides to compounds of the type:

$$[BrF_2^+] [AuF_4^-], [BrF_2]^+ [SbF_6^-]$$

Structure

The structure of BrF_3 is T-shaped.



Iodine trichloride, ICl_3

It can be obtained pure as lemon yellow crystals.

Preparation

(i) ICl_3 can be prepared by direct combination of elements. For this purpose chlorine is passed on iodine at – 80°C or Cl_2 is passed over iodine until ICl is formed and then raising the temperatures to 100°C.

$$I_2 + 3Cl_2 \longrightarrow 2ICl_3$$

(ii) ICl_3 can also be obtained by heating I_2O_5 in presence of HCl.

$$I_2O_5 + 10HCl \longrightarrow 2ICl_3 + 2Cl_2 + 5H_2O$$

Properties

ICl_3 is easily hydrolysed by water.

$$2ICl_3 + 3H_2O \longrightarrow ICl + HIO_3 + 5HCl$$

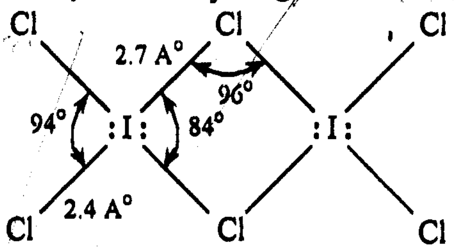
ICl_3 reacts with CS_2 to give CCl_4.

$$3CS_2 + 4ICl_3 \longrightarrow CCl_4 + 2CSCl_2 + 2S_2Cl_2 + 2I_2$$

ICl_3 combines with metal chlorides to form compounds of the type $MICl_4$.

Structure

X-ray analysis of the crystal of ICl_3 has given it a dimeric structure.



XX_5' Type Interhalogens

Only two interhalogens of this type are known:

Bromine pentafluoride	BrF_5	(Colourless liquid, b.p. 40.5°C)
Iodine pentafluoride	IF_5	(Colourless liquid, b.p. 98°C)

Both are fairly thermally stable.

Bromine Pentafluoride, BrF_5

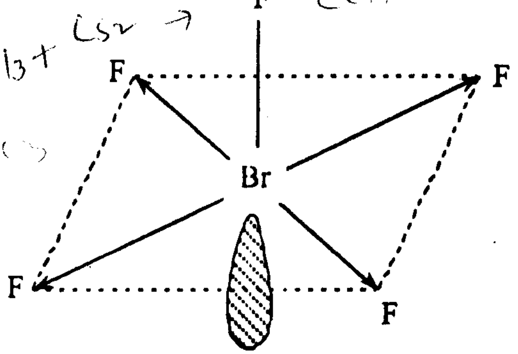
It is prepared by passing F_2 through BrF_3 at 100°C and heating the gaseous product to 290°C.

It is fairly stable but reacts readily with alkali metals, non-metals and their chlorides. It reacts violently with water.

Structure

The structure of BrF_5 is square pyramidal.

$ICl_3 + CS_2 \to CCl_4$



$PbI_2 + Cl_2$

Pbchloride

$\to ICl_3$

$ICl + Cl$

Iodine pentafluoride, IF_5

Preparation

(i) It can be prepared by the action of I_2 on AgF.

$$3I_2 + 5AgF \longrightarrow IF_5 + 5AgI$$

(ii) F_2 reacts with hot I_2O_5 to give IF_5.

$$2I_2O_5 + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

(iii) By the direct action of F_2 *overheated* iodine in a *quartz* vessel.

Properties

(i) IF_5 is quite reactive and fumes in air. It is readily hydrolysed by water.

$$2IF_5 + 5H_2O \longrightarrow I_2O_5 + 10HF$$

(ii) IF_5 reacts with most of the elements. Thus it combines with mercury to form $Hg(IF_5)_2$.

S, P, Si, Bi, etc., react violently with incandescence.

(iii) IF_5 reacts with I_2O_5, P_2O_5, V_2O_5, CrO_3 etc., to form oxyfluorides, *i.e.*, IOF_3, POF_3, VOF_3 and CrO_2F_2, respectively.

MoO_3 and WO_3 react with IF_5 to give addition products, $2Mo_3 . 3IF_5$ and $WO_3 . 2IF_5$.

(iv) ICl reacts with CCl_4 to form a mixture of CCl_3F, ICl and ICl_3.

$$CCl_4 + IF_5 \longrightarrow CCl_3F + ICl + ICl_3$$

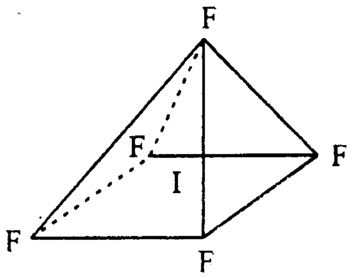
(v) Certain Potassium salts react with IF_5 to give addition products.

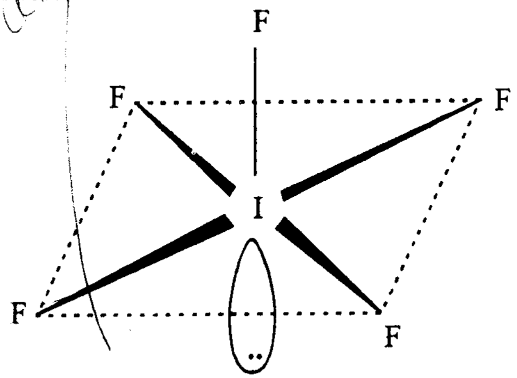
$$KIO_4 + IF_5 \longrightarrow KIO_4 . IF_5$$

$$KF + IF_5 \longrightarrow KIF_6$$

Structure

Infrared, Raman and Nuclear Magnetic Resonance spectroscopy have shown molecule to have tetragonal pyramid structure:





XX_7' Type Interhalogens

The only interhalogen known for XX_7' type is IF_7.

Iodine heptafluoride, IF_7 is prepared by the passing F_2 through liquid iodine pentafluoride at 90°C and then passing the mixture through a platinum tube at 270°C.

$$IF_5 + F_2 \longrightarrow IF_7$$

IF_7 molecule is inert because iodine possesses its maximum covalency in it without any lone pair of electrons. However, it is hydrolysed by water.

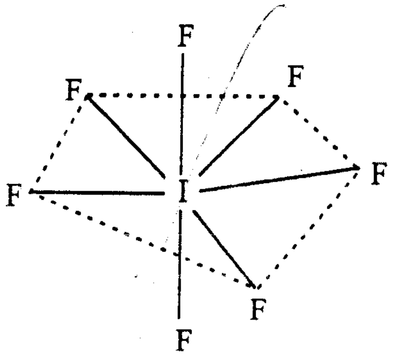
$$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$$

IF_7 acts as a fluorinating agent in presence of HgF_2 at 350°C. Thus, it fluorinates CCl_2F_2 to $CClF_3$.

$$CCl_2F_2 + IF_7 \longrightarrow CCl_2F_3$$

Structure

IF_7 molecule involves d^3sp^3 hybridization and has pentagonal bipyramidal structure.



N_3^- azide ion.

PSEUDOHALOGENS

Certain radicals show behaviour analogous to halogens and are called Pseudohalogens (Pseudo means false). ~~They would form covalent dimers just like halogen molecules. Some of the common examples of pseudohalogens are:~~

(SCSN)

Cyanogen	$(CN)_2$
Thiocyanogen	$(SCN)_2$
Selenocyanogen	$(SeCN)_2$
Azidocarbondisulphide	$(SCSN_3)_2$

Preparation of Pseudohalogen

They are usually prepared by methods similar to ~~those used for the preparation of halogens~~ halogen. For example,

سلور سائنائڈ $2AgCN \longrightarrow Ag + (CN)_2$. $N \equiv C - C \equiv N$

مرکیورک سائنائڈ $Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$

سلور سلفوسائنائڈ $2AgSCN + Br_2 \longrightarrow 2AgBr + (SCN)_2$ Thiyocyanide

$$2AgSeCN + I_2 \longrightarrow 2AgI + (SeCN)_2$$

hydrocynic acid $MnO_2 + 4HCN \longrightarrow Mn(CN)_2 + (CN)_2 + 2H_2O$ cyanogen

~~$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$~~

Azidocarbondisulphide $(SCSN_3)_2$ is prepared as white crystals from CS_2 and potassium azide. KN_3

$$CS_2 + KN_3 \xrightarrow{40°C} \overset{\text{aduct}}{KSCSN_3} \xrightarrow{H_2O_2} (SCSN_3)_2$$

$(SCSN_3)_2$ decomposes at room temperature to give N_2, S and $(SCN)_2$.

$$(SCSN_3)_2 \longrightarrow 2S + 2N_2 + (SCN)_2$$ Thiyocyanogen

Points of Similarities Between Pseudohalogens and Halogens

The following points of similarity are enough to give us an idea about the behaviour of halogens and pseudohalogens.

(1) ~~The hydrogen halides and hydrogen~~ Both halogen and pseudohalides behave as acids. The However acids formed by pseudohalogens are relatively weak acids,

weak	HN_3	Hydrazoic acid	Pka = 4.4	Pseudohalogen acid
	HCN	Hydrocyanic acid	Pka = 8.9	
Strong	HCl	Hydrochloric acid	Pka = – 7.0	→ halogen acid,

(2) The silver and mercurous salts of pseudohalides are insoluble in water just like ~~corresponding~~ halides.

(3) ~~The~~ Both pseudohalogens and halogens ~~are~~ ~~Both~~ volatile compounds and react with alkalies in ~~exactly the same manner~~. similiar way.

Pseudohalogen $(CN)_2 + 2OH^- \rightleftharpoons CN^- + OCN^- + H_2O$ oxyazidocarbon disulphide

$(SCSN_3)_2 + 2OH^- \rightleftharpoons SCSN_3^- + OSCSN_3^- + H_2O$

halogen $Cl_2 + 2OH^- \rightleftharpoons Cl^- + OCl^- + H_2O$ oxychloride

(4) Both pseudohalogens and halogens form addition compounds with unsaturated organic molecules.

Pseudohalogen → $CH_2 = CH_2 + (SCN)_2 \longrightarrow C_2H_4(SCN)_2$ $CNS - CH_2 - CH_2 - SCN$

halogen → $CH_2 = CH_2 + Br_2 \longrightarrow BrH_2C - CH_2Br$ $Br - CH_2 - CH_2 - Br$

They form covalent dimers just like Halogen.

(5) Pseudohalogens combine with halogens as well as with other pseudohalogen molecules to form interhalogen type compounds:

Pseudohalogen also form interhalogen type compound on reaction with halogen or

$$CNCl, CNBr, IN_3$$

$$CNBr + NaN_3 \longrightarrow CN.N_3 + NaBr$$

(6) Pseudohalides form ions similar to polyhalide ions.

Pseudohalogen

$NH_4(SCN)_3$ resembles KI_3.

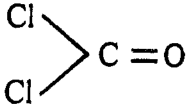
(7) Lead (IV) salts formed with halogens and pseudohalogens are covalent in nature and decompose to liberate free halogens and pseudohalogens, respectively.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

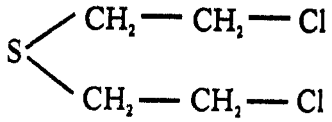
$$Pb(SCN)_4 \longrightarrow Pb(SCN)_2 + (SCN)_2$$

CHEMICALS IN WARFARE

Modern chemical warfare started with the use of chlorine. Later on, phosgene and mustard gas were used.



Phosgene
(Carbonyl chloride)



Mustard gas

Organophosphorus nerve gases were later developed. Chemical defoliating and riot control agents were subsequently developed. The infamous compound 2, 4, 5 – T or agent Orange is highly toxic.

Why iodine is soluble in water containing I^-?

I_2, molecular I_2 is insoluble in water, but get dissolved in the presence of KI.

$I_2 \rightarrow$ weak Lewis acid

$I^- \rightarrow$ lewis base have tendency to form coordinate covalent bond with I_2 resulting in its solution.

$KI + I_2 \longrightarrow \overset{+}{K}\overset{-}{I_3}$ Potassium triiodide

I_3 is a combination of $(I_2 + I^-)$

Questions

1. Discuss the general chemistry and group trends of the halogens. How would you correlate their general characteristics with the electronic configuration?
2. Give an industrial method for the manufacture of fluorine. Discuss its characteristic properties and anomalous behaviour with respect to other halogens.
3. Describe various processes for the manufacture of Cl_2, Br_2 and I_2. Discuss the general properties of halogens.
4. How is the electrolysis of brine carried out on a large scale? What are the products formed in this method? How would you prepare (a) Na_2SO_4, (b) HCl, and (c) NaOCl from the products?
5. Describe an electrolytic method for the preparation of chlorine. Explain what happens when:
   (i) Chlorine is passed over P.
   (ii) Chlorine reacts with NH_3.
   (iii) Chlorine is mixed with C_2H_4.
   (iv) Chlorine reacts with H_2S.
6. Mention two natural sources of bromine. How is bromine prepared from these sources? Describe a method for preparing Br_2 in the laboratory. Compare the properties of Cl_2 with F_2.
7. Describe at least one method for commercial preparation of iodine. What are its general properties and important uses?
8. A white solid is either potassium chloride, potassium bromide, or potassium iodide. What tests would be performed to identify them?
9. Give the points of resemblance between **chlorine** and **iodine** with reference to (i) its occurrence, (ii) physical properties, (iii) action on H_2S, (iv) reaction with NaOH, and (v) H_2.
10. Give an account of the oxides and oxyacids of chlorine.
11. Write a concise account of oxyacids of halogens.
12. Complete and balance the following equations:
   (i) $MnO_2 + HCl$
   (ii) $K_2Cr_2O_7 + NaCl + H_2SO_4$
   (iii) $FeCl_2 + Cl_2$

(iv) $I_2 + H_2S$

(v) $NH_3 + Cl_2$

(vi) $CaF_2 + H_2SO_4$ + heat

13. Describe the preparation and trend in acid strength of aqueous hydrogen halides. Discuss their chemistry.

14. Give names, formulas, preparation and structures of any two of the oxides of fluorine, chlorine, bromine and iodine.

15. Discuss the trends in (a) reducing action, (b) thermal stability, and (c) acid strength of hydrogen halides.

16. Which is the strongest acid of the following:

$$HClO, HClO_2, HClO_3 \text{ and } HClO_4$$

Draw structures of these acids and comment upon their acid trend.

17. What are the structures of the following species:

$$ClF_3, IF_5, IF_7, Cl_2O, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-, H_5IO_6$$

18. 'Iodine shows different colours in various solvents', comment on this statement.

19. How is hydrogen fluoride prepared? Why does it show polymeric nature? How does it differ from other hydrogen halides? Why is it weaker acid than HCl?

20. Which of the halogens (excluding astatine) provides (a) the weakest acid HX, (b) the largest atom, (c) the smallest ionization potential, (d) the strongest reductant, (e) the best hydrogen-bonder, and (f) the most reactive?

21. **Give short answers to the following questions:**

(i) Give the electronic configuration of the following elements with atomic numbers given in brackets:

(a) F(9) (b) Cl(17) (c) Br(35) (d) I(53)

(ii) Describe the general chemistry and group trends in halogen group.

(iii) What is the anamolous position of fluorine?

(iv) How is fluorine prepared on industrial scale?

(v) How is chlorine prepared on industrial scale?

(vi) How is bromine prepared from carnallite or sea-water?

(vii) How is iodine prepared from seaweeds?

(viii) What are the general characteristics of halogens?

(ix) Give reactions of the following:

(a) $Br_2 + H_2S$ (b) $HI + H_2SO_4$

(c) $NaOH + HCl$ (d) $I_2 + H_2SO_3$

(e) $PI_3 + H_2O$

(x) What are the type of oxides of halogens?

(xi) How is hydrochlorous acid prepared? What are its general characteristics?

(xii) How is chloric acid prepared? Give its characteristic features.

(xiii) How is perchloric acid prepared?

(xiv) Discuss the salient features of per-iodic acid.

(xv) What are interhalogens? Discuss their salient features.

(xvi) Draw structures of the following:

(a) ClF_3 (b) ICl_3 (c) BrF_3 (d) BrF_5 (e) IF_7

(xvii) What are pseudohalogens?

(xviii) What are the similarities of pseudohalogens and halogens?

22. **Give the correct answer:**

(i) The outer shell electronic configuration of iodine is:

(a) $5s^2\ 5p^5$ (b) $3s^2\ 3p^5$

(c) $4s^2\ 4p^5$ (d) $6s^2\ 6p^5$

(ii) Fluorine is the most reactive element due to:

(a) its smallest size in the group

(b) highest electronegativity

(c) low bond energy

(d) highest electron affinity

(iii) Fluorine oxidizes water to:

(a) O_2 (b) O_3

(c) O (d) H_2

(iv) F_2 can be prepared by:

(a) electrolysis of anhydrous HF

(b) electrolysis of aqueous HF

(c) electrolysis of fused KHF_2

(d) oxidation of HF by $KMnO_4$

(v) Electrolysis of brine solution in Nelson cell gives:

(a) Cl_2
(b) H_2 and NaOH
(c) Cl_2, H_2 and NaOH
(d) $NaClO_3$

(vi) Br_2 is obtained on large scale from:

(a) carnallite
(b) sea-water
(c) seaweeds
(d) ferric bromide

(vii) I_2 is prepared on a large scale from:

(a) seaweeds
(b) carnallite
(c) sodium iodate
(d) potassium iodide

(viii) Which of the following is not oxidized by $KMnO_4$?

(a) HF
(b) HCl
(c) HBr
(d) HI

(ix) HBr can be best prepared by:

(a) action of conc. H_2SO_4 on NaBr
(b) action of H_3PO_4 on NaBr
(c) passing Br_2 through SO_2
(d) reaction of Br_2 with H_2S

(x) Glass is attacked by:

(a) F_2
(b) HF
(c) HCl
(d) HBr

(xi) No precipitate is formed by adding $AgNO_3$ solution to the salt solution of:

(a) NaF
(b) NaCl
(c) NaBr
(d) NaI

(xii) According to VSEPR theory, the geometry of ClF_3 is:

(a) T-shaped
(b) pyramidal
(c) angular
(d) linear

(xiii) F_2 and Cl_2 are gases, Br_2 is liquid and I_2 is solid because:

(a) size of atom increases
(b) ionization energy decreases
(c) basic nature increases
(d) the magnitude of van der Waals' forces increases

(xiv) All the halogens show odd oxidation states of +1, +3, +5, +7 except:

(a) F (b) Cl

(c) Br (d) I

(xv) Which one of the following oxyacids is the most acidic?

(a) $HClO$ (b) $HClO_2$

(c) $HClO_3$ (d) $HClO_4$

(xvi) The weakest acid among the following:

(a) HF (b) HCl

(c) HBr (d) HI

(xvii) Which of the following is the best reducing agent?

(a) F^- (b) Cl^-

(c) Br^- (d) I^-

(xviii) Which of the following has the highest electron affinity?

(a) F (b) Cl

(c) Br (d) I

(xix) Bleaching powder is prepared by action of:

(a) Cl_2 on CaO (b) Cl_2 on $Ca(OH)_2$

(c) CaO with Cl_2 water (d) Cl_2 on $CaCO_3$

(xx) Theoretical percentage of Cl_2 in a good bleaching powder is:

(a) 48 % (b) 35 %

(c) 20 % (d) 15 %

(xxi) I_2 is estimated quantitatively by titration with:

(a) Na_2S (b) NaOH

(c) $KMnO_4$ (d) $Na_2S_2O_3$

(xxii) When Cl_2 is bubbled through hot alkali, he main products are:

(a) ClO^-, Cl^- (b) Cl^-, ClO_3^-, H_2O

(c) Cl^-, ClO^-, H_2O (d) ClO^-, H_2O

(xxiii) Which one of the following is not expected to oxidise?

(a) Br^- (b) I^-

(c) F^- (d) Mn^{2+}

(xxiv) Which reagent would not liberate I_2 from acidified KI solution?

(a) H_2O_2 (b) $NaNO_2$

(c) HNO_3 (d) SO_2

(xxv) HF is stored in:

(a) glass vessel (b) iron vessel

(c) lead vessel

(d) bottles made up of gutta percha

(xxvi) Photographic plates are coated with a film of:

(a) AgCl (b) AgBr

(c) AgI (d) $AgNO_3$

(xxvii) Which is the most volatile compound?

(a) HI (b) HCl

(c) HBr (d) HF

(xxviii) Which one is the anhydride of $HClO_4$?

(a) Cl_2O (b) ClO_3

(c) Cl_2O_5 (d) Cl_2O_7

(xxix) One of the following products between solid $KMnO_4$ and conc. HCl is:

(a) a red liquid (b) a greenish-yellow gas

(c) MnO_2 (d) KCl

(xxx) Which of the following halides is readily soluble in water:

(a) AgI (b) AgBr

(c) AgCl (d) AgF

(xxxi) In which of the following species does iodine show a positive oxidation state?

(a) NaI (b) IF_5

(c) KI_3 (d) KIO_3

(xxxii) Pure bromine free from HBr can be prepared from NaBr by warming with:

(a) acetic acid (b) conc. H_2SO_4

(c) conc. HNO_3 (d) conc. H_3PO_4

(xxxiii) Chlorine can or be used:

- (a) as bleaching agent
- (b) in preparation of antiseptic
- (c) for extraction of copper
- (d) n purification of water

(xxxiv) Which of the following statement is correct for $CsBr_3$?

- (a) it is a covalent compound
- (b) it contains Cs^+ and Br^- ions
- (c) it contains Cs^+ and Br_3^- ions
- (d) it contains Cs^+ and Br^- and Br_2.

(xxxv) The type of hybrid orbitals used by chlorine atom in ClO_2^- is:

- (a) sp^3
- (b) sp^2
- (c) sp
- (d) none of these

Uses of halogen and their compound.

Fluorine - Fluorides are used in toothpaste

=> Teflon (tetrafluoroethylene) C_2F_4 is non-sticky and non-toxic plastic.

=> Fluorocarbons are used as refrigerants

Chlorines => Used in manufacturing of different salts $AlCl_3$, HCl Chlorates, perchlorates, weeds killer and dry cleaning agents.

=> manufacture of medicinal compounds. such as chloral hydrates and mouth washes.

=> is used in the recovery of Tin (Sn) and aluminium (Al) scrap

Bromine: is used in petrol additives, used in photography, flame retardants, also used in medicine and agriculture

Iodine, => is used in the manufacture of dyes and colour photography

=> Picture of iodine Iodine vapour bulbs.

❀ ❀ 16 ❀ ❀

17

INERT GASES (ZERO GROUP ELEMENTS) (GROUP VIIIA)

Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) are members of the zero group. All these gaseous elements are generally called **inert gases** because they are chemically inert substances and exist only in the free state. These gases are also called **noble gases** because of the chemical inertness. Sometimes they are also called **rare gases** because they exist only in minute quantities in the atmosphere.

The chemical inertness of these gases is due to their stable electronic configuration. Except helium (atomic number 2) atoms of all other gases have fully occupied valence shells *i.e.*, $ns^2\ np^6$. Thus the outermost *s* and *p* orbitals are completely filled and, therefore, atoms of these elements would show a stable state. The electronic configuration of atoms of all these elements is shown in Table 17.1.

$A.ICl_3 \rightarrow HCl$ chlorates, perchlorated

TABLE 17.1

Element	Shell														
	1	2		3			4				5			6	
	s	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*
He (2)	2														
Ne (10)	2	2	6												
Ar (18)	2	2	6	2	6										
Kr (36)	2	2	6	2	6	10	2	6							
Xe (54)	2	2	6	2	6	10	2	6	10		2	6			
Rn (36)	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6

The electronic configuration assigned to any of these elements is called **inert gas configuration.**

The important **physical constants** of inert gases are shown in Table 17.2.

TABLE 17.2

Physical Constants of Inert Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic Number	2	10	18	36	54	86
Atomic weight	4.00	20.18	39.94	83.7	131.3	222
Melting point (°C)	–272.1	–248.6	–189.4	–156.6	–111.5	–71
Boiling point(°C)	–268.9	–246.0	–185.8	–152.9	–107.1	–65
Density (g/ml)	0.126	1.204	1.65(s)	2.6	3.06	4.4
Ionization potentials (KJ/mole) 1st	2371.5	2080.1	1519.6	2314.5	1170.3	1036.2
Ionization potentials (KJ/mole) 2nd	5248.5	3962.4	2664.8	2508.5	2026.1	—
Atomic radius (pm)	—	160	191	200	220	—
Water solubility (ml/l at 20°C)	13.8	14.7	37.9	73.0	110.9	—

DISCOVERY OF INERT GASES

The discovery of inert gases is very interesting. Until the end of the 18th century it was taken for granted that the atmosphere had been thoroughly explored and there was no need to search any new element in it. However, Cavendish in 1785 observed that on passing electric spark between the electrodes kept in a mixture of oxygen and air left some unconverted residual gases after the conversion of oxygen and nitrogen to nitrous oxide (absorbed in alkali solutions). Cavendish could not point out the existence of gases of zero group.

Raleigh (1894) observed that the density of nitrogen obtained from air was about 0.5 per cent higher than pure nitrogen obtained from NH_4NO_2,

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

This indicated the presence of a heavier gas along with nitrogen obtained from the atmosphere. The spectrum of the residual gas was found to be quite unfamiliar. Raleigh in collaboration with Ramsay removed oxygen and nitrogen from dry air by passing it over hot copper and magnesium (copper forms CuO and magnesium forms Mg_3N_2). The residual gas did not react under these conditions and gave spectrum different from nitrogen with atomic weight about 40. It was named **argon** (Greek — lazy or inert). Ramsay discovered helium (meaning the sun) from the spectrum of the chromosphere of sun.

In 1898, Ramsay and Travers carried out systematic refractionation of liquid argon and got **neon** (meaning new) in the first fraction. The other fractions were found to contain krypton (meaning hidden) and xenon (the stranger).

The last of the inert gases, **radon**, was discovered by Dorn (1900) as one of the disintegration products of radium.

Occurrence

The inert gases always occur in the free state and have the following chief sources:

1. **Air:** Air is the most important source of all the inert gases except radon. The percentage by volume of inert gases is:

He	0.0005	Kr	0.0001
Ne	0.0015	Xe	0.00001
Ar	0.932		

2. The **natural gas** found in U.S.A. and some parts of Canada contains up to 2 percent of helium along with methane and nitrogen.
3. The minerals *e.g.*, **monazite and pitchblende,** (containing radioactive elements) are found to contain some **helium.**
4. The dissolved gases of certain spring waters contain considerable amounts of **helium.**

Separation and Isolation of Inert Gases

The inert gases are separated and isolated from air (i) by fractional distillation from liquid air, (ii) by chemical methods. Let us consider these methods one by one.

(i) From Liquid Air

Inert gases are obtained as byproducts during the production of nitrogen from liquid air. All these gases boil at different temperatures from liquid air. The boiling points of the gases mainly present in air are shown in Table 17.3.

TABLE 17.3

Boiling Points of Inert Gases

Gas	Boiling Point
Helium	4 K (Kelvin or Abs.)
Neon	27 K
Nitrogen	77 K
Argon	87 K
Oxygen	90 K
Krypton	122 K
Xenon	164 K

Xenon and krypton boil at higher temperatures but helium and neon boil even at low temperatures and hence can be separated. The gases can be separated from liquid air by fractional liquefaction and evaporation at reduced pressure. The schematic outline of separation of inert gases is given in Figure 17.1.

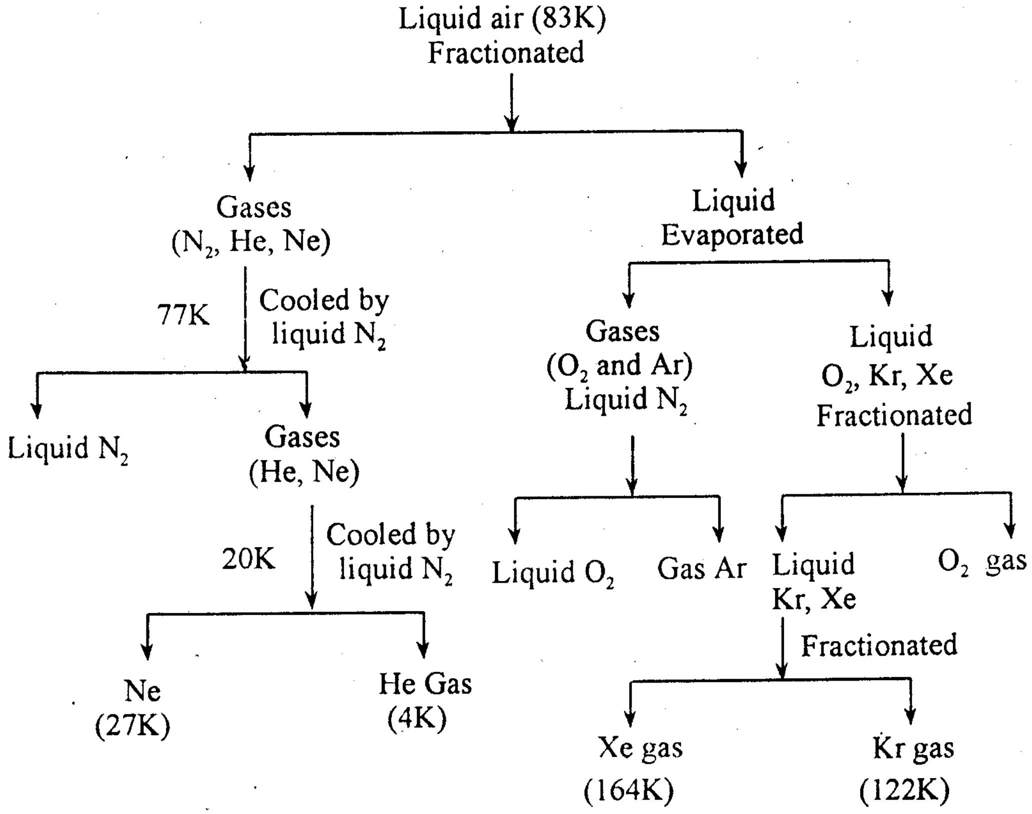


Fig. 17.1.

Helium is generally isolated from various other sources. The most important source is the natural gas in U.S.A. and Canada. The natural gas is cooled to low temperatures when other gases liquefy or solidify leaving helium in the gaseous state. Helium may also be obtained by heating the mineral monazite alone or in presence of dilute H_2SO_4.

(ii) Chemical Methods

These methods are based on the removal of nitrogen and oxygen through compound formation. In one method, electric discharge is passed through air containing slight excess of oxygen. Nitrogen reacts with oxygen under these conditions to form NO which takes up O_2 to form NO_2. NO_2 is absorbed in NaOH to form water soluble sodium nitrate and nitrite.

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

The inert gases remain unabsorbed in alkali solutions and continue accumulating in the flask which are later on separated. Excess oxygen is absorbed in alkaline solution of pyrogallol.

In another method, a mixture of CaC_2 (90 parts) and calcium chloride (10 parts) is heated in an iron retort at 800°C. Air is passed through this heated mixture and outcoming gases passed over red hot CuO to convert CO to CO_2 and then passed through KOH to absorb CO_2 and moisture. Traces of moisture and finally removed by passing through a layer of P_2O_5. The remaining gaseous mixture is either stored or subjected to further purification through fractionation.

The following chemical reactions are found to take place during the above process:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

$$2C + O_2 \longrightarrow 2CO$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$2CO_2 + 2CaC_2 \longrightarrow 2CaCO_3 + 4C$$

$$CO + CuO \longrightarrow Cu + CO_2$$

Radon is continuously formed through radioactive disintegration of radium metal.

$${}_{86}Ra^{226} \longrightarrow {}_{86}Rn^{222} + {}_{2}He^{4}$$

GENERAL CHEMISTRY OF INERT GASES

The electronic configuration of inert gases suggests the stable structure. They do not show any tendency to gain or lose any electron. Consequently, these gases are incapable of forming ionic or covalent bonds with other atoms or molecules. They are, therefore, incapable of forming compounds under ordinary conditions.

COMPOUNDS OF INERT GASES

A few unstable compounds of inert gases are found to exist. The following type of compounds have been studied:

(a) Hydrates

Argon, krypton and xenon form hydrates with up to $6H_2O$, which are similar to hydrates of other gases. They are obtained as colourless crystals by keeping gases in contact with water vapours at low temperatures.

$$Ar : x\,H_2O$$

$$Kr : x\,H_2O\ (x = 1 \text{ to } 6)$$

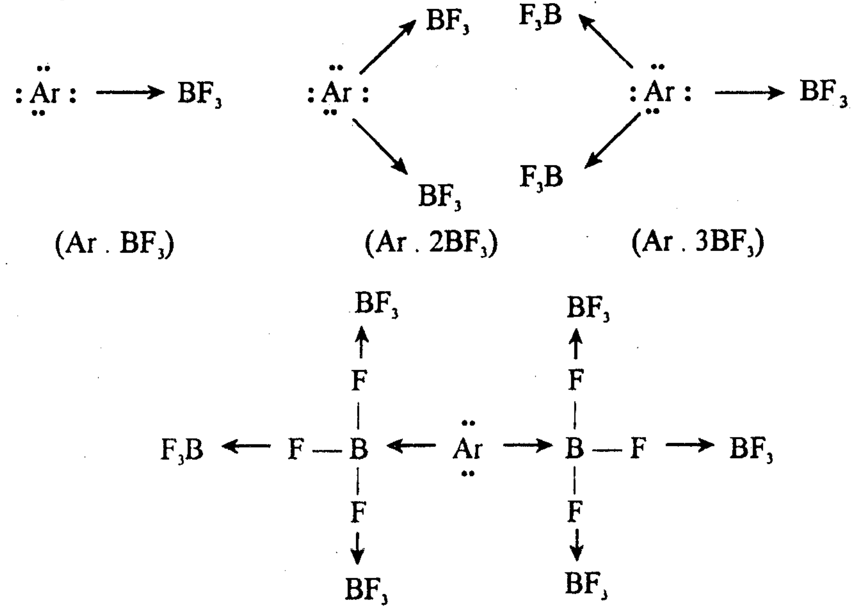
$$Xe : x\,H_2O$$

(b) Clathrates

The inert gases get incorporated into the crystals of some substances, *i.e.*, hydroquinone. The host molecules (hydroquinone etc.) hold the inert gases (guest molecules) by Van der Waals' forces. These type of compounds are known as **clathrates or cage compounds** because host molecules act like cages. Such ompounds are very unstable and break up when crystals are dissolved or melted en free gas is released from the cage structures.

(c) Compounds with BF_3

Boron trifluoride is an electron deficient compound. It can accept a lone pair of electrons from donor atoms to complete the octet of boron. Booth and Wilson have studied the combination of argon with BF_3. There is coordinate bond established between argon and BF_3 due to the donation of pair of electrons from $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ar}}:$ (donor) to BF_3 (acceptor). For example, the existence of compounds $Ar . BF_3$, $Ar . 2BF_3$, $Ar . 3BF_3$, $Ar . 6BF_3$, $Ar . 8BF_3$ and $Ar . 16BF_3$ has been revealed by studying the phase-rule system of boron trifluoride-argon at low temperatures. The structures and bond types of some of these compounds are shown in Figure 17.2.



$(Ar . BF_3)$ $(Ar . 2BF_3)$ $(Ar . 3BF_3)$

$(Ar . 8BF_3)$

Fig. 17.2.

(d) Halides:

Halides of some transition metals are known, *e.g.*, W, He_2, Fe, He, etc. These products are not true chemical compounds and are formed by the presence of small atoms like helium (see interstitial hydrides – Chapter 9) into the interstices in the crystal lattices of the metals. They represent a class of compounds called interstitial compounds.

XENON FLUORIDES

Xenon has been found to combine with the most electronegative element, fluorine to form XeF_2, XeF_4 and XeF_6. They are formed by discharge tube or thermal reactions. XeF_4 has been obtained in crystalline form.

$$Xe + 2F_2 \longrightarrow XeF_4$$

Chemical Reactivity

Xenon fluorides undergo the following typical reactions. In most of the reactions 'Xe' liberated is in free state.

(i) Xenon fluorides can be reduced with hydrogen at about 400°C.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

(ii) The acids especially HCl react rapidly even at low temperatures.

$$XeF_4 + 4HCl \longrightarrow Xe + 4HF + 2Cl_2$$

(iii) When XeF_4 is mixed with liquid ammonia. Xe and N_2 are suddenly liberated.

$$3XeF_4 + \underset{\text{(liquid)}}{4NH_3} \longrightarrow 3Xe + 2N_2 + 12HF$$

(iv) Xenon fluorides easily decompose and therefore, act as fluorinating agents. Even noble metals react to form corresponding fluorides.

$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$

$$XeF_2 + Hg \longrightarrow Xe + HgF_2$$

(v) XeF_2 is hydrolysed in water especially in alkaline solutions.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

Hydrolysis of XeF_4 gives XeO_3 (an explosive).

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

XeF_6 hydrolyses to give $XeOF_4$.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

(vi) XeF_4 reacts with KI to liberate iodine. It oxidises I^- to I°.

$$XeF_4 + 4KI \longrightarrow Xe + 2I_2 + 4KF$$

(vii) O_2F_2 oxidises XeF_4 to XeF_6.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Fluorides of other inert gases have also been reported i.e., KrF_2, KrF_4, RnF_4, etc.

Structures of Xenon Fluorides

XeF_2 has structure in which F – Xe – F bonds are linear (Figure 17.3a). XeF_4 molecule is stable and has square planar arrangement (Figure 17.3b). The structure of XeF_4 can be explained on the basis of d^2sp^3 hybridization of Xe orbitals. As d^2sp^3 hybridization would set up octahedral symmetry but only four positions (out of six in octahedron) will be occupied by F atoms and the rest two taken up by lone pair of electrons.

The structure of XeF_6 has not yet been fully established but it is most probably octahedral (Figure 17.3c).

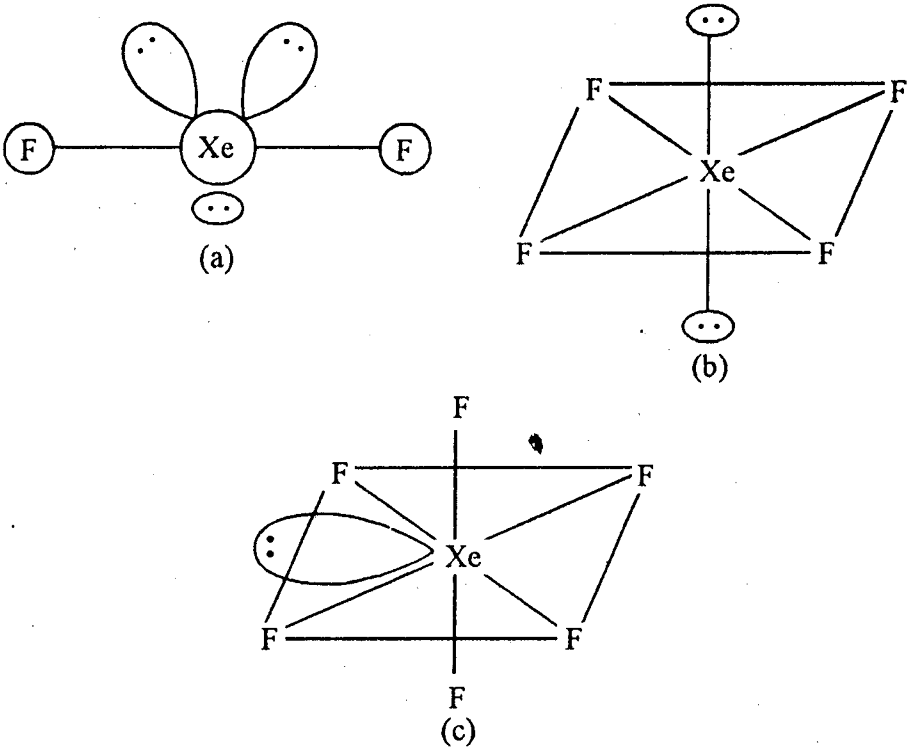


Fig. 17.3. Structures of (a) XeF_2 (b) XeF_4 (c) XeF_6.

Bonding Situation in Compounds of Inert Gases

The absence of ionic bonds in the compound of inert gases is indicated by volatility and observed crystal structures. The presence of Van Der Waals' forces is ruled out by the fact that observed bond energies in these compounds vary between 20 – 30 Kcal/mole. If Van der Waals' type forces were to exist the values of bond energies should only be 1 – 5 Kcal/mole.

Let us take the example of XeF_4 to elaborate the bonding type in such compounds. The electronic configuration of Xe and F are:

Xe(54): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
F(9): $1s^2\ 2s^2\ 2p^5$

In other words, Xe has the outermost $6s$ $6p$ orbitals completely filled in the ground state as shown in Figure 17.4. In the excited state two electrons would be promoted to d orbitals and thus 4 unpaired electrons appear. The formation of XeF_4 will, therefore, involve d^2sp^3 hybridization giving an octahedral structure in which two octahedral positions would be occupied by a set of two lone pair of electrons as shown in Figure 17.4.

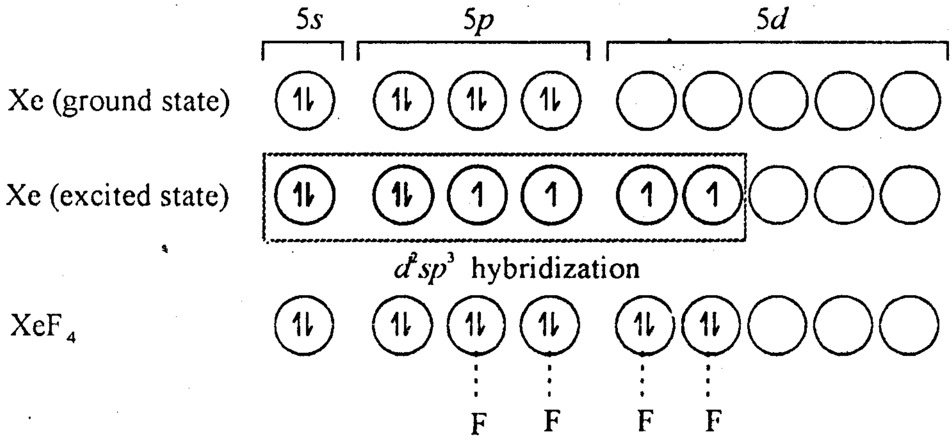


Fig. 17.4.

Molecular orbital theory gives more satisfactory bonding situation in Xenon compounds. Xe atom has all the orbitals with $n = 5$ fully occupied. Let us suppose that orbitals of Xe become available for overlapping with properly oriented $2p_z$ orbitals of two fluorine atoms. The outer electronic configuration in p orbitals of xenon and fluorine are:

Xe	$5p_x^2$	$5p_y^2$	$5p_z^2$
F	$2p_x^2$	$2p_y^2$	$2p_z^1$

The overlap of two atomic orbitals ($2p_z^1$) from two F atoms and one atomic orbital ($5p_z^2$) from xenon would result in the formation of a total of three molecular orbitals (bonding, non-bonding and anti-bonding) as shown in Figure 17.5.

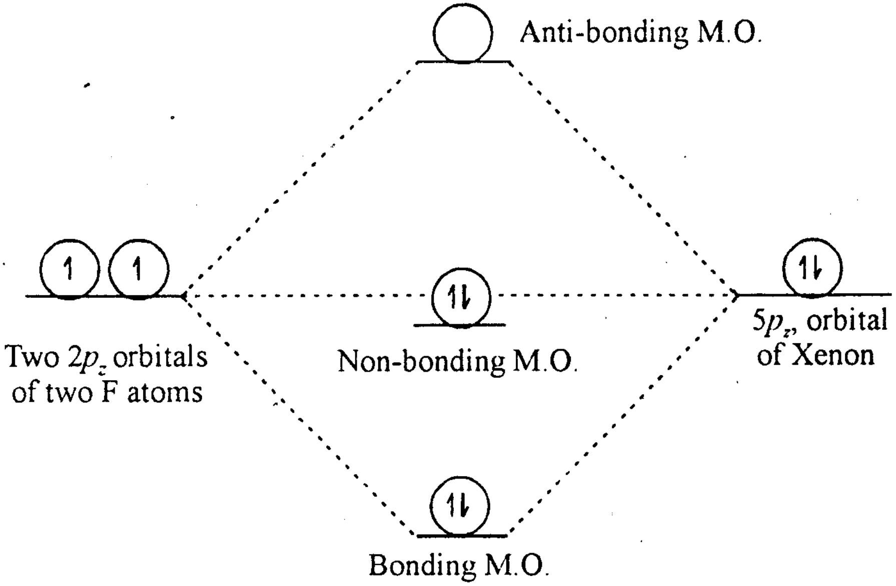


Fig. 17.5.

Commercial Utilization of Inert Gases

The electronic configuration of inert gases is the basis of the modern theory of valency. These gases have important applications.

Helium

1. Helium is used for filling observation balloons due to its lightness and inflammable nature.
2. Mixtures of He and O_2 are used for treatment of respiratory diseases.
3. Helium is also used in tyres of large aeroplanes.
4. Helium is used in signal lights.
5. Helium is less soluble in blood as compared to nitrogen. Therefore, a mixture of oxygen and helium is used by sea divers. If nitrogen as such is used along with oxygen it will remain in the blood even afterwards and would form bubbles known as 'bends'.
6. Helium is used in scientific research to produce inert atmosphere and to attain low temperature conditions.

Neon

1. Neon is mostly used in neon lamps and advertisement signs.
2. Neon is also used in television sets, sound movies, etc., to give ready response to changes in electrical potentials.

Argon

1. Argon is used in electric bulbs to keep an inert atmosphere in order to reduce the volatilization of tungsten filament and to lower the heat conductivity.
2. Geiger-counters (used to detect radioactivity) are also filled with argon.

Krypton and Xenon

1. Krypton is used in ionization chambers for the measurement of cosmic rays.
2. Krypton flash is used to produce intense light in cinematography.
3. Xenon has been used in bubble chambers for detecting γ-rays, neutrons and other nuclear particles.

Radon

Radon is a radioactive gas and is used in radiotherapy for cancer. Some of the gases are obtained as products of radioactive disintegration in minerals. Hence the amounts of inert gases evolved give a clue to the age of the specimen.

Questions

1. Draw the electronic configuration of inert gases. What is the reason of their inertness?
2. Name the inert gases. Discuss their position in the Periodic Table. Why do they show chemical inertness?
3. Write a short note on the important uses of inert gases.
4. (a) How were inert gases discovered? Why are they so called?
   (b) Discuss the separation procedures used for inert gases.
5. Relate the chemical inertness of inert gases to their electronic configuration.
6. Describe the methods used for the separation of inert gases. Discuss the physio-chemical principles involved.
7. Give the important sources of inert gases. Discuss their important properties.
8. Describe the possibility of compound formation of inert gases. Why are they able to react with F_2? What type of products are given by Xe? Describe their chemical reactions.
9. Discuss the bonding situation in xenon fluorides. Give their structures.
10. (a) Discuss the important compounds of Xe.
    (b) Give important applications of inert gases.
11. Give a brief review about the nature of inert gases with respect to their compound formation, chemical inertness and applications.
12. **Give short answers to the following questions:**
    (i) Give the electronic configuration of the following with atomic numbers given in brackets:
    (a) He(2) (b) Ne(10) (c) Ar(18) (d) Kr(36) (e) Xe(54)
    (ii) Write a short note on the discovery of inert gases.
    (iii) How are inert gases separated from liquid air?
    (iv) How chemical methods are used to separate inert gases?
    (v) Give an account of the compounds of inert gases.

(vi) Give salient features of the chemical reactivity of xenon fluorides.

(vii) Discuss the structures of xenon fluorides.

(viii) What is the bonding situation in compounds of inert gases?

(ix) Draw molecular orbital diagram of XeF_2.

(x) Give commercial utilization of inert gases.

13. **Give the correct answer:**

(i) The most abundant noble gas (0.9 % of air) in the atmosphere is:

(a) helium (b) neon
(c) argon (d) krypton

(ii) The separation of noble gases by fractional distillation of liquid air is based on:

(a) the difference in their boiling points
(b) the difference in their spectra
(c) the difference in their densities
(d) the difference in chemical properties

(iii) The noble gas atoms in the liquid or solid state are held by:

(a) H-bonds (b) covalent bonds
(c) Van der Waals' forces (d) ionic bonds

(iv) In which noble gas are the Van der Waals' forces strongest?

(a) Ne (b) Ar
(c) Kr (d) Xe

(v) Which noble gas does not have outer $ns^2\ np^6$ configuration?

(a) He (b) Ne
(c) Ar (d) Kr

(vi) Spectral line of which noble gas is used as a standard for the measurement of meter?

(a) Ne (b) Ar
(c) Kr (d) Xe

(vii) True compounds of only those noble gas can be formed which have:

(a) low ionization energy (b) high ionization energy
(c) unstable nuclei (d) small atomic size

(viii) What type of hybridization on Xe is found in XeF_2 and what is its geometry?

(a) dsp^3 pyramidal

(b) sp^3d trigonal bipyramidal

(c) sp^3d linear

(d) sp^3 tetrahedral

(ix) What type of hybridization is involved in XeF_4 and what is its geometry?

(a) d^2sp^3 octahedral

(b) sp^3d^2 octahedral

(c) sp^3d^2 square planar

(d) dsp^2 square planar

(x) Which shape XeO_3 has?

(a) trigonal bipyramidal

(b) pyramidal

(c) square planar

(d) distorted octahedral

(xi) Which noble gas reacts most rapidly with F_2?

(a) He

(b) Ne

(c) Kr

(d) Xe

(xii) The oxidation state of Xe in perxenic acid, H_4XeO_6 is:

(a) +2

(b) +4

(c) +6

(d) +8

(xiii) Which one of the following has tetrahedral geometry?

(a) XeO_3

(b) XeF_4

(c) XeO_4

(d) $XeOF_4$

(xiv) Square pyramidal shape is described for all except:

(a) BrF_5

(b) $XeOF_4$

(c) IF_5

(d) XeO_2F_2

(xv) In solid argon, the atoms are bonded by:

(a) ionic bonds

(b) hydrogen bonds

(c) Van der Waals' forces

(d) covalent bonds

(xvi) Maximum number of compounds are formed by:

(a) He

(b) Ne

(c) Ar

(d) Xe

(xvii) The noble gas whose ionization potential is almost equal to that of oxygen is?

(a) He (b) Ar

(c) Kr (d) Xe

(xviii) Noble gas used in radiotherapy is?

(a) Kr (b) Ar

(c) Rn (d) Xe

(xix) Which of the following gases does not have an octet or 8 electrons in the outer shell?

(a) Ne (b) Rn

(c) Ar (d) He

(xx) Which of the following statements is not correct?

(a) Helium is an inert gas.

(b) Xenon is the most reactive among the rare gases.

(c) The most abundant rare gas found in atmosphere is helium.

(d) Radon is obtained from the decay of radium.

(xxi) XeF_4 on partial hydrolysis produces:

(a) XeF_2 (b) $XeOF_2$

(c) $XeOF_4$ (d) XeO_3

(xxii) Helium is added to oxygen supply used by deep sea divers because:

(a) it is less soluble in blood than nitrogen at high pressure.

(b) it is lighter than nitrogen.

(c) it is readily miscible with oxygen.

(d) it is less poisonous than nitrogen.

(xxiii) The compound that attacks pyrex glass is:

(a) XeF_2 (b) XeF_4

(c) XeF_6 (d) all

(xxiv) He gas is filled in balloons and not H_2. Why?

(a) He is lighter than H_2. (b) H_2 is inflammable.

(c) H_2 is lighter than He.

(d) H_2 is not easily available.

(xxv) The number of unpaired electrons present in inert gases is:

(a) 0 (b) 1

(c) 2 (d) 4

❀ ❀ 17 ❀ ❀

CHEMISTRY OF *d*-BLOCK ELEMENTS

(GROUP IB TO VIIIB)

18

TRANSITION ELEMENTS

The purpose of this chapter is to introduce the transition elements and their chemistry with special emphasis on coordination compounds. The transition elements are defined as *those elements which possess partially filled d or f orbitals in the penultimate shells.* "The elements in which the *d* orbitals are incompletely filled are called *normal transition elements.*" Three normal transition series are known in the Periodic Table. The first transition series starts with scandium, Sc (At. No. 21, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$), the second transition series with yttrium, Y (At. No. 39, ... $4d^1\ 5s^2$) and the third transition series with lanthanum, La(At. No. 57,...... $5d^1\ 6s^2$) (Table 18.1). The elements such as Copper, Cu(At. No. 29, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$) will not be included among transition elements in the ground state of the free atom. Copper, in the ionic state adopts $3d^9$ configuration and would be included among transition elements. Thus, a broader definition of transition elements would be: *The elements in which the d (or f) orbitals are in the process of completion in the form of atoms or ions.*

The elements in which inner *f* orbitals are in the process of completion are called 'inner transition elements' *e.g.,* lanthanides and actinides. Lanthanides possess incompletely filled 4 *f* orbitals and actinides, the 5 *f* orbitals. The chemistry of these elements 'shall' not be considered over here.

The elements in which *d* orbitals are incompletely filled are also called *d-block elements.* The presence of incomplete *d* orbitals in transition elements attributes certain characteristic properties to them.

TABLE 18.1

Normal Transition Elements

1st series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic No.	21	22	23	24	25	26	27	28	29	30
2nd series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic No.	39	40	41	42	43	44	45	46	47	48
3rd series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic No.	57	72	73	74	75	76	77	78	79	80

GENERAL CHARACTERISTICS OF *d*-BLOCK ELEMENTS

1. Metals

All the transition elements are *metals*.

2. Melting and boiling points

Most of them are *hard, high melting and high-boiling* metals. They have relatively large enthalpies of vaporization.

3. Conductivities

All the transition metals are *good conductors* of heat and electricity. Copper, silver and gold are well-known for this behaviour.

4. Alloy formation

They *form alloys* with one another and with other metals *e.g.*, brass (Cu – Zn), bronze (Cu – Zn – Sn), German silver (Cu – Zn – Ni) etc.

5. Electrode potentials

Many transition elements are *'active' metals* as considered from thermodynamics point of view. Their electrode potentials indicate that they should react with 1MH$^+$ to yield aqueous solutions of their ions.

6. Variable oxidation states

The transition metals show *variable oxidation states*. The energy difference between $(n-1)\,d$ orbitals and ns orbitals of transition metals is very small. As a result the electrons may easily shift from $(n-1)\,d$ to ns orbitals or from ns to $(n-1)\,d$ orbitals. Thus the number of electrons responsible for oxidation states may vary and thus variation in oxidation states would occur. The highest oxidation state given by transition elements is 8. This is found in ruthenium (..... $4d^7\,5s^1$) and osmium (.... $5d^6\,6s^2$), *e.g.*, RuO_4 and OsO_4. It involves all the electrons present in $(n-1)\,d$ and ns orbitals. With increasing atomic number of elements in a group, the higher oxidation states usually become more stable and lower oxidation states, less stable.

7. Paramagnetic ions

The number of unpaired electrons in an atom can be manifested through their magnetic properties. It has been observed that the number of unpaired electrons (n) present is related to magnetic moment (μ, in Bohr magneton units) by the equation $\mu = \sqrt{n(n+2)}$. For one unpaired electron ($n = 1$), the value comes out to be 1.73 B.M. (Bohr magnetons). The values of μ are found near to 2.84 B.M. and 3.88 B.M. for 2 and 3 unpaired electrons, respectively (calculated) from $\mu = \sqrt{n(n+2)}$. The values of μ are experimentally found by means of magnetic balances (such as Gouy's balance) and the number of unpaired electrons determined. The transition metal ions and their compounds usually possess unpaired electrons and would show *paramagnetism*. The ions which possess unpaired electrons show *paramagnetic* behaviour and are attracted by the magnetic field. On the other hand, diamagnetic substances possess paired electrons and are repelled by a magnetic field e.g., $K_4Mn(CN)_6 . 3H_2O$, 1.73 Bohr Magneton, $CrSO_4 . 6H_2O$, 4.90 Bohr Magneton.

8. Coloured ions

All simple transition metal ions possess unpaired electrons and are coloured. The colour of the ions is related to the number of unpaired electrons:

Number of unpaired electrons	Colours of simple ions
0	Zn^{2+}, Ti^{4+} (colourless)
1	Ti^{3+} (purple), Cu^{2+} (blue)
2	V^{3+} (green), Ni^{2+} (green)
3	Cr^{3+} (deep green), Co^{2+} (pink)
4	Cr^{2+} (blue), Fe^{2+} (green)
5	Fe^{3+} (yellow)

The colour of the ions depends upon the electronic transitions between the available *d* orbitals. In such electronic shifts, absorption or emission of energy from white light takes place with consequent manifestation of colour. As different oxidation states of the same transition metal possess different number of electrons, different amounts of energy would be absorbed or emitted with difference in the colour of ions.

9. Formation of interstitial compounds

They form compounds of indefinite structures and proportions, called interstitial compounds. Small atoms such as H, B, C and N can reside within the interstices or holes present in their crystal lattices. Such compounds may be considered to be due to absorption of foreign atoms in the interstices of metal crystals and do not bear any stoichiometric composition, *e.g.*, $TiH_{1.73}$.

10. Catalytic behaviour

Most of the transition metals and some of their derivatives act as catalysts. For example, Pd, Pt, Ni, Ti and V metals and their compounds are used as catalysts in industry. Ni is used as a catalyst for the hydrogenation of vegetable oil to vanaspati ghee. V_2O_5 acts as a catalyst in the manufacture of H_2SO_4. Zeigler-Natta catalyst ($TiCl_4 . AlR_3$) is very useful in polymerisation of olefines.

11. Electropositivities

The ionization potential values of transition elements are intermediate between those of *s*-block and *p*-block elements. The transition elements are less electropositive than alkali and alkaline earth metals. They are more electropositive than *p*-block elements. They are ionic in their lower oxidation states but covalent in higher oxidation states.

12. Complex formation

Due to the presence of incompletely filled $(n-1)$ d orbitals, transition metals would act as Lewis acids (electron pair acceptors). They would, therefore, react with Lewis bases (electron pair donors) usually called ligands to form coordinate bonds and would give coordination compounds or complexes. Most transition metal ions are small and highly charged and would show marked tendency to form complexes.

IRON AND STEEL

Iron and steel is the mainspring of modern industry. Iron is perhaps the most useful of all metals.

Occurrence

Iron occurs abundantly in nature and constitutes 4.5 per cent of the earth's crust. There are three types of iron ores commonly available:

1. Magnetite, Fe_3O_4

It is usually very pure and gives high quality iron. It is primary constituent of igneous rocks.

2. Haematite (Fe_2O_3)

It is widely distributed as red mineral but brown mineral is also found.

3. Carbonate Ores

Most of them include ferrous carbonate, $FeCO_3$ along with varying amounts of silicious material.

Haematite deposits are found at Mazari Tang (Kohat District) and Langrial (Hazara district) in Pakistan. Magnetite is found to occur in Chagi district (Quetta division) and in Chitral state. Sedimentary iron deposits are also found in Kalabagh-Makarwal areas. Reserves of iron areas are estimated about 300,000,000 tons in Pakistan at present.

Iron pyrites, FeS_2 occur as pale yellow crystals and are called 'fool's gold'. This ore is not usually used for the metallurgy of iron.

Pig Iron

The iron metal which contains 3 – 4% C along with Si, P, Mn and small amounts of S is called Pig iron. It is brittle and usually converted to cast iron and steel.

Cast Iron

When pig iron is remelted and cooled, cast iron is obtained. Rapid cooling of molten pig iron produces *white cast iron*. The white appearance is due to the presence of iron carbide or cementite, Fe_3C in iron which is of light colour. If pig iron is cooled slowly, the carbon separates as graphite and gives grey appearance to iron. It is called *grey cast iron*.

Wrought Iron

Wrought iron is a pure form of iron. It is manufactured by melting pig iron with an excess of iron oxide which oxidises impurities. Carbon and sulphur are removed as CO_2 and SO_2. Oxides of Si and P react with flux (oxides of Mn, Fe or limestone) to form slag which is removed. Wrought iron is soft, malleable and ductile. It contains only 0.2% carbon. It possesses fibrous structure due to the presence of thin films of slag between layers of pure iron.

Steel

Iron which contains 0.05 to 2.5 % carbon and hardened by quenching is called *Steel*. Other metals such as Mn, Cr, Ni, Mo, W or V are added to iron in small amount, in order to produce different types of *alloy steels* for specific use.

Steel is free from P, S and Si which are present in cast iron. Steel possesses the useful properties of both cast iron and wrought iron, being both *hard* and *elastic*. Its hardness and elasticity can be varied as desired by *annealing* (heating to bright redness and cooling slowly) and quenching.

MANUFACTURE OF IRON

PIG IRON AND CAST IRON

The manufacture of iron is based on the principle of reduction of iron oxide with carbon monoxide. This reduction process is carried out in a furnace called **'blast furnace'**.

The iron ore is first washed, concentrated and roasted in order to remove impurities such as sulphur and phosphorus as oxides. The roasting process also decomposes carbonates to oxides and also oxidises sulphides. The roasted oxide ore is introduced from the top to the *blast furnace* along with sufficient amounts of limestone and coke. The blast furnace is provided at the top with *cup and cone* arrangement in order to drop the ore while furnace is on.

The blast furnace is made of steel and lined with fire bricks with cylindrical shape. The furnace is about 100 feet high and 23 feet in diameter. Hot air is forced into the furnace through openings or 'twyers' present between six to eight feet from bottom of the furnace. The bottom of the furnace is provided with outlets to remove molten iron and slightly above it is a slag hole (Figure 18.1). Different temperature zones are shown in furnace.

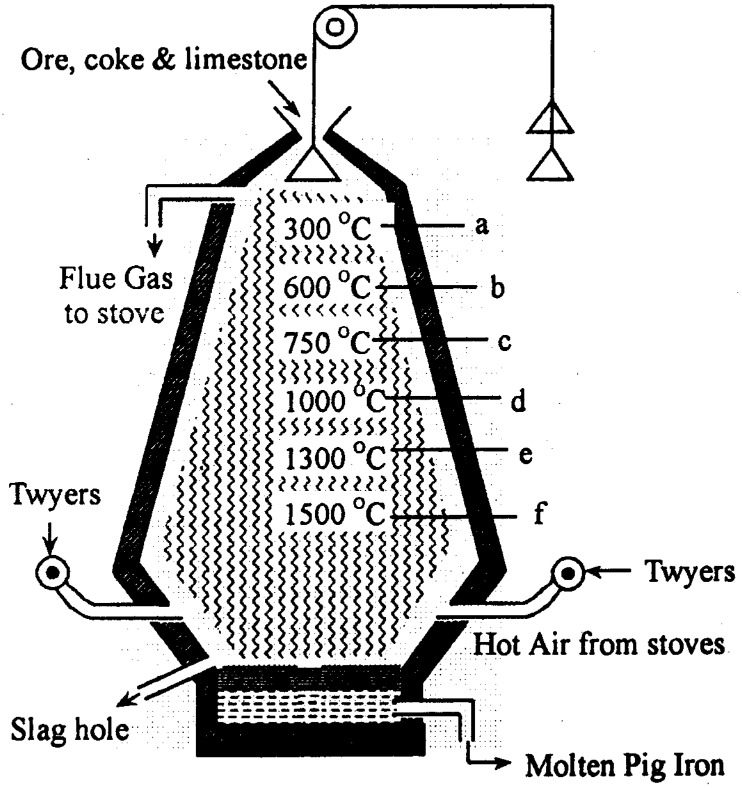


Fig. 18.1. Blast Furnace for Iron.

When the mixture of ore, coke and limestone descends through the top of the furnace, a blast of air comes across it in the upward direction. The mixture gets heated up and reactions take place in various zones of the blast furnace. The coke is first oxidised by the hot blast of air at the bottom to give CO and CO_2 with the liberation of large amount of heat which brings the temperature in zone *f* at about 1500°C. The excess of CO is produced in the furnace which reduces Fe_2O_3 or Fe_3O_4 to Fe.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

Near the middle of the furnace limestone decomposes to give lime, CaO and CO_2. CaO acts as flux and combines with silica present as gangue in the ore to form a slag of calcium silicate which is removed from slag hole. Iron meets near the bottom of the furnace and removed through an outlet.

The chemical changes which take place in the blast furnace during smelting of iron ore are somewhat complex. However, the following reactions are simplified representations.

Chemical reactions involved

(i) The reduction action between CO and iron oxide starts at 300°C to 600°C. In zone *a* and *b* the following reactions take place:

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

(ii) In zone *c* at about 750°C the following reactions occur:

$$FeO + CO \longrightarrow Fe + CO_2$$

$$C + CO_2 \longrightarrow 2CO$$

(iii) In zone *d* at 1000°C, $CaCO_3$ decomposes to give CaO and CO_2.

(iv) At about 1300°C, CaO (flux) combines with SiO_2 (present in the ore) to form calcium silicate (slag).

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

(v) At 1500°C, or above the iron descending from zone *c* meets and gets collected at the bottom of the furnace. Carbon (coke) burns in zone *f* to form CO which reduces the iron oxide while crossing it.

$$2C + O_2 \longrightarrow 2CO$$

The exhaust or flue gases which come out from the top of the *blast furnace* still contain large amounts of carbon monoxide. These gases are burnt and used to preheat the air blast.

Wrought Iron

It is prepared from cast iron by *puddling i.e.*, heating in special type of reverberatory furnace provided with doors DD. The furnace is lined with oxides of iron in haematite or magnetite. The iron oxide oxidises impurities present in iron. Thus C, S and P are removed as corresponding volatile oxides.

$$2C + O_2 \longrightarrow 2CO$$

$$S + O_2 \longrightarrow SO_2$$

$$P + 5O_2 \longrightarrow P_4O_{10}$$

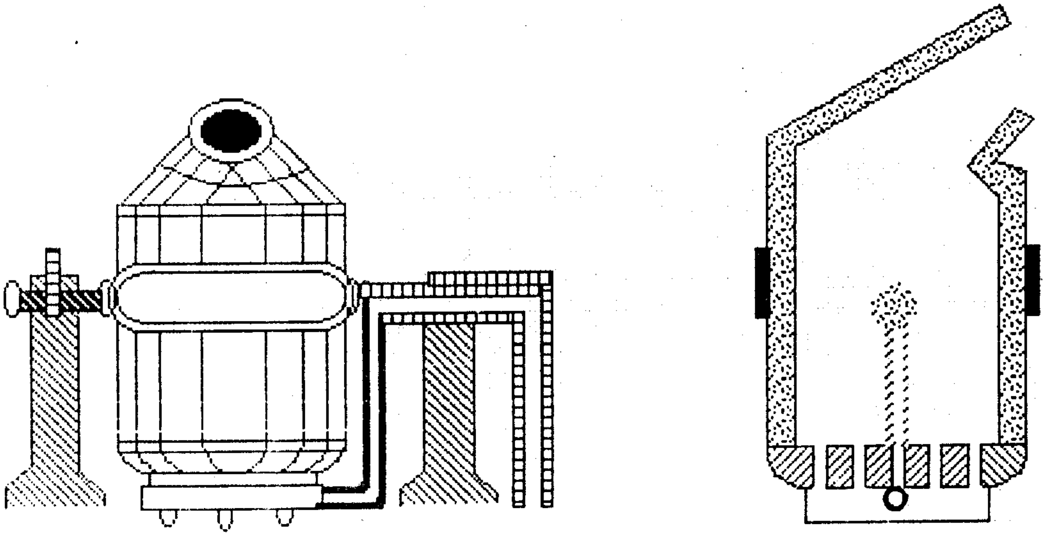
Heat is reflected and radiated from the roof of the furnace upon the molten iron etc., while blowing hot gases through it. The iron melts and is stirred or puddled by iron rods for thorough contact with furnace lining. The pasty mass of iron is collected in balls or *'blooms'* and removed from the furnace. Small amounts of slag remain present in wrought iron which gives fibrous structure to it but is helpful during welding. The wrought iron may be easily hammered and drawn into wires.

Manufacture of Steel

Steel is made by various methods but (a) Bessemer process, and (b) Open hearth process are important and commonly used.

1. Bessemer Process

This process is carried out in a pear-shaped furnace called *Bessemer converter* (Figure 18.2). The converter is made of steel plates and lined with silicious material (sand and small amount of clay) or bricks. A number of holes are present at the bottom of the converter to admit a blast of air.



Bessemer Converter

Fig. 18.2.

In the Bessemer process about 10 tons of molten pig-iron are run into the converter. When the converter has been charged and the blast of air is turned on, the temperature rises due to heat evolved during oxidation and combustion of impurities. Carbon is oxidised to CO, which burns at the mouth of the converter. The carbon monoxide flame gives an indication for the completion of the process. When carbon monoxide flame subsides, calculated amount of *spiegeleisen* (carbon and manganese or other metals) is added and the blast turned on again for a few minutes.

If Bessemer converter is lined with silica, it is called the *Acid Bessemer Process*. A *Basic Bessemer Process* involves lining of *dolomite* or *lime* or *magnesia* and is used to convert pig-iron (containing higher proportions of S, P and silicon) into steel.

The Bessemer process has revolutionized the manufacture of steel because it is cheaper and less time consuming.

2. Open Hearth Process (Siemens Martin Method)

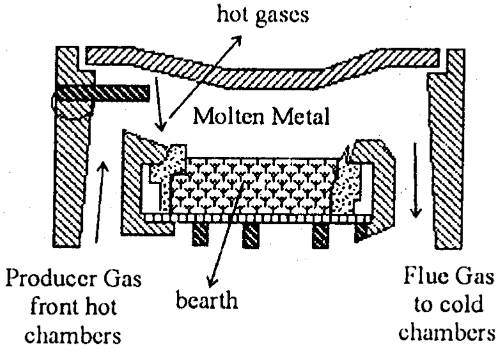


Fig. 18.3.

This method is now widely used for the manufacture of steel. The open-hearth furnace is shown in Figure 18.3. The furnace is charged with a mixture of pig-iron, scrap iron and haematite ore free from carbon. The mixture is melted in a shallow rectangular trough or hearth. The furnace is heated by producer gas. The direction of the burning gases is reversed after about 1/2 hour. In this way the heat of the flue gases is utilized in warming up chambers through which air and unburnt gases are passed. Thus this furnace is called Siemens' *regenerative furnace*.

The iron ore and scrap iron help in oxidising impurities. Carbon is oxidised to CO which goes off. Impurities such as P and S form corresponding oxides within 8 - 12 hours.

$$3S + 2Fe_2O_3 \longrightarrow 3SO_2 + 4Fe$$

$$3P_4 + 10Fe_2O_3 \longrightarrow 3P_4O_{10} + 20Fe$$

Fe_2O_3 and basic oxides (CaO from limestone added along with the charge in the furnace) act as flux and form slag with oxides of phosphorus and silicon. If sulphur and phosphorus are present in negligibly small quantities, the furnace may be lined with SiO_2.

When the required carbon content is reached during the process, the molten steel is removed. Small quantities of other metals such as Mn, Cr or Ni are added to prepare special type of steel

The steel obtained by open-hearth process is used for making heavy rails, guns, girders and ships, etc.

Advantages of Open-Hearth Process over Bessemer Process

(i) Scrap iron and the iron ore can be directly converted into steel by open-hearth process.

(ii) The external source of heat used in open-hearth process is more convenient and temperature can be accurately controlled.

(iii) The composition of steel is more uniform and accurate in open-hearth process and can be easily controlled.

(iv) Low grade cast iron can be used in this process.

(v) Steel obtained by open-hearth process is of high grade and of good quality

3. Electrical Processes

Electric furnaces, often of arc type, are used to get high quality steels. As no fuel is used, there are less chances of contamination by impurities. Electrical processes are popular for preparing good quality steel, especially when electric power is cheap. A number of steel alloys are made by these methods.

Various processes based upon heat treatment give steel of different qualities. *Annealing* is a process in which steel is heated to redness and allowed to cool slowly. *Quenching* refers to the process in which steel is heated to redness and cooled suddenly in water or oil. *Tempering* means heating steel at constant temperature for some time before cooling.

Alloy Steel

Many useful alloys of steel are manufactured by adding metals in small amounts. Some important alloys of such type are:

Stainless Steel

(Fe = 73 – 79%, Cr = 14 – 18%, Ni = 7 – 9%) is a corrosion resistant alloy used in cutlery and industry.

Invar

(Fe = 64%, Ni = 36%) has low coefficient of expansion and used in pendulum rods, meter scales, etc.

Silicon Steel

(Fe = 95 – 99%, Si = 1 – 5%) is hard and highly magnetic and thus used in magnets.

GENERAL CHEMISTRY OF 1ST TRANSITION SERIES

The metals of first transition series (Sc to Cu) resemble each other in a number of ways. The typical properties of these elements are shown in Table 18.2 for the sake of comparison. It can be seen that the atomic radii from Cr to Cu are very similar although they decrease from Sc to V. The increase in nuclear charge tends to set up more forces of attraction on electrons and should decrease the atomic radii by contracting the electron cloud. But the inter-electronic forces of repulsion have opposing effect. Consequently, the atomic sizes of transition metals remain almost constant and show a slight change. Thus the chemistry of transition elements is expected quite similar.

The ionization potential values are higher than those of alkali and alkaline earth metals. It may be noted that the difference in ionization potential values of adjacent elements is very nearly the same. The 2nd ionization potential values of Cr and Cu are relatively high. It is due to the presence of half-filled and completely filled *d* orbitals in these metals after the first electron has been removed. The stability of half-filled and completely filled *d* orbitals in Cr and Cu, respectively, is reflected in their chemistry.

The ionic radii (Table 18.2) show the same trend given by the atomic radii.

TABLE 18.2

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$
Ionization potential									
I_1	1.51	158	155	156	171	182	181	176	178
I_2	297	314	328	380	361	373	393	419	468
Atomic radius	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17
Ionic radius (M^{2+})	—	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.72
Melting point °C	1795	1750	2190	2176	1517	1812	1768	1728	1365
Boiling point °C	—	3550	3650	2900	2340	3150	3150	3160	2855
ΔH hyd. KJ/mole	—	1866	1895	1924	1861	1958	2079	2121	2121
Reduction potential $M^{2+}, 2e = M$ (v)	—	− 1.6	− 1.2	− 0.91	− 1.18	− 0.44	− 0.28	− 0.25	+ 0.34

The ionic radii of transition elements decrease slowly with increasing atomic numbers. The radii of doubly charged ions are somewhat smaller than that of Ca^{2+} and therefore, transition metals form oxides similar to, but less basic and less soluble than CaO. They form well defined aquo-ions, $[M(H_2O)_6]^{2+}$.

The standard electrode potential values show that metals of first transition series should be oxidised easily (except copper). So these metals are good reducing agents.

Metals of 1st transition series like others show wide variation in oxidation states. The highest oxidation state is VII, given by manganese. The oxidation state III is more important for Fe, Co and Cr. The IV oxidation state is important for Ti and VI state for Cr. Lower oxidation states (1, 0, −1) are shown by these transition metals with ligands of acid π-type *e.g.*, CO. Various oxidation states of metals of 1st transition series are shown in Table 18.3.

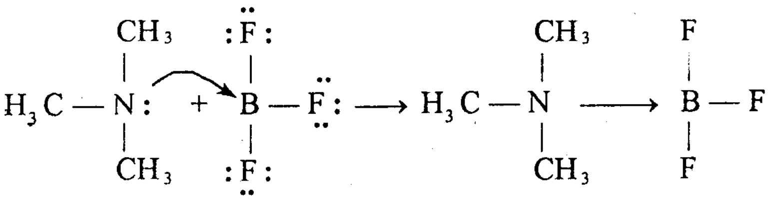
TABLE 18.3

Metal	**Oxidation States**										
Sc							III				
Ti			−I	0		II	III	IV			
V			−I	0	I	II	III	IV	V		
Cr		−II		0	I	II	III	IV	V	VI	
Mn	−III	−II	−I	0	I	II	III	IV	V	VI	VII
Fe		−II		0	I	II	III	IV	V	VI	
Co			−I	0	I	II	III	IV			
Ni			−I	0	I	II	III	IV			
Cu					I	II	III				

The aqueous chemistry of the elements of 1st transition series is interesting and quite well-known. The hydrated ions of all these metals are abundantly found. Thus pink $[Ti(H_2O)_6]^{3+}$, blue $[V(H_2O_6)]^{3+}$, violet $[Cr(H_2O)_6]^{3+}$, pale green $[Fe(H_2O)_6]^{2+}$ ions etc., are very common. Therefore, most of their salts are found in the hydrated state. The possibility for the formation of such complex ions is taken up in the subsequent discussion.

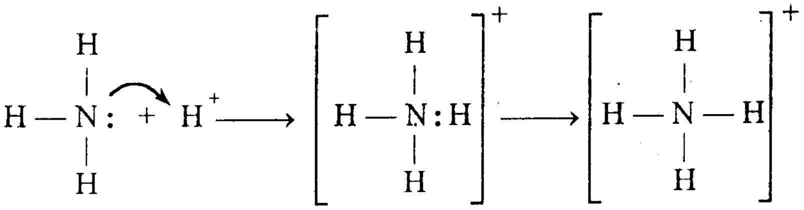
TRANSITION METAL COMPLEXES — NATURE OF COORDINATE BOND

When boron trifluoride (BF_3) gas is passed through trimethylamine $(Me)_3$ N, (in liquid), a rapid reaction takes place and white *solid settles*. The product is found to be 1 : 1 adduct (addition compound) $F_3B.\ N(CH_3)_3$. *Trimethylamine* $:N(CH_3)_3$ is a Lewis base and BF_3 being electron deficient molecule acts as Lewis acid. Lewis acid-base reaction results in the coordinate bond formation.



This 1 : 1 adduct, $(CH_3)_3\ N \longrightarrow BF_3$ is thus an example of a compound with coordinate bond.

The formation of NH_4^+ ion in solution from $:NH_3$ and H^+ also involves the Lewis acid-base type reaction in which $:NH_3$ donates a lone pair of electrons to H^+ and is linked through coordinate bond.



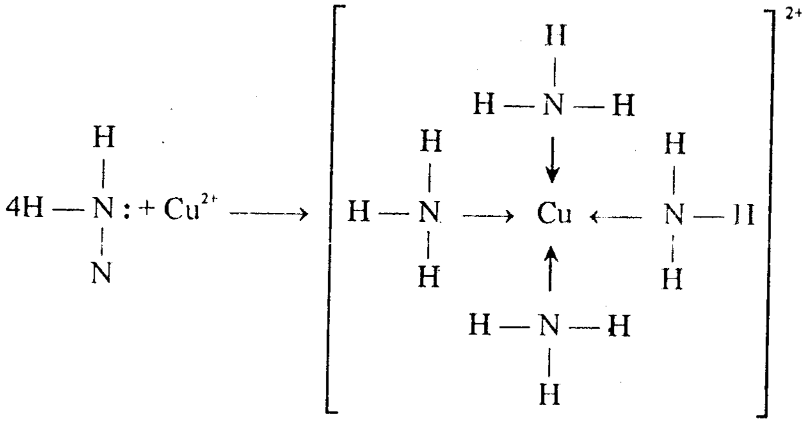
Similarly, when $AgNO_3$ solution is added to Cl^- ion, a white precipitate of AgCl settles, which dissolves in ammonia to form a complex or coordination compound.

$$Cl^- + AgNO_3 \longrightarrow AgCl + NO_3^-$$

$$AgCl + 2 : NH_3 \longrightarrow [H_3N \longrightarrow Ag \longleftarrow NH_3]Cl$$

(coordination compound)

Addition of ammonia to Cu^{2+} ions results in a deep blue solution due to the formation of a complex ion, $[Cu(NH_3)_4]^{2+}$.



It is obvious from the above reactions, that coordinate bond is established between electron pair donors (Lewis bases) and electron pair acceptors (Lewis acids). BF_3, Ag^+ and Cu^{2+} act as lone pair acceptors (Lewis acids) while ammonia and trimethylamine act as Lewis bases (lone pair donors) through nitrogen. Ag and Cu^{2+} are examples of transition metal ions. It is obvious that the transition metal ions behave as electron pair acceptors (Lewis acids) and would react with Lewis bases.

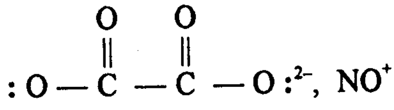
Let us analyse the behaviour of $[Ag(NH_3)_2]Cl$ and $[Cu(NH_3)_4]SO_4$ complexes. Although we can precipitate Cl^- or SO_4^{2-} ions from these complexes, but Ag^+ and Cu^{2+} cannot be precipitated or detected directly from the solution. Both the metal ions have lost their individual identity during the complex formation. *"Compounds containing the complex ions or complex molecules capable of independent existence are called coordination compounds or complexes."* The complexes are usually *formed by the combination of components which are already saturated according to the classical concept of valency and are not completely dissociated in solution.* They carry complex ions. Alum $K_2SO_4 \cdot Al_2(SO_4)_3.24H_2O$ is a double salt and not a complex because its individual ions, K^+, Al^{3+}, SO_4^{2-} can be detected due to complete dissociation.

DEFINITION OF TERMS

The *complex ion* is a charged molecular species consisting of a metallic atom or ion to which is attached one or more charged or uncharged molecules. The *metallic atom or ion* attached to other donor molecules around it is called *central metal atom or ion e.g.*, a transition metal. The charged or uncharged electron pair donor molecules which are linked to central metal atoms or ions are called ligands. Some of the commonly used simple *ligands* are neutral molecules containing P or

N or O atoms, *e.g.*, $:NH_3$, $H_2\overset{..}{O}:$, $(C_6H_5)_3\overset{..}{P}$, $:CO$, $H_2\underset{..}{N}\,CH_2\,CH_2\underset{..}{N}H_2$, $C_6H_5\,NH_2$, etc. The charged ions can also act as ligands:

$:\overset{..}{\underset{..}{Cl}}{}^{-}:$, $:\overset{..}{\underset{..}{O}}H^{-}$, NO_2^{-},



$$:O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O:^{2-},\ NO^{+}$$

(Oxalate ion)

The formulae of coordination complexes are written using square brackets [ ], called *coordination sphere*. Whatever would be within the coordination sphere is called *complex ion* (neutral complex molecule). The number of donor atoms establishing coordinate bonds to the central metal atom or ion is called its *coordination number*.

STRUCTURE OF THE COORDINATION OR COMPLEX COMPOUNDS

The complex compounds are known since times immemorial, *e.g.*, ***Prussion blue*** was known to Egyptians centuries ago for dyeing purposes. These compounds, created a great difficulty regarding the nature of bonding present in them. For example, molecular compounds of the type (a) $CoCl_3 \cdot 6NH_3$, (b) $CoCl_3 \cdot 5NH_3$ and (c) $CoCl_3 \cdot 4NH_3$ were known. When silver nitrate solution was added to these compounds, all the three Cl^- ions from compound (a) precipitated, but only $2Cl^-$ could be precipitated from compound (b) and only one Cl^- from that of (c). It is strange to note these facts in view of the presence of three Cl^- ions in all these compounds.

Many attempts were made in this direction but none was found satisfactory. In 1898, Alfered Werner put forward a revolutionary theory about the nature of these compounds which could explain the characteristics of these complexes and also predict the future developments in this field. For this great contribution, Werner was awarded Nobel Prize in chemistry.

POSTULATES OF WERNER'S THEORY

Werner's theory is based upon the following assumptions and is called the theory of coordination compounds:

1. Metals possess two types of valencies:
   (a) Primary valency, and (b) Secondary valency.
2. Every element tends to satisfy both its primary and secondary valencies.
3. The primary valencies are satisfied by positive or negative ions. The components united by primary valency are ionizable.

   In $AgCl \, . \, 2NH_3$, Ag^+ possesses one primary valency satisfied by Cl^-.

4. The secondary valencies are satisfied by groups of atoms or simple molecules which are capable of independent existence. The negative ions are also present in secondary valencies but none of them is able to ionize.

   In $AgCl . 2NH_3$, Ag^+ has two secondary valencies possessed by two ammonia molecules.

5. Each complex compound has a metal atom situated in the centre (within a coordination sphere) called central metal atom.

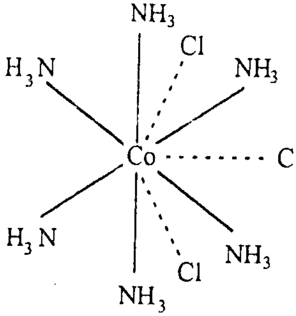
   The number of groups or ions (ligands) linked to the central metal atom is called the coordination number of the metal.

6. The number of secondary valencies (now called coordination number) for each metal ion is fixed.

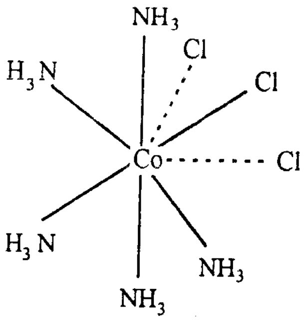
7. The secondary valencies are pointed in space along definite directions around the central metal atom or ion.

APPLICATIONS OF WERNER'S THEORY

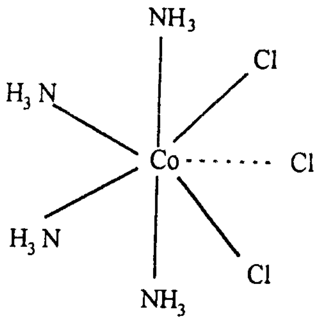
Werner's theory has successfully been applied to elucidate the structures, isomerism and nature of coordination compounds. Let us apply this theory to explain the structures and nature of cobalt chloride complexes described above, *e.g.*, $CoCl_3 . 6NH_3$, $CoCl_3 . 5NH_3$ and $CoCl_3. 4NH_3$. The structures of these compounds can be shown as follows based upon Werner's theory.



$CoCl_3 . 6NH_3$



$CoCl_3 . 5NH_3$



$CoCl_3 . 4NH_3$

The solid lines (–) between Co and other atoms or molecules represent the secondary valencies and dotted lines (…) indicate primary valencies. It is obvious from the above structural representations that no matter what is the formula of a coordination compound, the number of secondary valencies remains fixed in accordance with Werner's theory. It is six in all the three complexes of cobalt shown above. However, the number of primary valencies is three in $CoCl_3 . 6NH_3$, two in $CoCl_3 . 5NH_2$ and one in $CoCl_3 . 4NH_3$ as shown by dotted lines in the above structures.

According to Werner's Theory, the primary valencies are ionizable. In $CoCl_3 . 6NH_3$ the number of ionizable primary valencies is three and, therefore, all the chloride ions would be precipitated by $AgNO_3$. In the complex $CoCl_3 . 5NH_3$ one of the Cl^- ions gets attached through secondary valency and becomes un-ionizable. But the other two Cl^- ions remain attached through primary valencies, are ionizable, and would be precipitated by $AgNO_3$. The complex $CoCl_3 . 4NH_3$ contains only one Cl^- ion which possesses primary valency and is ionizable. The other $2Cl^-$ ions and NH_3 are bonded through secondary (un-ionizable) valencies to the central metal atom.

In terms of Werner's theory, the formulae of the above complexes can be written as:

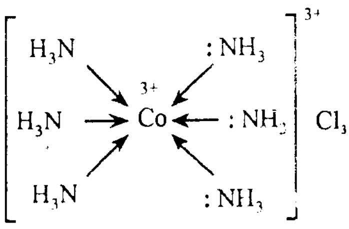
$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_4Cl_2]Cl$
$(CoCl_3 . 6NH_3)$	$(CoCl_3 . 5NH_3)$	$(CoCl_3 . 4NH_3)$

The number of molecules or ions (ligands) written within the coordination sphere (square brackets) represent the secondar valencies. It should be noted that the number of secondary valencies remains six in all the three cobalt complexes *e.g.*, the number of secondary valencies or coordination number remains fixed.

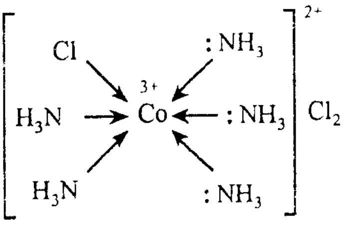
Electronic Interpretation of the Structures of Coordination Compounds

In 1923, Sidgwick made an attempt to explain the structure of coordination compounds with the help of electronic theory. According to that, the formation of coordination compounds involves the donation of a lone pair of electrons from coordinating group or ligand to the central metal atom. The coordinating group or ligand would act as *Lewis base* (electron pair donor) and central metal atom as *Lewis acid* (electron pair acceptor).

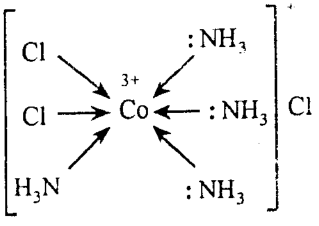
The structures of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ can be electronically represented as follows:



$[Co(NH_3)_6] Cl_3$



$[Co(NH_3)_5 Cl] Cl_2$



$[Co(NH_3)_4 Cl_2] Cl$

It is obvious that the net charge on the complex ion is algebraic sum of the oxidation number of the central metal and the charge on the ligands. For example, the net charge on complex ion, $[Co(NH_3)_5Cl]^{2+}$ is +2 because Co^{3+} possesses +3 oxidation state and Cl^- has −1 charge and the algebraic sum is $+3 - 1 = +2$ (on the complex ion). Thus +2 charge on complex ion is nullified by −2 charge on $2Cl^-$ ions in $[Co(NH_3)_5Cl]Cl_2$.

Sidgwick also pointed out that during the formation of coordination compounds, *the central metal atoms have tendency to attain the electronic configuration of next inert gas.* In other words, the effective atomic number of the central metal atom becomes equal to the atomic number of the next inert gas after complex formation. This is called *effective atomic number* (E.A.N.) *rule*.

$$\text{E.A.N.} = Z - E_l + E_g$$

Where Z is the atomic number of the metal atom.

E_l is the number of electrons lost by the metal during the formation of ions.

E_g is the number of electrons gained by the metal during the formation of coordination compounds.

For example, $[Co(NH_3)_6]Cl_3$ is formed by the donation of 6 electron pairs (12 electrons) by 6 : NH_3 groups and cobalt has lost 3 electrons (transferred to 3Cl) during the formation of Co^{3+} ions. The atomic number of cobalt is 27. The effective atomic number (E.A.N.) for Co^{3+} in this complex would be 36,

$$\text{E.A.N.} = 27 - 3e + 12e = \underline{36}$$

which is the atomic number of krypton (the next inert gas). The effective atomic number of some of the transition metal ions are given in Table 18.4.

TABLE 18.4

Effective Atomic Number (E.A.N)
of Some Transition Metal Ions in Complexes

Metal	Coordination number	Atomic Number of metal atom	No. of electrons lost in ion formation	Electrons gained by metals in coordination	E.A.N.
Fe^{2+}	6	26	2	12	36
Co^{3+}	6	27	3	12	36
Zn^{2+}	4	30	2	8	36
Pt^{4+}	6	78	4	12	86

Limitations of Sidgwick's Theory

Sidgwick's Theory has the following limitations with reference to coordination compounds:

1. The theory is unable to explain the geometry of the molecules.
2. The central metal atoms cannot gain so many electrons being fairly electropositive. This theory could not explain the accommodation of electrons during complex formation.
3. There are many coordination complexes which do not obey affective atomic number rule.

The Werner's theory and electronic theory of complex compounds have been further developed through modern theories of valency namely, *valence bond theory, molecular orbital theory* and *crystal field theory*. Let us discuss first the applications of valence bond theory to explain the structures of coordination compounds. The basic concepts of this theory have already been discussed in chapter 4.

Application of Valence Bond Theory to Coordination Compounds

Valence bond theory, developed by Professor L. Pauling can be conveniently applied to explain the structures of coordination compounds. The salient features of this theory as applied to coordination compounds are:

(a) When coordination groups or ligands are approaching the central metal atom or ion the electrons in the outer metal orbitals are disturbed and undergo re-arrangement in most cases.

(b) The vacant metal orbitals (*s*, *p*, *d* ...) accept a set of lone pairs of electrons from ligands and establish coordinate bonds. The number of coordinate bonds is equal to the number of lone pair of electrons donated or number of ligand atoms attached.

(c) The metal orbitals which accept the lone pair of electrons from ligands are hybridized. The possible geometrical shape of the coordination compound is determined by the type of hybridization. The following type of hybridization gives rise to the corresponding symmetries of the complexes.

sp hybridization ······ linear structure.

sp^3 hybridization ······ tetrahedral structure.

dsp^2 hybridization ······ square planar structure.

d^2sp^3 or sp^3d^2 hybridization ······ octahedral structure.

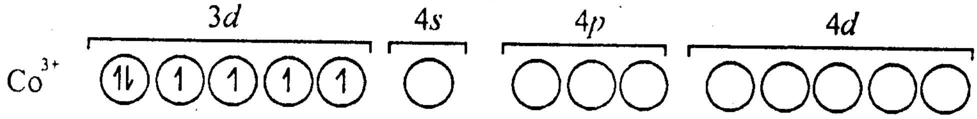
Structural Aspects of 6-Coordinate Complexes

Let us apply the principle of valence bond theory to elucidate the structural aspects of coordination compounds. For example, the structures of $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are octahedral because both involve d^2sp^3 hybridization. In both these complexes six ligands are attached to cobalt which is in +3 oxidation state. The electronic configuration of Co and Co^{3+} (Atomic number of Co = 27 which loses 3 electrons to leave 24 electrons on Co^{3+}) can be represented as:

Co(27*e*) $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^7$ $4s^2$

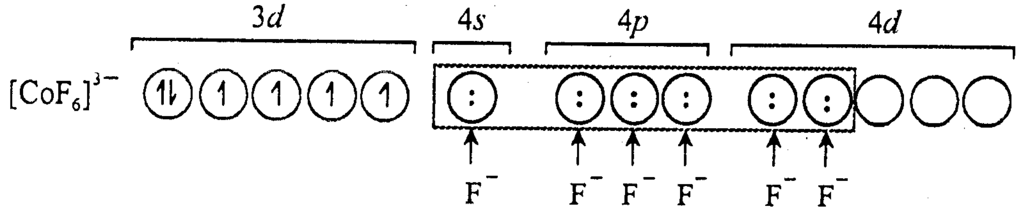
Co^{3+} (24*e*) .... $3d^6$ $4s^0$

If the orbitals involved in bond formation are indicated as circles and electrons shown as half arrows, the electronic configuration of Co^{3+} would be represented as:



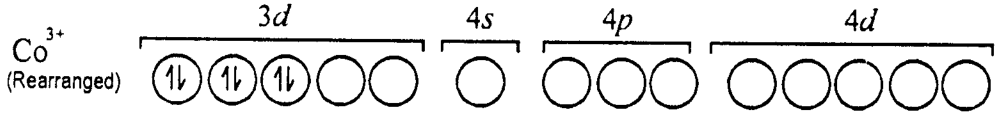
1. $[CoF_6]^{3-}$ Complex Ion

The F^- ions are weak ligands (cannot donate electrons more effectively) and will not affect much the electronic arrangement already present in *d* orbitals of Co^{3+} ion while forming the complex ion, $(CoF_6)^{3-}$. As a result of this, the $6F^-$ ions would donate 12 electrons to six vacant orbitals undergoing $4s\ 4p^3\ 4d^2$ or sp^3d^2 hybridization. $Na_3[CoF_6]$ complex is derived from $[CoF_6]^{3-}$ complex ion and is an example of *outer orbital complex*. A complex involving $ns\ np^3nd^2$ ($4s\ 4p^3\ 4d^2$ in $[CoF_6]^{3-}$ hybridization is called *outer orbital complex* because it uses *"outer" d* orbitals. It is obvious that $[CoFe_6]^{3-}$ has 4 unpaired electrons, the coordination compounds of this type are also called *spin-free* or *high spin* complexes. Such complexes usually show paramagnetic (attracted by external magnetic field or show magnetic properties) behaviour due to the presence of unpaired electrons. Each unpaired electron due to its spin would contribute to the paramagnetic behaviour. More the unpaired electrons present, more paramagnetism will be shown by coordination compounds. Another example of outer orbital complex is $[Fe(H_2O)_6]^{3+}$.

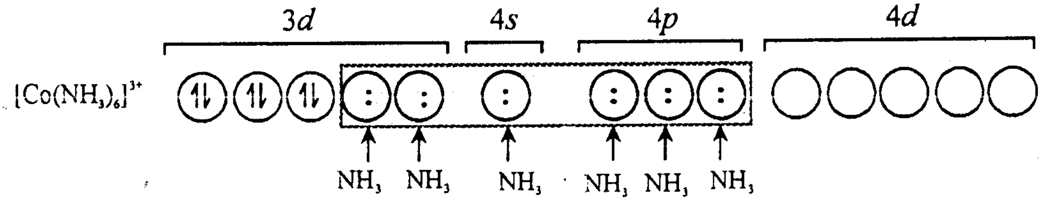


2. $[Co(NH_3)_6]^{3+}$ Complex Ion or $[Co(NH_6)_3]Cl_3$

Cobalt is again in +3 oxidation state in this complex or complex ion. The electronic configuration of Co^{+3} is already shown. Ammonia is a relatively stronger ligand (can donate electrons more effectively) and while approaching the Co^{3+} would force the electrons to pair up due to inter-electronic repulsion. The electronic configuration of Co^{3+} would thus be:



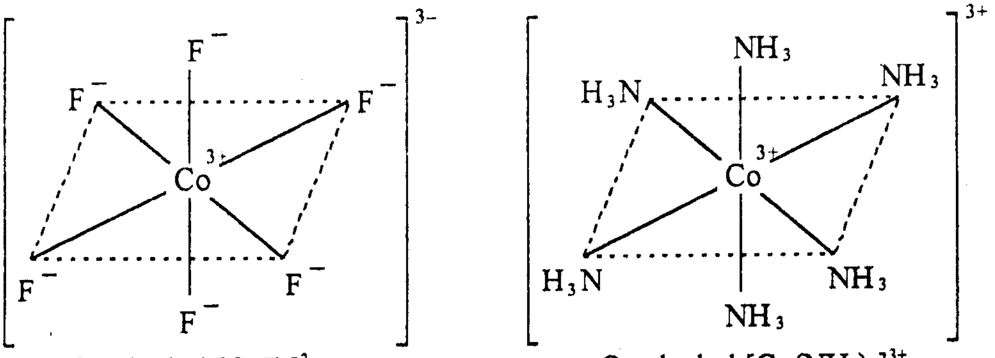
Two $3d$ orbitals become available for bond formation with ammonia molecules along with $4s$ and three $4p$ orbitals. Two $3d$, one $4s$ and three $4p$ orbitals would hybridize to give d^2sp^3 hybridization resulting in octahedral symmetry. Six : NH_3 groups will be attached and possess octahedral corners in the complex or complex ion.



$d^2\,sp^3$ hybridization

This type of complex is called *inner orbital complex* because it involves $(n - 1)$ d, ns and np orbitals in hybridization, *i.e.*, inner d orbitals are involved. Such type of complexes are also called *spin paired* or *low spin* complexes *e.g.*, $[Fe(CN)_6]^{3-}$. These usually show *diamagnetic* (repelled by external magnetic field) behaviour because all the electrons in various orbitals are paired up with opposite spins. The measurements of magnetic moment values (by magnetic balances) is of great value in elucidating the structures of coordination complexes. $[Co(NH_3)_6]Cl_3$ should have magnetic moment values near zero and $Na_3[CoF_6]$ complex has value near 4.9 B.M. (Bohr magnetons).

The structures of $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ are shown in Figure 18.4.

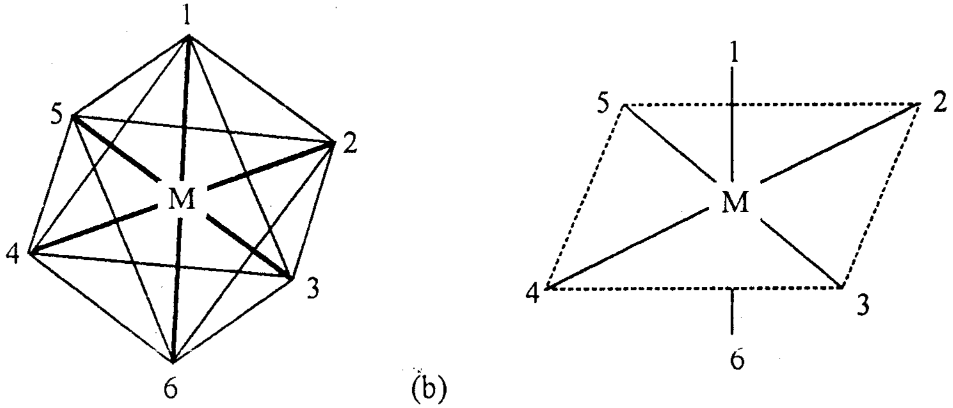


Octahedral $[CoF_6]^{3-}$

Octahedral $[Co(NH_3)_6]^{3+}$

(a)

Fig. 18.4(a). Structures of $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$.

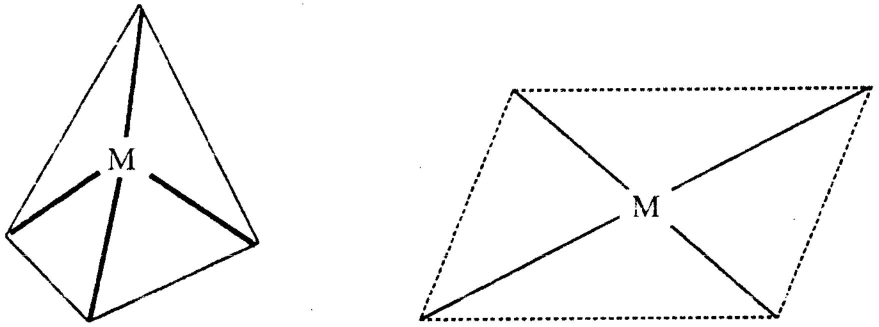


(b)

Fig.18.4(b). Octahedral symmetry.

Structural Aspects of 4-Coordinate Complexes

The 4-coordinate complexes are formed either by sp^3 hybridization or dsp^2 hybridization. A complex formed by sp^3 hybridization gives rise to tetrahedral structure and the complex obtained after dsp^2 hybridization of orbitals results in square planar structure (Figure 18.5). It should be noted over here that square planar arrangement of atoms lies in one plane *i.e.*, four corners of a square plane. However, tetrahedral symmetry is three dimensional.



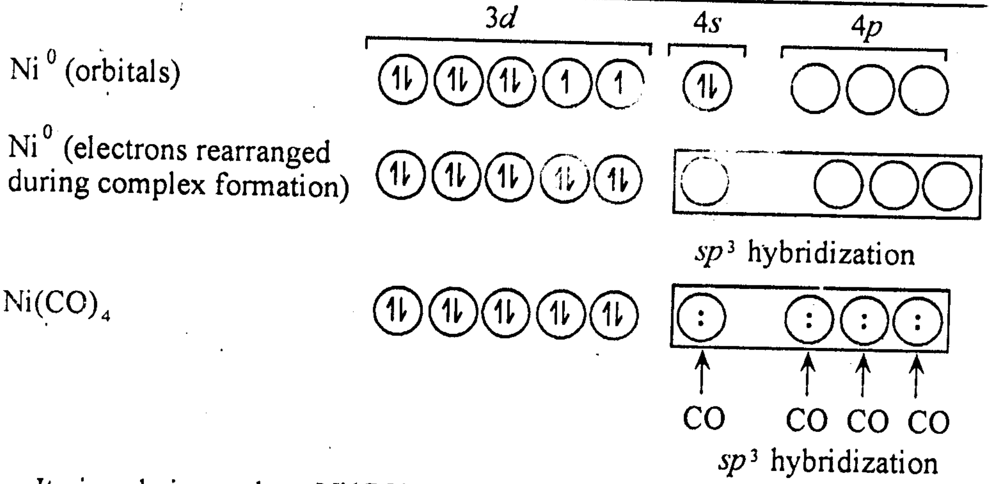
(a) (b)

Fig. 18.5(a) Tetrahedral symmetry. (b) Square planar symmetry.

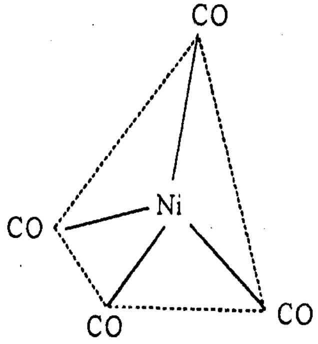
Let us apply the basic concepts of valence bond theory to $Ni(CO)_4$ and $K_2[Ni(CN)_4]$ complexes. Both these nickel complexes are examples of 4-coordinate complexes. The structures of both these complexes may be analysed taking into consideration the electronic configuration of Ni.

(1) $Ni(CO)_4$

In this complex, nickel is in zero valent state and the electronic configuration of Ni^0 (At. number = 28, Electronic configuration $1s^2$ $2s^2$ $2p^6$, $3s^2$ $3p^6$ $4s^2$ $3d^8$) during complex formation is:

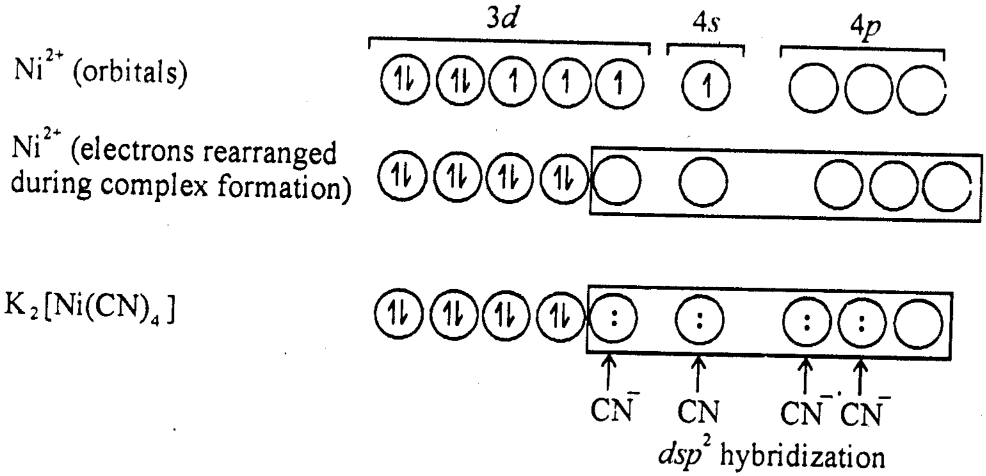


It is obvious that $Ni(CO)_4$ is formed by the sp^3 hybridization of metal orbitals which are rendered vacant during complex formation. Therefore, $Ni(CO)_4$ shows a *tetrahedral* structure. As none of the electrons is unpaired the complex would be diamagnetic. The structure of $Ni(CO)_4$ can be represented as:

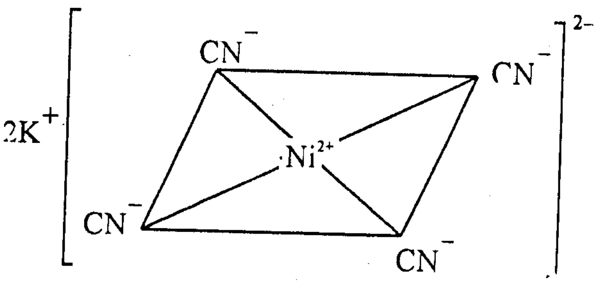


2. $K_2[Ni(CN)_4]$ Complex

Ni is in +2 oxidation state in this complex and overall charge on complex ion is –2, (Ni = +2, $4CN^- = -4$) which is counterbalanced by $2K^+$. The electronic configuration of Ni^{2+} ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^0$) and the resulting complex, $K_2[Ni(CN)_4]$ is:



The complex $K_2[Ni(CN)_4]$ involves dsp^2 hybridization and results in the formation of square planar symmetry. The absence of unpaired electrons indicates diamagnetic nature of the complex. The square planar structure of the complex, $K_2[Ni(CN)_4$ is:



Magnetic Properties of Complexes

It has already been indicated that presence of unpaired electrons in the orbitals of the metal atoms or ions is responsible for the paramagnetic behaviour of the complexes. The number of unpaired electrons depends upon the number of electrons present in *d* orbitals and the nature of the complex *e.g.*, low spin or high spin. Magnetic moments of some of the octahedral complexes are given in Table 18.5.

TABLE 18.5

Metal ion	*d* orbital configuration	Complex	Number of unpaired electrons	Magnetic moment μ in B.M.
Ti^{3+}	d^1	$[Ti(H_2O)_6]^{3+}$	1	1.7
Cr^{2+}	d^4	$[Cr(dipy)_3]\ Br_2 \cdot 4H_2O$ (low spin)	2	3.27
Mn^{3+}	d^4	$K_3[Mn(CN)_6] \cdot 3H_2O$ (low spin)	2	3.18
Mn^{3+}	d^4	$[Mn(ac \cdot ac)_3]$ (high spin)	4	4.95
Mn^{2+}	d^5	$K_4[Mn(CN)_6] \cdot 3H_2O$ (low spin)	1	1.80

Limitations of Valence Bond Theory

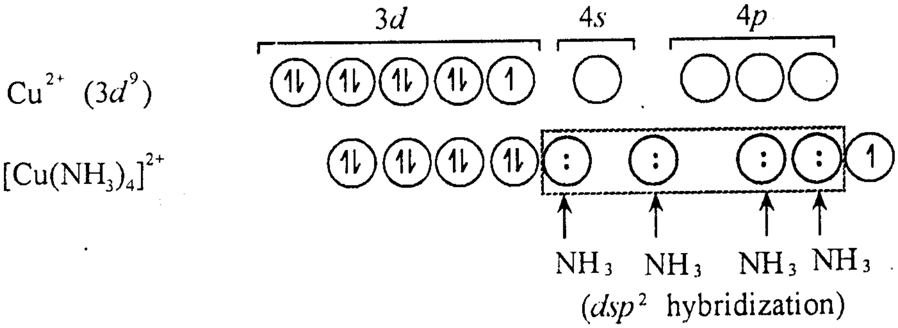
The valence bond theory has the following limitations:

(1) The valence bond theory is unable to explain the magnetic moment data of some of the complexes.

(2) The valence bond theory does not explain the colour of transition metal ions, absorption spectra and heats of formation etc.

(3) In the metal ions which involve dsp^2 hybridization, the reason for the non-involvement of third *p* orbital to give dsp^3 hybrid orbitals cannot be explained on basis of valence bond theory.

(4) One of the major drawbacks in valence bond theory is that it does not explain the bonding in Cu^{2+} complexes which are supposed to utilise dsp^2 hybrid orbitals. But Cu^{2+} is a d^9 ion and the complex derived from it *e.g.*, $[Cu(NH_3)_4]SO_4$ has square planar structure according to valence bond theory. It is clear from the following representation of electronic arrangements that one electron from 3*d* orbital must be promoted to higher energy orbital (4*p*) and should result in an unstable complex. The electron in 4*p* orbital should be easily given out to give Cu^{3+} ions which is against the facts *e.g.*, Cu^{3+} ions are not formed and Cu^{2+} complexes are stable. This is a serious drawback in valence bond theory.



Due to the serious drawbacks in valence bond theory as applied to coordination compounds, other theories were looked for their structural elucidation.

Stability of complexes is depicted by 18 electron rule. According to 18 electron rule, atomic number of transition metal – 18e + no. of electrons donated by ligands = 18. The complexes which obey this rule are more stable.

Application of Molecular Orbital Theory

The molecular orbital theory has been discussed in Chapter 4. The overlapping of *d* orbitals of transition metal atoms or ions with *s* and *p* atomic orbitals of ligands results in the formation of bonding, non-bonding and anti-bonding molecular orbitals in accordance with the principles of molecular orbital approach. The charge density tends to shift to low energy bonding molecular orbitals which gives stability to the complexes. The molecular orbital diagrams for $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ complex ions are shown in Figure 18.5 (a) and (b). Six bonding and six anti-bonding molecular orbitals are formed. Twelve electrons produced by six ligand orbitals go to bonding molecular orbitals.

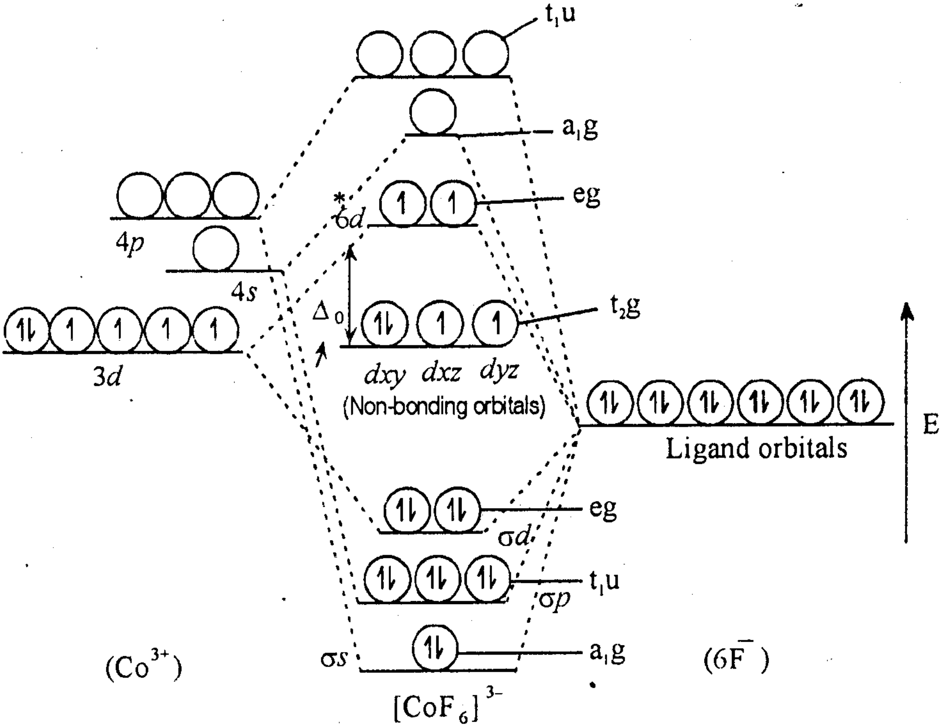


Fig. 18.5 (a) The Molecular Orbital diagram for $[CoF_6]^{3-}$.

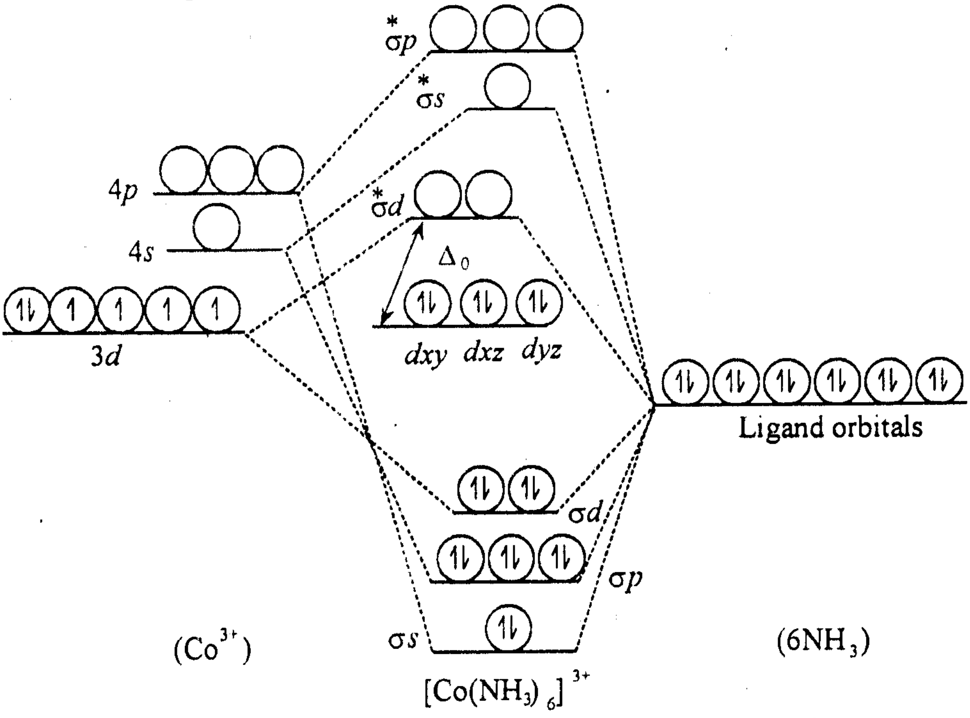


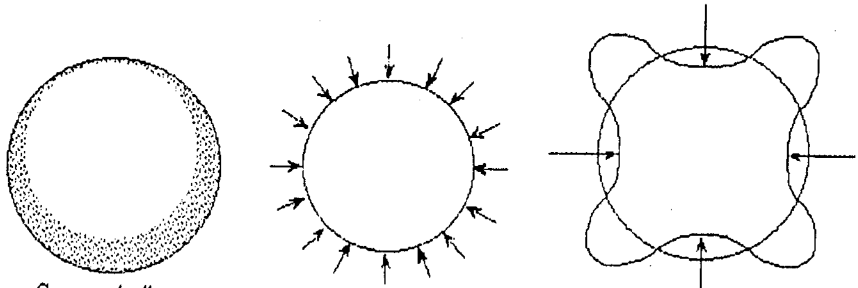
Fig. 18.5 (b) The molecular orbital diagrams for $[CoNH_3)_6]^{3+}$.

The value of energy difference between non-bonding *d* orbitals and $\overset{*}{\sigma}d$ orbitals Δ_0 is larger for $[Co(NH_3)_6]^{3-}$ complex ion than for $[CoF_6]^{3-}$ ion because NH_3 is a stronger ligand but F^- ion is a weak ligand. The energy of pairing of electrons is less than Δ_0 in $[Co(NH_3)_6]^{3+}$ and the electrons, therefore, remain paired. But in case of $[CoF_6]^{3-}$ the energy of pairing is larger than Δ_0 and, therefore, electrons remain unpaired. The presence of unpaired electrons in $\overset{*}{\sigma}d$ orbitals is responsible for paramagnetic behaviour of $[CoF_6]^{3-}$. The $[(Co(NH_3)_6]^{3+}$ is diamagnetic because all electrons are paired up.

CRYSTAL FIELD THEORY (CFT)

This theory gives a more comprehensive treatment to the structures and characteristics of coordination compound. Bethe and Van Vleck in 1930 developed this theory to explain the colours and magnetic properties of crystalline solids. In 1951, Crystal Field Theory was used to interpret spectra of transition-metal complexes. Later on, their theory was found useful to explain many characteristics of coordination compounds.

Let us take an analogy in order to understand the basic concepts of crystal field theory. Imagine the electron cloud of the metal ion similar to a sponge ball. If the external pressure on the ball is increased the system will attain higher energy and volume should decrease (Figure 18.6). If the external pressure is removed the ball will acquire its original position (Figure 18.6 a). This change in pressure corresponds to energy changes which result from the repulsive interactions between electrons of the ligands and electrons in the metal ion in the hypothetical complex. If the sponge ball is under localized pressure from four points the ball will attain the shape shown in Figure 18.6 (c). The ball will be pressed along the effected four points and would attain higher energy at these spots. The area under low pressure will bulge out and would have less pressure and at low energy state. Similarly, the *d* orbitals of metal ions which are directed along the approaching ligands would attain higher energy due to repulsion of electrons. These repulsive interactions will naturally be between electrons in *d* orbitals of metal ions and lone pair electrons carried by the approaching ligands As a result of this, some of the *d* orbitals will acquire higher energy states than the others. This change in energy of the degenerate *d* orbitals into higher and lower states is called crystal field splitting.



Sponge ball (Comparable to free metal ion) (a)

Sponge ball under pressure (Comparable to activated complex) (b)

Sponge ball under pressure from four-points (Formation of metal complex) (c)

Fig. 18.6. Visualization of Crystal field effects.

In order to understand the crystal field theory it is necessary to have a clear mental picture of the orientation of orbitals in space. The orientation of '*d*' orbitals in space is given in Figure 18.7. It may be noted that the set of 'orbitals' lying between x, y and z axes are denoted by d_{xy}, d_{xz}, d_{yz} and those '*d*' orbitals on the axis are $dx^2 - y^2$ and dz^2. The crystal field effects are produced by the interaction of the '*d*' orbitals of transition metal with orbitals of the ligand surrounding it. Let us consider the essentials of crystal field theory (CFT) by taking a simple example of an octahedral complex $[TiF_6]^{2-}$. In this complex Ti^{4+} ion has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^0$. All the five empty $3d$ orbitals have identical energies. *The orbitals which have the same energy are called degenerate orbitals.*

When Ti^{4+} ion is approached by six F^- ions during the formation of $[TiF_6]^{2-}$, energy of its d orbitals increases. A hypothetical complex with degenerate d orbitals but at a higher energy state than free metal ion is attained. Let us suppose that F^- ions are setting along the x, y and z axes to metal d orbitals and thereby set up an octahedral symmetry (Figure 18.7).

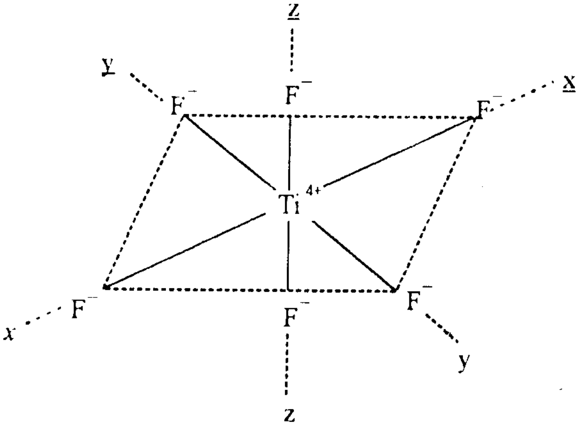


Fig. 18.7. Octahedral symmetry.

The *d* orbitals which would be lying on *x*, *y* and *z* axes are $dx^2 - y^2$ and dz^2. Thus, they will be effected more by the F^- ions and therefore increase in energy state (similar to areas of sponge ball under pressure). The *dxy*, *dyz*, *dxz* orbitals are pointing between the axes (Figure 18.7) and would not be effected much (similar to bulged portions of sponge ball). The set of $dx^2 - y^2$ and dz^2 orbitals are called *e.g.*, orbitals (*e* refers to a doubly degenerate set) and a set of *dxy*, *dyz* and *dxz* orbitals are called $t_{2}g$ (triply degenerate) orbitals (Figure 18.8).

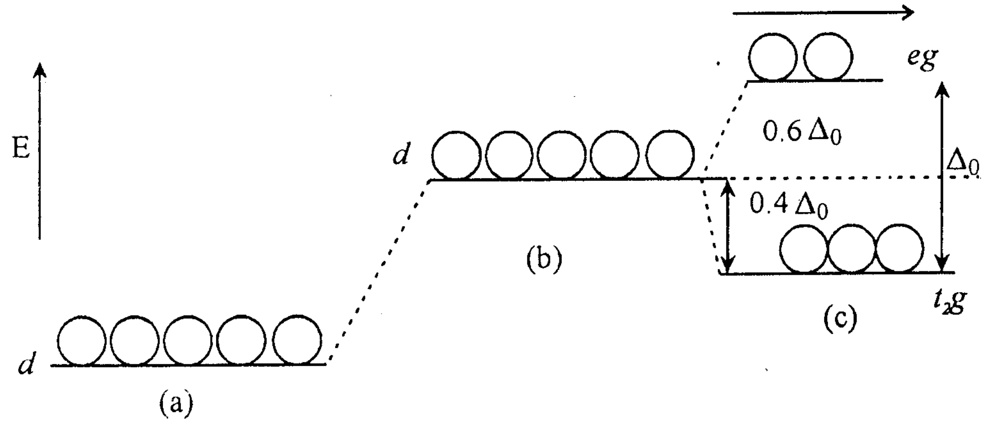


Fig. 18.8. The energies of d orbitals (a) in a free metal ion, (b) in a hypothetical complex state, and (c) in an octahedral complex.

During the complex formation, the *d* orbitals (*dxy*, *dyz*, *dxz*, $dx^2 - y^2$ and dz^2) separate into $t_{2}g$ and *eg* sets of orbitals. This is called *crystal field splitting*. The energy separation between $t_{2}g$ and *eg* orbitals is given by symbol Δ_0 (energy difference for octahedral system). The *eg* orbitals have increased their energy by 0.6 Δ_0. The $t_{2}g$ orbitals have Δ_0 less by 0.4 units from the five *d* orbitals in hypothetical degenerate state (Figure 18.8 b) and are said to be stabilized to this extent. The 0.4 Δ_0 is said to be the *crystal field stabilization energy* (CFSE) for the octahedral complex.

The crystal field stabilization energies for metal ions in octahedral complexes have been calculated by assigning a value of 0.4 Δ_0 for each electron present in $t_{2}g$ orbitals and 0.6 Δ_0 for each electron present in an *eg* orbital. Crystal field stabilization energies for metal ions in octahedral complexes are given in Table 18.6. Larger the value of crystal field stabilization energy greater will be the stability of the coordination complex.

TABLE 18.6

Crystal Field Stabilization Energies of Metal Ions in Octahedral Complexes

Number of Electrons in *d* orbitals of metal ions	t_2g			eg		Crystal Field Stabilization (Δ_0)
d^1 Ti^{3+}	↑	○	○	○	○	0.4 × 1 = 0.4
d^2 V^{3+}, Zr^{2+}	↑	↑	○	○	○	0.4 × 2 = 0.8
d^3 V^{2+}, Cr^{3+}	↑	↑	↑	○	○	0.4 × 3 = 1.2
d^4 Ph^{3+}	↑	↑	↑	↑	○	0.4 × 3 – 0.6 × 1 = 0.6
	↑↓	↑	↑	○	○	0.4 × 4 – 0 = 1.6
d^5 Fe^{3+}	↑	↑	↑	↑	↑	0.4 × 3 – 0.6 × 2 = 0.0
	↑↓	↑↓	↑	○	○	0.4 × 5 – 0 = 2.0
d^6 Co^{3+}, Rh^{3+}	↑↓	↑	↑	↑	↑	0.4 × 4 – 0.6 × 2 = 0.4
	↑↓	↑↓	↑↓	○	○	0.4 × 6 – 0 = 2.4
d^7 Co^{2+}	↑↓	↑↓	↑	↑	↑	0.4 × 5 – 0.6 × 2 = 0.8
	↑↓	↑↓	↑↓	↑	○	0.4 × 6 – 0.6 × 1 = 1.8

The magnitude of the crystal field splitting determines the pairing or unpairing of electrons. The extent of crystal field splitting depends upon several factors. The nature of the ligands is an important factor. With the same metal ion, the ligands with large negative charge which can approach the metal orbitals closely should provide *greater crystal field splitting*. Small and more electronegative ions will have less CF splitting *e.g.*, F^- ions. Ammonia with one lone pair of electrons can focuss its negative charge on *d* orbitals more effectively and causes greater crystal field splitting than F^- ions. The effect of NH_3 and F^- ions on CF splitting is shown in Figure 18.9 with reference to $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ ions. It may be noted that CFSE is zero for octahedral d^6, d^8 and d^{16} weak field (high spin) complexes.

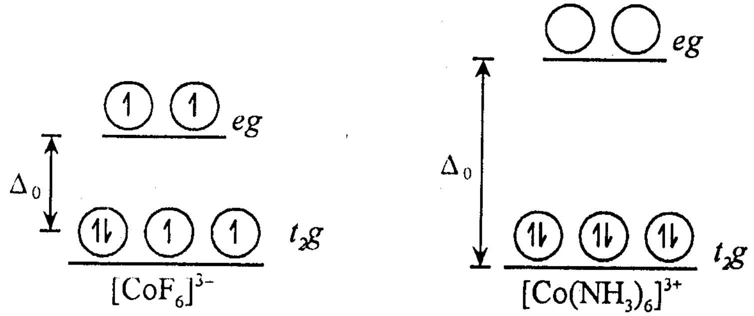


Fig. 18.9. Relative crystal field splittings (Δ_0) of d orbitals in Co(III) complexes.

In case of $[CoF_6]^{3-}$, the value of Δ_0 (the stability gained) is less than energy of pairing (stability loss due to electron pairing). Therefore, electrons would go to *eg* orbitals and become unpaired. This is an example of *high spin complex*. Complexes containing F^- ligands would be *paramagnetic* (due to unpaired electrons) and rather unstable. The crystal field splitting in $[Co(NH_3)_6]^{3+}$ being quite high Δ_0 (energy gained) is large enough to overcome the loss in stability due to pairing. Complexes containing $[Co[(NH_3)_6]^{3+}$ ions would be *diamagnetic* and are of *low-spin*. The CF splitting ability of ligands has been observed and is found to decrease in the following order:

$$CO, CN^- > NO_2^- > en > NH_3 > H_2O > F^- > OH^- > Cl^- > Br^- > I^-$$

Strong field ligands	Intermediate field ligands	Weak field ligands

Let us now consider tetrahedral complexes. We shall assume the ligands to occupy tetrahedral corners of a cube positioned so that the Cartesian coordinates of the metal atoms pass through the centers of the cube faces as shown in Fig. 18.10.

The lobes of the d_{xy}, d_{xz} and d_{yz} orbitals are directed toward the corners of the cube and come close to the ligands. The lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals are directed toward the cube faces. So electrons in d_{z^2} and $d_{x^2-y^2}$ orbitals are repelled less by the ligands than are the

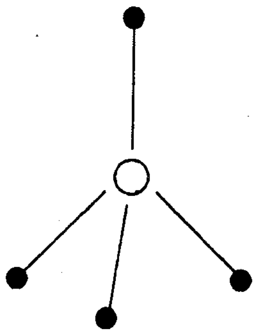
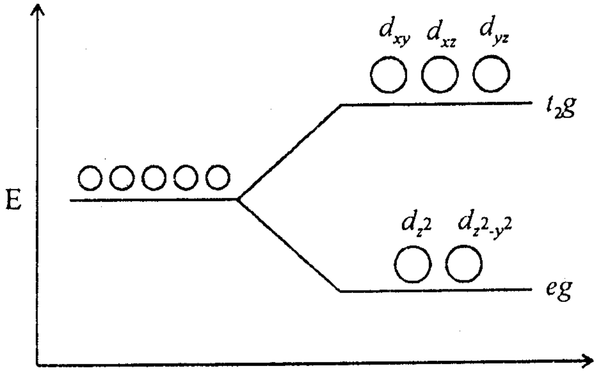


Fig. 18.10 Tetrahedral arrangement of negative ligands around a metal ion.

electrons in the dxy, dxz and dyz orbitals. As a result, splitting of the *d*-orbital energies into two levels takes place (Fig. 18.11). The energy of the triply degenerate t_2 set is raised by 0.4 Δt, and the energy of the doubly degenerate *e* set is lowered by 0.6 Δt (Δt = 0.444 Δ_0) because total negative charge is less for four lignads than for six ligands.



Charge distribution around ion

Fig. 18.11 Splitting of d-orbital energies in a tetrahedral field.

A nonlinear molecule in a degenerate electronic state may undergo distortion to remove the degeneracy in order to lower the energy. If a complex undergoes tetragonal distortion, the *eg* levels may be split. Such type of distortions are called John-Teller distortions and are found in $CuCl_2$ and CrF_2.

Colour and Absorption Spectra of Complexes

The best achievement of *crystal field theory* is its success in interpreting the colours and absorption spectra of transition-metal complexes. Why different transition metal compounds are coloured? For example, an aqueous solution of Ti(III) ion, (the oxidation state represented in Roman numerals) is violet. The colour of Ti(III) is an indication of its absorption spectrum (Figure 18.12). Aqueous solution of $[Ti(H_2O)_6]^{3+}$ ions are violet because they absorb the yellow light and transmit blue and red (a mixture of blue and red looks violet).

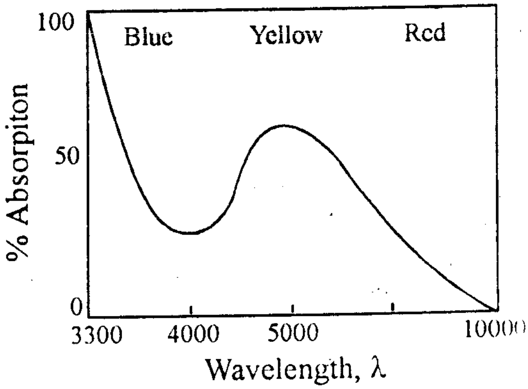


Fig. 18.12. The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ complex ions.

The amount of light energy and wavelength of light depend upon the energy difference (Δ_0) between t_2g and eg orbitals of metal ions for the excitation of electrons. In $[Ti(H_2O)_6]^{3+}$, the energy difference between t_2g and eg orbitals is 57k cals/per mole and, therefore; the same amount of energy will be absorbed in exciting an electron from t_2g to eg state (Figure 18.13).

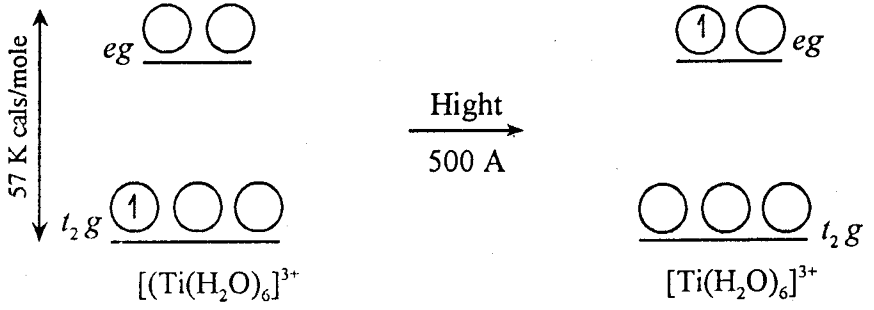


Fig. 18.13. The d – d electronic transition responsible for the violet colour of $[Ti(H_2O)_6]^{3+}$.

Colours of some chromium (III) complexes are given in Table 18.7.

TABLE 18.7

Colours of some chromium (III) complexes

$[Cr(H_2O)_4 Br_2] Br$	Green	$[Cr(H_2O)_4 Cl_2] Cl$	Green
$[Cr(NH_3)_4 Cl_2] Cl$	Violet	$[Cr(H_2O)_6] Br_3$	Bluish-grey
$[Cr(H_2O)_6] Cl_3$	Violet	$[Cr(NH_3)_6] Cl_3$	Yellow
$[Cr(NH_3)_5 Cl] Cl_2$	Purple		

It can be seen from the above discussion that crystal field theory is very useful in interpreting various characteristics of transition metal complexes. It should be noted over here that vacant d, s and p orbitals in metals would be responsible for bond formation with approaching ligands by accepting charge density from them.

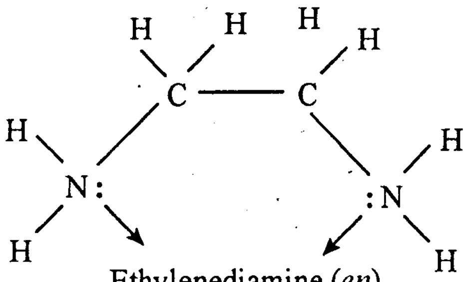
CHELATES

Certain ligands possess two or more unshared pairs of electrons suitably separated from each other in the molecule. These lone pairs have more than one coordinating positions within the molecules available for coordinate bond formation.

If a molecule or a single group occupies two or more coordination positions with the same metal ion, the ligand is called *bidentate or chelate or chelating group* (Chelate in Greek means crab's claw). The complexing process with chelates is called *chelation* and the complex formed is called a *chelate complex*.

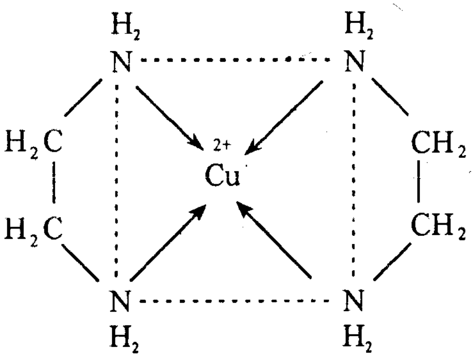
A ligand molecule may have three, four or more points of attachment to the central metal atom or ion and is called *tridentate*, *tetradentate* (*quadridentate*) or *polydentate ligand*.

Ethylenediamine molecule has two nitrogen atoms each carrying a lone pair of electrons and capable of donation to the transition metals and is an example of *bidentate* (*two teeth*) *ligand*. Ethylenediamine (*en*) has the following structure which clearly indicates its bidentate nature.



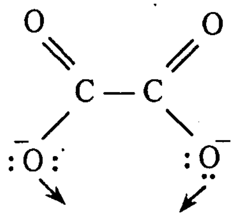
Ethylenediamine (*en*)

Ethylenediamine forms stable compounds with large number of metal ions through chelation. For example, it combines with Cu^{2+} to form the following complex:

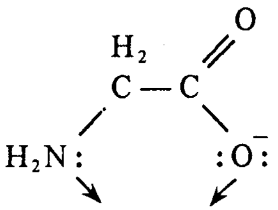


$[Cu(en)_2]^{2+}$

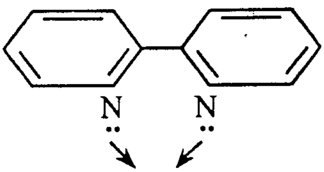
Other examples of bidentate ligands are:



Oxalate ion

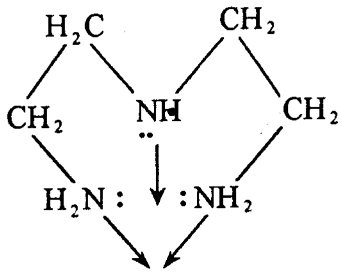


Glycinate ion

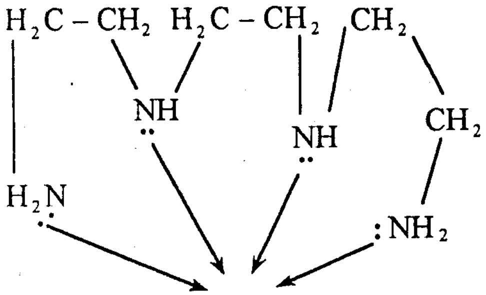


2, 2-bipyridine

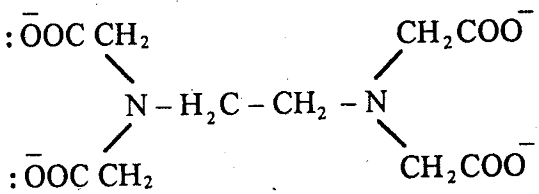
Many tridentate, quadridentate and hexa- or sexadentate ligands are known. Examples of such type are:



(Diethylenetriamine)
Tridentate



(Triethylene tetramine)
Tetradentate



(Ethylenediamine tetracetate)
Hexadentate

Ethylenediamine tetracetic acid (EDTA) or its ions have six coordination sites available for coordinate bond formation as shown in Figure 18.14.

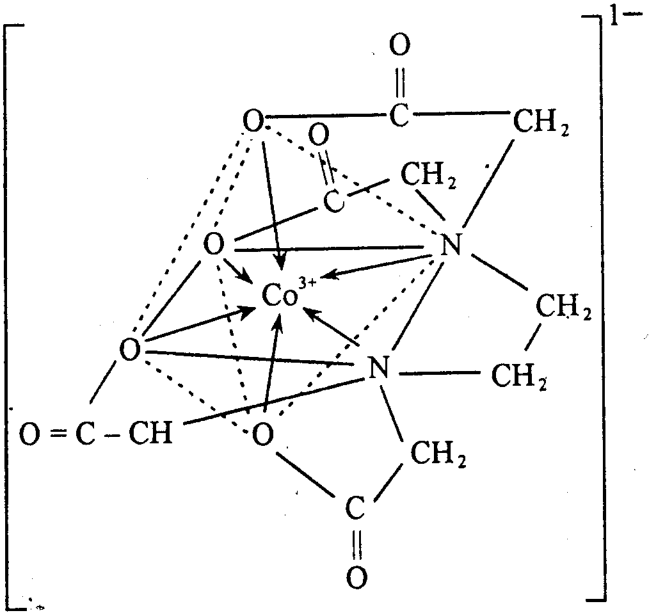
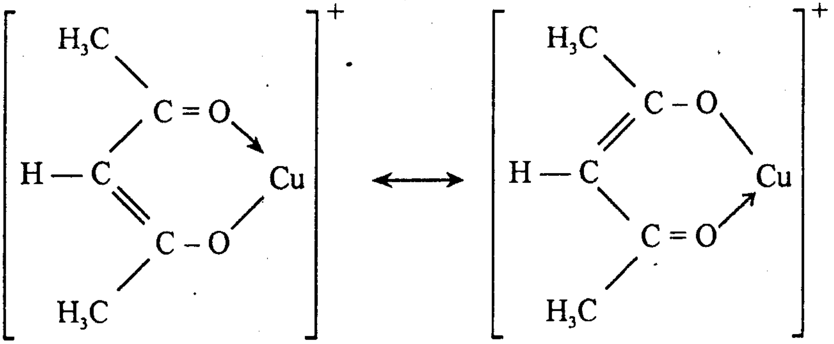


Fig. 18.14. Structure of Co(EDTA)$^-$.

Factors Influencing the Stabilities of Chelates

The stability of chelates is mainly due to ring formation. The vast majority of stable chelates have 5-membered or 6-membered ring systems. The chelate molecules which form 5-membered ring systems are rather more stable.

Chelates having rings which contain *alternate double bonds* are more stable. In such structures, the π-density spreads over the ring. In addition to that more than one resonating structures are possible which will be another stability contributing factor. For example, acetylacetone complex of copper is stabilised due to the following two resonating structures.



Big and heavy chelating ligands would form less stable complexes as compared to small and lighter molecules. Thus, the complexes of ethylenediamine $H_2NCH_2CH_2NH_2$ are more stable than those of the tetramethyl derivative of ethylenediamine, $(H_3C)_2\ NCH_2CH_2N(CH_3)_2$.

Importance of Chelates and Coordination Compounds

Coordination compounds play an important role in industry, analytical chemistry, plant, animal and human life. Following are some important aspects of chelates and coordination compounds:

(1) *Chlorophyll*, an important constituent of plants, is a chelate compound containing Mg^{2+} in the centre linked with pyrrole nuclei.

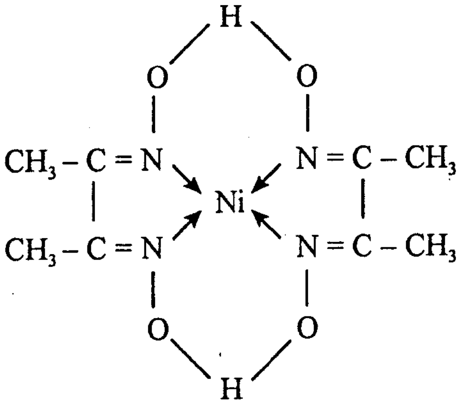
(2) *Hemoglobin*, the red colouring matter of blood, is an iron chelate structurally similar to chlorophyll.

(3) Vitamin B_{12} is a cobalt complex linked with 5-deoxyadenosyl (5, 6-dimethyl benzimidozole) group.

(4) In *analytical chemistry*, chelating agents are becoming increasingly important. For example, nickel is estimated with dimethylglyoxime through the formation of nickel-dimethylglyoxime complex.

Colorimetric determination of various metals is based on the complex formation.

Chelating agents are frequently used as *indicators* in the titration of certain metal ions.



Rose red nickel complex

(5) An important use of chelating agents is for *water softening*. Ion-exchange resins are used for this purpose based on coordination phenomena.

(6) Metal ions can be separated from the mixture based on the complex formation. The *water soluble chelates called squestering agents*, are used in aqueous solution for the effective removal of objectionable metal ions. Ethylenediamine tetracetic acid can be used to eliminate the harmful metal ions from the body.

(7) Coordination compounds are used in medicines, as detergents and anti-oxidants.

(8) They are used in dyeing and colouring agents.

(9) Invisible inks are mostly coordination compounds. For example, if we write with hydrated cobalt chloride and dry it, nothing would be visible. On keeping the paper near hot object the writing will become legible with blue colour. All this is due to the following changes in the complex compounds.

$$\underset{\substack{\text{Light pink}\\\text{(almost colourless)}}}{2[Co(H_2O)_6]Cl_2} \overset{\Delta}{\rightleftharpoons} \underset{\text{Blue}}{Co[CoCl_4] + 12H_2O}$$

(10) Complex compounds are also widely used as catalysts in synthetic reactions. For example, Zieglar-Natta (after the name of professors who discovered it) catalyst is widely used in polymerization of ethylene to form polyethylene. Similarly, $(Ph_3P)_3RhCl$ acts as a good catalyst for various reactions, i.e., polymerization, hydroformylation etc.

Isomerism in Coordination Compounds

The existence of two or more chemical compounds with identical chemical composition but different structures and properties is called isomerism. The phenomenon of isomerism is not restricted to organic compounds only but has also been found in inorganic substances. Coordination compounds show a variety of isomerism which is much more pronounced than that shown by organic compounds.

The following types of isomerism are commonly found in coordination compounds:

1. Ionization Isomerism

The compounds having the same empirical formula with different ions in solution are said to show ionization isomerism. For example, violet $[Co(NH_3)_5Br]SO_4$ and red $[Co(NH_3)_5SO_4]$ Br are ionization isomers, which yield sulphate and bromide ions, respectively. Other examples are:

$$[Co(NH_3)_5NO_2]^{2+}\ SO_4^{2-} \quad \text{and} \quad [Co(NH_3)_5SO_4]^{+}\ NO_2$$

$$[Pt\ (NH_3)_4Cl_2]\ Br_2 \quad \text{and} \quad [Pt\ (NH_3)_4\ Br_2]Cl_2$$

2. Coordination Isomerism

In this type of isomerism the same number of coordinating groups may be present in the complex but are linked to different metal ions. In these complexes

$$\underset{\text{(I)}}{[Co(NH_3)_6]\ [Cr(CN)_6]} \quad \text{and} \quad \underset{\text{(II)}}{[Cr(NH_3)_6]\ [Co(CN)_6]}$$

cobalt is linked to NH_3 in compounds (I) but linked to CN in (II). Other examples of coordination isomerism are:

$$[Co(NH_3)_6]\ [Cr(C_2O_4)_3] \text{ and } [Cr(NH_3)_6]\ [(Co(C_2O_4)_3]$$

$$[Cr(NH_3)_6]\ [Cr(C_2O_4)_3] \text{ and } [Cr(NH_3)_4C_2O_4]\ [Cr(NH_3)_2(C_2O_4)_2]$$

$$[Pt(NH_3)_4]\ [PtCl_6] \text{ and } [Pt\ (NH_3)_4Cl_2]\ [PtCl_4]$$

3. Polymerization Isomerism

Compounds are said to have polymerization isomerism if their molecular formulae are simple multiples of their stoichiometric arrangement. For example,

$$[Pt\ (NH_3)_2\ Cl_2] \text{ and } [Pt\ (NH_3)_4]\ [Pt\ Cl_4]$$

$$[Co(NH_3)_3(NO_2)_3] \text{ and } [Co(NH_3)_6]\ [Co(NO_2)_6]$$

4. Hydrate Isomerism

Water is a fairly strong coordinating group and would form many aquo complexes. The number of water molecules which are directly linked to the central metal ion and represented within the square brackets may vary. It depends upon various factors and conditions. The variation in the number of water molecules within the coordination sphere results in hydrate isomerism. For example, $CrCl_3.6H_2O$ has three different isomeric forms depending upon the number of H_2O within the coordination sphere. The formula of these three hydrates are:

$[Cr(H_2O)_6]Cl_3$ (Violet) $[Cr(H_2O)_5]\,Cl_2.H_2O$ (Green)

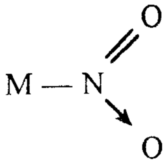
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (Green)

Another example showing hydrate isomerism is:

$[Cr(en)_2(H_2O)_2]\,Br_3$ and $[Cr(en)_2(H_2O)\,Br]\,Br_2.H_2O$

5. Structural or Salt Isomerism

This type of isomerism results from two possible ways of linking coordinating group to the central metal atom. For example, NO_2 group may either be attached to the central metal atom or ion through N or through O as shown below:



Nitro —

$M - O - N = O$

Nitrito —

Examples of isomers obtained from these two modes of linkage are:

$[CO(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

Nitropentammine deriv. (Yellow-brown) Nitritopentammine deriv. (Red)

$[Co(en)_2(ONO)_2]$ and $[Co(en)_2(NO_2)_2]$

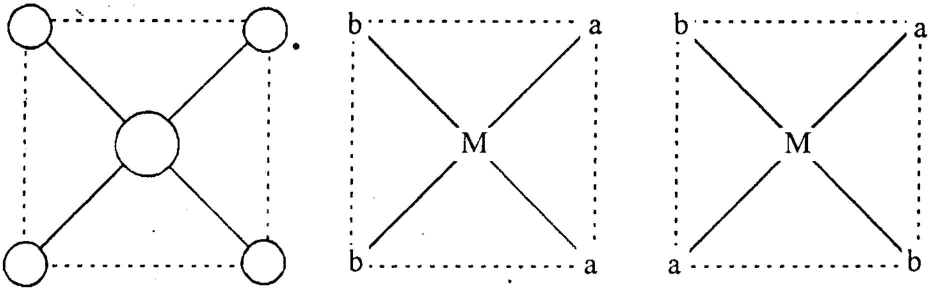
6. Stereoisomerism

This type of isomerism is found in two compounds which have the same composition and molecular formula but differ only in the relative positions of atoms or groups in space. This type of isomerism is also called *geometrical isomerism*. The two isomers may have the same geometrical form but may differ only with respect to the points of attachment of coordinating groups.

Stereoisomerism was predicted by Werner's theory. This is the most important type of isomerism found in coordination compounds. It is also called *cis-trans* isomerism. The variety of possible geometrical arrangements increases with the increase in coordination number.

Coordination No. 4

The complexes possessing coordination number 4 can adopt (a) square planar or (b) tetrahedral structure. *Cis-trans* isomerism can be predicted for complexes of the type [Ma_2b_2] having square planar arrangement (Figure 18.15).

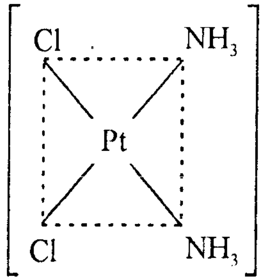


(a)
Square planar

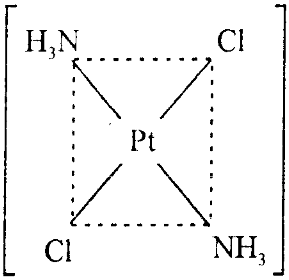
(b)
Cis
(I)

(c)
Trans
(II)

Fig. 18.15. (a) Square planar arrangement, (b) Cis-[Ma_2b_2], (c) Trans-[Ma_2b_2].



Cis
Pale yellow

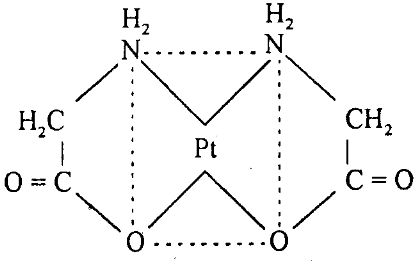


Trans
Dark yellow

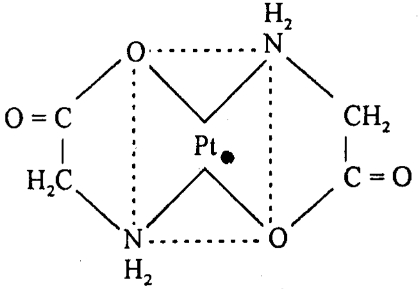
The isomeric form (I) in Figure 18.14 represents a *cis*-isomer with similar atoms (a or b) in vicinal positions and the form (II) is an example of *trans* (similar atoms at opposite corners) isomer. The complex [$Pt(NH_3)_2Cl_2$], square planar complex of [Ma_2b_2] type exists in *cis* and *trans* isomeric forms and is structurally represented as:

Cis – [$Pt(NH_3)_2 Cl_2$] and *Trans* – [$Pt(NH_3)_2 Cl_2$]

Geometrical isomerism is also given by square planar complexes containing unsymmetrical bidentate ligands of the type, [$M(AB)_2$]. For example, glycinate ion, $NH_2CH_2COO^-$ can coordinate with Pt(II) to give *Cis*- and *Trans*- [$Pt(glyc)_2$].



Cis – form



Trans – form

The complexes, $Pt(NO_2)_2$ $(NH_3)_2$ and $PtCl_2(Py)_2$ can also be isolated as *cis*- and *trans*-isomers.

Coordination No. 6

The complexes with coordination number six are relatively stable and many of them exhibit *cis-trans* isomerism. They possess octahedral symmetry (Figure 18.16) and *cis-trans* isomerism is commonly found in complexes of the general type $[Ma_4b_2]$. The typical example of this type is the occurrence of $[Co(NH_3)_4Cl_2]Cl$ as *cis*- $[Co(NH_3)_4Cl_2]Cl$ (violet) and *trans*- $[Co(NH_3)_4Cl_2]Cl$ (green). The *cis* and *trans* forms of $[Co(NH_3)_4Cl_2]^+$ complex ion can be structurally represented as shown in Figure 18.17.

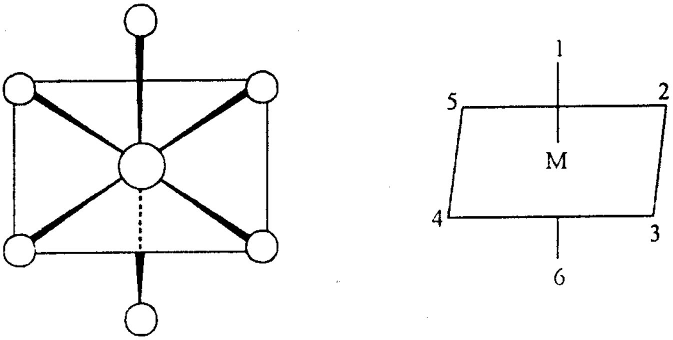
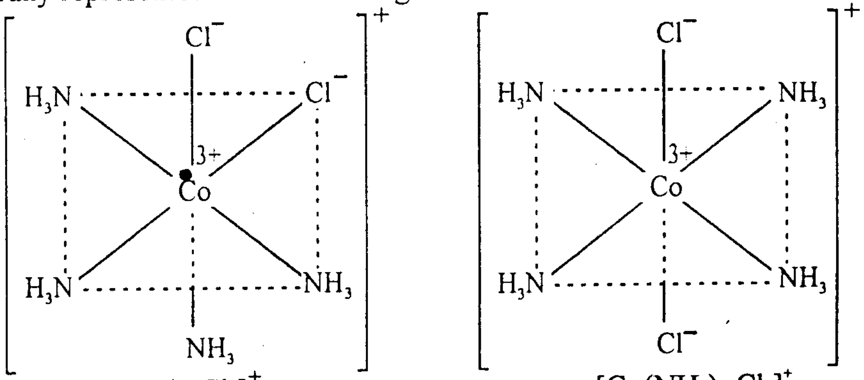


Fig. 18.16. Octahedral Symmetry.

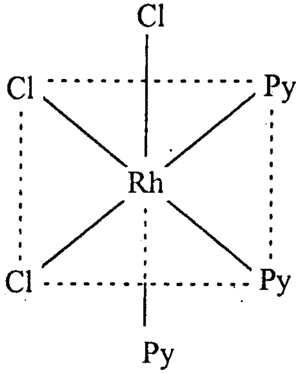


$[Co(NH_3)_4 Cl_2]^+$
Cis-form

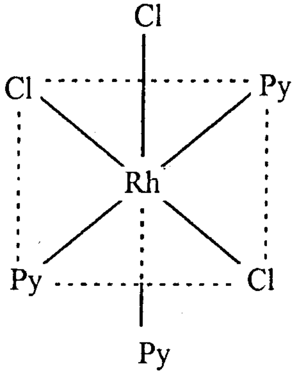
$[Co(NH_3)_4 Cl_2]^+$
Trans-form

Fig. 18.17. Cis and Trans- $[Co(NH_3)_4 Cl_2]Cl$

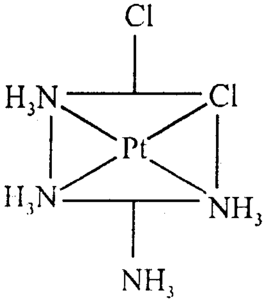
Large number of isomeric forms of complexes of the type $[Ma_4b_2]$, $[M(aa)_2b_2]$ (aa = bidentate ligand) etc., have been prepared. The octahedral complexes of the type $[Ma_3b_3]$ also exhibit *cis*- and *trans*-isomerism *i.e.*,



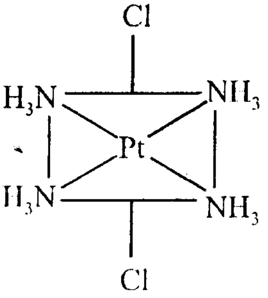
Cis- $[Rh(Py)_3Cl_3]$



Trans- $[Rh(Py)_3Cl_3]$



Cis



Trans

OTHER COORDINATION NUMBERS:

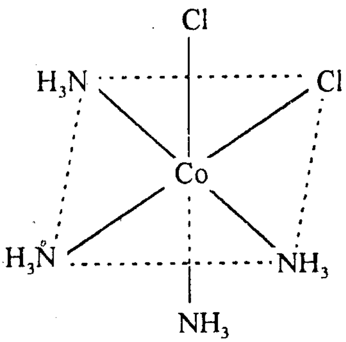
Coordination number 2, 3, 5, 7 and 8 also exist but are not very common:

Coordination number 2 e.g.,	$[Ag(NH_3)_2]Cl$
Coordination number 3 e.g.,	$[HgI_3]^-$, $Pt(Ph_3P)_3$
Coordination number 5 e.g.,	$Ni(CN)_5^{3-}$, $CdCl_5^{3-}$
Coordination number 7 e.g.,	TaF_7^{2-}, $UO_2F_5^{3-}$
Coordination number 8 e.g.,	$Mo(CN)_8^{3-}$, $W(CN)_8^{3-}$

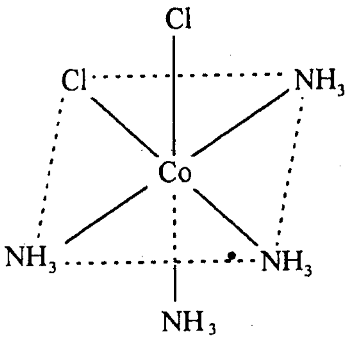
7. Optical Isomerism

The asymmetric (no symmetry) molecules show the property of rotating the plane polarized light (a beam of light vibrating in one plane only) either to left or right. Such molecules or compounds are said to be *optically active*. The isomeric form which rotates the plane polarized light to right is referred to *dextro* (*d*) isomer and that which rotates the light to left is called levo (*l*) isomer. The *d* and *l* mixture is called *racemic mixture*. The separation of two isomers (*d* and *l*) is called *resolution*.

The coordination compounds also show the property of optical isomerism. Some of these compounds exist in *dextro* and *levo* forms due to the presence of asymmetry in their molecules. The structures of such molecules are mirror images of one another and are asymmetric. For example, the *cis*–$[Co(NH_3)_4Cl_2]Cl$ is an asymmetric molecule and would be optically active but *trans*– $[Co(NH_3)_4Cl_2]Cl$ possesses symmetry and would not be optically active. The arrangement of atoms in *cis*-form and presence of *d* and *l* forms is shown as:

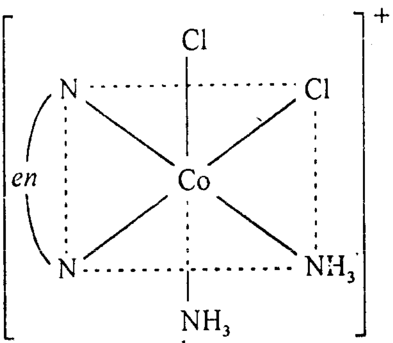


d-form

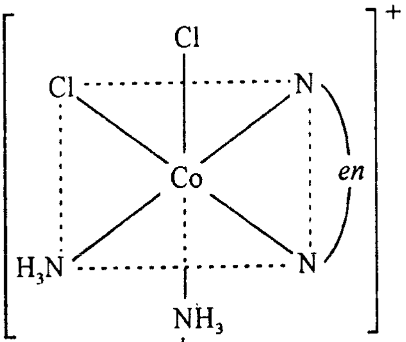


l-form

The complex ion $[Co(en)(NH_3)_2Cl_2]^+$ also exists in dextro and levo forms:

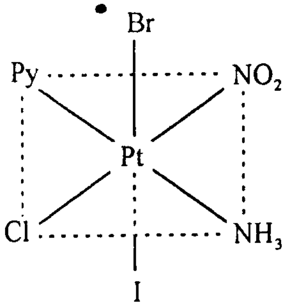


dextro

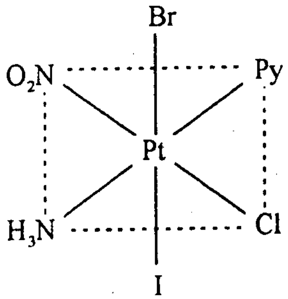


levo

The octahedral complexes containing six different ligands are also found to show optical isomerism. For example, $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$ exists in *d*- and *l*-forms.



dextro



levo

Nomenclature of Coordination Compounds

The following nomenclature is based upon the recommendations by the Inorganic Nomenclature Committee of International Union of Pure and Applied Chemistry (IUPAC).

Nomenclature of various aspects of coordination compounds is as follows:

(a) Order of Listing Ions

The cation is named before the anion; NaCl, sodium chloride.

$K_2[PtCl_6]$, Potassium hexachloroplatinate (IV).

(b) Names of Ligands

Neutral ligands are named as the molecule. Negative ligand end in – *O* and positive ligands end in – *ium*.

$H_2NCH_2CH_2NH_2$	Ethylenediamine
$(C_6H_5)_3P$	Triphenylphosphine
Cl^-	Chloro —
CH_3COO^-	Acetato
$NH_2NH_3^+$	Hydrazinium

Water and ammonia are called *aquo* and ammine, respectively.

(c) Order of Ligands

The ligands are named in the order of (a) negative ligands, (b) neutral ligands, and (c) positive ligands.

$[Pt(NH_3)_4(NO_2)Cl]SO_4$ Chloronitrotetraammineplatinum (IV) sulphate.

(d) Number of Ligands

The number of ligands are designated by prefixes di-(two), tri-(three), tetra-(four) etc. For example, presence of two NH_3 in a complex is indicated by the name diammine, three NH_3 by triammine and so on. The number of complex or chelate ligands are named by using prefixes bis –, tris –, tetrakis, etc.

$[Co(NH_3)_6]Cl_3$	Hexamminecobalt (III) chloride
$[Co(NH_3)_4Cl_2]Cl$	Dichlorotetramminecobalt (III) chloride
$[Co(en)_2Cl_2]Cl$	Dichlorobis (ethylenediamine) cobalt (III) chloride

(e) Oxidation States of Metals

The oxidation states of central metal atoms or ions are indicated by the corresponding Roman numbers (I, II, III, ...) in parentheses at the end of the name of the complex. For a negative oxidation state a minus sign is used.

$Na[Mn(CO)_5]$	Sodium Pentacarbonylmanganate (– I)
$Ni(CO)_4$	Tetracarbonylnickel (O)
$[Pt(NH_3)_2Cl_2]$	Dichlorodiammineplatinum (II)
$K_4[Fe(CN)_6]$	Potassium Hexacyanoferrate (II)

(f) Termination of Names

The anionic complexes are ended with the *–ate* after the name of the metal. In the cationic and neutral complexes the names end without any additions.

$Na[Co(CO)_4$	Sodium tetracarbonylcobaltate (– I)
$[Cr(H_2O)_6]Cl_3$	Hexaaquochromium (III) chloride
$[Ni(DMG)_2]$	Bis(dimethylglyoximato) nickel (II)

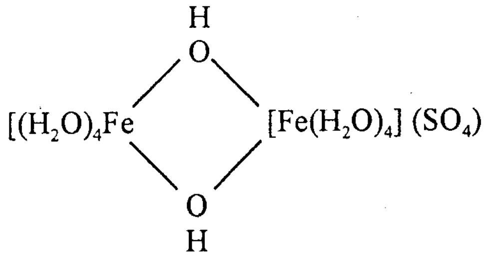
(g) Points of Attachment

Certain ligand molecules can have more than one points of attachment. The point of attachment must be indicated while naming the complexes. For nitrite and thiocyanate ions, the following names may be used which indicate their points of attachment.

$-NO_2^-$, nitro	$-SCN^-$, thiocyanato
$-ONO^-$, nitrito	$-NCS^-$, isothiocyanato

(h) Bridged Complexes

The bridging groups present in the complexes are indicated by using a Greek letter 'μ' before naming these isomers.



Octa-aquo–μ–dihydroxodi iron (III) sulphate

The isomeric forms of complexes are named by using prefixes *cis-* and *trans-* in geometrical isomerism and *d-* and *l-* in optical isomerism.

METAL IONS IN BIOCHEMISTRY

In the last few decades, the study of coordination compounds has grown tremendously in scope. It has now been realized that many important biochemicals are coordination compounds involving metal ions coordinated to organic groups of large size and complexity. This has been realized through modern instrumental techniques. Two important and famous compounds of this type are chlorophyll and hemoglobin. Chlorophyll is green colouring matter of plants which is key to photosynthesis. The heme unit of hemoglobin in blood transports oxygen molecule in the body. The O_2 molecule acts as a ligand and is coordinated to the iron atom of heme during its transport. The fairly complex vitamin, vitamin B_{12} or cobalamin has cobalt atom which is identifiable as Co^{3+} or Co^+ ion.

Enzymes are natures' catalysts for speeding up chemical reactions in the body to 100,000 times faster rates that would occur without catalysts. Many enzymes contain metal ions incorporated into the protein structure of the enzyme, called metalloenzymes. These are metal-activated enzymes. Some enzymes require the reversible coordination of metal ions in order to become active and are called metal-activated enzymes which are essential for animal life. The d-block metals with variable oxidation states are particularly useful in catalyzing biological oxidation-reduction reactions.

Metal ions can change the whole conformation of an enzyme or biomolecules containing negatively charged functional groups that are close together, such as triphosphate ion groups in DNA (Deoxyribonucleic acid) and RNA (Ribonucleic acid). In the absence of the charged metal ions, DNA and RNA double helices tend to unwind due to the repulsion of the triphosphate groups. The mutual attraction of the negatively charged triphosphate groups to the weakly acidic Mg^{+2} ions help retain the double helix.

The K^+, Na^+, Ca^{2+} and Mg^{2+} ions trigger and control certain biochemical mechanisms. The passage of Na^+ ions across nerve cell walls constitutes an electrical current involved in nerve impulse transmission.

Questions

1. Differentiate between a double salt and a complex compound. Elaborate your answer with suitable examples.
2. What are transition metals? Why do they occur in the Periodic Table where they are? Discuss their characteristic features.
3. Discuss the various aspects of the elements of First Transition Series.

4. (a) Describe what happens when ammonia is added to aqueous solution of cupric salt.
   (b) Why AgCl is soluble in NH_3?
   (c) What happens when BF_3 is passed through $(Me)_3N$?
5. Identify the types of stereoisomerism exhibited by the following complex ions or compounds:
   (a) Dichlorodiamminecopper (II).
   (b) Tetrachlorodiamminecobalt (III).
   (c) Dichlorotetramminecobalt (III).
   (d) Tris (ethylenediamine) platinum (IV).
6. Write formulae of the following complex ions or compounds:
   (a) Tetrammine copper (II) sulphate.
   (b) Di-pyridyl-bis (ethylenediamine) cobalt (III) ion.
   (c) Monochloropentamminecobalt (II) chloride.
   (d) Hexacyanoferrate (II) ion.
   (e) Tetracyanodiaquoferrate (III) ion.
   (f) Octa-amine – μ – amido – μ – hydroxodicobalt (III) sulphate.
   (g) Sodium tetracyanonickel (II).
   (h) Tris (ehtylenediamine) chromium (III).
7. Give the systematic names of the following compounds:
   (a) $K_5[Mn(CN)_6]$ (b) $K_2[Fe(CN)_6]$
   (c) $[Co(NH_3)_6]Cl_3$ (d) $[Co(NH_3)_4Cl_2]Cl$
   (e) $[Pt(NH_3)_4Cl_2]Cl_2$ (f) $[Cu(NH_3)_4]SO_4$
   (g) $[Cr(en)_2Cl_2]^+$ (h) $[Co(NO_2)_3(OH)_3]^{3-}$
   (i) $K_2[PtCl_6]$ (k) $Fe(CO)_5$
8. What do you mean by the coordination number of the central metal atom or ion? Give suitable examples to support your answer.
9. (a) What are the postulates of Werner's theory?
   (b) How does it account for the behaviour of:

$$CoCl_3 . 6H_2O, CoCl_3 . 5H_2O, CoCl_3 . 4H_2O?$$

10. How is Werner's theory explained in the view of the electronic theory of valency? What are its drawbacks as applied to coordination compounds?
11. What type of elements are able to give coordination compounds? Why?
12. Give a list of electron donors which may enter into complex formation.
13. What are chelates? Give four examples of such compounds and draw their structures.
14. How would you classify chelates? What factors give stability to chelate compound? Discuss their importance.

15. What is isomerism? Distinguish between ionization, coordination and polymerization isomerism.
16. Draw the diagrammatic structures of the isomers of $[Cr(en)_2Cl_2]^+$.
17. Discuss the possibility of stereoisomerism in coordination compounds. What type of complexes are expected to give this type of isomerism?
18. How many isomers are possible for $[Co(NH_3)_4Cl_2]^+$.
19. What type of complexes would give optical isomers? Discuss their structures.
20. How are the structures of coordination compounds explained on the basis of valence bond theory? Explain with respect to $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$. What are limitations of this theory?
21. Draw molecular orbital diagrams of $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$. How is the paramagnetic character of complexes obtained on the basis of molecular orbital theory?
22. Discuss the essentials of crystal field theory. What are the merits of this theory? How can we explain the colour of complexes on the basis of this theory?
23. What is crystal field splitting? What does it depend upon? How would you proceed to calculate the crystal field stabilization of a complex?
24. Distinguish between cast iron, wrought iron and steel. Describe the blast furnace for the manufacture of pig iron.
25. Describe Bessemer Process for the manufacture of steel from cast iron with special emphasis on various reactions.
26. Give the open-hearth process for the manufacture of steel. Compare the Open-Hearth process with Bessemer process.
27. Give an account of the metallurgy of iron. Discuss various chemical reactions which take place in the blast furnace.
28. Describe a process for converting pig-iron into steel together with the nature of chemical changes involved.
29. How is steel manufactured? Describe the reaction taking place in blast furnace.
30. **Give short answers to the following questions:**
    (i) Give the electronic configuration of the following transition elements with atomic numbers in brackets:
    (a) Ti(22) (b) Cr(24) (c) Fe(26) (d) Cu(29)
    (ii) What are the characteristics of *d*-block elements?
    (iii) How is Cast iron manufactured?
    (iv) What is Wrought iron? How is it manufactured?
    (v) How in Steel manufactured by Bessemer process?
    (vi) How in Steel manufactured by Open-Hearth process?

(vii) What are the advantages of Open-Hearth process over Bessemer process?

(viii) What are alloy steels? Give some examples.

(ix) What is the general chemistry of 1st Transition Series?

(x) What is the nature of Coordinate bond?

(xi) Give postulates of Werner's Theory.

(xii) What are the applications of Werner's Theory?

(xiii) What are the electronic interpretation of the structures of coordination compounds?

(xiv) How Valence Bond Theory is applied to structural aspects of 6-coordinate complexes?

(xv) How Valence Bond Theory is applied to structural aspects of 4-Coordinate complexes?

(xvi) How the magnetic properties of transition metal complexes are explained on the basis of Valence Bond Theory?

(xvii) What are the limitations of Valence Bond Theory?

(xviii) How Molecular Orbital Theory is applied to explain the structure of transition metal complexes?

(xix) What is Crystal Field Theory? How is it applied to explain the colour and absorption spectra of complexes?

(xx) What are Chelates? Draw structures of some important chelates.

(xxi) What are the factors which influence the stabilities of chelates?

(xxii) What is the importance of coordination compounds in chemistry?

(xxiii) What are the types of isomerism depicted in coordination compounds?

(xxiv) Discuss stereoisomerism depicted by coordination compounds.

(xxv) What is optical isomerism? What type of coordination compounds depict optical isomerism?

(xxvi) Discuss important aspects of nomenclature of coordination compounds.

31. **Give the correct answers:**

(i) *d*-block elements show strong paramagnetic properties because:

(a) these atoms have all paired electrons

(b) these atoms have all unpaired electrons

(c) these atoms have a number of unpaired electrons

(d) these atoms have a number of paired electrons

(Ans: c)

(ii) *d*-bock elements show catalytic activity because:
(a) of their large surface area
(b) of their large atomic volume
(c) of their ability to exist in multiple oxidation states
(d) of their ability to form coloured compounds **(Ans: c)**

(iii) *d*-block elements form coloured compounds because their ions:
(a) cannot absorb the colours of these radiations
(b) involve *d* transition which falls in the visible region
(c) involve *d*-*d* transitions which fall in the visible region
(d) involve *d*-*s* transition in the visible region **(Ans: c)**

(iv) *d*-block elements form coordination compounds because of:
(a) small cationic size (b) large ionic charge
(c) unfilled *d*-orbitals (d) filled *d* orbitals
(Ans: c)

(v) The outer shell configuration of Cr is:
(a) $3d^4\,4s^2$ (b) $3d^5\,4s^1$
(c) $3d^3\,4s^2\,4p^1$ (d) $3d^6\,4s^0$ **(Ans: a)**

(vi) The number of unpaired electrons in Cr atom is:
(a) 2 (b) 3
(c) 4 (d) 5
(e) 6 **(Ans: e)**

(vii) Stainless steel contains:
(a) 12% Cr and 0.3% C (b) 12% Cr and 1% C
(c) 18% Cr and 9 % Ni (d) 10% Cr and 6% V
(Ans: c)

(viii) The principal oxidation states shown by Cr are:
(a) +2, +3, +4 (b) +2, +4, +6
(c) +2, +3, +5 (d) +2, +3, +6 **(Ans: d)**

(ix) The conversion of CrO_4^{2-} into $Cr_2O_7^{2-}$ is brought about by:
(a) H_2O (b) NH_3
(c) NaOH (d) H_2SO_4 **(Ans: d)**

(x) The outer shell configuration of Mn is:
(a) $3d^5\,4s^2$ (b) $3d^6\,4s^1$
(c) $3d^4\,4s^2\,4p^1$ (d) $3d^7\,4s^0$ **(Ans: a)**

(xi) Which of the following transition metals show largest number of oxidation states:
(a) Cr (b) V
(c) Mn (d) Ti **(Ans: c)**

(xii) An acidified solution of $KMnO_4$ gives a yellow precipitate with:
(a) SO_2 (b) SO_3
(c) KI (d) H_2S **(Ans: d)**

(xiii) It is dangerous to add $KMnO_4$ to hot conc. H_2SO_4 because:
(a) explosive MnO_2 is formed
(b) explosive $MnSO_4$ is formed
(c) explosive Mn_2O_7 is formed
(d) K_2MnO_4 is formed explosively **(Ans: c)**

(xiv) The outer shell electronic configuration of Fe is:
(a) $3d^5\,4s^2$ (b) $3d^6\,4s^2$
(c) $3d^8\,4s^0$ (d) $3d^7\,4s^2$ **(Ans: b)**

(xv) An alloy used for making surgical instruments is:
(a) silicon steel (b) stainless steel
(c) Mond steel (d) nichrome **(Ans: b)**

(xvi) Nickel is purified by:
(a) Krolli process (b) Mond's process
(c) Haber process (d) Van Arkel's process
(Ans: b)

(xvii) Cobalt chloride paper provides a test for the presence of:
(a) NH_3 (b) CO
(c) CO_2 (d) H_2O **(Ans: d)**

(xviii) Brass is an alloy of:
(a) Cu and Zn (b) Cu, Ni, Zn
(c) Cu and Ni (d) Cu, Al, Zn **(Ans: c)**

(xix) Fool's gold is:
(a) gold (b) KI
(c) copper glance, Cu_2S (d) iron pyrites, FeS_2
(Ans: d)

(xx) When AgCl dissolves in NH_3, the principal cations produced are:
(a) $Ag(NH_3)_2^{2+}$ (b) $[Ag(NH_3)]^+$
(c) $[Ag(NH_3)_4]^+$ (d) NH_4^+ **(Ans: a)**

(xxi) The roasting of metal is due to:

(a) burning (b) combustion

(c) slow oxidation (d) slow reduction(**Ans:** c)

(xxii) The number of unpaired electrons in Ti^{4+} ion are:

(a) 2 (b) 3

(c) 5 (d) 0 (**Ans:** d)

(xxiii) Oxidation state of zero is shown in:

(a) $Fe(CO)_5$ (b) CrO_2Cl_2

(c) $K_4[Fe(CN)_6]$ (d) $Na_2Ni(CN)_4$ (**Ans:** a)

(xxiv) The existence of Cu^+ ions in aqueous solution is very rare owing to its ready:

(a) oxidation (b) reduction

(c) disproportionation (d) dimerisation (**Ans:** a)

(xxv) The highest oxidation state of Fe is:

(a) +2 (b) +3

(c) +6 (d) +8 (**Ans:** c)

(xxvi) In which of the following complexes silver has an oxidation state of +3:

(a) $Ag(NH_3)_2Cl$ (b) $NaAg(CN)_2$

(c) $Na_3Ag(S_2O_3)_2$ (d) $KAgF_4$ (**Ans:** d)

(xxvii) The highest magnetic moment is exhibited by the transition metal ions with the following configuration:

(a) $3d^2$ (b) $3d^5$

(c) $3d^7$ (d) $3d^8$ (**Ans:** b)

(xxviii) Rust is:

(a) $FeO + Fe(OH)_2$ (b) $Fe_2O_3 + Fe(OH)_2$

(c) Fe_2O_3 (d) $Fe_2O_3 + Fe(OH)_3$

(**Ans:** c)

(xxix) Which of the following transition metals show the highest oxidation state?

(a) Fe (b) Mn

(c) V (d) Cr (**Ans:** b)

(xxx) Chromium has the most stable oxidation state:

(a) +3 (b) +4

(c) +5 (d) +6 (**Ans:** d)

(xxxi) Element of atomic number 24 is placed in Periodic Table in:

(a) *s*-block (b) *p*-block

(c) *d*-block (d) *f*-block **(Ans: c)**

(xxxii) The 3rd transition series have atomic numbers:

(a) 44 – 75 (b) 21 – 30

(c) 39 – 48 (d) 57 – 80 **(Ans: d)**

(xxxiii) Which of the following is diamagnetic ion?

(a) Ti^{4+} (b) V^{3+}

(c) Cr^{3+} (d) Co^{2+} **(Ans: a)**

(xxxiv) Which of the following ions forms most stable complex compound?

(a) Cu^{2+} (b) Ni^{2+}

(c) Fe^{2+} (d) Mn^{2+} **(Ans: c)**

(xxxv) The effective atomic number of Cr(24) in $Cr(NH_3)_6Cl_3$ is:

(a) 18 (b) 36

(c) 54 (d) 86 **(Ans: b)**

(xxxvi) The name of the complex $[Co(en)_2 Cl_2]Cl$ is:

(a) Trichlorodiethylene cobalt (II)

(b) Dichlorobis (ethylenediamine) cobalt (II) chloride

(c) Diethylenediaminedichloro cobalt (II) chloride

(d) Dichlorobis (ethylenediamine) cobalt (III) chloride

(Ans: d)

* * 18 * *

19

NUCLEAR CHEMISTRY

The chemical properties of elements depend upon the electronic arrangements of the atoms and the behaviour of electrons in the valency shells. Nothing happens to the nuclei of the atoms during chemical changes.

Recently, a new type of transformation of matter involving changes in the atomic nuclei is studied under a new branch of chemistry called Nuclear Chemistry. *Nuclear Chemistry is the study of properties, compositions and reactions of the atomic nuclei.*

The atoms of certain elements (uranium and radium) undergo spontaneous disintegration to produce atoms of other elements along with emission of radioactive rays. In 1895, Becquerel discovered that uranium salt, potassium uranyl sulphate, $[K_2UO_2(SO_4)_2]$ gave out rays which affected photographic plates kept in darkness and wrapped in a black paper. These rays are called *radioactive rays* and the phenomenon is called *radioactivity*. *Radioactivity is the phenomenon of spontaneous production of invisible rays from chemical substances. The invisible rays affect the photographic plate and ionize the gas or air through which they pass.*

Radioactive substances emit three type of rays:

(a) α-Rays (Alpha rays)

1. These rays are actually helium nuclei having charge $+2(He^{+2})$.
2. The kinetic energy of α-rays is between 3 to 9 MeV. They cannot penetrate the matter to large extent. They are obstructed even by thick paper.
3. The velocity of α-rays is about 20,000 miles per hour. They ionize the air while passing through it.
4. They are deflected from straight path by a magnetic or electric field indicating their positive charge.

(b) β-Rays (Beta rays)

1. They are negatively charged and are actually electrons having negative charge.
2. They are deflected from straight path by a magnetic or electric field indicating their negative charge.
3. β-rays are more penetrating than α-rays. A 3 mm. thick lead plate will be able to obstruct them.
4. The velocity of β-rays is almost equal to the velocity of light.
5. They ionize the air or molecules while passing through them.

(c) γ-Rays (Gamma rays)

1. They are photons and consist of electromagnetic radiations.
2. They travel with the velocity of light and have strong penetrating power.
3. These rays do not carry any charge and therefore, are not deflected by magnetic and electric fields.
4. They ionize the air or gas while passing through it.

Natural Radioactivity

Rutherford and Soddy suggested that radioactivity (of uranium) involves a decomposition of its nuclei into other elements. The alpha, beta and gamma rays are emitted from the nucleus during the course of this transformation. The spontaneous decomposition of uranium into thorium involves the emission of alpha rays in the first step as:

$$\underset{\begin{pmatrix}\text{Mass No.} = 238\\ \text{Atomic No.} = 92\end{pmatrix}}{\text{Uranium}} \longrightarrow \underset{\begin{pmatrix}\text{Mass No.} = 234\\ \text{Atomic No.} = 90\end{pmatrix}}{\text{Thorium}} + \underset{\begin{pmatrix}\text{Mass No.} = 4\\ \text{Atomic No.} = 2\end{pmatrix}}{\alpha\text{-Particle}}$$

This change may be represented as:

$${}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$$

It should be noted that the sum of the atomic numbers and atomic masses of reactants and products should be equal.

Radioactivity is a nuclear property and is independent of the state of chemical combination or physical conditions. Thus, uranium will have the same radioactivity whether it is in metallic, solution, solid or mineral form. It has been seen that ${}_{92}U^{238}$ disintegrates with the emission of α-rays. The thorium isotope, Th^{234} disintegrates with emission of β-rays to give proactinium (Pa^{234}).

$${}_{90}Th^{234} \longrightarrow {}_{91}Pa^{234} + {}_{-1}e^{0} \ (\beta\text{-rays})$$

Group Displacement Law

The emission of α and β-rays from atomic nuclei of radioactive elements gives rise to the displacements in positions of the products of disintegration in the Periodic Table. This is due to the change in atomic number of the parent element. These displacements of the elements of disintegration are described by Group Displacement Law. It states that:

1. *When an element emits an α-particle, the product obtained moves to the left of the Periodic Table by two positions (Atomic No. decreases by 2) and mass of the element is decreased by 4 units.*
2. *When an element emits a β-particle, the product moves by one position to the right (higher) in the Periodic Table (Atomic No. increase by 1).*

Radioactive elements may undergo successive disintegrations to give a chain of species known as *radioactive series*. There are three naturally occurring radioactive series which include most of the naturally occurring elements:

1. The Uranium series.
2. The Actinium series.
3. The Thorium series.

These three series undergo transformations from the parent elements (U, Ac and Th) to the end product of stable isotopes (Table 19.1).

TABLE 19.1

The Uranium Series	The Actinium Series	The Thorium Series
$_{92}U^{238}$ $\downarrow \alpha$ $_{90}Th^{234}$ $\downarrow \beta$ $_{91}Pa^{234}$ $\downarrow \beta$ $_{92}U^{234}$ $\downarrow \alpha$ $_{90}Th^{230}$ $\downarrow \alpha$ $_{88}Ra^{226}$ $\downarrow \alpha$ $_{86}Rn^{222}$ $\downarrow \alpha$ $_{84}Po^{218}$ $\downarrow \alpha$ $_{82}Pb^{214}$ $\downarrow \beta$ $_{83}Bi^{214}$ $\downarrow \beta$ $_{84}Po^{214}$ $\downarrow \alpha$ $_{82}Pb^{210}$ $\downarrow \beta$ $_{83}Bi^{210}$ $\downarrow \beta$ $_{84}Po^{210}$ $\downarrow \alpha$ $_{82}Pb^{206}$ (Stable)	$_{92}U^{225}$ $\downarrow \alpha$ $_{90}Th^{231}$ $\downarrow \beta$ $_{91}Pa^{231}$ $\downarrow \alpha$ $_{89}Ac^{227}$ $\alpha \swarrow \quad \searrow \beta$ $_{87}Fr^{223} \qquad _{90}Th^{227}$ $\beta \nwarrow \quad \nearrow \alpha$ $_{88}Ra^{223}$ $\downarrow \alpha$ $_{86}Rn^{219}$ $\downarrow \alpha$ $_{84}Po^{215}$ $\downarrow \alpha$ $_{82}Pb^{211}$ $\downarrow \beta$ $_{83}Bi^{211}$ $\downarrow \beta$ $_{84}Po^{211}$ $\downarrow \alpha$ $_{82}Pb^{207}$ (Stable)	$_{90}Th^{232}$ $\downarrow \alpha$ $_{88}Ra^{228}$ $\downarrow \beta$ $_{89}Ac^{228}$ $\downarrow \beta$ $_{90}Th^{228}$ $\downarrow \alpha$ $_{88}Ra^{224}$ $\downarrow \alpha$ $_{86}Rn^{220}$ $\downarrow \alpha$ $_{84}Po^{216}$ $\downarrow \alpha$ $_{82}Pb^{212}$ $\downarrow \beta$ $_{83}Bi^{212}$ $\downarrow \beta$ $_{84}Po^{212}$ $\downarrow \alpha$ $_{82}Pb^{208}$ (Stable)

Equation of Radioactive Disintegration or Decay

The rate of radioactive disintegration is independent of all physical and chemical characteristics. The rate of radioactive disintegration is a first order reaction.

The rate of disintegration of a radioactive element at any time is proportional to the number of atoms of the element present at that time.

If N is the number of atoms of a radioactive element present at time t, the number of atoms present in a small interval of time dt would be dN. The rate of disintegration would be $-\frac{dN}{dt}$ (minus sign indicates that the amount decreases with time).

Rate of disintegration $\left(-\frac{dN}{dt}\right)$ would be proportional to N (the total amount of radioactive element). Thus,

$$-\frac{dN}{dt} \ \alpha \ N$$

or $$-\frac{dN}{dt} = KN$$

K is called *decay* or *disintegration constant*. If $dt = 1$ second, we have,

$$-dN = KN$$

or $$-\frac{dN}{N} = K$$

Hence, K or the decay constant is defined as the fraction of the total *number of atoms of the radioactive element which disintegrates per second.* The value of K is characteristic of the radioactive disintegration. However, the most dependable property of a radioactive substance is its *half-life.*

Half-Life

The half-life of a radioactive element is the time required to disintegrate one half of it. A radioactive element would disintegrate in proportion to its quantity present at that time. So, the half-life would also mean the time required to get 50% of the total activity of the radioactive element of a given amount. If Nt is the number of atoms present at times t and No, the number of atoms initially present,

$$\frac{Nt}{No} = \frac{1}{2} = 0.5$$

or $$\ln\frac{1}{2} = -Kt\frac{1}{2}$$

$$\begin{aligned}
\text{or} \qquad Kt\frac{1}{2} &= -2.303 \log\frac{1}{2} \\
&= -2.303 \log 2 = 0.693 \\
\text{or} \qquad t\frac{1}{2} &= \frac{0.693}{K}
\end{aligned}$$

Half-life of a radioelement is independent of its total mass. The half-life of radium is 1590 years and that of U^{238} is 4.5×10^9 years but Po^{214} has $t\frac{1}{2} = 19^{-8}$ seconds.

If a radioactive substance has half-life of one day and we have 100 grams of it, 50 grams would be left after one day, 25 grams of it after 2 days and 12.5 grams after the end of 3 days and so on.

Units of Radioactivity

Curie is the unit of radioactivity. A curie is defined as the quantity of a radioactive substances which undergoes 3.7×10^{10} disintegrations per second.

Artificial Radioactivity

Some of the elements do not disintegrate as such but are made to disintegrate by the bombardment of high energy α-particles or neutrons. Sometimes, these elements are found to retain the radioactive phenomenon even after the removal of α-rays etc., source. *The process of getting radioactive products by the bormbardment of high energy particles is generally called artificial radioactivity.*

Artificial radioactivity gained by the bombardment of particles is exemplified below:

1. **By the bombardment of neutrons:**

$$\begin{aligned}
{}_7N^{14} + {}_0n^1 &\longrightarrow {}_6C^{14} + {}_1H^1 \\
{}_{47}Ag^{107} + {}_0n^1 &\longrightarrow {}_{47}Ag^{108}
\end{aligned}$$

2. **By the bombardment of alpha particles:**

$$\begin{aligned}
{}_5B^{10} + {}_2He^4 &\longrightarrow {}_7N^{13} + {}_0n^1 \\
{}_{12}Mg^{24} + {}_2He^4 &\longrightarrow {}_{14}Si^{27} + {}_0n^1
\end{aligned}$$

3. **By the bombardment of deuterons:**

$$\begin{aligned}
{}_{12}Mg^{24} + {}_1H^2 &\longrightarrow {}_{11}Ne^{22} + {}_2He^4 \\
{}_3Li^7 + {}_1H^2 &\longrightarrow {}_4Be^8 + {}_0n^1
\end{aligned}$$

4. **By the bombardment of protons:**

$$\begin{aligned}
{}_8O^{18} + {}_1H^1 &\longrightarrow {}_9F^{18} + {}_0n^1 \\
{}_5B^{11} + {}_1H^1 &\longrightarrow {}_2He^4 + {}_4Be^8
\end{aligned}$$

Measurement of Radiation

Radiations emitted from radioactive material is measured by means of detectors. The main type of nuclear radiations are:

(a) charged particles *i.e.*, protons, alpha and beta particles;

(b) uncharged particles *i.e.*, neutrons;

(c) electromagnetic radiations.

The basic principle of detectors is ionization technique or excitation of atoms.

Ionization Technique :

The principle of ionization technique is that charged particles are passed through a gaseous medium *e.g.*, air, CO_2, N_2, argon etc., which causes ionization of the gas. The intensity of the incident radiation can be measured by collecting the ions.

The ionization chamber consists of an inert gas filled in a container closed at both ends and fitted with a thin mica window at one end. The electrode system containing a central rod acts as positive end and outer metal cylinder to negative end of the d.c. supply (Fig. 19.1).

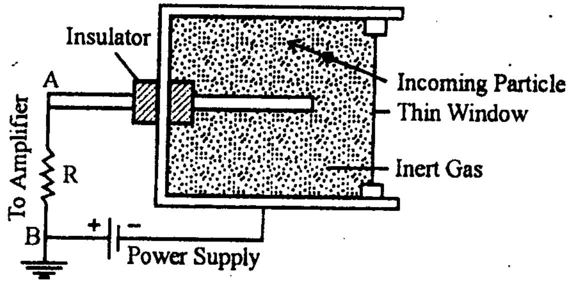


Fig. 19.1. Ionisation chamber.

The radiation to be detected is passed through the mica window. As soon as radiation enters the container, ionization of inert gas already in the chamber takes place. The number of ion pairs produced are proportional to the intensity of radiation. The negative particles or electrons are attracted towards the positive end on central rod. The positive ions are accelerated towards the negative ends of outer metal cylinder. An e.m.f. appears across the rod and the container and produces a current, *i*.

$$i = 2ne / CR$$

Where *ne* is number of positive (*ne*) and negative (*ne*) charges, C is capacity of electrodes and R is the resistance.

Different types of particles of the same energy produce different ionization currents in travelling through the chamber at the same pressure. So Ionization

Chambers are used to measure the radiation due to charged particles like electrons, protons, positrons, beta-particles, X-rays.

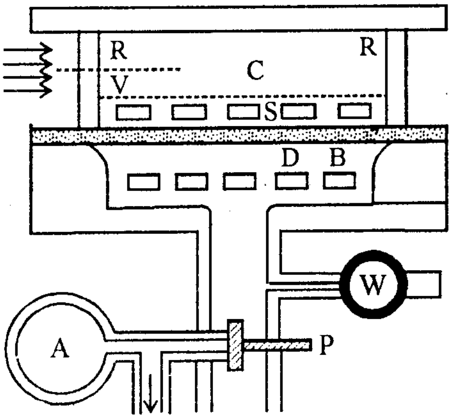
Commonly used detectors are:

(i) Wilson's Cloud Chamber

(ii) Geiger-Muller Counter

(i) Wilson's Cloud Chamber

Wilson developed a cloud chamber in which the tracks of charged particles can be seen. The principle of this technique is that when a gas containing vapours at saturation pressure is expanded suddenly it gets cooled and becomes supersaturated. In presence of dust particles, droplets are formed around the dust particles. In a dust free atmosphere condensation could be produced on a negative ion present in the gas and expansion of gas is made 1.31 – 1.4 times its volume.



To Vacuum Pump

Fig. 19.2. Wilson's Cloud Chamber.

The Wilson's Cloud Chamber consists of a cylindrical glass chamber, C. It is provided with a glass plate cover and a perforated metal plate base. The metal plate is covered by a dark velvet cloth V. Water is sprinkled on velvet cloth to provide water vapour to saturate the air in the chamber, C. The rubber diaphragm D forms an air-tight seal between chamber C and space S below it. A is an evacuated container kept closed by a piston P (Fig 19.2).

Operation

When a piston P is withdrawn, the space S is connected to the container A. The pressure in S suddenly falls. This pulls down the diaphragm D, and the air in the chamber C undergoes expansion. After expansion, container A is closed by the piston P and air is slowly admitted into the space S through a small valve V. The diaphragm R goes to its original position. The pressure in the chamber C reverts to its original value. The second perforated plate B is kept below the diaphragm D and expansion ratio adjusted.

The water droplets are condensed on charged ions. The Chamber is illuminated and tracks can be viewed through the top glass plate and photographed. After that potential difference is adjusted to 100V and electric field sweeps the ions from the chamber. The chamber is then made ready for next operation.

Alpha-particles ionize to large extent and produce thick tracks. Beta particles ionize to less ionization and tracks are thin.

Demerits

1. It is not practicable to build Cloud Chamber large enough to show the entire path of an extremely high energy particle.
2. High energy bubble chambers or photographic emulsions have to be used to observe the tracks.
3. The Cloud Chamber is less sensitive as the duration of super saturation is of the order of one second.

(ii) Geiger-Muller Counter

Geiger and Muller designed the device in 1928 and is still considered to be an efficient detector. It consists of a number of ionization chambers with high field applied to one of the electrodes. Due to high voltages, electrons produced by ionization are accelerated to such a high velocity that they further produce ionization by collision with the neutral molecules. So ion pairs are sharply multiplied to $10^4 - 10^6$ times. This process is called amplification and giyes rise to greater ionization current. So the device becomes highly sensitive.

Operation

C is metal chamber containing air or some other gas at a pressure of about 10 cms of Hg. W is a fine tungsten wire along the axis of the tube, which is insulated from the tube by ebonite plugs E. The wire is kept at a high positive potential of about 1000-3000 volts maintained between the wire and the chamber. Few ions are produced first but due to high potential difference these ions are multiplied and electrons thus produced move towards the central wire, which gives a small current impulse which flows through resistance R (Fig. 19.3). The critical potential is lowered suddenly and a discharge passes through resistance R. Such discharge clears the ions from the chamber and the counter is ready to register the next particle.

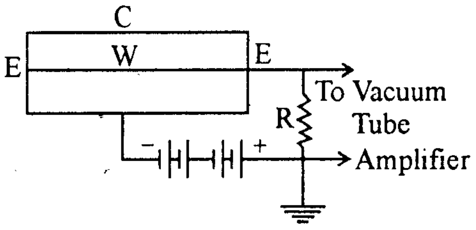


Fig. 19.3. Geiger-Muller counter.

A plot of the count rate of particles and voltage is shown in Fig. 19.4. There is a threshold applied voltage below which the counter does not work. When applied field is increased a continuous discharge takes place and count rate increases rapidly.

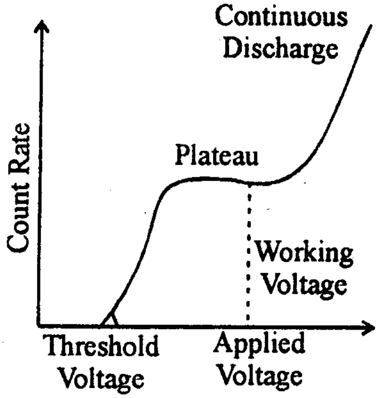


Fig. 19.4. Applied voltage vs. Count rate.

Merits

(1) Geiger-Muller counter produces a large pulse which requires no further amplification.

(2) The pulse size is independent of the nature of incident radiation.

(3) The technique is very sensitive.

(4) The radiation serves only to trigger a discharge.

Demerits

(1) The counter is not sensitive for very high counting rates.

(2) It cannot provide information about the nature of the particle which causes a pulse.

Scintillation Counters

When alpha-particles strike the fluorescent screen, tiny flashes of light called scintillations are produced. The energy of the particles is converted into light energy.

The scintillation counters consist of a phosphor material which produces a tiny flash of light when a charged particle is passed through it. Anthracene, naphthalene or sodium chloride saturated with silver and silver iodide activated with thallium can be used a phosphor. The flashes of light fall on photo sensitive cathode of photomultiplier tube. The photomultiplier tubes emit electrons which are proportional to the energy of the particles and can be measured.

Nuclear Reactions: Nuclear reactions include nuclear fission and nuclear fusion.

When ${}_{92}U^{235}$ is bombarded with slow neutrons the uranium nucleus is split into two fragments. Such process is called *nuclear fission.*

$$ {}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 2 \text{ to } 3\,{}_{0}n^{1} + E $$

The products written on the right side of equation are called *fission products*. In this type of process loss of mass occurs which releases large amount of energy according to the equation $E = mc^2$. If we take equal weight of U^{235} and C to get energy, uranium will produce 2.5 million times more energy.

The neutrons produced along with the products of the nuclear fission would initiate further reaction and *a chain process* would start.

Nuclear Reactors and Atomic Energy

The system of producing self-sustaining nuclear reaction is referred to as *atomic reactor* or *pile* or *nuclear reactor*. The chain process can be controlled by means of substances called *moderators*, such as graphite, heavy water or water. They lower down the speed of neutrons.

Nuclear reactors are essentially sources of neutrons under controlled conditions. They are used to produce radioactive isotopes such as Co^{60}, P^{32} and C^{14} etc.

Atomic Energy

The heat energy generated during the fission reaction in atomic reactor can be utilised for power production through dynamos and turbines. The technological advancements regarding atomic energy as a source of energy would play an important role in near future. The uncontrolled nuclear chain reaction results in ultimate liberation of tremendous amount of heat and other forms of energy which is the principle of atom bomb. In this connection the *critical mass* of the fissionable material is essentially attained.

Nuclear Fusion (The Hydrogen Bomb)

Two or more nuclei may fuse to produce new nuclei and the process is called *nuclear fusion*. Nuclear fusion involving hydrogen and its isotopes is an exothermic reaction. Examples of nuclear fusion reactions are:

$$ {}_{1}H^{2} + {}_{1}H^{3} \longrightarrow {}_{2}He^{4} + {}_{0}n^{1} $$

$$ {}_{1}H^{3} + {}_{1}H^{3} \longrightarrow {}_{2}He^{4} + 2\,{}_{0}n^{1} $$

$$ {}_{3}Li^{7} + {}_{1}H^{2} \longrightarrow 2\,{}_{2}He^{4} + {}_{0}n^{1} $$

Fusion reactions are highly exothermic and release tremendous amounts of energy and are used in hydrogen bombs. Large amounts of energy are required to start these reactions. High energy required for fusion may be derived from the nuclear fission.

It is believed that solar energy is due to a series of hydrogen fusion reactions taking place in the sun. Hydrogen is transformed to He with the release of large amounts of energy.

$$4\,{}_1H^1 \longrightarrow {}_2He^4 + 2e^+ + \gamma$$

The two positrons ($2e^+$) and two electrons interact and release large amount of energy.

DIFFERENTIATION BETWEEN NUCLEAR FISSION AND FUSION

NUCLEAR FISSION	NUCLEAR FUSION
1. Nuclei of heavy elements undergo fission.	1. Nuclei of light elements are in involved in the process of fusion.
2. Heavy nuclei split into lighter nuclei of comparable atomic masses.	2. Lighter nuclei fuse to form heavy nuclei.
3. The reaction initiates at normal temperatures.	3. Fusion initiates at 10^8 K.
4. The fission process liberates about 200 MeV energy.	4. The energy released in 24 MeV.
5. Nuclear fission can be controlled and can be used for peaceful purposes.	5. The reaction cannot be controlled.
6. Efficiency of energy conversion is low.	6. Efficiency of energy conversion is high.
7. Fission products are radioactive and dangerous.	7. Fusion products are not radioactive.
8. Fast neutrons are also released.	8. Nature of the ejected particles depends upon the type of thermonuclear reaction.
9. Probability of fission depends on the nuclear cross-section of slow neutrons.	9. Probability of fusion depends on temperature and density of plasma.
10. Fuel is either solid or liquid.	10. Fuel is in plasma state.
11. Fuel can be stored for any length of time.	11. Fuel cannot be stored.
12. Sum of atomic masses of the fission products is less than the mass of the fissile element.	12. Sum of the masses of fusionable isotopes is greater than the compound nucleus formed on fusion.
13. The reaction can be made self-sustained and chain reaction is possible.	13. A high temperature has to be maintained to fuel materials.

Transuranium Elements

Uranium (Atomic No. 92) was the last element known uptil 1940. Afterwards, a few other elements were artificially prepared from uranium (U^{238}) by bombarding it with high velocity electrons or deuterons or neutrons. *The elements which are made artificially and occur after uranium in the Periodic Table are known as transuranium elements.* The higher transuranium elements up to atomic number 104 have been reported and are usually prepared as shown by the following reactions:

$$_{92}U^{238} + {}_{1}H^{2} \longrightarrow {}_{92}U^{239} + {}_{1}H^{1}$$

$$_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

(Neptunium)

$$_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + {}_{-1}e^{0}$$

(Plutonium)

$$_{94}Pu^{239} + {}_{2}He^{4} \longrightarrow {}_{96}Cm^{242} + {}_{0}n^{1}$$

(Curium)

$$_{96}Cm^{242} + {}_{2}He^{4} \longrightarrow {}_{98}Cf^{252} + 2{}_{0}n^{1}$$

(Californium)

$$_{98}Cf^{252} + {}_{5}B^{11} \longrightarrow {}_{103}Lr^{257} + 6{}_{0}n^{1}$$

(Lawrencium)

Nuclear Stability Nuclear Stability

The protons and neutrons are held together within the nucleus by means of forces known as *Nuclear Forces*. Neutrons and protons together are called *nucleons*. Nuclear forces are at least millions of times more than those which bind atoms in molecules.

It is found that as the number of protons increases in nucleus the number of neutrons also correspondingly becomes more. It is assumed that neutrons provide a type of *'Nuclear Glue'* for the nucleus. Nuclei containing even number of nucleons (protons + neutrons) are found to be more stable. Similarly, nuclei containing protons or neutrons equal to 2, 8, 20, 50, 82 or 126 are also stable.

The stability of the nucleus of an atom depends upon the ratio of the number of neutrons to the number of protons in it. For elements up to atomic number 20, the *n/p* ratio should be close to 1 for stability. But for elements of higher atomic numbers, the *n/p* ratio should be 1.52 at the most for stability. If the ratio of neutrons to protons is beyond 1.52, excessive neutrons impart unstability to the nuclei.

Radioisotopes

Isotopes are atoms of the same element which have same atomic number but different mass numbers. Radioisotopes (radioactive isotopes) are usually produced in nuclear reactors as a result of neutron bombardments. Thus ${}_9F^{18}$ is conveniently obtained by irradiating ${}_3Li^6$ with neutrons in a reactor.

$$
{}_3Li^6 + {}_0n^1 \longrightarrow {}_1H^3 + {}_2He^1
$$

$$
{}_1H^3 + {}_8O^{16} \longrightarrow {}_9F^{18} + {}_0n^1
$$

Another useful source of radioisotopes is the fission of uranium in a reactor. Thus Sr^{90} can be produced from fission products. Radioisotopes can also be prepared by bombardment of protons or deuterons in the cyclotron.

The mixture of radioisotopes can be separated from the parent by *solvent extraction, volatilisation, electrodeposition, ion exchange or precipitation technique.*

APPLICATIONS OF RADIOISOTOPES

1. USES IN ANALYTICAL CHEMISTRY

(a) Radiometric analysis

The analysis of inorganic compounds can be carried out with the help of radioactive reagent. For example, labelled P^{32} is used to determine the amount of Zn (II) in the given sample. The radioactivity in the product is noticed with counters and amount of unknown Zn (II) determined. This method is less time consuming and very convenient and more accurate at the same time.

(b) Isotope Dilution

This technique is now very commonly used. It is quite helpful in separating a complicated mixture of various components to get them in free state. The purity of the separated components is tested through radiation counts.

(c) Determination of Metals in Compounds

Let us exemplify this technique by taking an example of the complex $[Co(NH_3)_5H_2O]\ Cl_3$. A drop of $Co^{60}Cl_3$ (Cobalt chloride containing Co^{60} radioisotope) is added to at least 100 mg of the complex. The complex $[Co(NH_3)_5\ H_2O]\ Cl_3$ is converted into $K_3\ [Co\ (NO_2)_6]$ and radiation count in this product would give an idea about the amount of Co present in it.

2. USES IN PHYSICAL AND INORGANIC CHEMISTRY

The radioisotopes are now commonly used in studying the molecular structures, reaction kinetics and mechanism, catalysis and diffusion of gases. The transuranium elements have been studied by this technique.

3. USES IN ORGANIC CHEMISTRY

The radioisotope technique is very useful in elaborating the mechanism of organic reactions. In this way the mechanism of the reactions between alcohol and organic acids to form esters can be studied quite efficiently by means of tracers (radioisotopes). C^{14} radioisotope is usually used as tracer in organic reactions.

4. USES IN MEDICINES

Radioisotopes are commonly used for diagnosis and treatment of various diseases. They are very popular in diagnosing heart disease, cancer, vitamin deficiency and for metabolism. The rate of gaining water and food by plants can be estimated by this technique.

5. USES IN INDUSTRY

Radioactive tracers are commonly used in catalysis, detergents, dyes, etc. They are found to give excellent results in cigarette, paper, plastic industries and in various metallurgical operations. They are also used in determining the structures of polymers.

The tracers are useful in detecting the cracks in pipes. I^{131} is used to detect the leakage point in underground pipes. As I^{131} has half-life of only eight days, its use is harmless because its activity dies down after a short time.

6. USES IN AGRICULTURE

The use of radioisotopes is found to give excellent results in studying the genetic changes of plants. The preservation of food and vegetable is a problem which will hopefully be solved in future with the help of radioisotope techniques.

7. RADIOISOTOPE DATING

The age of certain objects has been calculated by means of radioisotope tracers. C^{14} has half-life of about 5,568 years. The age of a dead body of fossil can be determined by noting C^{14} activity in it. The approximate age of Egyptian pyramids has been calculated by noting the activity of C^{14} and found present since 2600 B.C. Libby (1960) calculated the dates of various monuments and got Nobel Prize for that work.

NUCLEAR HAZARDS

In neutron capture reactions the recoil nucleus acquires high energy and causes perturbations in the orbital electrons. As a result, it breaks the bonds with other atoms in the molecules. The recoil atom initially loses its kinetic energy by elastic collision with inactive isotope atom in accordance with the laws of conservation of momentum.

For fission, the sample must exceed the critical mass before explosion takes place. In an atom bomb, several pieces of fissionable material, all below the critical mass, are held sufficiently apart for no chain reaction to occur. When these are suddenly brought together, an atomic explosion results instantaneously.

Radiation exposure causes following risks:

(a) Risk of fatal cancer in various body organs.

(b) Life span is list.

(c) Morbidity due to non-fatal cancers.

(d) Serious hereditary diseases in future generation.

Non-malignant effects are mainly on skin, hair, sweat glands, hormones, lungs, thyroid gland, eyes, ears, gonad, embryo. Growth retardation damage to is one of the major problem. Burns and ulceration on skin, loss of hair, blood forming tissues, damage to biochemical make up of genes and induction of cancer are of serious nature.

Two general types of stochastic effects are induction of cancer and hereditary disorder. Hereditary disorder is a pathological condition arising as a consequence of mutation or chromosomal aberration transmitted from one human generation to the next.

Carbon Dating

A radioisotope can be identified by its radioactivity and an inactive isotope of particular mass is identified by means of mass spectrometer. Carbon with atomic weight 12 is inactive isotopes but carbon with an atomic weight 14 is radioisotope. Radiocarbon (C) is produced in the upper atmosphere by the transmutation of nitrogen atom under the influence of cosmic rays (free neutrons).

$$_7N^{14} + {_0n^1} \longrightarrow {_6C^{14}} + {_1H^1}$$

$$_7N^{14} + 3{_0n^1} \longrightarrow {_6C^{14}} + {_1H^3}$$

Carbon-14 may enter into carbon dioxide cycle and CO_2 is absorbed by plants during photosynthesis and later becomes part of their bodies. Animals consume C^{14} by eating plants. On death, organisms cease to take in fresh carbon dioxide or carbon atoms. Carbon-14 thus begins to decay. Half-life of Carbon-14 is 5,568 years. After 5,568 years a fossil (animals or plant) will lose half of the amount of Carbon-14 present in the living state. So the amount of C^{14} is an ancient organic sample may thus indicate its age.

Methodology

The sample of bones, wood, coal or organic matter are first cut into chips. The material is heated in a tube and converted to CO_2. The gas is purified and frozen to a solid and stored. Geiger-Muller counter is used to determine the rate of emission of radiation from frozen CO_2. By suitable calculations, age of the sample is worked out.

Errors may crop in due to solar radiations involving cosmic rays but by proper manipulation of experiment these errors can be avoided.

Carbon dating helps in establishing historical facts.

Solved Examples

Example 1:

For a given sample, the counting rate is 47.5 alpha particles/minute. After 5 minutes the counts are reduced to 27 per min. Find the decay constant and half-life of sample.

Solution:

Rate of disintegration is given by

$$-dN/dt = Nt_{1/2}$$

No is the number of atoms at $t = 0$ when rate of disintegration is 47.5 min^{-1} and N is the number of atoms at $t = 5\ \text{min}^{-1}$ when the rate of disintegration is 27 min^{-1}.

$$\begin{aligned}
-dN/dt &= N \times t_{1/2} \\
-47.5 &= t_{1/2}\,No \\
-27 &= t_{1/2}\,N \\
N/No &= 27/47.5 \\
N/No &= e^{-t1/2 \times t} = e^{-t1/2 \times 5} \\
27/47.5 &= e^{-t1/2 \times 5} \\
t_{1/2} &= 0.1129 \text{ minutes}
\end{aligned}$$

Example 2:

Determine the amount of $_{84}Po^{210}$ necessary to provide a source of alpha particles of 5 millicuries strength. Half-life of polonium is 138 days.

Solution:

$$\begin{aligned}
-dN/dt &= N \times t_{1/2} \\
-dN/dt &= 5 \text{ millicuries} = 5 \times 3.7 \times 10^{7} \text{ disintegrations/sec.} \\
5 \times 3.7 \times 10^{7} &= N\sqrt{}\ (\sqrt{} = 0.693 / t_{1/2}) \\
\sqrt{} &= 0.6993 / 138 \times 24 \times 60 \times 60 \\
N &= 5 \times 3.7 \times 10^{7} / t_{1/2} \\
&= 5 \times 3.7 \times 10^{7} \times 138 \times 24 \times 60 \times 60 / 0.693 \\
N &= 3.18 \times 10^{15} \text{ atoms}
\end{aligned}$$

Since 210 g of polonium contains 6.023×10^{23} atoms (Avogadro Number), the amount necessary to obtain a source of the required strength is

Amount Po to produce / 5 millicuries of alpha-particles $= 210 \times 3.18 \times 10^{5} / 6.023 \times 10^{23} = 1.11 \times 10^{-6}$ g

Questions

1. What are alpha particles? Describe certain reactions which take place by alpha particle bombardments. What other particles are utilized for nuclear reactions?
2. What do you understand by half-life period? What is its significance?
3. Differentiate between natural and artificial radioactivity.
4. What is meant by radioactivity? How was it discovered? What is this property due to?
5. Complete the following nuclear reactions:

$$_{1}H^{1} + {}_{4}B^{9} \longrightarrow ? + {}_{2}He^{4}$$

$$_{13}Al^{87} + {}_{0}n^{1} \longrightarrow {}_{12}Mg^{27} + ?$$

$$_{12}Mg^{24} + {}_{2}He^{4} \longrightarrow ? + {}_{0}n^{1}$$

$$_{3}Li^{7} + {}_{1}H^{2} \longrightarrow {}_{4}Be^{8} + ?$$

$$_{9}U^{235} + {}_{0}n^{1} \longrightarrow {}_{56}Ba^{141} + ? + 2 \text{ to } 3\ {}_{0}n^{1} + E$$

6. Explain the following terms giving suitable examples:
   - (a) Half-life
   - (b) Artificial radioactivity
   - (c) Atomic fission
   - (d) Atomic fusion
   - (e) Atomic reactor
7. Give a possible nuclear reaction involved in hydrogen bomb. What is the principle of the bomb itself?
8. What is the fundamental principle of radio-carbon dating?
9. What are radioisotopes? How are they usually produced? Give some of their important applications in daily life.

10. Discuss the group displacement law in light of uranium, actinium and thorium series.

11. Derive the equation of radioactive disintegration. What is meant by decay or disintegration constant?

12. Write a comprehensive note on radioactivity. What are its units?

13. How are isotopes of various elements produced through artificial radioactivity?

14. Describe the use of radioisotopes in medicine and industry.

15. (a) What do you understand by half-life of a radioactive substance?

    (b) The half-life of Sn^{110} is 4 hours. If 10 mg. of this neuclide is present at 8 a.m. on Friday morning, how much of it would be at 8 a.m. on Saturday?

16. Describe a preparative route from U^{238} to Cf^{241}.

17. **Give short answers to the following questions:**

    (i) What is nuclear chemistry?

    (ii) Give characteristic features of alpha rays.

    (iii) What are the characteristics of beta rays?

    (iv) What are the characteristics of gamma rays?

    (v) What do you understand by Natural Radioactivity?

    (vi) Discuss Group Displacement Law.

    (vii) Derive equation of Radioactive Disintegration or Decay.

    (viii) What is the significance of half-life in radioactivity?

    (ix) Describe the salient features of Artificial Radioactivity.

    (x) Discuss Nuclear Fission.

    (xi) How is radiation measured?

    (xii) Describe Wilson's Cloud Chamber used to measure radiation.

    (xiii) What is the function of Geiger-Muller Counter?

    (xiv) Write a brief note on nuclear hazards.

    (xv) What is the usefulness of carbon dating?

    (xvi) Describe Transuranium Elements.

(xvii) Write a brief note on nuclear fusion.

(xviii) What are radioisotopes?

(xix) What are the applications of radioisotopes?

(xx) Discuss nuclear structure and nuclear stability.

18. **Give the correct answer:**

(i) One of the following radioisotope is used to determine Zn(II):

(a) P^{32} (b) H^3

(c) F^{18} (d) U^{239}

(ii) Becquerel discovered the uranium soft:

(a) $KuO_2(SO_4)_2$ (b) UO_2Cl_2

(c) $UO_2(NO_3)_2$ (d) UCl_6

(iii) Alpha rays are:

(a) H^+ (b) electrons

(c) He^{+2} (d) He^+

(iv) The velocity of beta rays is almost equal to:

(a) velocity of alpha rays (b) velocity of sound

(c) velocity of light (d) velocity of gamma rays

(v) In uranium series ${}_{92}U^{238}$ disintegrates to:

(a) ${}_{82}Pb^{206}$ (b) ${}_{82}Pb^{207}$

(c) ${}_{82}Pb^{208}$ (d) ${}_{82}Pb^{209}$

(vi) The bombardment of neutrons on ${}_7N^{14}$ gives:

(a) ${}_6C^{14}$ (b) ${}_7N^{13}$

(c) ${}_{14}Si^{27}$ (d) ${}_9F^{18}$

(vii) The bombardment of protons on ${}_8O^{18}$ produces:

(a) ${}_8O^{16}$ (b) ${}_8O^{17}$

(c) ${}_9F^{18}$ (d) ${}_2He^4$

(viii) On bombardment of neutrons with ${}_{92}U^{235}$:

(a) ${}_{56}Ba^{141}$ and ${}_{36}Kr^{92}$ (b) ${}_{56}Ba^{142}$ and ${}_{36}Kr^{91}$

(c) ${}_{56}Ba^{140}$ and ${}_{36}Kr^{93}$ (d) ${}_{56}Ba^{143}$ and ${}_{36}Kr^{90}$

(ix) The bombardment of alpha particles on ${}_{12}\text{Mg}^{24}$ produces:

(a) ${}_{14}\text{Si}^{27}$ (b) ${}_{7}\text{N}^{13}$

(c) ${}_{9}\text{F}^{18}$ (d) ${}_{6}\text{C}^{12}$

(x) The bombardment of deuterons on ${}_{3}\text{Li}^{7}$ produces:

(a) ${}_{4}\text{Be}^{8}$ (b) ${}_{4}\text{Be}^{9}$

(c) ${}_{5}\text{B}^{11}$ (d) ${}_{5}\text{B}^{12}$

❀ ❀ 19 ❀ ❀

INDUSTRIES

20

IMPORTANT METALLURGIES AND METALLURGICAL OPERATIONS

In this chapter, we shall discuss the production of some important metals such as Cu, Ag, Ca, Al and Fe. Except for gold, platinum, silver, mercury etc., most of the metals occur in nature in the combined state. The metals which are found in metallic or free state are said to be ***native***. *The compounds of metals which occur in nature are called* ***minerals****. The minerals from which metals can be economically extracted are known as* ***Ores****.*

Metallurgy is the art of extracting metals from their ores. The worthless material present in the ore is called *gangue* or *matrix*. The first step in metallurgical operation is to crush the ores in order to bring them to suitable size, followed by screening and sizing. The ores are *concentrated* to reduce the amount of gangue from valuable minerals. The products of concentrated ores are called *'concentrate'* and *'tailings'*. The valuable minerals are called concentrates and waste material or gangue refers to tailings. Gravity concentration and froth flotation processes are commonly used for this purpose.

Concentration Processes

The most important concentration processes are:

1. Gravity Separation

This process is based upon the difference in specific gravity of useful part of the ore and gangue. The separation is carried out on Wilfley tables or shaking machines called jigs. In Wilfley tables the crushed ore is carried by a stream of water over a surface provided with riffles or obstructions. The lighter gangue particles are washed away leaving the useful ore particles entangled in riffles. In jigs or shaking machines, the crushed ore is shaken in a box with a perforated bottom. In this way, the heavier ore particles carrying metals are separated from gangue.

2. Froth Flotation Process

This method is extensively used for concentrating low-grade ores such as sulphides of copper and zinc. The finely crushed ores are thoroughly agitated with the help of a blast of air in presence of water and a little pine or eucalyptus oil (Figure 20.1).

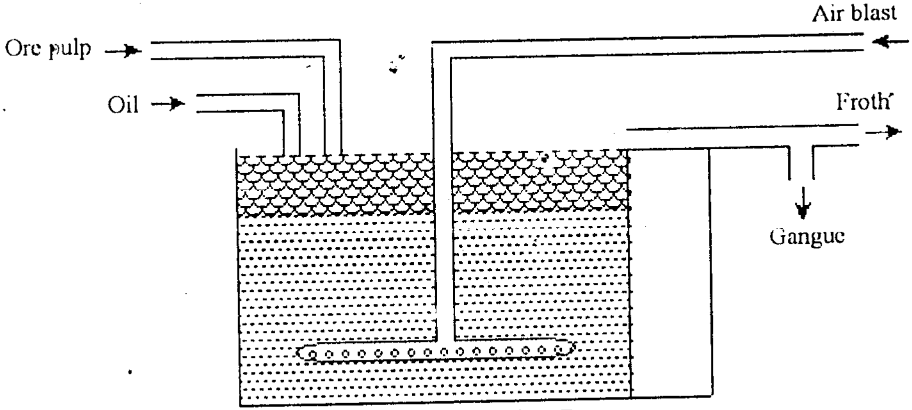


Fig. 20.1. Froth Flotation Process.

The ore is preferentially wetted by oil and the gangue by water. A froth appears at the top of liquids which carries ore particles and is skimmed off.

It is worth noticing that froth flotation process is just the reverse of gravity concentration. In froth flotation process heavy ore particles rise to the top instead of sinking as in gravity process.

3. Electromagnetic Separation

This method is usually applied for separating minerals of equal densities, especially when one of them shows magnetic behaviour or can be easily converted into a magnetic product. This *tinstone* (density 6.4 – 7.1) and *wolfram* (density 7.1 – 7.9) which occur together in nature, can be separated by this process. Wolfram is magnetic while tinstone is not. In order to separate them, the crushed ore mixture is allowed to run over a travelling belt passing over a magnetic roller, RM (Figure 20.2). The tinstone falls undeflected at T and wolfram is attracted by the magnet and falls at a separate heap, W.

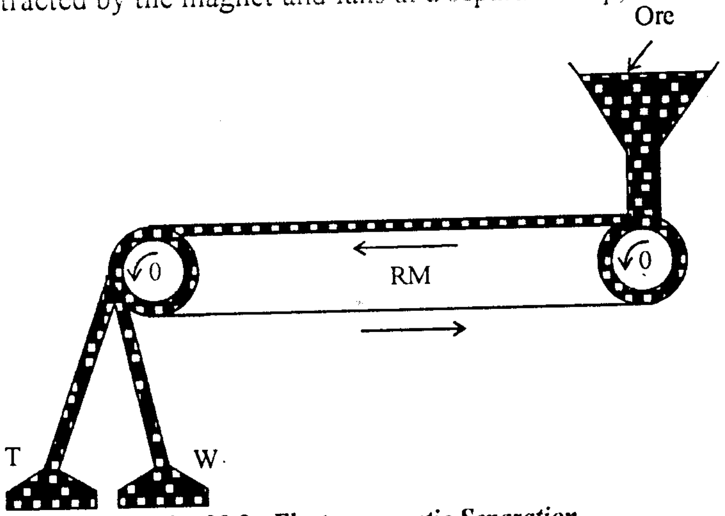


Fig. 20.2. Electromagnetic Separation.

After the ores have been concentrated, the subsequent steps for the production of metals vary depending upon their nature and type of ore. Therefore, the other metallurgical operations will be discussed along with the metallurgy of the corresponding metal.

METALLURGY OF COPPER

Copper occurs mostly in the combined state though rarely in the free state.

OCCURRENCE

The important ores of copper are:

(a) Sulphide Ores

Copper pyrite	or	Chalcopyrite,	$Cu_2S.\ Fe_2S_3$
Copper glance	or	Chalcocite,	Cu_2S
Bornite	or	Peacock ore,	$3Cu_2S.\ Fe_2S_3$

(b) Oxide Ores

Cuprite,	Cu_2O
Malachite,	$CuCO_3.Cu\ (OH)_2$
Melaconite,	CuO

Native copper crystallizes in the cubic system. Copper minerals generally occur in veins or in grains disseminated through host rock and in scales. In Pakistan, copper ores are found in North Waziristan Agency, Chitral State, Dir State, Gilgit Agency, Hazara District and in Quetta Division (in Chaghi, Loralai, Pishin and Zhob Districts).

Extraction of Copper from Sulphide Ores

Large amounts of copper (75%) are obtained from copper pyrite, $CuFeS_2$ by smelting. Ores containing 4% or more of copper are treated by *smelting process*. Very poor ores are treated by *hydrometallurgical process*.

1. BY SMELTING

In this process the concentrated sulphide ore is oxidised by air. Sulphur burns to SO_2, iron is converted to FeO, which is removed as FeSiO . Cuprous sulphide is partially oxidised to cuprous oxide which reacts immediately with unoxidised Cu_2S to give metallic copper. The following steps are involved during smelting:

(a) Concentration

The finely crushed ore is concentrated by *froth-flotation* process. The finely ground ore is suspended in water containing a little pine oil. A blast of air is passed through the suspension. The particles of sulphide ore get wetted by oil and float as froth which is skimmed (Figure 20.1). The gangue sinks to the bottom and is removed.

(b) Roasting

The concentrated ore is then roasted in a furnace in presence of a current of air. Sulphur is oxidised to SO_2 and the impurities of arsenous and antimony are removed as volatile oxides. The ore now contains a mixture of cuprous and ferrous sulphides.

$$Cu_2S.\ Fe_2S_3 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

(c) Smelting

The ore is now transferred into a water jacketed blast furnace (Figure 20.3). A little coke and sand (or silica) are also added. The furnace is provided at the base with a row of *twyers* for the supply of air. The combustion of ore itself provides a lot of heat and, therefore, less amounts of coke are usually needed. The smelting serves to oxidise sulphides to corresponding oxides.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

Some limestone is also added to remove excess SiO_2.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The iron and other silicates rise to the top and are removed as slag. A mixture of Cu_2S and some unreacted FeS forms the lower layer and is called **matte**.

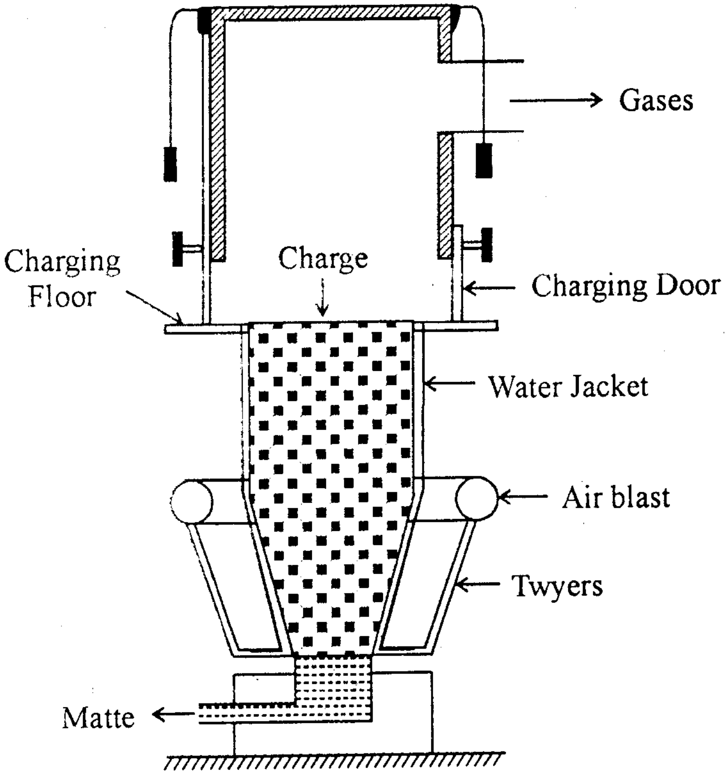


Fig. 20.3. Blast Furnace for Copper.

(d) Bessemerization

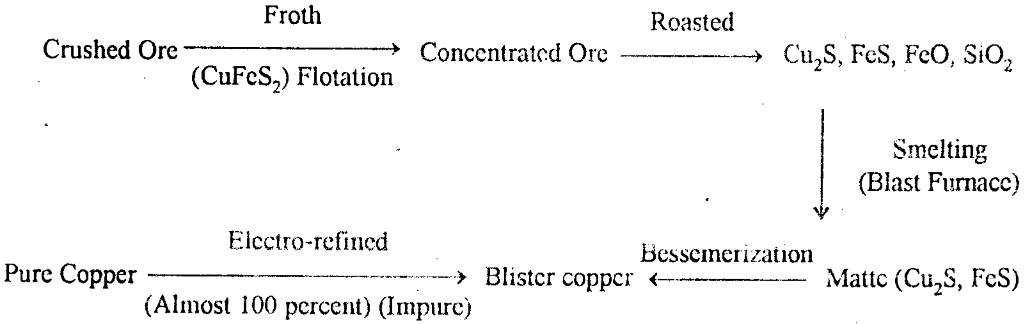
The **matte** is removed in a Bessemer converter (Figure 20.4) by blowing the air through the molten material. FeS is first oxidised to FeO and SO_2. Sand is added to remove FeO as $FeSiO_3$. The blast of air converts Cu_2S to Cu_2O. Cu_2O thus formed reacts instantaneously with Cu_2S to give metallic copper.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Some cupric oxide CuO is also produced by the air blast. It is removed by stirring the molten metal with poles of green wood. The resulting gases reduce CuO. The copper obtained through Bessemerization has characteristic appearance due to evolution of gases from within and is called **'blister copper'**. Blister copper is about 98 percent pure copper. The rest is some iron with small traces of silver and gold (if present). Blister copper is further refined by electrolytic process given under the heading 'Refining of Copper'.

The entire process may be schematically represented as:



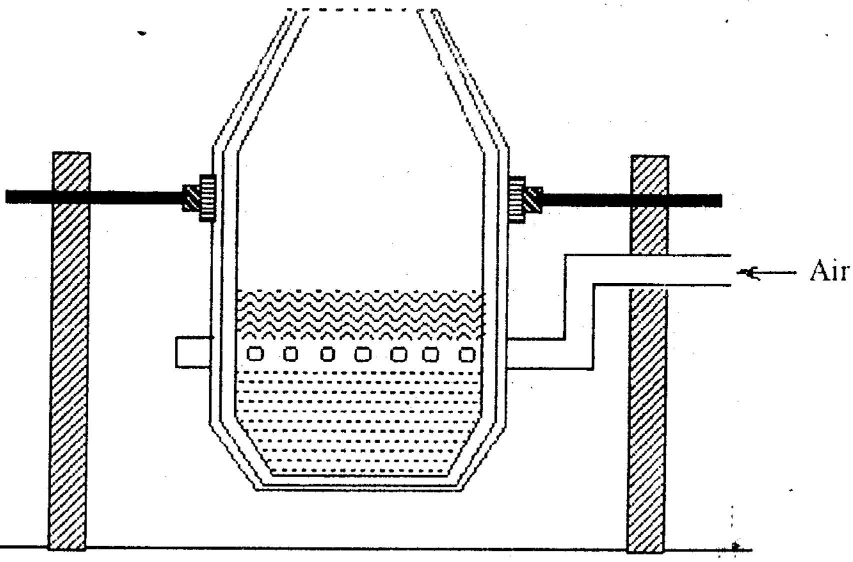


Fig. 20.4. ***Bessemer Converter for Copper.***

2. HYDROMETALLURGICAL PROCESS

The low-grade sulphide ores of copper are subjected to hydrometallurgical process. The crushed ore in bulk (about 100,000 tons) is allowed to whether in contact with water. Water is also allowed to percolate from the top. After about one year copper sulphide is oxidised to $CuSO_4$. At the same time $FeSO_4$ and H_2SO_4 are also formed.

$$2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$$

$$2Fe_2S_3 + 11O_2 + 2H_2O \longrightarrow 4FeSO_4 + 2H_2SO_4$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

Copper is precipitated from pale green solution coming out of the bottom of the heap by means of iron.

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$$

The precipitated copper is dried, melted and then refined.

Extraction of Copper from Non-Sulphide Ores

The following two methods are in common use:

1. Reduction with Carbon

The oxide or carbonate ore is mixed with powdered coke and reduced in a reverberatory furnace.

$$CuCO_3 \longrightarrow CuO + CO_2$$

$$CuO + C \longrightarrow Cu + CO$$

2. Leaching with H_2SO_4

The non-sulphide ores of copper may be leached with H_2SO_4 in concrete tanks with wooden bottom. The leaching of ore with dilute sulphuric acid is done on counter current principle. As a result, a fairly concentrated solution of copper sulphate is obtained. Electrolysis of copper sulphate solution using *lead anodes* and copper sheet *cathodes* is carried out to get pure copper. The copper left behind in the residual liquor is recovered by treating it with scrap iron.

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$

Refining of Copper

The modern method of refining copper is by electrolysis. For this purpose crude metal is cast into plates. These plates act as anodes and are hung at intervals in lead-lined tanks containing copper sulphate solution. The *cathodes* consist of a series of thin sheets of pure copper (Figure 20.5). The cathode plates are coated with graphite so that the deposited copper may be removed readily. During electrolysis, the impurities due to less active metals settle at the bottom of the tank as *anode mud*. The voltage employed is 1.3 volts and at this voltage only copper is deposited at the cathode. The copper obtained in this way is almost 100 per cent pure.

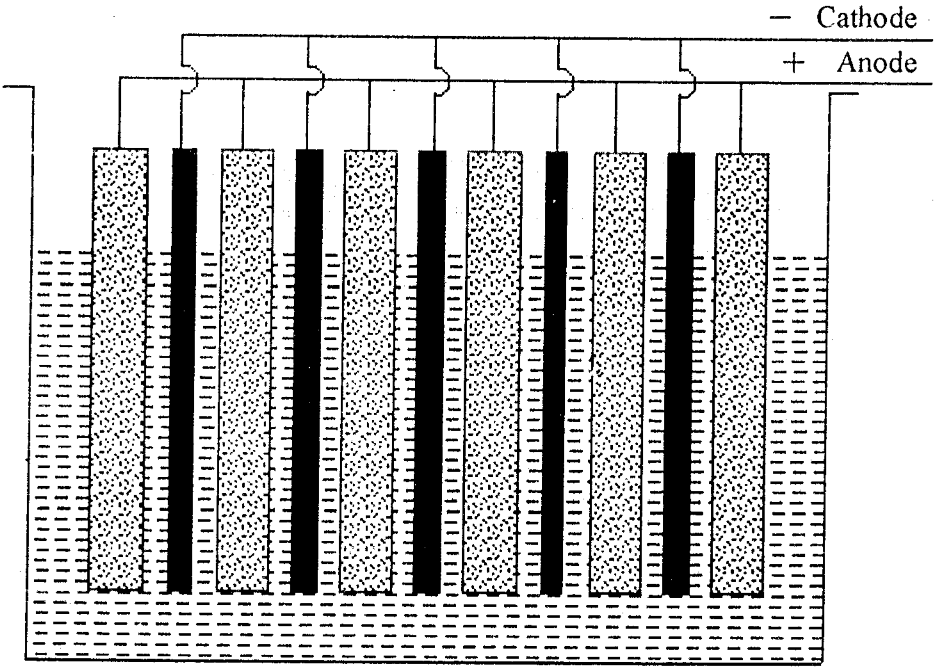


Fig. 20.5. Electrolytic Refining of Copper.

USES

1. Copper is extensively used in preparing water-stills, vacuum pans, steam coils, etc.
2. Copper is used in electrical equipment due to its high electrical conductivity.
3. Large quantities of copper are used for the fireboxes of locomotive boilers.
4. Copper forms a large number of useful alloys, *i.e.*, brass, bronze, monel-metal German silver etc.

METALLURGY OF SILVER

Silver is usually found in nature in native form along with gold and copper.

OCCURRENCE

The important ores of silver are

Argentite or silver glance,	Ag_2S
Horn-silver,	$AgCl$
Pyroargyrite,	Ag_5SbS_4

The silver ores are often found associated with galena, PbS. Another source of silver is the *anode mud* obtained during the electro-refining of copper.

Extraction of Silver

The extraction of silver is carried out by various techniques which usually depend upon the type of ore. The following processes are usually used:

1. Cyanide Process

Mostly silver is now extracted by this procedure. The principle of the procedure is to get Ag^+ into solution as dicyanoargentate ion, $[Ag(CN)_2]^-$ in presence of CN^- ions. Silver metal and its compounds are easily soluble in alkali cyanide solutions in presence of air. The metallic silver is deposited from cyanide solution in presence of reducing agents such as zinc or aluminium (hydroquinone may also be used as investigated by authors).

The finely divided ore, usually silver sulphide, is agitated with about 1% NaCN solution for about 48 hours in a current of air. Silver gradually goes into solution as sodium dicyanoargentate, $Na[Ag(CN)_2]$.

$$Ag_2S + 8NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

OR

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

If ore contains AgCl, the reaction is:

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl$$

The silver is usually deposited from $Na[Ag(CN)_2]$ by treatment with Zn.

$$Zn + 2Na[Ag(CN)_2] \longrightarrow Na_2[ZN(CN)_4] + 2Ag$$

The precipitated silver is filtered, washed and then melted with KNO_3 to oxidize any zinc.

The process of extraction of silver may be shown schematically as:

$$\begin{tikzcd}
\text{Finely Ground Ag ore} \arrow[r, "\text{Froth}", "\text{Flotation}"'] & \text{Concentrated ore} \arrow[r, "\text{dilute}", "\text{NaCN Soln.}"'] & \text{Solution of } Na[Ag(CN)_2] \arrow[d, "Zn"] \\
& \text{Metallic Silver} & Ag \arrow[l, "\text{Dried and}"', "\text{Fused}"]
\end{tikzcd}$$

2. Amalgamation Process

The ore (Ag_2S) is ground to a paste with water and treated with cupric chloride (or NaCl and ($CuSO_4$) when Ag_2S is converted into AgCl.

$$Ag_2S + CuCl_2 \rightleftharpoons 2AgCl + CuS$$

The products are mixed with metallic mercury when silver is deposited.

$$2AgCl + 2Hg \longrightarrow 2Ag + Hg_2Cl_2$$

The silver thus obtained may form an amalgam in presence of excess mercury. Excess mercury may be removed by distillation in retorts.

3. Extraction from Commercial Lead

Small quantities of silver present in lead or lead ores can be economically extracted by **Parkes' Process**. This process is based upon the *Partition Law*. According to that, molten lead dissolves about 1 % Zn and molten zinc dissolves about 1% Pb. But Ag is completely soluble in molten zinc. Thus, by adding molten zinc to fused lead-silver alloy, silver goes in molten zinc forming Zn – Ag alloy which solidifies and floats on the surface of molten lead. Silver is obtained pure by distilling zinc. This process is also called desilverisation of lead.

The small quantity of lead which may remain in silver is removed by **Cupellation Process.** The mixture is placed in cupellation furnace (Figure 20.6) and a blast of hot air passed over it. Lead is converted PbO. PbO is blown off leaving behind silver.

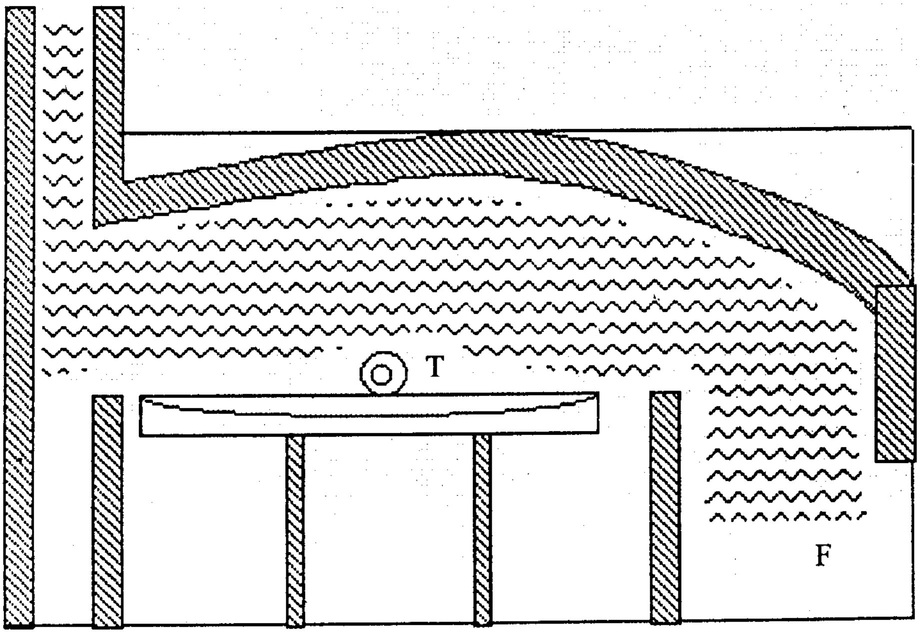


Fig. 20.6. Cupellation Furnace (F) Fire Gate, (T) Twyer for the blast of air.

4. Electrolytic Process

This process is principally used to refine the crude silver. The electrolytic cell contains $AgNO_3$ solution as electrolyte with 1 per cent HNO_3 in it. A slab of impure silver is used as anode and a plate of pure silver as cathode. Silver is deposited on the cathode and gold, if any is left as a mud.

Uses of Silver

1. Large amounts of silver are used for making silver ware, ornaments and coins.
2. The metal is also used for coating copper articles.
3. Silver is used to prepare silver nitrate, an important chemical.
4. Silver leaf is used in Ayurvedic system of medicine.
5. Various compounds of silver are used in photography.

METALLURGY OF CALCIUM

Calcium compounds are abundantly available in nature. Limestone ($CaCO_3$), Gypsum ($CaSO_4.2H_2O$) and Dolomite ($CaCO_3 . MgCO_3$) are very common in Pakistan, especially in Karachi, Peshawar, Multan, Hyderabad, Kalat and Rawalpindi divisions.

Extraction

The mineral is converted to $CaCl_2$ which is subjected to electrolysis in the fused state mixed with alkali metal halides or CaF_2.

The electrolytic cell (Figure 20.7) consists of a circular *iron box* A and through its bottom projects a conical *iron cathode* B insulated from the box A. The *carbon* C acts as anode and insulated form the iron box. The metal is collected in *collecting ring* E at the top of molten chloride mixture. The metal is allowed to accumulate until the ring is full. The top of the metal solidifies and this solid part is fastened to a *hook* F which gradually rises and carries metal along with it. The heat due to electric current keeps the salts in molten state. The metal is protected from air by the layer of fused salts.

The calcium obtained in this way is only 85 percent pure and is distilled under vacuum to get pure metal.

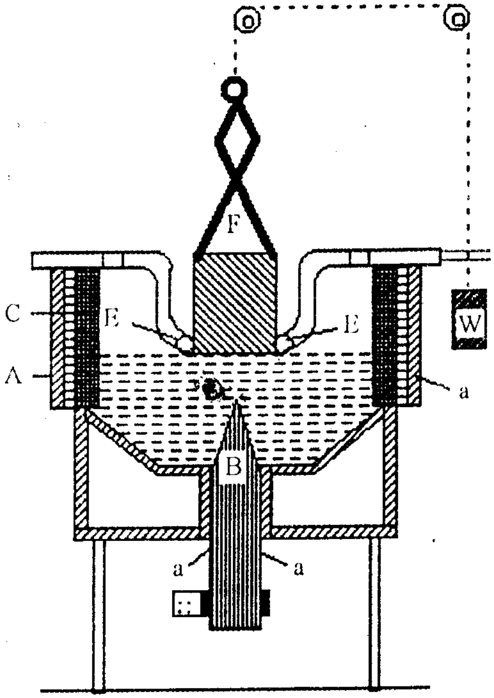


Fig. 20.7. Molar Electrolytic Cell for Manufacture of Calcium.

METALLURGY OF CHROMIUM:

In the 18th century analysis of Siberian ore, crocoite, $PbCrO_4$ was found to contain lead and chromium. In 1797, chromium oxide CrO_3, was discovered by Vanquelin. Heating of this oxide with charcoal in an oven produced chromium metal.

ORES:

The chief ores of chromium are:

Chromite	$FeCr_2O_4$	(46.46 % Cr)	Black or brown black
Crocoite	$PbCrO_4$	(15.89 % Cr)	Red orange

EXTRACTION OF CHROMIUM:

(a) From Chromite Ore:

The chromite ore is finely ground and then roasted with Na_2CO_3 at 800 – 1000°C in rotary kilns. Cr_2O_3 produced during the reaction is converted into Na_2CrO_4.

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2$$

The roasted product is leached with water and filtered to separate the soluble Na_2CrO_4 from the iron oxide and gangue present in the ore. The Na_2CrO_4 is converted to $Na_2Cr_2O_7$ by treatment with H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The $Na_2Cr_2O_7$ in the aqueous solution is selectively crystallized by evaporation and crystals are separated by filtration. The dried $Na_2Cr_2O_7$ crystals are then converted to Cr_2O_3 by sulphur reduction in a furnace.

$$S + Na_2Cr_2O_7 \longrightarrow Na_2SO_4 + Cr_2O_3$$

The Cr_2O_3 in finally reduced by Al or silicon to yield metallic chromium

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

$$2Cr_2O_3 + 3Si \longrightarrow 4Cr + 3SiO_2$$

(b) Electrolytic Chromium:

In the chrome alum process, chromite or ferrochromium is converted to $NH_4Cr(SO_4)_2 \cdot 12H_2O$ by dissolving it in H_2SO_4 and then adding $(NH_4)_2SO_4$. Ammonium chromium sulphate is electrolyzed in a cell with a diaphragm. This diaphragm is used to prevent the sulphuric acid and the chromic acid from mixing with chromium at the cathode. The cell is operated at 4.2 V at 53°C at a current density of 8 A / mm^2.

(c) Chrome Acid Process:

In the chromic acid process, chromic acid is produced by treating $Na_2Cr_2O_7$ with H_2SO_4.

$$Na_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2NaHSO_4 + H_2O$$

The chromic acid cell operates at 4 g/L concentration of H_2SO_4 and 85°C. The solution containing chromic acid is electrolysed at current density 10 A/mm^2 to get chromium.

Properties:

Chromium is a lustrous steel gray metal with density 7.19 g/cm^3 at 20°C. M.P. 1856.9°C B.P. 2671.9°C. It is hard and corrosion resistant metal.

Uses:

1. Chromium is used for the manufacture of stainless steel and other alloys.
2. It is widely used as catalyst.
3. It is used in glass to give green colour.
4. Lead chromate is used as chrome yellow in pigments.
5. Chromium compounds are used in the textile industry as mordants.
6. It is used in the aircraft industry for anodizing aluminium.
7. Dichromate is used in tanning leather and as oxidizing agent in quantitative analysis.

METALLURGY OF NICKEL:

As early as 200 BC, the Chinese made a white alloy from zinc, copper and nickel. Nickel was first isolated in 1751.

ORES:

Some important naturally occurring ores of nickel are:

Millerite	NiS	(51.24 % Ni)	Brass yellow
Niccolite	NiAs	(43.92 % Ni)	Pale copper red
Violarite	$FeNi_2S_4$	(38.94 % Ni)	Violet grey
Pentlandite	$(Fe, Ni)_9S_8$	—	Light Bronze yellow

The chief sulphide ore of nickel is pentlandite. It also occurs to a minor degree as violarite, $FeNi_2S_4$.

PYROMETALLURGICAL EXTRACTION OF NICKEL FROM SULPHIDE ORES:

ROASTING:

The ore is well ground and subjected to froth flotation process. The concentrates are then roasted in presence of air. Some of sulphur is oxidized to SO_2 and Ni_3S_2 is formed. The temperature rises to 850°C.

SMELTING:

The roasted ore is smelted in a blast furnace to produce a matte (20 % Ni, 7 % Cu, 40 % Fe and 27 % S). The slag contains gangue and oxidized iron.

$$NiO + 6FeS + 2O_2 + 3SiO_2 \longrightarrow 2Ni_3S_2 + 3(2FeO\ .\ SiO_2) + 2SO_2$$

$$2Cu_2O + 2FeS + SiO_2 \longrightarrow 2Cu_2S + 2FeO\ .\ SiO_2$$

The furnace used is similar to that described for smelting of copper (Fig. 20.3).

Bessemerization:

The matte is transferred to the Bessemer converter (Fig. 20.4) by allowing air through the molten material. FeS is oxidized to FeO and SO_2. FeO is removed as $FeSiO_3$. The blast of air converts nickel sulphide to granular nickel oxide. Some of nickel oxide is converted to Ni by carbonyl process and other by electrolytic repining.

Nickel Carbonyl or Mond Process for Refining of Nickel:

Mond discovered a novel process for refining nickel. From bessemerization nickel oxide is reduced by CO which combines with carbon monoxide at 40 – 90°C to form gaseous nickel carbonyl, $Ni(CO)_4$. At 150 – 300°C, the nickel carbonyl decomposes to give pure nickel.

$$Ni + 4CO_4 \xrightarrow{50°C} Ni(CO)_4$$

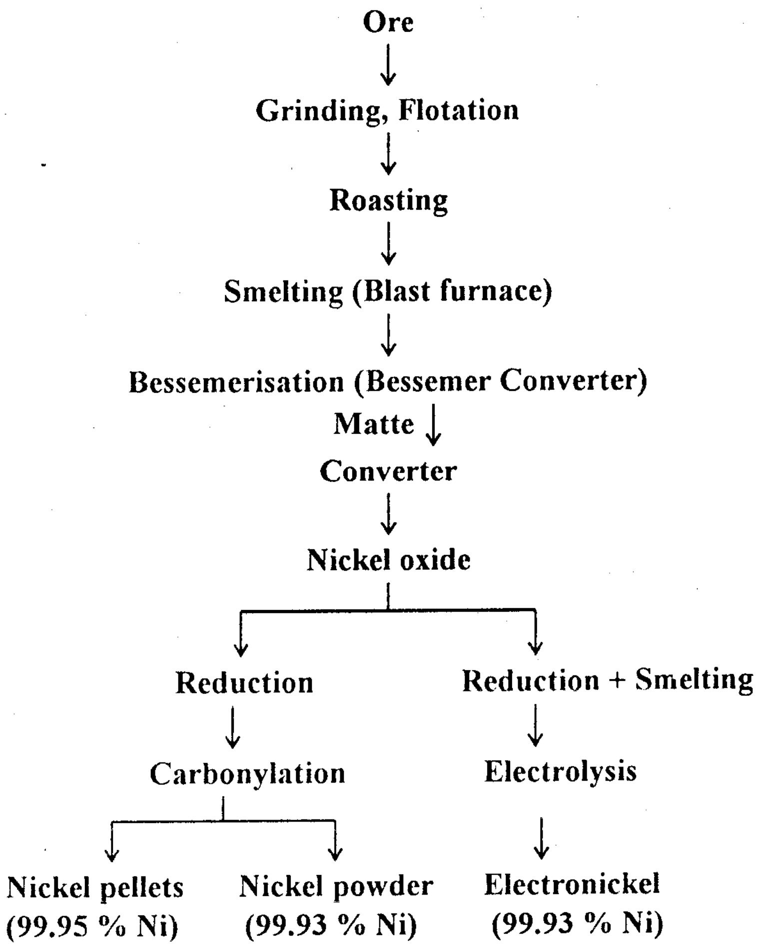
$$Ni(CO)_4 \xrightarrow{230°C} Ni + 4CO$$

Iron, too, forms a volatile carbonyl, $Fe(CO)_5$ but its rate of reaction is slow.

ELECTROLYTIC REFINING OF NICKEL:

The nickel oxide is reduced by smelting with coke in an electric furnace and then cast into nickel metal anodes. The electrolysis is carried out at 60°C at a current density of $170 A/m^2$. Pure nickel (99.93 %) is deposited at the cathode.

The flow sheet diagram for extraction and refining of nickel is given below:



Properties:

Nickel is a silvery white lustrous metal. It has density 8.9 g/cm^3 at 20°C.

M.P. 1452.9°C B.P. 2731.9°C

It exhibits high electric and thermal conductivity. The metal is corrosion resistant and forms alloys.

Uses:

1. Nickel is valuable in the form of alloys, i.e. stainless steel, copper-nickel alloy used in desalination plants for converting sea water into fresh water.
2. It is extensively used as coinage metal.
3. It is used to make steel for artillery and burglar proof vaults.
4. Nickel is added to glass for producing green colour.
5. It used in batteries and in electroplating.
6. Finely divided nickel is used as a catalyst for hydrogenation of vegetable oil to vegetable ghee.

Questions

1. How is copper usually found in nature? Give details of the extraction of copper from sulphide ores. Describe a method adopted from very poor ores. How is copper refined?
2. Give an account of the extraction of silver from
   (a) sulphide ore (b) from an alloy of lead and silver.
3. Describe the electrolytic refining of copper
4. Discuss the cyanide process for extracting silver.
5. Describe the extraction of copper from copper *pyrites*. How is it obtained in pure state?
6. Give salient features of the metallurgy of chromium.
7. How is nickel manufactured from its ore? Give the steps for refining of nickel.
8. **Give short answers to the following questions:**
   - (i) What is gravity separation?
   - (ii) Write a note on froth flotation process.
   - (iii) Describe electromagnetic separation.
   - (iv) What are the common ores of copper?
   - (v) How is copper extracted from sulphide ores?
   - (vi) Discuss smelting process for copper extraction.
   - (vii) Describe the function of Bessemer Converter for Copper.
   - (viii) Describe hydrometallurgical process for copper extraction.
   - (ix) How is copper extracted from non-sulphide ores?
   - (x) How is silver extracted by cyanide process?
   - (xi) How is silver extracted from commercial lead?
   - (xii) Discuss the steps involved in metallurgical operation of calcium.
9. **Give the correct answer:**
   - (i) Smelting process for copper extraction is used for:
     (a) sulphide ores (b) non-sulphide ores
     (c) oxide ores (d) carbonate ores
   - (ii) In Froth Flotation process the following oil is used:
     (a) mineral oil (b) diesel oil
     (c) pine oil (d) castor oil
   - (iii) *Chalcopyrites* is:
     (a) $Cu_2S . Fe_2S_3$ (b) Cu_2S
     (c) $3Cu_2S . Fe_2S_3$ (d) Cu_2O

(iv) The following mixture is called 'Matte':

(a) Cu_2S and FeS
(b) CuS and FeS
(c) CuS_2 and Fe_2S_3
(d) CuS and Fe_2S_3

(v) Leaching of non-sulphide ores of copper with H_2SO_4 produces:

(a) $CuSO_4$
(b) Cu_2SO_4
(c) $CuSO_4 . H_2SO_4$
(d) $CuSO_4 . Cu_2S$

(vi) Silver glance is:

(a) Ag_2S
(b) AgCl
(c) Ag_5SbS_4
(d) $AgNO_3$

(vii) Ag_2S and NaCN produce:

(a) Na_2S
(b) $Ag(CN)_2$
(c) NaAgS
(d) $NaAg(CN)_2$

(viii) AgCl and Hg react to give:

(a) Ag and $HgCl_2$
(b) Ag and Hg_2Cl_2
(c) Ag and $HgCl_3$
(d) Ag and Hg

(ix) Cu_2S when heated in oxygen gives:

(a) $CuSO_4 + CuO$
(b) $CuSO_4 + CuS$
(c) $CuSO_4 + Cu_2O$
(d) $CuSO_4 + Cu$

(x) On heating Fe_2S_3 in oxygen, the following are produced:

(a) $FeSO_4 + H_2SO_4$
(b) $FeSO_4 + FeO$
(c) $FeSO_4 + F_2O_3$
(d) $FeSO_4 + SO_2$

(xi) Chromite ore is:

(a) K_2CrO_4
(b) $FeCr_2O_4$
(c) $PbCrO_4$
(d) Cr_2O_3

(xii) Violarite ore is:

(a) $FeNi_2S_4$
(b) NiS
(c) NiAs
(d) $(Fe, Ni)_9S_8$

❀ ❀ 20 ❀ ❀

21

ACID-ALKALI INDUSTRIES

Nitric acid, sulphuric acid, sodium carbonate and sodium hydroxide are important chemicals for industrial use. The industrial processes commonly used for their manufacture shall now be discussed.

Nitric Acid, HNO_3

Nitric acid is usually obtained from nitrates, from air or from ammonia.

1. From Nitrates

HNO_3 can be produced on large scale from sodium or potassium nitrate and sulphuric acid. (This method can also be used in the laboratory). On industrial scale, the charge of $NaNO_3$ or KNO_3 and H_2SO_4 is taken in cast iron retorts and heated to about 200°C. At this temperature nitric acid produced distills off.

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

Under ordinary conditions the reaction is reversible and an equilibrium is established. As HNO_3 boils at 83°C compared to H_2SO_4 which boils at 338°C, it is distilled off. The distillate is passed through water cooled silica tubes to condense HNO_3. Uncondensed fumes are passed through cold water and collected as dilute HNO_3. Nitric acid usually has a yellow colour which is due to the dissolved NO_2 which can be removed by distillation.

The flow sheet for the manufacture of HNO_3 from sodium nitrate is shown in Figure 21.1.

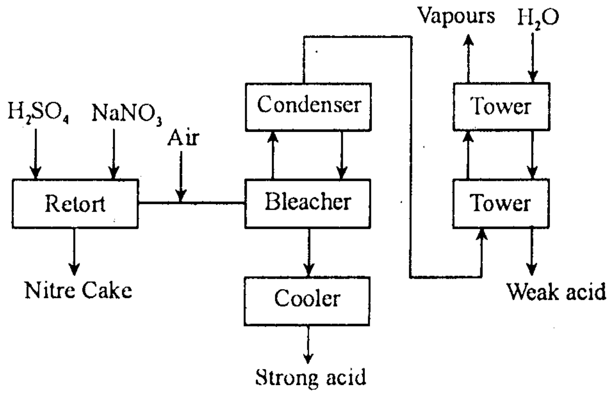


Fig. 21.1. HNO_3 from sodium nitrate.

2. From Air (Arc Process)

Air contains mainly N_2 and O_2. It is subjected to high tension electric discharge or heated through an are at about 3000°C in order to fix nitrogen.

$$N_2 + O_2 \rightleftharpoons 2NO - 180.75 \text{ KJ/m.}$$

Applying *Le-Chatelier's principle*, the forward reaction would be favoured by a rise in temperature whereas pressure should not affect the equilibrium. At 3000°C, about 5% of NO is present. The temperature of the gases should be suddenly dropped below 1000°C otherwise equilibrium shifts backwards and only N_2, and O_2 would be left. Below 1000°C, the decomposition of NO is negligible. On cooling, NO combines with more O_2 to form NO_2.

$$2NO + O_2 \longrightarrow 2NO_2$$

The brown fumes of NO_2 are brought into contact with water on *counter current* principle, *i.e.*, the gases and vapours going upwards when water trickles down the absorption towers. As a result of this, HNO_3 is obtained due to the following reactions:

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

The unconverted gases which escape the towers contain some NO and NO_2 which are absorbed in sodium carbonate solution to produce $NaNO_2$.

$$NO + NO_2 + Na_2CO_3 \longrightarrow 2NaNO_2 + CO_2$$

Birkeland-Eide process is used in Norway in which arc is struck between electrodes in U-tubes made of copper, cooled externally by water.

This process is no more used for the manufacture of HNO_3 due to the high cost of electricity and low yield of nitric acid.

3. By Oxidation of Ammonia (Ostwald's Process)

This process is based on oxidation of NH_3 by O_2 when NO and NO_2 are obtained. The oxidation of ammonia

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O + 945.6 \text{ KJ}$$

$$2NO + O_2 \longrightarrow 2NO_2 + 116.3 \text{ KJ}$$

is an exothermic process and proceeds smoothly without supply of heat. Ammonia is mixed with 10 times its volume of air heated to 700°C and passed through the converter (Figure 21.2) containing platinum gauze catalyst or an alloy of 10% platinum and 10% rhodium.

The gaseous mixture containing NO, NO_2, etc., is passed through absorption towers in which water is sprayed over gases. NO_2 is converted to nitric acid.

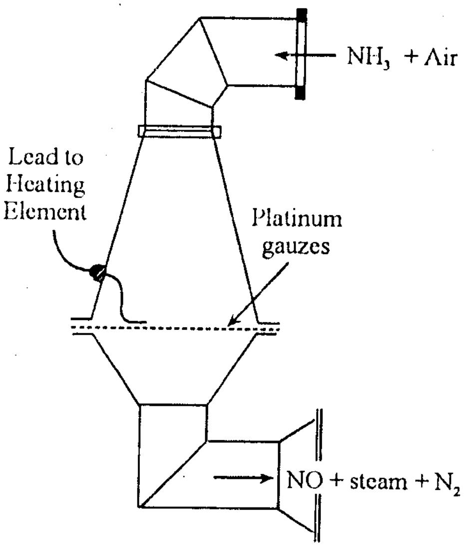


Fig. 21.2.

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$$

The unabsorbed NO is returned to absorption towers along with more air so that NO_2 is formed which gets dissolved in water to form HNO_3.

Pure HNO_3 is made by distillation of the product under reduced pressure.

A flow sheet of ammonia oxidation process is shown in Figure 21.3.

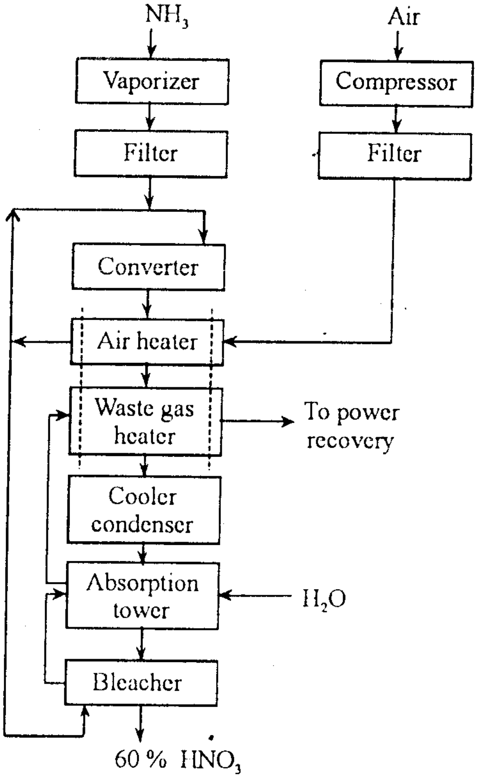


Fig. 21.3. Ammonia Oxidation Process for the manufacture of HNO_3.

Materials of Construction

Nitric acid is a strong acid and good oxidizing agent. Therefore, special materials of construction are chosen to withstand various concentrations of the acid. Chromium steel or iron-silicon steel is used for plant construction.

Aluminium is resistant to the attack by hot concentrated HNO_3 because of the formation of an acid film which prevents further attack. Al is, therefore, used to prepare heat exchangers in the plants. Ceramic material may be used in the plant if normal pressure is required.

Marketing

Nitric acid is usually supplied in the market in the strengths from 36° Be′ (52% HNO_3) to 42°Be′ (67% HNO_3). If the quantity is less than 24 litres or so, HNO_3 is shipped in carboys. Larger shipments of 90 – 95% HNO_3 are made in aluminium or stainless steel drums.

Sulphuric Acid, H_2SO_4

Sulphuric acid is very important in chemical industries and is generally called the *king of chemicals*. The advancement in chemical process industries is estimated on the basis of amounts of sulphuric acid prepared. Sulphuric acid is widely used in chemical industries *i.e.*, fertilizers, paints, explosives, petroleum refining, drugs, etc.

· The following are the two well-known processes used for the manufacture of H_2SO_4:

1. Lead Chamber Process.
2. Contact Process.

1. LEAD CHAMBER PROCESS

This process is carried out in large lead-lined chambers where SO_2 is reacted with O_2 in presence of NO.

SO_2 is obtained either by burning sulphur or by roasting pyrites or sulphides such as iron sulphide. Instead of metal sulphides or sulphur, gypsum ($CaSO_4$) has

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

also been used to produce SO_2. Thus, a mixture of $CaSO_4$, SiO_2, C and clay is heated in a furnace to produce a mixture of gases containing SO_2, N_2 and oxygen called *burner gases*.

$$CaSO_4 + C \longrightarrow CaO + SO_2 + CO$$

$$CaSO_4 + CaS + O_2 \longrightarrow 2CaO + 2SO_2$$

$$2CaS + 4CaO + 6SiO_2 + 3O_2 \longrightarrow 6CaSiO_3 + 2SO_2$$

$$2CaS + 4CaO + 2Al_2O_3 + 3O_2 \longrightarrow 6CaO.2Al_2O_3 + 2SO_2$$

This method of obtaining SO_2 is suitable in Pakistan where large amounts of gypsum are available.

Sulphur dioxide is passed through lead chambers in presence of air or O_2, NO and NO_2 along with steam. SO_2 is converted to H_2SO_4. Reactions in the lead chambers are represented as:

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + 2SO_2 + H_2O \rightleftharpoons 2NO(HSO_4) + NO$$

$$2NO\,(HSO_4) + H_2O \rightleftharpoons 2H_2SO_4 + NO + NO_2$$

The overall reaction in lead chambers is oxidation of SO_2 to SO_3.

$$SO_2 + [O] \longrightarrow SO_3$$

The mixture of NO and NO_2 is recirculated which functions as 'oxygen carrier.'

The acid from Chamber Process is 60 – 70% H_2SO_4. A schematic outline of the process is given in Figure 21.4.

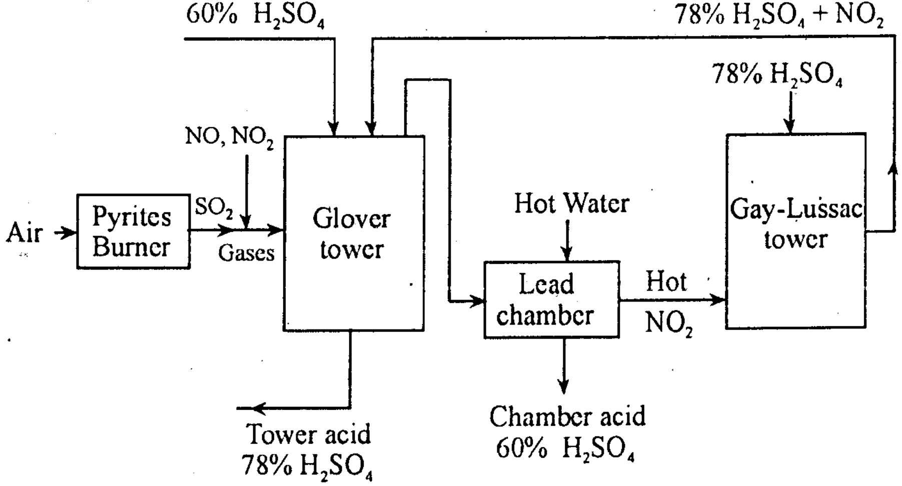


Fig. 21.4. A schematic outline for the manufacture of H_2SO_4 by Lead Chamber Process.

The plant employed in the process consists of:

(i) Pyrites Burners

The combustion of S or sulphides is carried out in mechanical furnace or the flash roaster.

(ii) Nitre Pots

The nitre pots contain a mixture of $NaNO_3$ and H_2SO_4.

The tower is about 15 × 50 feet and lined with acid proof cement. The mixture of gases are sprayed by a mixture of 60% H_2SO_4 from the lead chambers and strong nitrated acid from the base of the Gay-Lussac tower.

(iii) Glover Tower:

The major functions of Glover tower are:

(i) Cooling the gases from the burner.

(ii) Concentration of the dilute acid for the chambers.

(iii) Conversion of some SO_2 into H_2SO_4. This reaction is similar to that taking place in lead chambers.

(iv) Recovery of the oxides of nitrogen from nitrated H_2SO_4 coming from Gay-Lussac tower.

(v) Cleaning of the burner gases.

(iv) Lead Chambers

These are box-like rooms made of sheet lead. The number of chambers varies and is usually between 3 to 12. The gases enter the chambers at about 99°C. The operation of the chambers is controlled through colour of the chamber gases, by analysis, and through temperature control.

The functions of the chambers are:

(i) To afford space and time for the mixing of the gases and conversion of SO_2 to SO_3.

(ii) To radiate heat produced by the chemical reaction.

(iii) To furnish surfaces for condensation of the acid mist formed.

(v) Gay-Lussac Tower

The construction of this tower is essentially the same as the Glover tower. It is filled with tile with tile packing to provide maximum area for contact. The major function of the Gay-Lussac tower is the recovery of the oxides of nitrogen from gases coming from lead chambers.

(vi) Coolers

The coolers consist of a number of tanks (at least three) set in series made of sheet lead. Coils of lead pipes carrying cold water are present in them. The acid from the Glover tower enters the first cooler at 130° – 150°C and leaves the last at 30 – 40°C.

PURIFICATION OF CHAMBER ACID

Chamber acid is usually used for ordinary purposes without further purification *i.e.*, fertilizers, pickling of iron, etc. If chamber acid is prepared from sulphur, the acid is relatively pure and contains only small amounts of lead, oxides of nitrogen, iron or aluminium dissolved from towers or chambers. Dissolved oxides of nitrogen are removed by adding 0.2 – 0.5 percent ammonium sulphate and heating the acid to 100°C.

$$NO + NO_2 + (NH_4)_2\,SO_4 \longrightarrow 2N_2 + H_2SO_4 + 3H_2O$$

The purified acid is further concentrated by distillation and by the addition of *oleum* (H_2SO_4 saturated with SO_3).

2. THE CONTACT PROCESS

The contact process for the manufacture of H_2SO_4 is based on the catalytic oxidation of SO_2 to SO_3 in presence of atmospheric oxygen.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 189.1\ KJ$$

The reaction is reversible and exothermic. Therefore, the most favourable conditions of the reaction are:

(i) Composition

An excess of air must be passed but too much excess is avoided to prevent dilution of gases.

(ii) Temperature

Since the reaction is exothermic, the temperature of the reaction should be kept at 400 – 500°C (Le-Chatelier's Principle).

(iii) Pressure

According to Le-Chatelier's principle, increase of pressure should increase the yield of SO_3. Pressure is usually kept between 1.5 to 1.7 atmospheres.

(iv) Use of catalyst

The different catalysts used in the contact process for the manufacture of H_2SO_4 are given below. They enhance the yield of SO_3 from SO_3.

(a) Platinized Asbestos: It is very useful catalyst and in its presence conversion of SO_2 to SO_3 is almost 100%. The temperature is kept between 420°C – 430°C.

(b) Platinized Magnesium Sulphate: This catalyst is prepared by moistening hydrated magnesium sulphate with a solution of platinum chloride and heating the salt till it swells up.

(c) Vanadium Pentoxide: V_2O_5 is an efficient catalyst and is not affected by poisons.

Process

Sulphur is burnt in a *sulphur burner*. The gas leaving the sulphur burner contains 5 – 7% by volume of SO_2, some moisture and dust. The vapours of gases are cooled by passing through pipe cooler made of cast iron.

The gases pass on to a *coarse coke filter* from scrubber towers. The last traces of suspended matter are removed by Cotterell electrostatic mist precipitator. The purified gases then pass through the heat exchangers, and cooled to 250°C. From heat exchangers, the gases go to the catalyst chambers called converters. Sulphur trioxide is formed with evolution of heat. SO_3 is cooled and passed through absorption towers. A stream of water or dilute H_2SO_4 is run into the towers. By restricting the supply of water and acid, oleum or fuming sulphuric acid is obtained. The oleum tower is made of brick-lined steel packed with quartz and fed with 98% H_2SO_4

$$H_2SO_4 + SO_2 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

Appropriate amounts of water are added to oleum to convert $H_2S_2O_7$ to H_2SO_4.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Sulphuric acid obtained by the contact process is quite pure and concentrated and it is a better method.

The flow sheet for contact process is shown in Figure 21.5.

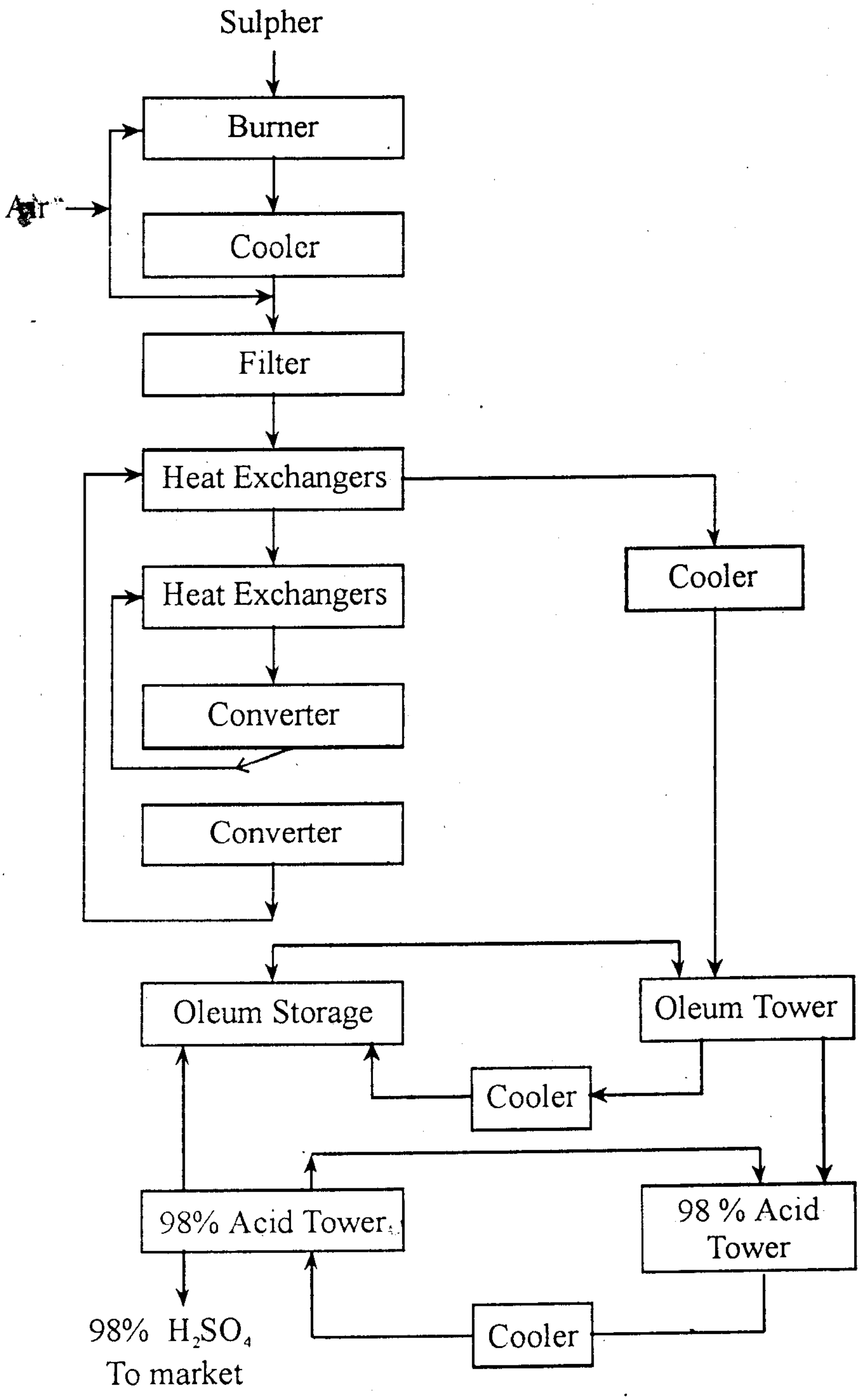


Fig. 21.5. Flow sheet of the Contact Process.

Comparison of the Contact and Lead Chamber Processes

The contact is overall superior to the lead chamber process and has the following major advantages:

(i) The acid obtained in contact process is extremely pure.

(ii) Sulphuric acid of any concentration can be easily obtained in the contact process.

At present contact process is mainly used, especially when acid is required for the manufacture of explosives, fine chemicals, lead accumulators, indigo, etc.

The lead chamber process is comparatively cheaper. Whenever commercial acid is required, lead chamber process is employed.

MANUFACTURE OF SODIUM CARBONATE (SODA ASH), Na_2CO_3

Sodium carbonate is an important chemical and is used from the earliest times. Sodium carbonate can be manufactured by three methods:

(i) by the Leblanc process — now almost obsolete.

(ii) by the ammonia-soda or Solvay process.

(iii) from naturally occurring sodium carbonate.

The first two processes are usually used and would be discussed over here:

1. The Leblanc Process

This method is not in much use now. It involves the following three stages during the manufacture of sodium carbonate:

(a) Sodium chloride is converted into sodium sulphate by treatment with sulphuric acid.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

(b) The salt-cake of Na_2SO_4 is converted into *black-ash* (a mixture of CaS and Na_2CO_3) by heating it to high temperatures in presence of limestone and coke in revolving furnaces.

$$Na_2SO_4 + CaCO_3 + 2C \longrightarrow Na_2CO_3 + CaS + 2CO_2$$

(c) The sodium carbonate is extracted from black ash by leaching it with water. The solution is filtered to get sodium carbonate in it which can be obtained in solid form by crystallisation. The calcium sulphide can be used in the manufacture of $Na_2S_2O_3$.

Economics of the Process

A sulphuric acid industry is to be established in order to run this process. The purity of soda ash (Na_2CO_3) is poor. The recovery of byproducts also involves a lot of expenditure. The Leblanc process died due to the high fuel cost, high labour costs and extra necessities to run the process.

2. Ammonia Soda or Solvay Process

This is the modern method used for the manufacture of sodium carbonate and is commonly known as Solvay Soda process.

The process is based on the fact that on mixing sodium chloride and ammonium bicarbonate solutions, a precipitate of $NaHCO_3$ is obtained under these conditions:

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

The sodium bicarbonate is filtered off and heated to get sodium carbonate.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

The working of the process is shown by flow sheet diagram shown in Figure 21.6.

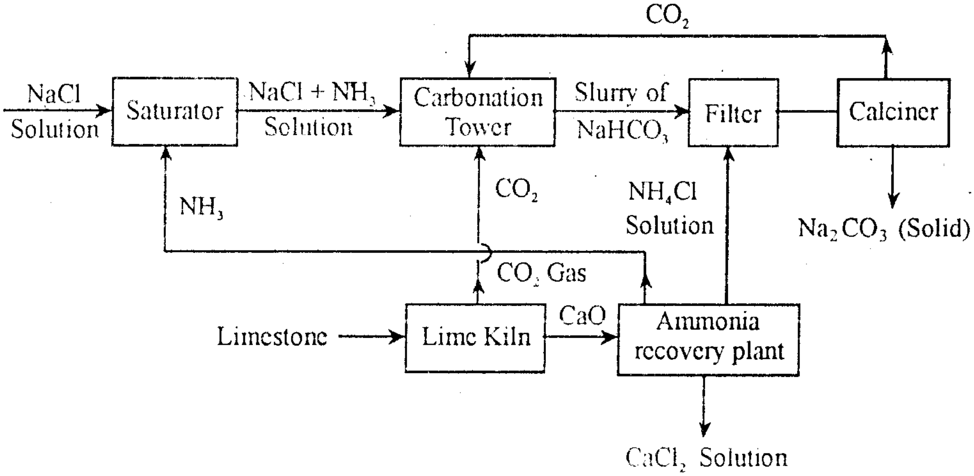


Fig. 21.6. Flow sheet of Solvay process.

The process shall now be discussed on the basis of the various parts of the plant.

(a) Saturator

A strong solution of sodium chloride or brine is admitted into saturating tank. The saturating tank is cylindrical (15 × 12 feet) with conical bottom. The brine solution is here saturated with ammonia. Calcium and magnesium present in the form of salts as impurities in brine are precipitated by CO_2 accompanying NH_3 from ammonia recovery plant.

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + 2NH_4Cl$$

$$MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3\downarrow + 2NH_4Cl$$

The saturated brine is allowed to stand in setting tank where precipitates of carbonates of calcium and magnesium settle down.

(b) Carbonation Tower

The carbonation of ammoniacal brine (sodium chloride solution) is carried out in carbonation tower provided with partitions and cooling coils. The CO_2 gas from lime kiln is passed from the bottom and solution trickles form the top (counter current principle). As a result of this ammonium bicarbonate is formed which precipitates $NaHCO_3$.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$$

Actually a milky liquid containing suspended sodium bicarbonate crystals is obtained. The solution is filtered to get $NaHCO_3$. The solid sodium bicarbonate is heated in rotary furnace called *calciner* to get solid sodium carbonate.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

The carbon dioxide set free is recirculated to carbonation tower.

(c) Lime Kiln

Limestone is burnt in lime kiln to get calcium oxide and carbon dioxide.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

CO_2 is sent to carbonation tower. The lime, CaO is slacked by adding large quantities of water and pumped to *ammonia recovery plant* to regenerate NH_3 from NH_4Cl.

(d) Ammonia Recovery Tower

The solution from filters is run into ammonia recovery plant where it is mixed with $Ca(OH)_2$ coming from lime kiln and heated in presence of steam. Ammonia (mainly) and some carbon dioxide are regenerated which are pumped to *saturator* (Figure 21.6)

The following reactions take place in ammonia recovery tower.

$$NH_4HCO_3 \xrightarrow{\Delta} NH_3 + H_2O + CO_2$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$

The ammonia soda or Solvay process is almost self-sufficient. The only raw materials mainly consumed are NaCl and limestone ($CaCO_3$).

Sodium carbonate crystallises as $Na_2CO_3.10H_2O$ (washing soda). It is used in the manufacture of glass, soap, paper and pulp and in petroleum refining as well as in water softening.

Baking soda ($NaHCO_3$) is also a useful intermediate used as baking powder and in medicines.

MANUFACTURE OF CAUSTIC SODA OR SODIUM HYDROXIDE, NaOH

Sodium hydroxide is a very important chemical and is manufactured on large scale by the following two methods:

(i) By causticizing sodium corbonate of soda ash.

(ii) By electrolysis of sodium chloride solution (brine).

1. By Causticizing Sodium Carbonate (Gossage's process)

Caustic Soda is mainly manufactured by causticizing sodium carbonate (soda ash) with slaked lime, Ca $(OH)_2$ according to the following reaction:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3\downarrow$$

The efficiency of the process decreases by increasing the concentration of sodium carbonate solution treated with lime. In actual practice, a 20% solution of sodium carbonate is used. The liquid is kept at 85°C.

The causticization of sodium carbonate is carried out in a tank provided with stirrer. A 20% Na_2CO_3 solution is run into the tank and a slight excess of milk of lime (slaked lime) is added. The temperature of the solution is kept at 80° – 85°C and stirred. After one hour, stirring is discontinued and precipitated calcium carbonate allowed to settle. The supernatant liquid (containing 1% NaOH) is run into concentration tank. The solution is heated in multiple effect evaporators to get 50% NaOH solution. In order to get solid sodium hydroxide, the 50% solution is heated in cast iron pots over the naked flame until water is driven off. The caustic soda obtained by the above procedure is above 98% pure. (The only impurities are 0.9% Na_2CO_3, 0.3% NaCl and 0.2% Na_2SO_4).

2. By Electrolysis of Sodium Chloride (Brine)

The electrolysis of a solution of sodium chloride commonly known as brine produces sodium hydroxide and chlorine. The electrolytic cell is made in such a way as to prevent contact of Cl_2 set free from the anode with NaOH at the cathode.

The principle of the procedure is indicated by the following electrochemical changes.

$$2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$$

$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

At Cathode

$$2Na^+ + 2e \longrightarrow 2Na$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2H^+ + 2e \longrightarrow H_2$$

At Anode

$$2Cl^- - 2e \longrightarrow Cl_2$$

$$2OH^- - 2e \longrightarrow H_2O + [O]$$

In order to keep the products obtained at the cathode and the anode, two type of cells are commonly used:

(a) Porous Diaphragm Cell.

(b) Mercury Cell or Kellner Cell.

(a) Porous Diaphragm Cell

A large number of porous diaphragm cells have been devised but one of the widely used cell is Gibbs cell (shown in Figure 21.7). In this cell a ring of carbon rods are used as anodes which are separated from the cathode consisting of a cylinder of iron gauze by a diaphragm made of asbestos paper. The brine solution is kept at 85°C and is introduced into the cell in a slow stream from the top into anode compartment. On electrolysis, any NaOH produced is collected at the bottom of the cell and removed. Chlorine comes out on top of the cell and is collected in cylinders or earthenware pipes.

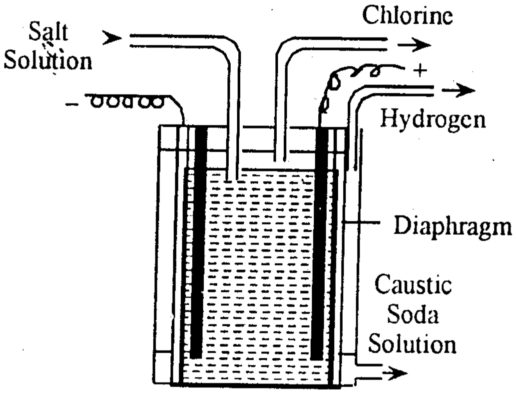


Fig. 21.7. Porous Diaphragm Cell.

The other type of diaphragm cell commonly used is Nelson cell.

(b) Mercury Cell or Kellner Cell

A cell using mercury diaphragm is called Kellner Cell (Figure 21.8). Graphite anodes and a mercury cathode is used in this cell. The cathode consists of a layer of mercury at the bottom of the cell through which it flows slowly. Na^+ ions are discharged at the mercury cathode. The sodium deposited at mercury cell forms sodium amalgam (Na.Hg) which is treated with water in iron vessel outside the cell compartment to get sodium hydroxide and mercury and hydrogen is evolved. The mercury flows through the cell either by giving slanting position to the cell or by using Archimedean screw. Chlorine obtained at the anode is removed from the top of the cell.

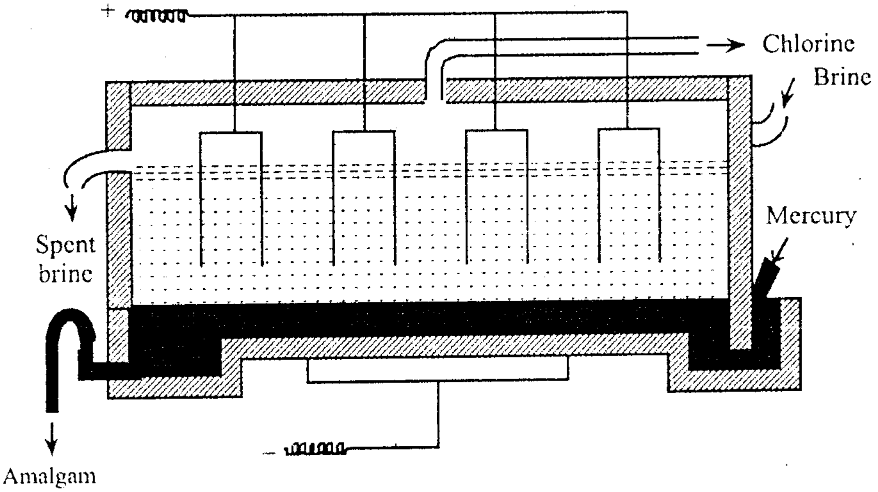


Fig. 21.8. Mercury or Kellner Cell.

The caustic soda obtained from mercury cell has a concentration of 50% and is almost free from impurities. At present more than 75% of electrolytic caustic soda is obtained by mercury cells.

The chlorine obtained by electrolytic process is an important byproduct and is used to prepare various other chemicals such as bleaching powder.

Purification of Caustic Solution

The demand for iron free caustic soda is increasing in rayon and wood pulp industries. Purification processes are necessary for 50% NaOH obtained from diaphragm electrolytic cell.

Iron, silica and alumina etc., are removed by treating 50% caustic soda solution with finely divided strontium sulphate. It absorbs the impurities and settles down.

The presence of sodium chloride in caustic soda is also objectionable. NaCl is removed from caustic soda by cooling.

Marketing of Caustic Soda

The materials which are seriously attacked by caustic soda are copper, brass, bronze, silicon-iron alloys, aluminium and its alloys, hard rubber, etc. Caustic soda is sold either as a solid or in the form of solution. The solid caustic soda is marketed in drums. Solid sticks or pellets of caustic soda are considered superior and have higher prices.

MANUFACTURE OF SOAP:

Soap is sodium or potassium salt of fatty acids, mainly oleic, stearic, palmitic, lauric and myristic.

Raw Materials:

Tallow is the principal fatty material in soap making. It contains mixed glycerides obtained from the solid fat of cattle. This solid fat is digested with steam. The tallow forms a layer above water and is easily removed. Tallow is usually mixed with coconut oil to increase the solubility of soap. Greases are also used as raw material for soap making. These are important source of glycerides of fatty acids. The soap made from coconut oil lathers well. Inorganic chemicals added to soap are called builders e.g., soda ash, sodium tripolyphosphate, tetrasodium pyrophosphate.

Manufacture:

Soap is manufactured by saponification of glycerides of fatty acids. The basic chemical reaction in soap making is saponification of fat.

$$\underset{\substack{\text{Glyceryl stearate}\\ \text{(fat)}}}{(CH_{17}H_{35}COO)_3C_3H_5} + \underset{\substack{\text{Caustic}\\ \text{soda}}}{3NaOH} \longrightarrow \underset{\substack{\text{Sodium}\\ \text{stearate}}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}$$

The following two steps are involved in soap making:

The fat is hydrolyzed to get fatty acid and glycerine. The fatty acid is neutralized with caustic soda solution to form soap.

$$\underset{\text{Glyceryl}}{(CH_{17}H_{35}COO)_3C_3H_5} + 3H_2O \longrightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerine}}{C_3H_5(OH)_3} \qquad (1)$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + NaOH \longrightarrow \underset{\substack{\text{Sodium}\\ \text{stearate}}}{C_{17}H_{35}COONa} + H_2O \qquad (2)$$

The fatty oil is deaerated under vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower, which breaks the fat into droplets. These towers are about 20 m high and 60 cm in diameter and are made of stainless steel. At the same time deaerated, demineralised water is fed to the top of contacting section to separate glycerine from fatty phase. They fatty acids are discharged from the top of the hydrolyser to a decanter and glycerine – water solution from the bottom. The molten fatty acid is run into pans and neutralized with 50 % caustic soda to get soap.

The neat soap is discharged at 93°C into blending tank and extruded, milled, flaked or spray – dried. The soap is heated at about 200°C under high pressure steam exchanger. The heated soap is released to a flash tank at atmospheric pressure, where partial drying takes place. The soap is cooled from 105°C to about 65°C and cut into bar lengths.

The main classes of soap are toilet soaps and industrial soaps. All soaps contain 10 – 30°C water. If soap is anhydrous, it would be too hard to dissolve it. Toilet soaps contain 10 – 15 % moisture and have perfume and a fraction of a percent of titanium dioxide as a whitening agent. Shaving soaps are potassium salts of mainly stearic acid.

Questions

1. How is Nitric Acid manufactured? What is the action of nitric acid on copper, zinc and tin?
2. How is Nitric Acid manufactured from (a) air, (b) ammonia?
3. Starting from nitrogen and hydrogen, how would you prepare Nitric Acid?
4. Describe in detail the Solvay process for the manufacture of sodium carbonate. Give important applications of sodium carbonate.
5. Sketch and explain the flow sheet for the manufacture of Sulphuric Acid by the Contact process. Compare the efficiency of different catalysts employed. Discuss the advantages of Contact process over the Chamber process.
6. What is the function of NO in the manufacture of H_2SO_4 by Chamber process? Discuss the process and reactions involved.
7. Compare the Contact and Chamber processes for the manufacture of Sulphuric Acid.
8. Discuss the conditions necessary to obtain a maximum yield of Sulphuric Acid from Sulphur. What is the fundamental reaction of the Contact process for the manufacture of Sulphuric Acid?
9. Briefly discuss the basic conditions and reactions governing the conversion of SO_2 to H_2SO_4 by the Contact Process.
10. Liebig declared "A nation's industrial pre-eminence may be measured by its consumption of sulphuric acid." Justify this statement.
11. Discuss the process and reactions involved in the production of Sulphuric Acid by Chamber process. What is the quality of acid obtained by this process?
12. Explain the process for the manufacture of sodium hydroxide. How is it obtained pure in solid state?
13. Describe briefly with diagram the electrolytic method for the manufacture of caustic soda. Mention its commercial uses.
14. How would you compare the quality of caustic soda obtained from diaphragm cell and mercury cell?
15. Discuss the prospects of acid-alkali industry in Pakistan.
16. Describe the manufacture of soda ash.
17. What are the steps involved in the manufacture of soap?
18. **Write short answers to the following questions:**
    - (i) How is nitric acid produced from nitrates?
    - (ii) How is nitric acid obtained from air?
    - (iii) What is the Ostwald's process for the formation of HNO_3?
    - (iv) How is sulphuric acid produced by Lead Chamber Process?
    - (v) Discuss Contact process for the production of sulphuric acid.

(vi) Why sulphuric acid is called king of chemicals?

(vii) Draw comparison of the Contact and Lead Chamber processes.

(viii) How is soda ash manufactured by Leblanc process?

(ix) Elaborate the steps involved in the manufacture of soda ash by Solvay process.

(x) Discuss the formation of caustic soda from brine.

19. **Give the correct answer:**

(i) Leblanc process for the manufacture of Na_2CO_3 involves:
(a) electrolysis (b) $CaCl_2$ (c) $CaCO_3$ (d) CO_2
(Ans: c)

(ii) In Solvay process, the following is the raw material:
(a) NaCl (b) $NaNO_3$ (c) KCl (d) KNO_3
(Ans: a)

(iii) Caustic soda can be produced by the reaction of:
(a) Na_2CO_3 and $Ca(OH_2)$ (b) Na_2CO_3 and $CaCl_2$
(c) $CaCO_3$ and NaCl (d) CaO and $CaCl_2$
(Ans: a)

(iv) Slaked lime is:
(a) CaO (b) $CaCO_3$ (c) $Ca(OH_2)$ (d) $CaCl_2$
(Ans: c)

(v) Baking soda is:
(a) Na_2CO_3 (b) NaOH (c) $NaHCO_3$ (d) Na_2SO_4
(Ans: c)

(vi) The brine solution is aqueous solution of:
(a) Na_2CO_3 (b) $NaNO_3$ (c) NaCl (d) KCl
(Ans: c)

(vii) On heating $NaHCO_3$, the following is produced:
(a) $Na_2CO_3 + CO_2$ (b) Na_2CO_3 (c) Na_2O (d) Na_2CO_3 and Na_2O
(Ans: b)

(viii) On heating NH_4HCO_3; we get the following:
(a) $NH_3 + CO_2$ (b) NH_3 (c) CO_2 (d)$(NH_4)_2CO_3$
(Ans: a)

(ix) Cl^- liberates Cl_2 at:
(a) anode (b) cathode (c) anode and cathode (d) None of the above
(Ans: a)

(x) The container for caustic soda is made of:
(a) glass (b) brass (c) iron (d) earthen ware
(Ans: d)

❀ ❀ **21** ❀ ❀

22

AN INTRODUCTION TO MODERN MATERIALS

Systematic developments in Chemistry have tremendous contributions in the modern civilization. Chemists have now invented entirely new substances and developed means for processing naturally occurring materials to form fibers, films, adhesives and other substances with special electrical and magnetic, or optical properties. The advances in technology depend much more than ever upon the discovery of useful new materials. Thin and light electronic-display devices will make it possible to mount a television set on a wall like a picture. The forth coming era of nano-technology will be more fascinating when cheap materials will be commonly available i.e., computers, T.V. etc. Repositories of vast information, solar cell technology etc., will develop side by side with the development of modern materials. In this chapter a concise treatment of this subject-matter will be developed. At this stage we cannot cover all kinds of modern materials. However, liquid crystals, inorganic polymers, engineering ceramics, fiber glass, thin films and semi-conductors shall be discussed.

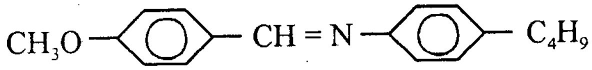
Liquid Crystals

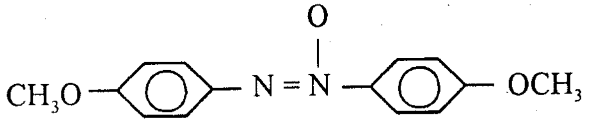
In 1888, F. Reinitzer, an Austrian botanist, discovered unusual properties of an organic compound called *cholesteryl benzoate*. When heated, the substance melts at *145°C to form a milky liquid* which becomes clear at *179°C*. This work represents the first report on liquid-crystal behaviour.

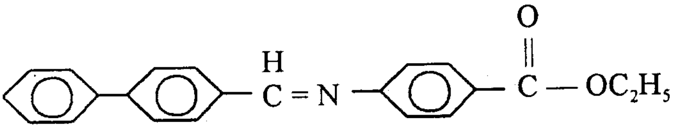
As the liquid crystals melt, many of them pass through a temperature range in which they possess properties intermediate between solid and liquid phases. The intermediate phase is called liquid crystal phase. In this phase the substances have some ordering of molecules like solids.

Structure of Liquid Crystals

Liquid-crystalline substances have characteristic molecular structures and shapes. The molecules tend to possess long, rod-like shape and are somewhat rigid. The characteristic rod-like shape allows intermolecular interactions and maintains a parallel ordered form of liquid phase. The molecules which behave as liquid crystals are required to possess long axis with double bonds and three dimensional network which does not coil in random ways and appears to be rod-like rather than round. The characteristic rod-like shape allows intermolecular interactions that maintain a parallel ordering in the liquid phase. The following molecular structures of typical liquid crystals are rather long, rigid and permit alignment and ordering of molecules with respect to one another.

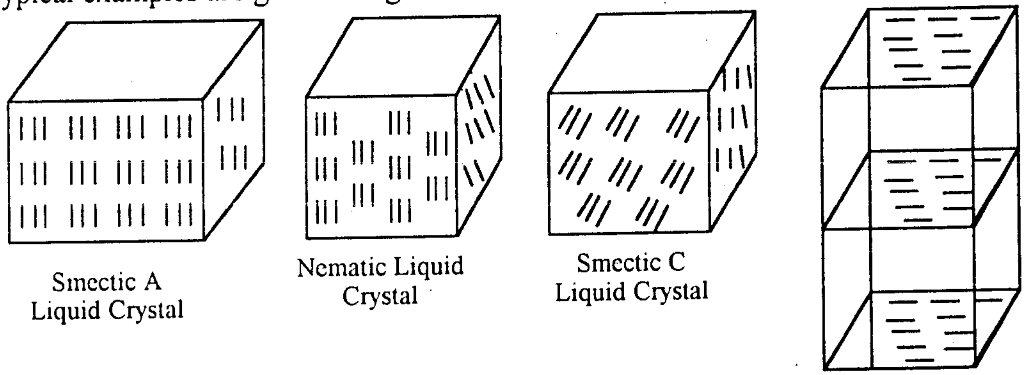






Types of Liquid Crystalline Phases

Different ordering arrangements are known for liquid crystals. Some typical examples are given in Fig. 22.1.



Smectic A Liquid Crystal

Nematic Liquid Crystal

Smectic C Liquid Crystal

Cholesteric Liquid Crystal

Fig. 22.1. Ordering Arrangements for Liquid Crystals.

Applications of Liquid Crystals

The attractive forces that cause the alignments of molecules in liquid crystals are not large as compared to energies of chemical bonds. These relatively weak interactions lead to physical properties of considerable technological importance. These are considered to be chemical curiosities and are now widely used in electrically controlled "liquid-crystal-display" (LCD) devices in watches, calculators and computer screens. These applications are based on the ability of an applied electrical field to cause a change in the orientation of liquid-crystal molecules which affects the optical properties of a layer of liquid-crystalline material.

The liquid-crystal devices are marketed in different designs. Ordinarily liquid-crystalline material is placed between two glass plates coated with transparent electrically conducting material. Light passes through the liquid-crystal without applying any voltage and is reflected at the bottom of the material causing bright surface. On applying voltage changes in orientation of liquid-crystal molecules take place and light is unable to pass through the liquid-crystalline phase. The area of display to which the voltage has been applied appears dark. The result is different patterns on display.

Liquid-crystalline materials also change colour as temperature changes which is the cause of colour displays. The computers have liquid-crystal display (LCD) panel.

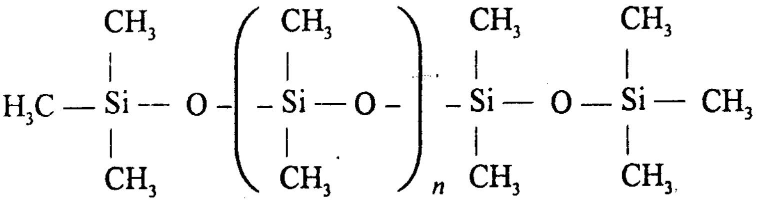
Inorganic Polymers

Polymers are large molecules formed by linking together large number of small units called monomers. Polyethylene – $(CH_2 - CH_2)_n$–, made from ethylene. $CH_2 = CH_2$, is a typical example. Other examples of organic polymers are nylon, dacron, tetralyne and poly vinyl chloride (PVC). The 'backbones' of organic polymers are mostly carbon atoms, and usually they tend to become brittle when cold and deteriorate on heating. They tend to be flammable and swell in organic solvents. These problems are minimized with inorganic polymers whose molecular backbones consist of atoms other than carbon.

The following three types of inorganic polymers will be discussed:

(a) Silicon Polymers

The silicon polymers are widespread and are called silicones. These polymers contain an alternating silicon-oxygen backbone with organic groups attached to each silicon atom. A silicon polymer chain is:



$$H_3C - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}} - O - \left(- \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}} - O - \right)_n - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}} - O - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}} - CH_3$$

Silicon polymers (Silicones) are formed by hydrolysis of compounds such as $(CH_3)_2SiCl_2$. The Si – OH bonds subsequently expel water and form, Si – O – Si – linkages.

Silicones are present in the form of oils, greases or rubbers. These are used in polishes, waterproofing treatments for fabrics and leather, paints, lubricants, medical preparations, etc.

(b) Phosphazenes

In phosphazenes, the polymer backbone consists of alternating phosphorus and nitrogen atoms. Polyphosphazenes are prepared by polymerizing the ring-shaped molecules, $(PNCl_2)_3$ and then substituting chlorines with various groups. The phosphazenes are generally non-flammable or flame retarding. Some of them are glasses and others are elastomers which retain their elasticity at low temperatures. They do not react with living tissue and are used to replace blood vessels. It has been observed that certain biologically active molecules can be incorporated into these polymers without losing their activity.

(c) Electrically Conducting Polymers

One of the most interesting conducting polymer is formed by heating tetrasulphur tetranitride, S_4N_4. The ring-shaped molecule initially breaks down into a smaller ring, S_2N_2, which then polymerizes to give crystals of poly (sulphurnitride), $(SN)_n$, a shiny metallic solid. The crystals contain long chains of alternating sulphur and nitrogen atoms. These polymers behave like metallic conductors and even become superconductors if cooled to near absolute zero.

Kevlar is advanced polymer material. Kevlar ropes have replaced steel ropes and cables in many applications, especially on off shore oil-drilling platforms. Kevlar ropes in sea-water have 20 times the strength of steel.

Ceramics

Ceramics are inorganic, non-metallic, solid materials and can be crystalline or non-crystalline. Glass is an example of non-crystalline form. Ceramics possess a covalent network structure or ion bonding or a combination of the two. Ceramics are hard and brittle but stable to high temperatures. Common examples of ceramic materials are pottery, china clay, cement, roof tiles, refractory bricks used in furnaces and the insulators in spark plugs.

Ceramic materials are present in a variety of chemical forms, such as silicates (silica, SiO_2, with metal oxides), oxides, carbides, nitrides and aluminates (alumina, Al_2O_3, with metal oxides).

Engineering Ceramics

Ceramic materials which might be used to replace other engineering materials, such as metal, wool or plastics, are termed engineering ceramics. These ceramics are highly resistant to heat, corrosion, wear and tear and used in high temperature devices. Some ceramics are used in aircraft, missiles and spacecraft which may have about 40% by weight of ceramic materials. The only disadvantage in their use is that they are brittle.

Ceramic Composites

Ceramic objects become much tougher when they are mixed with other materials such as ceramic fibres. Such mixture is called a composite. The composites are highly resistant to crack failure. An example of ceramic fibre is silicon carbide, SiC or Carborundum.

Applications of Ceramics

Ceramics, particularly new ceramic composites are widely used in cutting-tool equipment. For example, alumina reinforced with silicon carbide is used to cut cast iron and nickel-based alloys. Ceramic materials are also used in grinding wheels and as abrasives. Ceramic materials are also used in the electronic industry. Semi-conductor integrated circuits are mounted on ceramic substance, usually alumina.

Thermistors are ceramic materials with limited electrical conductivity that increases with temperature. Thermistors are devices which measure or control temperature. They are used as heating element and electrical switches.

Ceramic oxides containing lanthanum, barium and copper show superconducting behaviour. The discovery of high temperature conductivity is of great significance and has applications in electrical generators and electric motors and could lead to the production of smaller and faster computer chips.

Fibre Glass

Fibre glass is produced by dropping molten glass onto a refractory rotating disc. The glass flies off the disc and forms fibres.

Optical fibres are made from silica glass. Silica glass has excellent optical transparency and should be extremely pure. Impurities such as copper and iron have to be reduced to less than one part per billion. The silica glass used for optical fibres is made directly by the vapour-phase reaction of oxygen and silicon (IV) chloride. Optical fibres consist of a central core region in which light is transmitted. The fibre of thickness of a human hair can be prepared and is protected by a thin film of silicone or organic polymer.

Fibre glass is used to make panels in cars and is useful material for aircraft components. Optical fibres are used to transmit television programmes, telephone conversations, computer outputs, etc. It is expected that copper wire cables used conventionally will eventually be replaced by optical fibres.

THIN FILMS

The term thin film refers to films with thickness ranging from 0.1 μm to about 300 μm. It does not refer to coatings which are much thicker. Thin film must possess the following properties:

(a) It should be chemically stable in the environment in which it is to be used.

(b) It should adhere well to the object it covers.

(c) It should have a uniform thickness.

(d) It should be chemically pure.

(e) It should have low density.

(f) It may possess some special properties such as that of insulator, semiconductor or may have special optical or magnetic properties.

The bonding energies between the thin film and the substrate may be of the same magnitudes as chemical bonds or may be of the magnitude of intermolecular Van der Waals' and electrostatic forces.

Thin films can be formed by vacuum deposition. The material to be deposited as thin film is heated either electrically or by electron bombardment in a high vacuum chamber (10^{-5} mm Hg or less). The uniformity of thin film is obtained by rotating the object to be coated. The materials which can be vapourized or evaporated without undergoing any chemical change or decomposition can be used to form thin films. For example, optical lenses are coated with inorganic materials such as MgF_2, SiO_2 and Al_2O_3.

Thin films can also be formed on a material surface by sputtering. Sputtering involves the use of a high voltage to remove material from the source or target. Atoms are removed from the target material and carried through the ionized gas within the chamber and deposited on the substrate. The target surface is the cathode and the substrate is made the anode. The chamber contains an inert gas such as argon. The sputtered atoms have a lot of energy. The initial atoms striking the surface may penetrate several atomic layers into the substrate, which helps to ensure good adhesion of the thin film to the object. Another advantage of sputtering is that it is possible to change the target material from time to time to get multilayer thin films without disturbing the system. Sputtering is widely used to form thin films of silicon, titanium, tungsten, aluminium, gold and silver. It is also employed to form thin films of refractory materials such as carbides, borides and nitrides on metal tool surfaces and to form lubricating films.

In chemical-vapour deposition, the surface is coated with a volatile, stable chemical compound at a temperature below the melting point of the surface. The compound then undergoes a chemical reaction to form stable coat. It is thus possible to make titanium thin films on ceramic or other material by passing mixture of gaseous $TiBr_4$ and hydrogen over the surface of the material at 1300°C.

$$TiBr_{4(g)} + 2H_{2(g)} \longrightarrow Ti_{(s)} + 4HBr_{(g)}$$

Films of silicon nitride can be formed by the reaction of silane, SiH_4, with ammonia at 900°C – 1100°C.

$$3SiH_{4(g)} + 4NH_{3(g)} \longrightarrow Si_3N_{4(g)} + 12H_{2(g)}$$

Thin films were first used for decorative purposes. These are even today used for decorative or protective purposes, to form conductors, resistors and other types of films in microelectronic circuits. They are also used to form photovoltaic devices for the conversion of solar energy to electricity. Thin films are also used as optical coatings on lenses to reduce the amount of light reflected from the lens surface and to protect the lens. Metal tool surfaces are coated with ceramic thin films to increase their hardness. For example, a hard steel drill may be coated with a thin film of tungsten carbide. Diamond thin films are used to get hardness and wear resistance on cutting tools and to enhance the hight frequency response of diaphragms in audio speakers.

Semi-Conductors

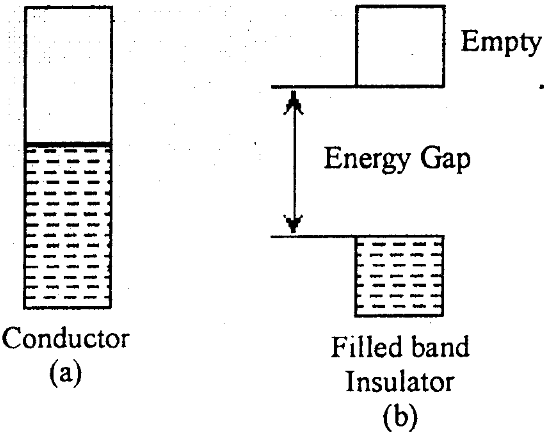


Fig. 22.2. (a) Metallic conductors have partially filled energy bands. (b) Insulators have filled or empty energy bands.

A metal is a good conductor of electricity because it has partially filled energy band as shown in Fig. 22.2 (a). There are more molecular orbitals in the band than are needed to accommodate all the bonding electrons present in it. Thus, an excited electron can move easily to the vacant orbitals and is responsible for conduct of electricity. In some solids, however, the electrons completely fill the allowed energy bands *e.g.*, diamond. The carbon 2*s* and 2*p* atomic orbitals combine to form two energy bands. One of these bands is completely filled and the other remains unfilled with electrons (Fig. 22.2 b). There is large energy gap between the two bands. As there is no readily available vacant orbital in the filled band and there is energy barrier between the filled and empty band, the electrons cannot move even under the influence of an applied electrical potential, diamond is not a good conductor of electricity. Such solids in which energy bands are either completely filled or completely empty are called electrical insulators.

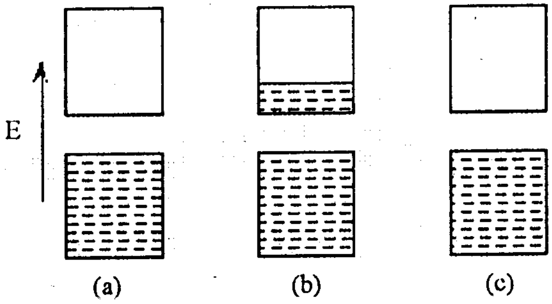


Fig. 22.3. (a) Pure Silicon, (b) Silicon doped with phosphorus, (c) Silicon doped with gallium.

Silicon and germanium have electronic structures similar to diamond. But the energy gaps in them are smaller down the group IV. As a result of it the empty bands permit the flow of electrons to some extent. Therefore, silicon and germanium behave as semi-conductors (Fig. 22.3 a).

The electrical conductivity of a semi-conductor or insulator can be modified by adding small amounts of other substances. This process is called doping. When silicon is doped with phosphorus, the phosphorus atoms substitute for silicon atoms at random sites in the structure. The excess electrons with phosphorus have access to empty bands and are responsible for the conductance of electricity (Fig. 22.3(b)). Silicon doped with phosphorus in this manner is called an *n*-type semi-conductor, because this doping introduces extra-negative charges (electrons) into the system.

If elements, such as gallium are doped with silicon, enough electrons are not available to be transferred to silicon. The valence band is thus nor completely filled (Fig. 22.3(c)). Under the influence of an applied field, electrons can move from occupied molecular orbitals to the vacant valence band. A semi-conductor of this type is called *p*-type semi-conductor.

The modern electronics industry is based on integrated circuits in which silicon or germanium doped materials are used to get the desired electronic characteristics. Semi-conductors are responsible for tremendous miniaturization of electronic devices.

Questions

1. What are modern materials? What is their usefulness?
2. What are liquid-crystals? Discuss their structures and liquid-crystalline phases. Describe their applications in modern technologies.
3. What are polymers? Discuss the type of inorganic polymers used in modern industry.
4. What are ceramics? Discuss engineering ceramics with reference to their applications.
5. What is fibre glass? Describe its usefulness.
6. Give the characteristic features of thin films. How are these formed? What is the advantage of preparing thin films?
7. Discuss the theory of semi-conductors. What is their usefulness?
8. Write notes on: (a) Liquid crystals. (b) Thin films. (c) Semi-conductors. (d) Fibre glass. (e) Engineering ceramics.
9. **Give short answers to the following questions:**
    - (i) What are liquid crystals?
    - (ii) Describe the structure of liquid crystals.
    - (iii) What are the applications of liquid crystals?
    - (iv) Classify inorganic polymers.
    - (v) What are ceramics?
    - (vi) What are the applications of ceramics?
    - (vii) What is fibre glass?
    - (viii) What are thin films? What should be their characteristic features?
    - (ix) How are thin films produced?
    - (x) Describe salient features of semi-conductors.
10. **Give the correct answer:**
    - (i) Semi-conductors have:
        - (a) partially filled energy bonds
        - (b) low energy bonding molecular orbitals
        - (c) low energy antibonding molecular orbitals
        - (d) fully filled orbitals

      (**Ans:** a)
    - (ii) Thin films have:
        - (a) uniform thickness
        - (b) non-uniform thickness
        - (c) high density
        - (d) chemically impure

      (**Ans:** a)

(iii) Fibre glass is used to make:
(a) panels in cars (b) balloons
(c) tyres (d) optical glass
(Ans: a)

(iv) Ceramic materials are applied for making:
(a) thermistors (b) thin films
(c) optical fibres (d) Kevlar
(Ans: a)

(v) Lubricants are made of:
(a) liquid crystals (b) semi-conductors.
(c) silicon polymers (d) plastic material
(Ans: c)

(vi) Liquid crystals have molecular structures with:
(a) trigonal shape (b) tetrahedral shape
(c) long rod-like shape (d) octahedral shape
(Ans: c)

(vii) Phosphazenes contain:
(a) Alternate P and N atoms
(b) Alternate P and H atoms
(c) Alternate P and O atoms
(d) Alternate P and Cl atoms
(Ans: a)

(viii) Liquid crystals are used in:
(a) calculators (b) clocks
(c) radio (d) cars
(Ans: a)

(ix) Semi-conductors are made up of:
(a) selenium
(b) silicon doped with gallium
(c) selenium doped with gallium
(d) selenium doped with silicon
(Ans: b)

(x) Titanium thin film can be obtained by passing gaseous $TiBr_4$ at 1300°C over:
(a) oxygen (b) carbon
(c) hydrogen (d) bromine
(Ans: c)

❀ ❀ **22** ❀ ❀

23

SOLVENT EXTRACTION AND CHROMATOGRAPHIC TECHNIQUES

SOLVENT EXTRACTION:

Solvent extraction is a technique that involves the distribution of a solute between two immiscible liquid phases. This is a rapid and clean technique of separating organic and inorganic substances.

Basis Principle of Solvent Extraction Technique:

The method is used for separation of dissolved substances from solutions by extraction with immissible solvents. It can be used for the separation of one constituent from a solid mixture and for the removal of undesirable impurities from mixtures.

Extraction of a substance with a second solvent is based on Nerst Distribution or Partition Law.

Distribution Law:

The ratio of the concentrations of the solute 's' in the two phases will be constant for immiscible solvents at particular temperature.

$$K_D = \frac{So}{Sw}$$

So = Organic solvent phase
Sw = Water

Distribution Coefficient:

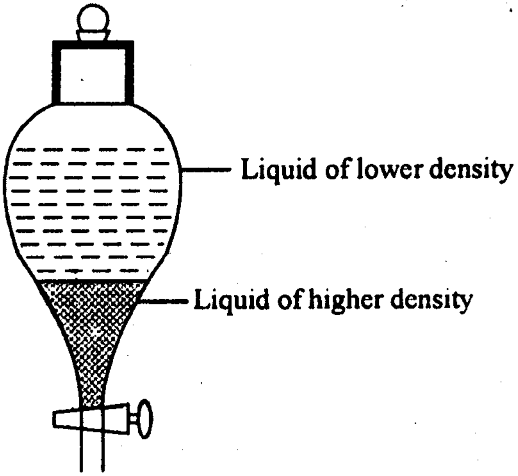
K_D is called distribution coefficient. If distribution coefficient, K_D is large, the value of So would be large and the solute would tend towards organic phase and distribution may be quantitative.

Immiscible solvents are used in solvent extraction and common apparatus used is separating funnel. The two solvents are easily separated with it. This is an example of batch extractor when K_D is large. This is applicable to liquids of different densities. The common organic solvents used for extraction in the laboratory are diethyl ether, isopropyl ether, petroleum ether or benzene. A good solvent for extraction should satisfy two important conditions:

(a) The substance extracted should be highly soluble in the solvent;

(b) Solvent should be easily separable from water and the solute.

The efficiency of extraction is increased by the addition of a salt like sodium chloride in aqueous layer as it decreases the solubility of solute in water.



Separating Funnel

If a substance is partially ionized in the aqueous layer (such as weak acids), a pH effect on extraction will be noticed. If benzoic acid is extracted from an aqueous solution of an organic phase, the distribution coefficient is

$$K_D = \frac{[C_6H_5COOH]_o}{[C_6H_5COOH]_W}$$

Benzoic acid ionizes in aqueous layer to H^+ and B_Z^-.

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$

Benzoic acid

$$Ka = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

In such cases quantitative separation may not be possible and solvent extraction will be pH dependent.

Distribution Ratio:

It is ratio of all species of the solute in organic and aqueous phase. It is designated by D. For benzoic acid in organic and aqueous phase,

$$D = \frac{[C_6H_5COOH]_o}{[C_6H_5COOH]_w + [C_6H_5COO^-]_w}$$

Relationship between distribution coefficient, K_D and distribution ratio, D can be derived as:

For benzoic acid,

$$K_a = \frac{[H^+]_w [C_6H_5COO^-]_w}{[C_6H_5COOH]_w}$$

$$[C_6H_5COO^-]_w = \frac{Ka\,[C_6H_5COOH]_w}{[H^+]_w}$$

$$K_D = \frac{[C_6H_5COOH]_o}{[C_6H_5COOH]_w}$$

$$[C_6H_5COO]_o = K_D\,[C_6H_5COOH]_w$$

$$D = \frac{K_D[C_6H_5COOH]_w}{[C_6H_5COOH]_w + Ka[C_6H_5COOH]_w / [H^+]_w}$$

$$D = \frac{K_D}{1 + Ka / [H^+]_w}$$

If $[H^+]_w$ is small Ka will be small and D is nearly equal to K_D. If K_D is large, more benzoic acid will be extracted into organic layer.

The Percent Extraction:

The distribution ratio D is a constant which is independent of volume ratio of solvents. However, fraction of the solute extracted will depend on the volume ratio of the two solutes. More solute will dissolve in larger volume of organic layer.

Fraction of the solute extracted is equal to m moles of solute in the organic phase divided by total number of m moles of solute. The m moles = molarity × ml

The percentage extraction (% E) is:

$$\%\,E = \frac{[S]_o\,V_o}{[S_o]\,V_o + [S_o]_w\,V_w} \times 100\,\%$$

$$\%\,E = \frac{100\,D}{D + V_w / V_o}$$

If $V_w = V_o$

$$\%\,E = \frac{100\,D}{D + 1}$$

If D is less than 0.001 the solute can be considered to have been quantitatively retained. If D is 100, solute is quantitatively extracted.

Problem:

20 ml of an aqueous solution of 0.10 M butyric acid are shaken with 10 ml of ether. After the layers are separated, it is determined by titration that 0.5 m mole of butyric acid remains with aqueous layer. What is the distribution ratio and what is the percent extracted?

Solution:

m moles = molarity × ml = 0.10 × 20 = 2.0 m moles

Concentration of butyric acid in aqueous layer = 0.5 m moles

Concentration of butyric acid in organic layer = 2.0 – 0.5 = 1.5 m moles

$$\text{Molarity} = \text{m moles / ml} = \frac{0.5}{20} = 0.025$$

$$D = \frac{0.15}{0.025} = 6.0$$

If 1.5 m moles are extracted, the percent extracted $= \frac{1.5}{2.0} \times 100 = 75\,\%$

$$\text{Percentage Efficiency (\% E)} = \frac{100 \times 6.0}{6.0 + 1} = 85.7\,\%$$

Simple Extraction:

Single-step solvent extraction provides one of the simplest, cleanest and most rapid methods of performing a separation. The mixture dissolved in one solvent is shaken with another immiscible solvent and the phase allowed to settle. Usually one solvent is water and the other organic. The ionic species prefer to be remain in aqueous layer and neutral species in organic phase. In order to separate two ions, one is converted to electrically neutral species by forming ion association complex e.g., $FeCl_4^-$, I_3^- or a chelate with acetyl acetone, 8-hydroxy quinoline, dithizone etc.

Double and Multiple Extraction:

When partial separation is obtained in one extraction step, complete separation may be achieved by repeated extractions. One of the simplest schemes has the following steps:

(1) Take a series of tubes (0, 1, 2, 3, ······) containing a fixed amount of a suitable solvent, e.g., an aqueous solution of known pH.

(2) Place the mixture in aqueous solution to be separated in tube 0 and add a fixed amount of organic solvent, e.g., chloroform.

(3) Shake the tube 0 to achieve distribution of solutes between the two phases and allow the layers to separate.

(4) Transfer the chloroform layer to tube 1 and add a fresh aliquot of chloroform to tube 0.

(5) Shake tubes 0 and 1 and allow the layers to separate.

(6) Transfer the chloroform layer of tube 1 to tube 2 and that of tube 0 to tube 1 and add a fresh aliquot of chloroform to tube 0.

(7) Continue the cycle until separation is complete.

The process is known as Craig counter-current multistage extraction.

The apparatus can be simple; gadolinium has been separated from rare earth ores by using beakers and a stirrer.

A lot of work has to be carried out for a multi-stage solvent extraction. It is therefore better to select conditions for a good degree of separation with minimum transfers. Optimum values of pH are taken into consideration.

Batch Extraction (Single, Double and Multiple Extraction):

In this method to a given volume of the solution a known volume of another solvent is added until equilibrium is obtained and the two layers are separated. When partial separation is obtained in one extraction step, complete separation may be obtained by repeated or multiple extractions.

Let vm*l* of solution in Phase I containing wg of the solute be extracted with S m*l* of another solvent (phase II) immiscible in the first. Let w_1 be the weight of solute remaining in phase I after equilibrium is attained.

$$\text{Concentration in phase I } (C_1) = \frac{w_1}{v}$$

$$\text{Concentration in phase II } (C_2) = \frac{w - w_1}{S}$$

$$D = \frac{C_2}{C_1} = \frac{(w - w_1)/S}{w_1/v}$$

$$w_1 = w\left(\frac{v}{D(S+v)}\right)$$

This is the concentration in single extraction. If another extraction of phase I is made with another portion of S m*l* of solvent, w_2g will be the weight remaining in phase I. After second extraction,

$$w_2 = w_1\left(\frac{v}{DS+v}\right)$$

$$w_1 = w\left(\frac{v}{DS+v}\right)$$

$$w_2 = w\left(\frac{v}{DS+v}\right)^2$$

If successive or multiple extractions with the same volume of solvents are made,

$$w_n = w\left(\frac{v}{DS+v}\right)^n$$

For complete extraction S should be made small and n large.

Problem:

If the distribution coefficient for a metal chelate partitioning between water and chloroform is 6.4, calculate the fraction of chelate extracted when 25.0 mL of water containing solute of concentration 1 M is shaken with:

(a) One 10.0 ml portion of chloroform and

(b) Two successive 10.0 ml portions of chloroform.

Solution:

According to equation,

$$w_1 = w\left(\frac{v}{DS+v}\right)$$

(a) The fraction w_1 remaining after one extraction is:

$$w_1 = 1\left(\frac{250}{6.4 \times 10.0 + 25.0}\right) = 0.281$$

The fraction of metal chelate extracted is:

$$w_1 = w - w_2 = 1 - 0.281 = 0.719$$

$$\% \text{ extraction in chloroform} = \frac{0.719}{1} \times 100 = 71.9\,\%.$$

(b) The fraction remaining after two extractions is:

$$w_2 = 1 \times \left(\frac{25.0}{6.4 \times 10.0 + 250}\right)^2$$

$$= 0.0790$$

The fraction of metal chelate extracted = 1 – 0.0790 = 0.921

$$\% \text{ extraction in } CHCl_3 = \frac{0.921}{1} \times 100$$

$$= 92.1\,\%$$

Thus, % extraction in double extraction is more than in single extraction and % extraction would increase with multiple extractions approaching 100 %.

Continuous Extraction:

Continuous extraction is applicable when distribution ratio, D is relatively small. In most continuous extraction devices, the extracting solvent is distilled and condensed into the solid to be extracted or in the solution.

For separation of the components of a solid mixture by continuous extraction, the soxhlet apparatus is used. The solid is kept in a porous thimble and the extracting solvent is taken in the boiling flask. The solvent is heated to reflux and the distillate drops on to the porous thimble containing the solid mixture. Extraction of the components in thimble and draining of the solution into the boiling flask continues till it is over. On cooling the flask, the components are isolated by solvent extraction or distillation of the solvent.

Extraction of components in solution is also possible by using lighter or heavier immiscible solvent than that from which components are to be extracted.

In continuous extraction efficiency depends on:

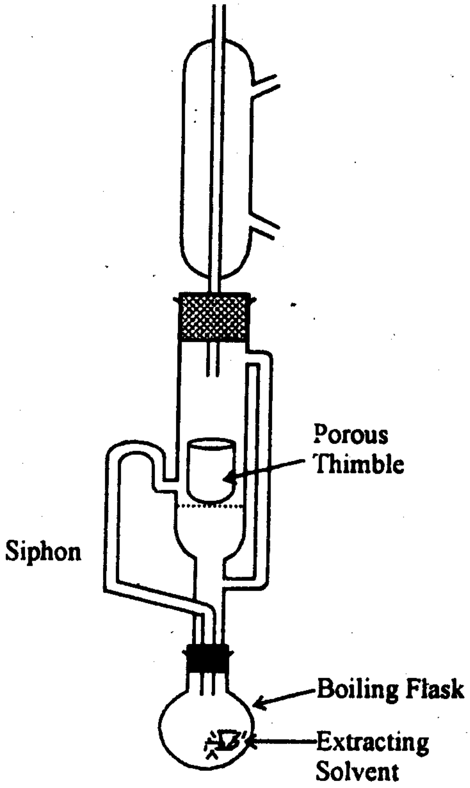
(a) Viscosity of solvents.

(b) Distribution ratio, D

(c) Distribution coefficient, K_D

(d) Relative volume of two phases.

(e) Area of contact of two phases.



Soxhlet Extractor

PROCESS OF SOLVENT EXTRACTION:

The following aspects are important in the process of solvent extraction.

(1) Choice of Solvent:

Distribution ratio of the solute in the solvent of choice must be high to get early separation. Nature of solvent, viscosities, miscibility, tendency to form emulsions, boiling points etc. are important factors to choose. The solvent should not be toxic or flammable.

(2) Stripping:

Stripping is the removal of organic solvent for analysis. In conventional methods further steps are required for analysis. Colorimetric estimation may be carried out directly in organic solvent. Radioactive counting can directly be applied on organic phase.

Organic solvent has to be destroyed by heating to evaporation or by treatment with sulphuric acid or nitric acid before carrying out analysis in aqueous solution.

(3) Back Washing:

The Organic phase containing the solute after extraction is treated with water. The impurities, if any may go back to the aqueous phase leaving pure compound in organic layer.

(4) Treatment of Emulsions:

Continuous process is applied for emulsions. Viscosity of organic liquid should be low and density difference between the organic liquid and water should be high.

(5) Variation of Oxidation States:

Extraction efficiency is affected by change in oxidation states. $FeCl_3$ extraction in organic phase is prevented by reducing Fe(III) to Fe(II).

(6) Use of Masking Agents:

Masking agents are metal complexing agents which mask the extraction of a substance. An example is the extraction of aluminium in presence of iron with 8-quinolinol into chloroform. Addition of alkali cyanide prior be extraction forms ferrocyanide ion which acts as masking agent and Fe is not extracted.

Extraction Strategies:

Extraction can be carried out with non-chelated complexes, chelated complexes and oxonium systems.

Bulky cations and anions are extracted as ion pairs or aggregates without further coordination. For example, permanganate ions can be extracted with chloroform by association with tetraphenyl arsonium ions.

$$Ph_4As^+Cl^- + MnO_4^- \longrightarrow \underset{\text{(ion pair)}}{Ph_4As^+MnO_4^-} + Cl^-$$

Tri-n-butyl phosphate (TBP), and tri-n-octyl phosphine oxide (TOPO) extract uranium, actinides and lanthanides.

Metal chelates can be extracted at specific pH which is correlated to the stability constants of chelates. Common solvents used for extraction of chelates are:

Hexane, cyclohexane, toluene, carbon tetrachloride, chloroform, diethylether, tri-n-butyl phosphate, TBP.

Alkali metals do not form stable complexes or chelates. Interesting macromolecules called crown ethers (cyclic ethers) which overlap certain metal ions in a protective pockets of oxygen atoms enable their transfer from aqueous to organic solvents.

Applications of Solvent Extraction in Chemistry and Industry:

The ease with which solvent extractions are performed and the possibility of analysis through it make this technique popular. This technique is mainly used for selective extraction and spectroscopic determination of metals in geological samples, petroleum products, food stuffs, body fluids, plant and animal tissues.

Common uses are:

(1) Extraction of precious metals such as gold, palladium, platinum etc.

(2) Separation of impurities.

(3) Extraction of uranium.

(4) Extraction of trace metals in sea.

(5) Extraction of rare metals in meteorites

(6) Study of the effect of K, Ca and Mg on tomato crop.

(7) In nuclear technology for the separation of nuclear fuel poisons.

(8) In oil and fat industry.

(9) Separation and analysis of metallurgical and geological samples.

(10) Separation of petroleum products.

(11) Quality control of foodstuffs.

(12) Analysis of plant, animal and body fluids.

CHROMATOGRAPHIC TECHNIQUES

The most difficult step in an analytical procedure is often the separation of chemically similar species. The most widely used, the most powerful, and the most effective separation technique is chromatography. First of all F.F. Runge separated mixtures of dyes and plant extracts on unglazed paper, blotting paper, and cloth in 1850s. In 1893, L. Reed separated potassium dichromate from eosin, and ferric chloride from copper sulphate on columns of powdered Kaolin. D.T. Day separated many crude oil samples into their components i.e., aliphatic and aromatic hydrocarbons, organic, nitrogen and sulphur compounds on large columns of powered fullers earth. M. Tswett, developed column chromatographic technique. In 1906, he described in detail the separation of leaf pigments into chlorophyll a, chlorophyll b, xanthophyll etc. In 1941, Martin and Synge developed partition chromatography.

Chromatography is basically a separation technique of great flexibility with variety of applications and is popular in modern laboratories. Chromatography is a physical method of separation based on distribution of the solute between a stationery and a mobile phase.

Chromatographic methods are classified into two types on the basis of mobile and stationary phases.

(1) Adsorption chromatography

(2) Partition chromatography

ADSORPTION CHROMATOGRAPHY:

The chromatographic separation of the components in a mixture by adsorption from a mobile liquid stream onto the surface of a powdered solid as stationary phase is called adsorption chromatography. It has liquid mobile phase and solid stationary phase. Typical examples are (a) column adsorption technique and (b) thin-layer chromatography.

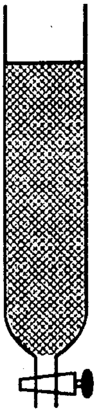
(a) Column Chromatography:

The experimental factors of column chromatography are: (i) The nature of adsorbent; (ii) The nature of solvent used to elute the sample; (iii) The nature of solute; (iv) The operating parameters.

A glass column is used to carry out the separation.

(i) Nature of Adsorbent:

An adsorbent is usually a finely divided solid possessing an extremely large surface area. Three most commonly used adsorbents in chromatography are metal oxides (alumina and silica gel) magnesium silicate (Florisil) and carbon.



Glass Column

The characteristics of a solid that must be considered when selecting an adsorbent to effect the chromatographic separation are:

(1) Surface area — preferably 50 m^2/g adsorbent

(2) Particle size — 100 - 200 mesh (150 - 75 μ) provide a minimum resistance to flow.

(3) Surface Activity — Higher surface activity of adsorbent will lower the separation efficiency because solutes will be bound too long on surface of adsorbent.

(4) Class of adsorbent: Adsorbents have been classified according to relative strength of adsorption and polarity. Examples of strong adsorbents are; alumina, silica gel, magnesium silicate (Florisil), and carbon. Intermediate adsorbents are calcium carbonate, calcium phosphate and magnesia, whereas weak adsorbents include sucrose, starch, and talc. The strength of adsorbent is determined by measuring the rate of movement of a solute band. The faster the band moves down the column, the weaker the adsorbent is. Most adsorption chromatographic separations use strong adsorbents.

Silica gel and magnesium silicate are acidic adsorbents, whereas alumina is a basic adsorbent. Acidic adsorbents should be used for the separation of acidic compounds and basic adsorbents for the separation of basic compounds. If an acidic adsorbent is used in an attempt to separate basic compounds, chemisorptions may occur so the solute cannot be eluted from the column.

(ii) Nature of Solvents:

The solvent in which a sample is dissolved will compete with the components of the sample for surface sites upon which to be absorbed. A solvent which is strongly adsorbed on the surface will act as a strong eluent and will displace solutes easily and thus results in shorter retention time of solutes. Solvents which are poorly adsorbed upon the adsorbent surface act as weak eluents and do not compete with the solute molecules. Hence they do not displace the solutes from the surface of adsorbent as rapidly and result in longer retention times.

The relative ability of solvents to elute a solute from a adsorbent is known. The listing of solvents according to the order in which they elute a given solute is in increasing order of polarity of the solvent e.g., Ethanol > Acetone > Diethyl ether > Carbon Tetrachloride > n-Hexane.

(iii) Nature of the Solute:

The most important feature of an adsorption chromatographic separation is the extent of separation of the components of the solute sample for a given solvent-adsorbent system. In order to achieve better separation, there must be a large difference in the retention time of the components of the solute. The differences in molecular size, solute polarity and specific adsorptivity of solute are important factors for separation.

(iv) Operating Parameters:

The effect of general experimental conditions, such as method of packing, flow rate, and temperature are important for the efficiency of a column adsorption chromatographic separation.

(a) Packing:

Technique of column packing is important. One common method is to pour dry, powdered solid slowly onto the top of the glass column. The column is gently tapped or vibrated till the solid settles. Solvent is then added and drained to get a slurry.

Another method most often used in to form slurry of the adsorbent and the solvent. The slurry is then poured into the column and solid allowed to settle until desired height of the adsorbent in obtained. A general rule of thumb is to use about fifty grams of adsorbent for each gram of sample to be separated.

(b) Flow Rate:

The rate of flow of solvent through the column is very important in achieving successful chromatographic separation. If flow rate is too rapid, there will be insufficient time for the adsorption - desorption equilibrium to become established. Too rapid a flow rate can produce tailing, band overlapping and incomplete separation. If the rate of solvent flow is too slow, diffusion of the separated solutes from regions of higher concentration to those of lower concentrations can upset the separation. The optimum flow rate is compromise between the two.

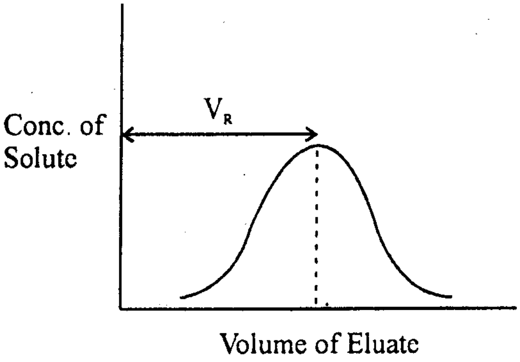
(c) Temperature:

Increasing the temperature of the column will cause a slight decrease in the adsorption of all the components into sample. This decrease is on the order of 1 – 2 % per degree centigrade.

Retention volume (VR) and Retention Time:

The retention volume (VR) in chromatography is defined as the volume of solvent that must be used in order to elute one half of the solute.

The retention time is merely the time elapsed from the beginning of the development of the chromatogram to the appearance of the maximum in the elution peak of the solute provided the rate of flow of eluent is constant.



The motion of a solute compared to the motion of the flowing solvent in the column is known as the principle of selective retardation. Each solute in a mixture moves through the column at a rate that is determined by the position of equilibrium between the solute in the flowing solvent and the solute on the stationary solid surface. These rates of movement are characteristic of each solute in a column with reference to a particular solvent. The relative time taken by the solute to emerge from the bottom of the column is used to identify the solute. Each solute has its own degree of retardation or retardation factor, R_f

$$R_f = \frac{\text{linear velcoity of a band of the solute}}{\text{linear velcoity of the flowing solvent}}$$

$$= \frac{\text{distance moved by the solute band in time 't'}}{\text{distance moved by the flowing solvent in time t}}$$

There are three different methods by which a column chromatogram can be developed.

(a) frontal analysis (b) displacement analysis and

(c) elution analysis.

Frontal analysis is one of the earliest methods used in column chromatography. A very large volume of the sample solution is poured continuously into the top of the column. The liquid coming out of the column is identified for the solute either as coloured band or through analysis. Only one solute can be obtained in a pure condition by this method.

Displacement method is based on placing a narrow band of the solute sample in small volume at the top of the chromatographic column. A second solution containing solute that is very strongly adsorbed is slowly poured through the column. The solution is called displacing agent or the developer. As the developer passes through in column, it displaces all the components of the sample from their positions on the stationary phase, forcing them into the mobile liquid. At the same time each of the components of the sample begins to displace other components weakly adsorbed. The components gradually separate and emerge out of the column one by one.

The sample in a solvent is poured into the column and another solvent which is less strongly adsorbed onto the column called eluting ligind or eluant is poured into the column. On elution one component of the solute will come off the column more rapidly than the other and so on.

Applications:

The column chromatography has the following applications:

1. It is used for the separation in organic chemistry and biochemistry.
2. It is also applicable for the separation of inorganic chemicals.

3. Fillinger developed a rapid chromatographic qualitative analysis scheme using alumina as adsorbent in a small 6 mm inner diameter glass tubing.

   The Group I ions (Ag^+, Pb^{2+}, Hg_2^{2+}) are developed with K_2CrO_4 and identified as coloured bands. Similarly copper, arsenic, aluminium, alkaline earth and alkali metals can be separated on small column.
4. The technique is used for the separation of hydrocarbons and petroleum products.
5. Sugars have been separated on alumina, silica gel or carbon columns.
6. Mixture of alkaloids can be separated on alumina, sila gel or kieselguhr columns.
7. Mixture of dyes and pigments can be separated by this technique.
8. Vitamins and steroid hormones have been separated by column chromatography.
9. Purification of antibiotics can be carried out.
10. Separation of isomers. DL-Mandelic acid, $C_6H_5CHOHCOOH$ has been resolved into its two enantiomers on stereo specific columns and cis and trans- isomers of stilbene, $C_6H_5CH = CHC_6H_5$ have been separated.

(b) Thin-Layer Chromatography (TLC):

The stationary phase in thin layer chromatography is glass, metal, or plastic sheet which merely serves as a support of solid adsorbent slurry spread on it which is dried. The mobile phase is a liquid which moves through the stationary phase by capillary action. The equilibrium processes upon which separation is based may be adsorption, ion-exchange or gel filtration. Thin layer chromatography as originally developed is based on adsorption equilibrium process and majority of the applications of thin-layer chromatography use adsorption as the separation mechanism. In 1938, Ismailof and Shraiber first developed thin-layer chromatography. A slurry of alumina was spread 2 mm thick onto a glass microscope slide, dried, and the spotted with a drop of tincture of belladonna, or rhubarb. The drop was separated into concentric circles by dropping alcohol in the center. The components of these tinctures were identified by colours of the circles. In 1951, Kirchner, Miller and Keller used thin-layer chromatography to identify flavouring compounds in citrus fruits.

Parameters and Experimental Variables:

1. Backing Sheets or Plates:

The most common backing sheets or plates used are of glass or microscope slides, but stainless steel, aluminium or plastic materials may be used.

2. Stationary Phase:

The stationary phase is a finely powdered solid which acts as adsorbent. A binder such as plaster of paris or gypsum is used to adhere stationary phase to the backing sheet or plates.

Thin-layer chromatography plates are prepared by spreading an aqueous slurry of the solid adsorbent uniformly in a very thin layer (0.1 – 0.3 mm) over the surface of the backing. After the solvent is evaporated off, the adsorbent layer is activated by drying it in the oven at 110°C. The activated plates are stored in a desiccators until ready for use.

3. Adsorbents:

Silica gel is the most commonly used adsorbent in thin-layer chromatography.

Alumina, magnetism silicate, calcium silicate and activated charcoal are also used as adsorbents in thin-layer separations.

Polyamides such as perlon or nylon (polyhexamethylenediamine adipate) is also used as thin layers to separate polar compounds.

Ion-exchange resins, such as Dowex 50 W and Dowex 1, are available. For Gel filtration thin-layers are prepared from sephadex superfine.

4. Plate Preparation:

Precoated TLC plates are available from commercial sources. The standard sizes are 10 × 20 cm or 20 × 20 cm. Silica gel, alumina, and cellulose coated plates are available.

There are many ways to coat the plates in the laboratory, but the two most common techniques are dipping and spreading. The ideal adsorbent layer is thin, uniform in thickness free from cracks and lumps, and adheres well to the plate.

Microscope slides are usually coated with thin films by dipping. A. slurry of adsorbent (about 5 g in 100 ml of water) is prepared and two microscope slides with flat surfaces are held together and dipped into the slurry in a beaker. The plates are withdrawn slowly and the excess slurry allowed to drain off. The two slides are separated and the solvent allowed to evaporate from the surface. This is by for the easiest and simplest method of coating plates.

The plates (10 × 20 cm or 20 × 20 cm) are coated by means of commercially available spreaders. There are two type of spreaders, the stationary trough or

Kirchner type or the movable trough or Stahl type. In both these spreaders, the slurry is poured into a narrow trough that is as long as the plate width. The rear wall of the trough can be raised vertically above the plate surface to specified heights, so that the slurry emerges from the bottom of the back wall of the trough, coating the plate. The thickness of the adsorbent layer is accurately adjusted. In the Kirchner-type spreader the trough is fastened permanently at a fixed position on the bed of the apparatus. The plates to be coated are pushed under the trough, which deposits a fixed thickness of slurry on their surfaces. In Stahl-type spreader the plates are clamped on to the bed of the equipment and the trough is moved, depositing even layer of slurry on the plates.

(5) Mobile Phases:

The solvents used in thin-layer chromatography are hexane, cyclohexane, carbon tetrachloride, chloroform, diethylether; ethylacetate, acetone. The developing solvents used as mobile phase must be of high purity. The solvent of more viscosity will slow down the process.

(6) Sample Application:

It requires more skill and patience to apply a spot on thin-layer. The sample should be spotted 1.5 cm up from the lower edge of the plate, and 1.0 cm in from either sides of the plate. The sample is applied by a syringe, micropipette or with a platinum loop. The drop of the sample is touched to the surface of the plate, quickly and cleanly, and not allowed to contact with the thin layer for which practice is needed.

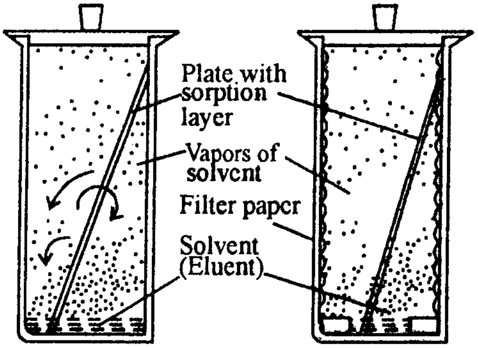
(7) Development:

Ascending development is more common in thin-layer chromatography. The developing liquid is placed in the bottom of the closed chamber at room temperature with relative humidity of 40 – 65 %. Development chambers are usually small which allow rapid saturation with solvent vapour.

They may be jam jars, glass bottles or small tanks.

Horizontal development of thin-layer is also occasionally carried out.

The development chamber should be saturated with the solvent vapour before the plate is put in to develop. The degree of saturation of the chamber is an important variable in TLC.



Development Chamber for ascending thin-layer chromatography

(8) Detection of Spots:

The spots in TLC are detected by the following methods:

(i) The TLC plate is held under ultraviolet light to locate spot of the sample.

(ii) Locating agents such as ninhydrin, dithizone or iodine vapour are used to locate the spot.

(iii) Dyes such as rhodanine B and fluorescein may be used.

R_f Values:

R_f values in TLC are much less reproducible and reliable than the other techniques.

R_f values are used for the qualitative analysis of the components in a mixture or to find out the purity of the substance.

Quantitative Analysis:

Thin-layer chromatography (TLC) can be used for quantitative analysis in addition to its value for qualitative separations. It is of course not as accurate as acid-base titrations and other techniques used for quantitative analysis.

A comparison of the spots of unknown samples with the known compounds as regards their intensity and size is important. Relationship between the area of spot and amount of material has been established.

The intensity of the fluorescence of the spot of unknown with that of compound of known concentration gives quantitative information.

The spot can be removed from thin-layer plate with a razor blade or through suction and analyzed by any suitable technique depending on the nature of substance present.

Preparative TLC:

Thin-layer chromatography can be scaled up and used for the isolation of large (10 – 100 mg) quantities of pure component which may be analysed. The bands of components are scrapped off with a razor blade or spatula and the component is washed off with a suitable solvent and analysed.

Preparative TLC is an ideal quantitative technique for radioactive and toxic substances. It is used for isolation of expensive pharmaceutical and fine chemicals.

Advantages and Limitations:

The advantages of thin-layer chromatography over other chromatographic methods that make it a popular method are:

(1) Speed: Separation can be accomplished in 5 – 30 minutes.

(2) Simple Equipment: Microscope slides, ordinary bottles, sheets and strips can be used for coating the adsorbents.

(3) **Efficiency:** Very complex mixtures of solutes can be resolved into separate spots within a distance of 10 cm. TLC can resolve well the mixtures of very similar chemicals.

(4) **Versatility:** The basis of separation can be adsorption (most common), partition, ion exchange or gel filtration.

(5) **Adaptibility:** The method is excellent for preliminary studies for column chromatography.

(6) **Microanalysis:** The sample size of TLC is in micrograms. So it is an excellent technique for analysis of mixtures available in small amounts.

The limitations of TLC are:

(1) Lack of reproducibility of R_f values.
(2) Large scale preparative work is not possible as TLC deals with small amounts of material.

Applications:

TLC has been applied to just about everything that one would imagine as enumerated below:

(1) It is used for the detection and analysis of mixtures of terpenes, natural oils, chlorophylls.
(2) It is used for identification and separation of steroids, lipids, vitamins, etc.
(3) It is used in pharmaceuticals such as antihistamines, analgesics, hypnotics, bactericides, diuretics, laxatives, antibiotics etc.
(4) It is used for identification of dyes, food additives (antioxidants, preservatives, artificial sweetners, emulsifiers, colorants etc.)
(5) It is used for the separation of amino acids, nucleic acids.
(6) Plasma, urine and sera have been analysed for sugars, amino acids, fats, lipids, cholesterol, phospholipids, steroids and any foreign materials in case of poisoning and in therapy.
(7) It is used to identify insecticides.
(8) It is useful in forensic science to detect poisons, metal ions, drugs, tranquilizers in body fluid.
(9) It can be used to identify explosives in residues and smoke of the explosion.
(10) It is commonly used in study of organic compounds e.g., separation of anthraquinones.

Partition Chromatography:

Paper chromatography is an example of partition chromatography in which cellulose of paper holds firmly 2 – 3 per cent of water which acts as a stationery phase for a solute soluble in water and another solvent is used as a mobile phase. Further discussion on partition chromatography is available elsewhere.

Questions

1. What is the basic principle of solvent extraction? State partition or distribution law.
2. What do you understand by distribution coefficient and distribution ratio? How are these correlated?
3. What is meant by the percent extraction?
4. What are simple, double and multiple extractions? Explain with examples.
5. Explain the functioning of solvent extraction.
6. Give salient features of the process of solvent extraction.
7. What is meant by batch extraction? Explain with suitable examples.
8. What extraction strategies are required for efficient extractions?
9. Give significant applications of solvent extraction.
10. What are the major experimental factors on which column chromatography depend?
11. Give significant applications of column chromatography.
12. What features distinguish thin-layer chromatography from other forms of chromatography?
13. Which of the adsorbents used in thin-layer chromatography would you try first in attempting each of the separations listed below?
    (a) Methylamine, ethylamine, n-propylamine.
    (b) Resorcinol, phenol
    (c) Mixture of naturally occurring lipids.
    (d) Biphenyl, o-triphenyl, and m-triphenyl.
14. What solvent wouid you try first for each of the thin-layer separations given below?
    (a) Ammonium salts of carboxylic acids on silica gel
    (b) Long-chain alcohols on silica gel
    (c) Amino acids an alumina
    (d) Fatty acids an Kieselgulr
15. What influence does each of the factors given below have on the measured R_f value of a solute?
    (a) The thickness of the thin-layer on the plate.
    (b) The purity of the eluent.
    (c) The concentration of the solute in the drop used to spot the plate.
    (d) The temperature of development of the plate.
16. **Give the correct answer:**
    (i) Solvent extraction is based on:
        (a) adsorption (b) partition
        (c) distribution of solute in two liquids
        (d) oil extraction

(Ans: c)

(ii) Distribution coefficient is:
(a) Ratio of concentrations of solute in two phases
(b) Ratio of all species in organic and aqueous phase
(c) Ratio of solvents (d) Ratio of solute mixture
(Ans: a)

(iii) Percentage extraction depends on:
(a) Distribution ratio (b) Distribution coefficient
(c) Distribution law (d) Distribution of solvents
(Ans: a)

(iv) Simple extraction is:
(a) Crude (b) Clean
(c) Not good (d) Slow
(Ans: b)

(v) Soxhlet extraction uses:
(a) Porous thimble (b) Glass beads
(c) Chips (d) Stainless Steel
(Ans: a)

(vi) Column chromatography is:
(a) Partition chromatography (b) Gel chloromatography
(c) Adsorption chromatography
(d) Ion-exchange chromatography
(Ans: c)

(vii) R_f is:
(a) Ratio of distance moved by solute and solvent
(b) Rate of flow of solvent (c) Rate of flow of solute
(d) Rate of reaction
(Ans: a)

(viii) Thin layer chromatography
(a) takes longer time for separation
(b) takes less time for separation
(c) requires expensive materials
(d) requires lot of equipment
(Ans: b)

(ix) The ideal adsorbent layer on TLC is:
(a) Thin coating (b) With lumps
(c) Uneven coating (d) With cracks
(Ans: a)

(x) The most common adsorbent used in TLC is:
(a) Calcium silicate (b) Glass beads
(c) Alumina (d) Silica gel
(Ans: d)

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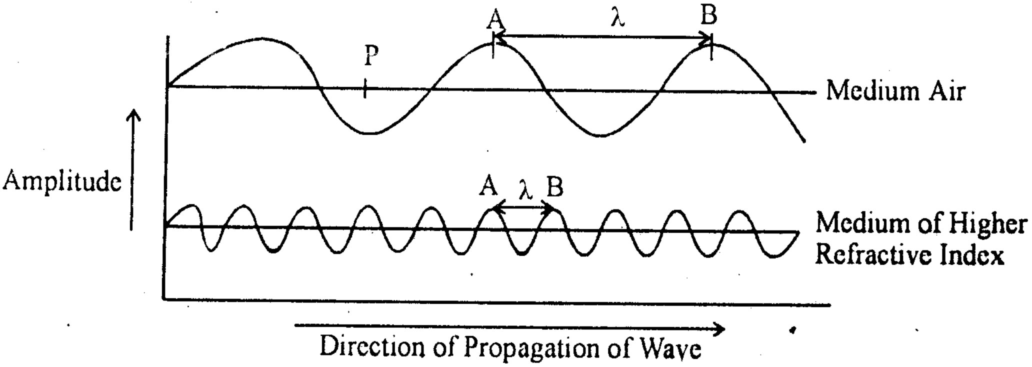
SPECTROSCOPY

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter. It deals with the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecule, or atom, or ion of a sample moves from one allowed energy state to another. Every atom, ion, or molecule has a unique and characteristic relationship with electromagnetic radiation. Atoms and molecules are capable of absorbing radiant energy, thereby undergoing various types of excitations.

Beam of radiation may be regarded as an electromagnetic waveform disturbance or photon of energy propagated at the speed of light. A photon has the property of a particle as well as of a wave extending over a broad area of space. The Heisenberg uncertainty principle shows that it is not possible to measure wave and particle nature of a photon simultaneously. However, it is useful to keep both properties in mind.

A photon originating at a point in space radiates from that point a wave characterized by electric field vectors which have periodic maxima perpendicular to the direction of propagation. The wavelength of radiation, λ, can be visualized as the distance between these maxima i.e. from crest to crest.



When a beam of polychromatic light is passed through a prism or grating, it splits up into seven different colours. The set of colours thus obtained is called a spectrum. The complete spectrum may extend from γ-rays of wavelength 10^{-13} m to visible, ultraviolet (UV), infrared (IR) and radiowaves of wavelength 10^{5} m.

The study of spectroscopy can be carried out as under:

1. Atomic Spectroscopy

It deals with the interaction of electromagnetic radiation with atoms most common in their lowest energy state.

2. Molecular Spectroscopy

It deals with the interaction of electromagnetic radiation with molecules. This results in transition between rotational and vibrational energy levels in addition to electronic transitions.

Designation	Wavelength limits		Frequency limits, Hz	Wave number limits, cm^{-1}
	Usual units	Metres		
X-ray	$10^{-1} - 10^{3}$ A°	$10^{-12} - 10^{-8}$	$10^{20} - 10^{15}$	
Far ultraviolet	10 – 200 nm	$10^{-8} - 2 \times 10^{-7}$	$10^{16} - 10^{15}$	
Near ultraviolet	200 – 400 nm	$2 \times 10^{-7} - 4.0 \times 10^{-7}$	$10^{16} - 7.5 \times 10^{14}$	
Visible	400 – 750 nm	$4.0 \times 10^{-7} - 7.5 \times 10^{-7}$	$7.5 \times 10^{14} - 4.0 \times 10^{14}$	25,000 – 13,000
Near infrared	0.75 – 2.5 pm	$7.5 \times 10^{-7} - 2.5 \times 10^{-6}$	$4.0 \times 10^{14} - 1.2 \times 10^{14}$	13,00 – 4000
Mid infrared	2.5 – 50 pm	$2.5 \times 10^{-5} - 5.0 \times 10^{-8}$	$1.2 \times 10^{14} - 6.0 \times 10^{12}$	4000 – 200
Far infrared	50 – 1000 pm	$5.0 \times 10^{-5} - 1 \times 10^{-3}$	$6 \times 10^{12} - 10^{11}$	200 – 10
Microwaves	0.1 – 100 cm	$1 \times 10^{-1} - 1$	$10^{11} - 10^{8}$	$10 - 10^{-1}$
Radio waves	1 – 1000 m	$1 - 20^{2}$	$10^{8} - 10^{5}$	

CLASSIFICATION OF SPECTRA

There are two main classes of spectra namely emission spectrum and absorption spectrum.

1. Emission Spectrum

When the light emitted by a substance is passed through a prism and examined directly with a spectroscope, the spectrum obtained is referred to as emission spectrum. Emission spectrum is further classified according to appearance as line, band and continuous spectrum.

2. Absorption Spectrum

When white light (i.e. having all the wavelengths) is passed through an absorbing substance and then observed through a spectroscope, it is found that certain wavelengths are missing and dark lines appear at their places. The spectrum so obtained is called absorption spectrum. These dark lines or bands depend upon the nature of the absorbing material.

ELECTROMAGNETIC RADIATION

Electromagnetic radiation may be defined as the energy, the propagation and transfer of which takes place as a wave motion without transfer of matter. It ranges from the electric waves of low frequency through UV, visible and IR to the high frequency (low wavelength) X-rays and γ-rays. Our eyes see sun light as white light but it is a mixture of lights each of which evolves a sensation of color. Newton first gave the name spectrum to the continuous band of seven colours. Visible radiation represents only a small part of electromagnetic radiation. An electromagnetic radiation is said to have a dual nature exhibiting both **wave and particle** characteristics. This duality is not confined to the visible portion of the electromagnetic spectrum but can be demonstrated for the whole region of electromagnetic radiation.

1. Wave Properties of Electromagnetic Radiation

The wave nature of electromagnetic radiation (emr) can be represented by electrical and magnetic vector. Besides being perpendicular to each other, the two fields are perpendicular to the direction of propagation. It is because of these associated electric and magnetic fields that the radiation is called **electromagnetic radiation**. In emr it is the electrical field that interacts with the electrons in matter and as a consequence representation of radiation by the electrical vector alone has been found to be sufficient for most cases. *A radiation in which all electric displacements are in one plane, as the wave progresses, is said to be polarised.* Emr having all the waves of single wavelength are termed as **monochromatic,** i.e., one coloured. On the other hand, a **polychromatic** radiation consists of waves of various wavelengths.

An electromagnetic wave is characterised by the following parameters:

(a) **Wavelength (γ):** The linear distance between successive maxima or minima of a wave is known as wavelength. It is usually expressed in cm. The units of wavelength are:

(i) Angstrom, Å; 1 Å $= 10^{-8}$ cm $= 10^{-10}$ m

(ii) Nanometer (nm); 1 nm $= 10^{-7}$ cm $= 10^{-9}$ m

(iii) Micron (μ); 1 μ $= 10^{-4}$ cm $= 10^{-6}$ m

(iv) Micrometer (μm); 1 μm $= 10^{-3}$ nm

(b) **Frequency (ν):** The number of waves per second is called frequency of an electromagnetic radiation. Frequency (ν) = speed of light in cms^{-1} / wavelength in cms. Frequency is generally expressed in cycles per second (cps) or **Hertz** (Hz) or in **Fresnel**.

Other units are kilocycles per second (kcps or kHZ) and mega cycle per second (Mcps or MHz) 1 MHz = 10^6 Cps.

(c) **Wave Number ($\bar{\nu}$):** It is the number of waves spread in a length of 1 cm. $\bar{\nu} = 1/\lambda$. The wave number is the direct measure of the energy of radiation.

(d) Velocity (V): The product of wavelength and frequency is equal to the velocity of the wave in the medium, i.e. Wavelength x Frequency = Velocity

$$\lambda \times v = V$$

Velocity has the unit of cm s^{-1} or m s^{-1}. At a particular frequency, the relationship between the wavelength, frequency and velocity of light in a vacuum is $\lambda v = c$.

Relation between Frequency, Velocity and Wave Number

$$\bar{v} = 1/\lambda \qquad \text{But} \qquad v = c/\lambda \qquad \text{OR} \qquad \lambda = c/v$$

$$\therefore \quad \bar{v} = v/c \qquad \text{OR} \qquad v = c\bar{v}$$

where c is the velocity of light in a vacuum (3×10^8 ms^{-1}).

2. Particle Properties of Electromagnetic Radiation

The wave nature of electromagnetic radiation fails to explain several phenomenon like photoelectric effect. Hence it is assumed that electromagnetic radiation consists of a stream of discrete packets (particles) of pure energy, called **photons or quanta.** These have definite energy and travel in the direction of propagation of the radiation beam with the velocity equal to that of the light. *The energy of photon is proportional to the frequency of radiation and is given by the relationship,* $E = hv$

Where E is the energy of photon in ergs, v the frequency of electromagnetic radiation in *cps,* h is Planck's constant (6.626×10^{-34} Js).

Relation between Wavelength and Particle Properties of Electromagnetic Radiation

The relation between wave and particle nature of radiation was suggested by **Planck**. According to him, if a transition occurs between the energy states of a system such that a photon of energy E is emitted or absorbed, the frequency, v, of the emitted or absorbed radiation is given by:

$$E = hv \qquad \text{or} \qquad E = hc/\lambda \qquad \text{Since} \qquad v = c/\lambda$$

INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

When electromagnetic radiation passes through matter, a variety of phenomenon may occur as follows:

1 *If the photons of radiation possess the appropriate energies, they may be absorbed by the matter and result in electronic transitions, rotational changes, vibrational changes or combination of these. After absorption, atoms and molecules become excited. They give out energy quickly either*

by losing energy in the form of heat or by re-emitting electromagnetic radiation.

2. *The radiation passing through the matter may not be absorbed completely. The portion of electromagnetic radiation that passes into matter, instead of being absorbed, may undergo scattering or reflection or may be re-emitted at the same or different wavelength.*
3. *When electromagnetic radiation is neither absorbed nor scattered, it may undergo changes in orientation or polarization.*

ATOMIC SPECTRA

The electrons in any atom occupy the lowest energy level. The electrons can be excited by electromagnetic radiation to higher energy states. The process of transfer of an electron from one energy level to the other is referred to as **electronic transition.** Excited atoms or molecules are relatively short lived, and tend to return to their ground state after about 10^{-8} sec. Both excitation and de-excitation processes follow the law of conservation of energy. Thus the electron may return to its normal position directly or in steps with the emission of certain amount of energy. *When the emission of light is instantaneous, the phenomenon is called fluorescence, but if occurs after sometime, it is known as phosphorescence. When the absorbed energy is stored by the atom or molecule and used in producing some chemical reaction, fluorescence and phosphorescence disappear and the resulting chemical reaction is known as photochemcial reaction.*

Electronic Transitions in Molecules

In a molecule the electrons are present in various types of orbitals e.g., **bonding, non-bonding and antibonding.** The electrons from these levels are excited to molecular orbitals of higher energies and thus several possible excited states are obtained. Thus in a molecule, there are several transitions from the ground state to the various excited states. Hence on the basis of electronic transitions the spectra are conveniently classified into $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$.

Charge-transfer Transition

When the electron is transferred from an atom or group to another atom or group in a molecule, the transition is said to be **charge-transfer**. These transitions are very intense. For example, in **MnO^-_4 and $Cr_2O^{2-}_7$ ions** the electron is transferred from non-bonding orbitals of oxygen to Mn and Cr respectively involving transition of the type $n \rightarrow \pi^*$.

MOLECULAR ABSORPTION SPECTRA

Transitions within the molecules are usually studied by the selective absorption of radiation passing through them.

When a molecule emits or absorbs a photon, its energy is decreased or increased and one or more of the vibrational or rotational quantum numbers change. Some important possibilities are:

(a) **Rotational Spectra** arise when the rotational quantum numbers change and occur in the far infra red and microwave regions.

(b) **Electronic spin resonance** involves a change in the direction of the resultant spin in the presence of a magnetic field. For electron spin resonance (ESR) microwave frequencies from 1000-25000 MHz are used.

(c) **Nuclear Magnetic Resonance** involves a change in the direction of nuclear spin quantum number in presence of magnetic field. When nuclei or electrons of certain elements are subjected to a strong magnetic field, additional quantized energy levels are produced as a result of magnetic properties of these elementary particles. For nuclear magnetic resonance (NMR) nuclei are subjected to magnetic field.

(d) **Electronic Spectra** occur in the visible and ultraviolet regions and arise when the electronic energy level normally changes.

(e) **Vibrational-Rotational spectra** occur when the vibrational change, possibly with a simultaneous rotational change takes place. These spectra are found in infra red region.

(f) **Raman Spectra** involve change in the vibrational and rotational energy levels.

SPECTROSCOPIC TECHNIQUES

The following spectroscopic techniques shall be discussed here:

1. Atomic Emission Spectroscopy
2. Atomic Absorption Spectroscopy
3. Ultraviolet Spectroscopy
4. Infrared Spectroscopy

1. ATOMIC EMISSION SPECTROSCOPY

Atomic emission spectroscopy pertains **to electronic transitions in atoms** which use an excitation source like flames, arcs or sparks and argon plasma sources. Emission spectroscopy is related to atoms. It was known since the work of **Bunsen and Krichoff** (1860) that many metallic elements under suitable excitation emit radiations of characteristic wave lengths in visible region. The use of this fact has been made in the qualitative analysis of alkali and alkaline earth metals which impart characteristic colours to the flame. **Emission spectroscopy** is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states. The wave length of a spectral line is inversely proportional to the energy difference between the initial and final energy levels. Since no two elements have identical energy levels, no two elements will have the same spectra.

Principle

The source vapourises the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy, E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy, $h\nu$ is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

Instrumentation:

The essential parts of an emission spectrometer are the excitation source, sample holder, optical system, monochromators, slits, detectors or a camera for recording the spectrum. (Fig.24.1).An electrical source produces a steady electrical discharge. The sample is introduced into the discharge, where it is vaporized and excited. The excited sample emits radiation which is detected and measured by the detector

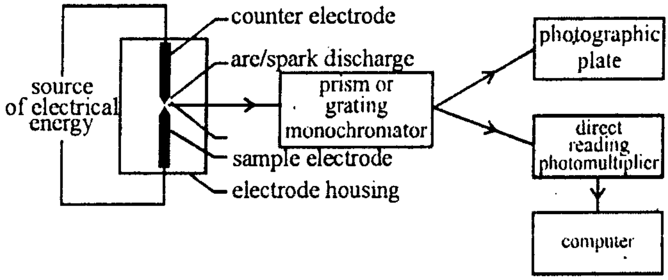


Fig. 24.1 Schematic diagram of an emission spectrometer

1. Excitation Sources

The source of emission analysis differs from that used in absorption analysis. The source must accomplish the following:

Flame, alternating current are (AC arc), gas discharge tube and laser beam are the sources used in emission method.

i. The source should provide both sufficient and constant intensity.

ii. The sample should dissociate into atoms.

iii. The electrons in the atoms must be excited to higher energy levels from the ground state.

Laser Beam

Laser beam has been used for exciting the atoms or ions of a sample, particularly when the beam is focused to irradiate only a small area of the specimen. The method of excitation by laser is non-destructive since a very small portion of the sample is vapourised. The use of **laser beam is advantageous** as it helps in studying variations in composition from one small region of the sample to another and can give continuous as well as pulsed outputs.

Laser can be generated with a variety of materials. A glass matrix containing a small amount of neodymium or yttrium aluminum garnet (YAG) can be used to get laser beam. Helium, neon, argon, nitrogen and carbon dioxide can be used to lase by electric discharge.

2. Sample Holder

The function of the sample holder is to introduce the sample into the electrical discharge. There are two types of sample holders, those for **solid samples** and those for liquid samples.

3. Optical System

The region of greatest importance for emission analysis is 2500-4000 Å but longer and shorter wavelengths are also sometimes useful. Thus the optical components through which radiation is transmitted must be of fused silica or quartz.

4. Detectors

Two types of detectors are widely used: **photomultipliers and photographic plate**. For all quantitative analysis photographic plate is used on which all the emission lines from the sample are recorded. This photograph of the emission spectrum helps in the measurement of wavelength of radiation lines. From these lines emitting elements can be identified. The instrument with photographic recording is called **spectrograph** and the one using photoelectric device as spectrometer.

Photomultipliers are more suitable for quantitative work because their response is less dependent on wavelength.

Advantages of Emission Spectroscopy

Emission method is extremely important in analysis.

1. The technique is highly specific.
2. The method is **extremely sensitive**. With this technique all metallic elements can be detected even if they are present in very low concentration (0.0001%).
3. Even **metalloids** (arsenium, silicon and selenium) have been identified by this technique.

4. The analysis can be performed either in **solid or liquid state** with almost equal convenience.
5. The technique requires **minimum sample preparation**, as a sample can be directly introduced in to the arc or spark.
6. The sample requires no preliminary treatment and can be analysed as received.
7. Spectra can be taken simultaneously for more than two elements. No separation is required. A very small amount of sample (1-10 mg) is sufficient for analysis.
8. The technique provides results very rapidly. If automated, time required is just 30 seconds to one minute.
9. This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, and forensic material, environmental and biological samples.
10. The technique permits **non-destructive** analysis.

Disadvantages of Emission Spectroscopy

1. The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.
2. Recoding is done on a photographic plate which takes some time to develop, print and interpret the results.
3. Radiation intensities are not always be reproducible.
4. Relative error exceeds 1 to 2 %.
5. The **accuracy and precision** are not high.

Specific Applications

(a) **Metals and Alloys:** Emission spectroscopy has been employeed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes. The percentage determined is 0.001% in iron. **Alloys** of Zn, Cu, Pb, Al, Mg and Sn have been analysed.

(b) **In Oil Industry:** Lubricants oils have been analysed for Ni, Fe, Cr, Mn, Si, Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and the need for engine overhaul. Some of these metals can poison the catalyst used in the cracking process. **In petroleum** industry oil is analysed for V, Ni, Fe, the presence of which makes fuel poor.

(c) Solid samples and animal tissues have been analysed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc.

(d) Emission Spectroscopy has been used to detect 40 elements in plants and. soil. Thus metal deficiency in plants and soil can be diagnosed. Hence one can make up the deficiency through soil applications or through sprays on to the leaves.

(c) The following materials have been analysed by emission spectroscopy.

(i) Trace and major constituents in ceramics.
(ii) Traces of Co, Ni, Mo and V in Graphite.
(iii) Trace metal impurities in analytical reagents.
(iv) Rare earths in spent nuclear fuels.
(v) Trace of Ca, Cu, Zn in blood.
(vi) Zinc in pancreatic tissues.

Flame Photometry

The characteristic coloured flames of elements such as sodium and potassium are well known in qualitative analysis. Their flame emission lines in the visible region are readily observed through a spectroscope. Some elements e.g. alkali metals produce intense lines at temperature of 2000° C. The flame photometer is a simple, accurate and inexpensive instrument **(Fig. 24.2).**

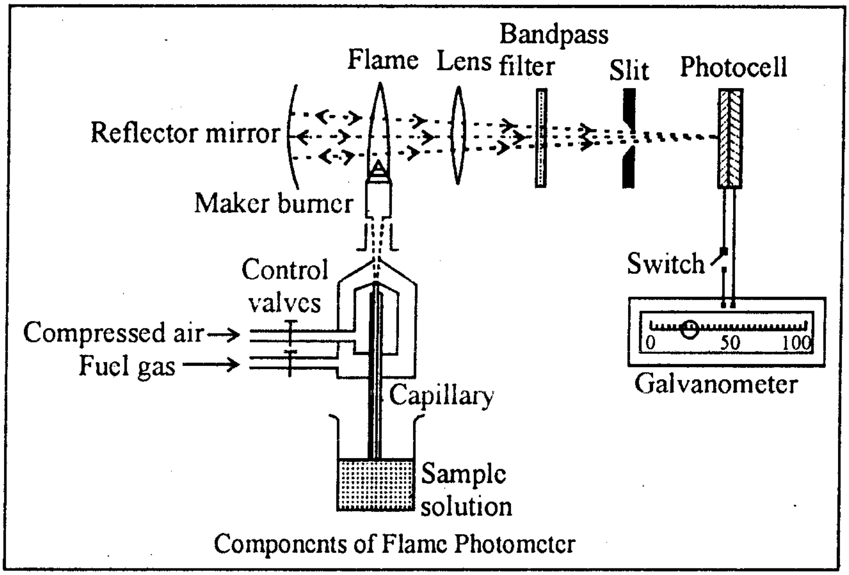


Fig. 24.2

The solution of the sample to be analysed is prepared and sprayed by means of an atomizer into the flame of a Maker-type burner. Air together with the entrained spray is blown through the throat of the burner where it mixes with the fuel gas. The radiation emitted is passed through a filter and the intensity of the selected band measured with a photocell detector.

The use of flame photometers is restricted to a few elements e.g., Na, K, Li and Ca. These elements can be determined individually to an accuracy of 2-5 percent. In case of mixtures, due to interferences, the accuracy varies with the proportion of element present. For example, Ca interferes with Na because it gives a weak band in the Na region (589 nm).

Applications:

The flame photometer has widespread use in pathological laboratories for the determination of Na, K and Ca in clinical samples. The recent availability of interference filters, which have a much narrower band pass, has extended the range of such instruments to include more elements for analysis such as magnesium, thallium and indium.

2. ATOMIC ABSORPTION SPECTROSCOPY

The first observation of atomic spectra was made by **Fraunhofer** while studying dark lines in the solar spectrum. The potential use of atomic absorption spectroscopy (AAS) for the analysis of metallic elements was first pointed by **Walsh, Alkemade and Miltaz in 1955**. The technique has been particularly useful in the determination of trace metals in liquids. The versatility of AAS can be realized from the fact that 60-70 elements have been analysed by this method in concentration as low as 1 ppm. The greatest advantage of AAS is the analysis of one metal in the presence of another metal, thus saving time and eliminating error.

Principle of AAS

Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible by neutral atoms in the gaseous states. *If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground-state atoms present in the flame.* This is the underlying principle of AAS

Absorption of Radiant Energy by Atoms

Atoms absorb light at a definite wavelength depending upon the nature of the element, e.g., sodium absorbs at 589 nm. Light at this wavelength has adequate energy to excite atoms to another electronic state. From the ground state an atom is excited to a higher energy state by absorption of energy.

Measurement of Atomic Absorption

Analytical methods based on atomic absorption are highly specific because the lines observed are extremely narrow and the energy corresponding to electronic transition is unique for each element. **Beer's Law** can also be applied, if the band width is narrow with respect to the width of absorption peak.

There are two fundamental laws which express respectively the relationship between absorption of radiation by a substance and its molar concentration and the length of the path through which the light passes. These laws are:

Beer's Law: *When a beam of monochromatic light is passed through a substance in a solvent, the absorption of light is directly proportional to the molar concentration of the absorbing substance.*

Lambert's Law: *When a beam of monochromatic light is passed through a substance, the absorption of light is directly proportional to the path length of the sample.*

The above two laws are combined to get a **Beer-Lambert Law.** According to it *the absorption of light by a substance at a particular wavelength is proportional to molar concentration in a fixed path length.* Mathematically, it can be expressed as:

$$\log_{10} \frac{I_0}{I} = \epsilon . c . l$$

Where, I_0 = Intensity of incident light, I = Intensity of transmitted light, c = Concentration of the absorbing substance in mol/litre, l = Path length or thickness in cm of the cell containing the sample. ε = Proportionality constant known as molar absorptivity or **molar extinction coefficient.**

The term $\log_{10}\frac{I_0}{I}$ is called optical density or absorbance. It is represented as A.

$$A = \log_{10} \frac{I_0}{I} = \varepsilon . c . l$$

I_0 / I *is* the ratio of intensity of incident light to that of transmitted light.

Deviations of Beer's Law

The deviations of Beer's law from ideal behaviour are caused by instrumental factors or by interactions with the solution. These can cause positive or negative deviations.

(i) Instrumental Factors:

(a) Too Wide a Slit: The law is only strictly applicable for monochromatic radiation. This condition can be maintained with narrow slits.

(b) Stray Radiation: Scattered radiation from another part of the spectrum and unabsorbed by the sample may fall on the detector. The errors caused by such radiation are serious.

(c) Reflection Losses: Losses will occur due to reflection from the front and back surface of the windows in the path of radiation beam. These effects worsen as the windows deteriorate due to scratching and wear.

(d) Path Length Errors: If cells are not placed perfectly normal to the beam the path length traversed through the solution will be greater than the measured cell thickness, *l*. Repeated measurements are preferred.

(ii) Solution Interactions:

(a) Inhomogeneity: The deduction of Beer's law assumes that the absorbing substance is uniformly and finely dispersed. If it is coagulated into small number of large units there will be large open areas through which radiation can pass freely and the observed absorption will diminish. Further more, large particles will cause turbidity, i.e., scattering. Scattering of the radiation beam will give an apparent increase of absorption.

(b) Solute-Solute Interactions: The nature of the absorbing species may change with concentration due to molecular self-association. The effect will be particularly strong for hydrogen-bonding substances such as alcohols.

(c) Solute-Solvent Interactions: Hetero association between solute and solvent can give rise to changes in the concentration.

(d) Chemical Side Reactions: The absorbance may be altered greatly by altering the chemical conditions, e.g. change of pH, addition of complexing agent, in such a way that the concentration of absorbing species is altered.

It should be remembered that strict obedience of data to Beer's law is not essential for performing precision quantitative analysis, provided adequate calibration curves are obtained

Instrumentation for Atomic Absorption

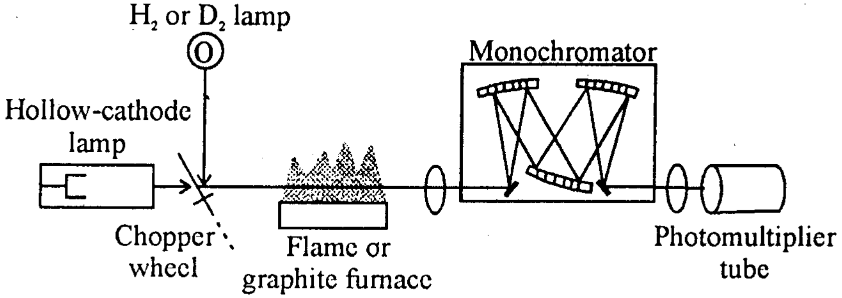
The following basic components of an AAS instrument are shown in Fig. 24.3

1. **Radiation Source (A):** A hollow cathode is used as the radiation source. (A high voltage (300-500 V) is put across the anode and cathode. Ar or He are ionized at the anode and attracted towards cathode. The fast moving ions strike the surface of the cathode and physically displace the metal atoms into the atmosphere. The displaced atoms are excited and emit the characteristic spectrum of the metal used as cathode. Hollow metal cylinder acting as cathode, is 10 to 20 mm in diameter. The cylindrical design of cathode tends to concentrate the radiation in a limited region of the tube. The argon or helium gas filled in the hollow cathode lamp performs three functions:

(i) It is responsible for excitation of the ground state metal atoms.

(ii) It dislodges atoms from the surface of the cathode.

(iii) It is the main source of current. Pressure maintained in the hollow cathode lamp is 1 to 5 torr.



AA spectrometer with H_2 (or D_2) lamp for background correction.

Fig. 24.3

Generally a flame is not preferred due to interferences and back striking effect. In case of non-flame atomizers, an electrical heating device is used. In **graphite furnace**, the temperature can be raised gradually in stages, in order to evaporate, dissociate or vapourise the compound. Non-flame methods are preferred as they are more safe.

2. **Chopper:** It is a rotating wheel interposed between the hollow cathode lamp and the flame.
3. **Burners:** Totals consumption burner and the premixed burners are used in AAS.
4. **Monochromators:** Prisms and gratings are the most common monochromators. *The function of a monochromator is to select a given absorbing line from spectral lines emitted from the hollow cathode.*
5. **Detectors:** Film and photomultiplier are the commonly used as detectors.
6. **Amplifier:** The electric current from the photomultiplier detector is fed to the amplifier which amplifies the electric current several times. Generally, **Lock-in amplifiers** are preferred which provides a narrow frequency band and help to achieve an excellent signal-to-noise ratio.
7. **Read-out device:** Chart recorders or digital readout devices are used in AAS.

Two types of spectrophotometers are used in AAS:

1. **Single-beam Spectrophotometers:** In this instrument, the optical system is very simple.
2. **Double-beam Atomic Absorption Spectrophotometers:** A double beam system compensates for changes in radiation intensity.

Applications of Atomic Absorption Spectroscopy

The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration and has several advantages over conventional absorption or emission spectroscopic methods. AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed. The technique is firmly established in analytical chemistry, ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

It is well known that sample for AAS must be in the form of solution. So solid and gaseous samples are first obtained in the solution form.

1. **Solid** samples should be dissolved in a suitable solvent and then analysed. Examples include metal alloys, soils, fertilizers, ores, polymers, cement, bone ash, plant and animal materials.
2. **Liquids** may be analyzed directly. Examples are pollutants in water, electroplating solutions, blood, petroleum products etc.
3. **Gases** should be collected from the gas sample by absorption or by trapping in solution.

3. ULTRAVIOLET AND VISIBLE SPECTROSCOPY

The ultraviolet and visible spectra of compounds are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone pair orbital and antibonding orbitals. Absorption of energy is quantized and results in the promotion of electron from low-energy orbitals in the ground state to higher energy orbitals in an excited state. The main difference between ultraviolet and visible methods is that ions, atoms or molecules absorbing in the ultraviolet region absorb more energy for excitation than in the visible region.

Absorption of radiation in the visible and ultraviolet regions of the electromagnetic spectrum results in electronic transitions between molecular orbitals. Alongwith the electronic transitions there are always simultaneous changes in rotational and vibrational energies (Fig. 24.4). At room temperature all molecules will be in the ground electronic state and almost in the lowest vibrational level. Transitions to any vibrational level in the first electronic state will be allowed by the spectroscopic selection rules and a spectrum will be obtained as broad band. These are characterised by maximum absorption band at λ_{max}.

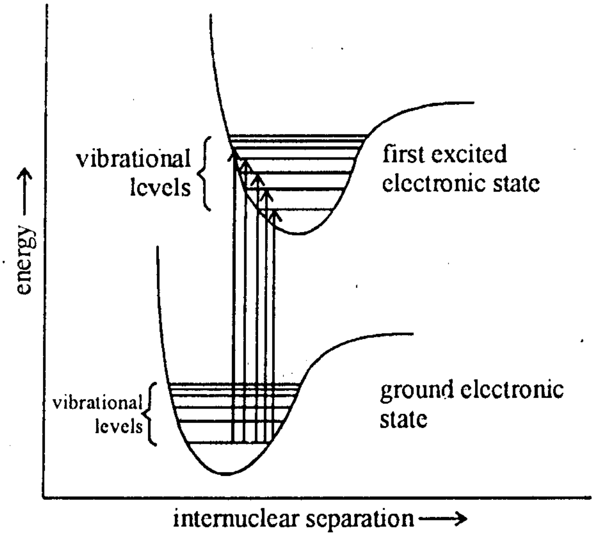
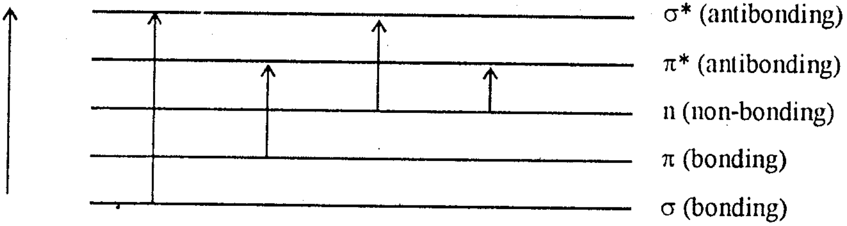


Fig. 24.4

In most organic compounds the bonding and non-bonding orbitals are filled and the antibonding orbitals are vacant. The lowest energy and therefore longest wavelength transitions are from non-bonding orbitals to antibonding π^* orbitals i.e., $n \rightarrow \pi^*$.

These give rise to bands in the near UV and visible regions and are used in analysis. Other allowed transitions in order of increasing energy i.e., shorter wavelength are $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$. These occur in UV region and $\sigma \rightarrow \sigma^*$ occurs in far UV little used analytically. Intense bands are produced by $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions but those arising from $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ are weak.



Relation of energies of orbitals and possible transitions

Chromophores:

The term chromophores is used to describe the system containing electrons responsible for absorption of radiation. Typical chromophores and their absorption characteristics are given in Table 24.2

Table 24.2

Absorption Characteristics of some typical Chromophores

Chromophores	Example	Transition	λ_{max} in mμ
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	ethane	$\sigma - \sigma^*$	150
$>C=C<$	ethylene	$\pi - \pi^*$	165
$>C=O$	acetone	$\pi - \pi^*$	188
$-\ddot{O}-$	ether	$n - \sigma^*$	185
$-N<$	amine	$\pi - \pi^*$	195
$-N=N-$	azomethane	$\pi - \pi^*$	347
$-N=O$	nitrosobutane	$n - \pi^*$	300
	benzene	$\pi - \pi^*$	615

The following terms are commonly used, while discussing the visible / UV spectra.

Red shift of bathochromic effect. It is a shift of an absorption maximum towards longer wavelength. It may be produced by a change of medium, or by the presence of an auxochrome.

Auxochrome: A substituent on a chromophore which leads to a red shift. For example, the conjugation of the lone pair on the nitrogen atom of an enamine shifts the absorption maximum from the isolated double bond value of 190 m to about 230 $m\mu$, nitrogen substitutent acts as auxochrome. Examples of auxochromes are – OH, – Cl, – NH_2.

Blue shift or hypsochromic effect: It is a shift towards shorter wavelength. This may be caused by a change of medium and also by the removal of conjugation.

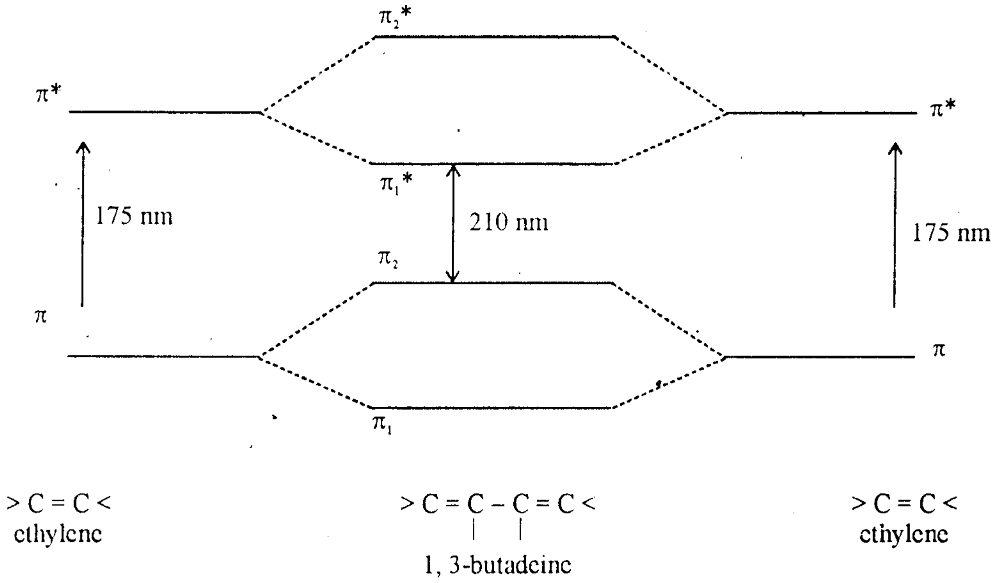
Hyperchromic effect: An effect leading to increased absorption intensity.

Hypochromic effect: An effect leading to decreased absorption intensity.

Isosbestic point: A point common to all curves produced in the spectra of a compound taken at several pH values.

Conjugation Effects:

Absorption bands due to conjugated chromophores (with alternate single and double bonds) are shifted to longer wavelength (bathochromic or red shift) and intensified shift can be explained on the basis of delocalization of the $\pi - \pi^*$ orbitals of each chromophore to produce new orbitals in which highest π orbital and the lowest π^* orbital are closer in energy. Effect of conjugation on absorption of > C = C < (double bond) is depicted as:



Extent of conjugation will determine the shift to higher wavelength. Thus γ-carotene with 11 conjugated double bands is a coloured compound and absorbs in visible region at 460 nm. Benzene absorbs at 184, 203.5 and 254 nm.

Effect of Auxochromes:

In general, auxochrome substitution of chromophores causes bathochromic shifts (to longer wave length) and increases in intensity for $\pi - \pi^*$ transitions. These shifts can be explained in terms of mesomeric (resonance) effects caused by interaction of lone pair electrons associated with auxochromes such as $-OH$, $-Cl$, $-NH_2$ with the π-system of the chromophere. This leads to change in energies.

Emperical rules have been devised by Woodward and others to calculate the additive effects of auxochromic substitution on the absorption of aromatic and conjugated systems.

The rules of diene absorption are reproduced below:

	Wavelength λ (nm)
Base value for heteronuclear diene	214
Base value for homonuclear diene	253
Increments added for:	
double bond extended conjugation	30
alkylsubstituent or ling residue	5
exocyclic double bond	5
Polar groups	
O Alkyl	6
S Alkyl	30
Cl, Br	5
N (Alkyl)$_2$	60
Calculated λ_{max} Total	

Problem: Calculate the absorption maximum in the ultraviolet spectrum of 2, 4-hexadiene.

Solution: The basic unit in 2,4 hexadiene is butadiene. There are two alkyl substitutions (one on each double bond) on it.

$$CH_3 - CH = CH - CH = CH - CH_3$$

2, 4- hexadiene

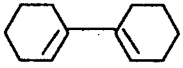
Parent value = 217 nm

2- Alkyl substituents (2x 5) = 10 nm

Calculated λ_{max} = 227 nm

Observed λ_{max} = 227 nm

Problem: Calculate absorption maximum for



Solution: The compound is an example of heteroannular diene.

Parent Value = 214 nm
4-Ring residues (4x5) = 20 nm
Calculated λ_{max} = 234 nm
Observed λ_{max} = 234 nm

Solvent Effects:

Adsorption bands arising from $n \rightarrow \pi^*$ transitions undergo hypsochromic shifts on increasing the solvent polarity and the $\pi - \pi^*$ transitions undergo bathochromic shift.

The positions and intensities of $\pi \rightarrow \pi^*$ bands in such compounds as phenols and amines exhibit a marked sensitivity to pH changes.

Metal Complexes:

Complexes of metals with organic and inorganic ligands which absorb in the visible region of the spectrum are of great significance in quantitative analysis.

The following three types of transitions are found in coloured complexes:

a. d-d transitions within a metal ion. These are usually of low intensity and of little use in analysis.

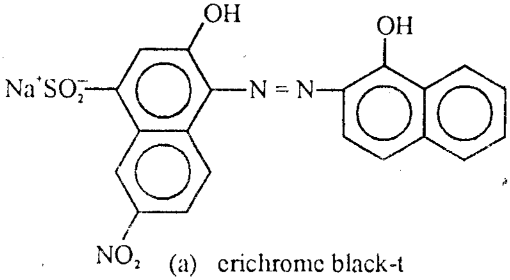
b. Excitations within an organic ligand. These are usually $n-\pi^*$ and $\pi-\pi^*$ transitions in presence of metal.

c. Charge-transfer transition. These involve the transfer of an electron between two orbitals one of the ligand and the other from the metal.

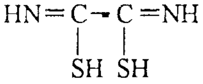
These last two (b&c) types give rise to strongly coloured complexes suitable for trace analysis. Bands due to d-d transitions are responsible for the colours of transition metal ions in aqueous solutions. Absorption of radiation is due to the movement of electrons from filled d orbitals to half – filled or empty d orbitals of transition metals. As a result of it various colours are obtained depending on the metal and the nature of coordinating ligand. The absorption band shifts towards UV region in the following order named as *spectrochemical series*.

$I^- < Br^- < Cl^- < OH^- < H_2O < NH_3 <$ ethylenediaxmine $< CN^-$

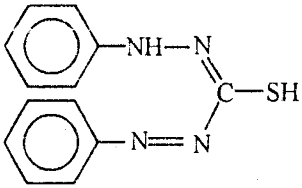
A series of coloured complexes of transition metals with ligands, both chelating and non- chelating are found. They include excitations within an organic ligand and charge transfer transitions. These are useful for quantitative analysis of metals.



(a) eriochrome black-t



$$HN{=}\underset{\overset{|}{SH}}{C}-\underset{\overset{|}{SH}}{C}{=}NH$$



(b) dithiooxamide (rubeanic acid) (c) dithizone (diphenylthocarbazone)

Examples:

i. Coloured complexes of eriochrome black- T, rubeanic acid and dithizone with transition metals

ii. The intense red colour of Fe (III) - thiocyanate complex, orange colour of Ti(IV) peroxy complex and the purple permangarate ions are all charge transfer complexes where electrons transfer from metals to ligand orbitals.

Measurement of UV/Visible Spectrum

1. The ultraviolet or visible spectrum is usually taken of a very dilute solution.
2. An appropriate quantity of the compound (often about 1 mg when the compound has a molecular weight of 100 to 200) is weighed accurately. It is dissolved in a suitable solvent and made upto 100 ml.
3. A portion of this solution is transferred to a silica cell. The cell is so made that the beam of light passes through a 1 cm thickness of solution.
4. A comparison cell containing pure solvent is also prepared. Each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of UV are passed, one through the solution of the sample and one through the pure solvent.
5. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument.
6. The spectrum is plotted automatically on most UV/visible spectrophotometers.

Quantitative analysis by visible and UV spectrometry is in common practice. Most of the inorganic and biochemical substances can be quantitatively estimated either directly or after the formation of a complex.

This is one of the most sensitive and common technique available for the determination of trace and even ultra-trace level of constituents. The estimations are based on selectivity and sensitivity by proper choice of the organic reagent, use of masking agents or by solvent extraction with high degree of precision and accuracy.

The following are some examples of the applications of UV/visible spectrometry for quantitative analysis.

Applications of quantitative visible and ultraviolet spectrometry

ELEMENT OR COMPOUND DETERMINED	REAGENT	EXAMPLE OF APPLICATION
Fe	o-phenanthroline	natural waters, petroleum products
Cu	neocuproine	minerals, alloys
Mn	oxidation to MnO_4^-	steels
Cr	diphenylcarbazide	alloys, minerals
Hg, Pb	dithizone	food products, fish
P, PO_4^{3-}	reduction to molybdenum blue	fertilizer residues, soils
F^-	lanthanum alizarin complexone	drinking water
aspirin	—	analgestic preparations
cholesterol	Liebermann-Burchard reaction	body fluids
vitamin A	glycerol trichlorohydrin	foodstuffs
sulphonamides	diazo derivatives	drug preparation
proteins	biuret reaction	tissue, body fluids
DDT	nitrated derivative	soils, fish

Applications of Ultraviolet Spectroscopy in Analysis:

Ultraviolet spectrophotometric methods find extensive use in the identification of various hydrocarbons, vitamins, steroids, heterocyclic and aliphatic compounds.

The following applications are common.

1. **Detection of Functional Groups in Organic Compounds:**

The absence of a band at a particular wavelength marks the absence of a particular group in the organic compound. If the spectrum above 200nm is transparent, it shows the absence of conjugation, aldehydes, ketones, aromatic compounds etc.

2. **Elucidation of Structures of Vitamins:**

The UV spectra help in the elucidation of structures of Vitamins. Vitamin A, absorbs at 325 nm and Vitamin A2 at 287 and 351nm.

3. **Identification of Tautomeric forms:**

Tautomeric forms can be identified by UV.

4. **Identification of Geometrical Isomers:**

Cis and trans forms can be identified by UV. Cis forms absorb at lower wavelength. Cis- stilbene absorbs at 283 nm and trans-stilbene at 290 nm.

5. **Chemical Kinetics:**

UV spectroscopy can be used to follow the path of a reaction even in fast reactions.

6. **Detection of Impurities:**

UV is one of the best methods for detecting impurities in organic compounds.

7. **Determination of Metal Halide Complexes:**

The halide complexes of metals are the main inorganic compounds absorbing UV radiations. Tellurium can be determined as its iodide complex $[\text{Te I}_6]^{2-}$ by measurements at 335 nm.

8. **Ozone Concentration in the Atmosphere:**

The concentration of ozone in the environment can be determined by measuring absorption at 260 nm.

9. **Determination of Lanthanides:**

Characteristic intense absorption bands of lanthanides appear in UV region and can be used to determine them.

INFRARED SPECTORSCOPY

Infrared spectroscopy is one the most powerful analytical techniques which offers the possibility of chemical identification. **IR** technique when coupled with intensity measurements may be used for quantitative analysis. Infrared has been of tremendous use to chemists and is currently more popular as compared to other physical techniques in the elucidation of the structures of unknown compounds.

The Range of Infrared Radiation

The infrared radiation refers broadly to that part of the electromagnetic spectrum which lies between the visible and microwave regions. From instrumentation and application point of view, the infrared region has been subdivided as follows:

a. The near infrared region (overtone region). It ranges from 0.8 to 2.5μ (12500-4000 cm^{-1}).

b The mid infrared region (vibration-rotation region). It ranges from 2.5 to 15μ (4000-667 cm^{-1}).

c. The far infrared region (rotation region). This ranges from 15 to 200μ (667-50 cm^{-1}).

An infrared spectrum show downward peaks corresponding to absorption, plotted against wavelength (λ) or wave number (ν). Wavelength is expressed in μ (microns) or μm (1μm = 10^{-4} cm). Since λ is inversely proportional to energy, the wave number in cm^{-1} is mostly used to measure the position of a given infrared absorption.

Requirements for Absorption of Infrared Radiation

For a molecule to absorb infrared (IR) radiation, it has to fulfill certain requirements, which are as follows (selection rules):

i. **Correct Wavelength of Radiation**. A molecule absorbs radiation only when the frequency of vibration of some part of a molecule is the same as the frequency of the incident radiation.

ii. **Electric Dipole**. A molecule can absorb IR radiation when its absorption causes a change in its electric dipole (dipole moment).

Each non-linear molecule has 3n-6 internal degrees of freedom and the linear molecules have 3n-5 (n = No of atoms in the molecule). For a vibration to be IR-active, there must be electrical coupling between oscillating electric field of electromagnetic radiation and molecular motion and should have a change in dipole moment.

Origin of Infrared spectra

When a molecule is placed in an electromagnetic field, e.g., infrared radiation, a transfer of energy from the electromagnetic field to the molecule occurs when,

$$\Delta E = h\nu$$

Where ΔE is the difference in energy between two quantized states, h is Planck's constant (6.624 × 10^{-27} erg sec), ν is the frequency of light. When the molecule is excited, it absorbs energy from the lower energy state E_1 to higher energy state E_2 and emits radiations of the same frequency when the molecule reverts from the higher energy state to lower energy state.

$$\Delta E = E_1 - E_2 \qquad \text{(Absorption)}$$
$$\Delta E = E_2 - E_1 \qquad \text{(Emission)}$$

Actually the energy of a molecule can be resolved into:

(a) *The energy* associated with the rotation of the molecule as a whole (**rotational energy**).

(b) *The energy associated with the vibration of the constituent atoms in the molecule (***vibrational energy**).

Molecular Vibrations

The molecules undergo vibrations in the following ways.

1. **Stretching Vibrations.** A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. The symmetrical stretching vibration is inactive in the infrared since it produces no change in the dipole moment of the molecule, e.g., $O=C=O$.

The stretching vibrations are of two types.

(a) *Symmetrical Stretching.* When the stretching and compression occur in a symmetrical fashion, it is called symmetrical stretching.

(b) *Asymmetric Stretching.* When one bond is compressing while the other is stretching.

2. **Bending or Deforming Vibrations.** A bending vibration may consist of a change in bond angles between bonds with a common atom, or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group. Bending vibrations are of four types:

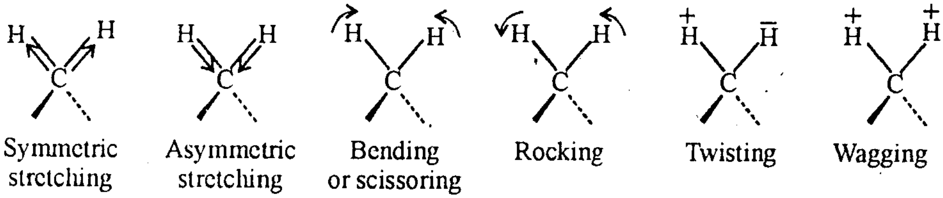
(a) **Scissoring:** When the two atoms join to a central atom move toward and away from each other with the deformation of the angle between them (in plane bending).

(b) **Rocking:** When the structural unit swings back and forth in the plane of the molecule (in plane bending).

(c) **Wagging:** The structural unit swings back and forth out of the plane of the molecule (out of plane bending)

(d) **Twisting:** The structural units rotate about the bond which joins to the rest of the molecule (out of plane bending)

In a molecule containing more than two atoms, all the four types of vibrations may be possible. However, only those vibrations that result in a change in the dipole moment of the molecule are observed in the infrared. Various modes of vibrations for an **AX_2** group are shown below.



Electronic Effects

Changes in the absorption frequencies for a particular group take place when the substituents in the neighborhood of that particular group are changed. The frequency shifts are due to electronic effects which include:

(i) Inductive effects

(ii) Mesomeric effects and

(iii)Field effects etc

(i) Inductive Effect. The introduction of an electronegative atom or group causes the inductive effect which results in the increase of bond order. The force constant increases and hence the wave number of absorption rises. Consider the wave numbers of absorption in the following compounds:

(a) Acetone (CH_3 $COCH_3$) 1715 cm^{-1}

(b) Chloroacetone (CH_3 $COCH_2$ CI) 1725 cm^{-1}

(c) Dichloroacetone (CH_3 $COCHCI_2$) 1740 cm^{-1}

(d) Tetrachloroacetone (Cl_2 $CHCOCHCl_2$) 1750, 1778 cm^{-1}.

(ii) Mesomeric Effect: It causes lengthening or the weakening of a bond leading to the lowering of absorption frequency. In most of the cases, mesomeric effect works along with inductive effect.

(iii) Field Effect: In ortho substituted compounds, the lone pair of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is known as **field effect.**

Hydrogen Bonding:

Hydrogen bonding brings about remarkable downward frequency shifts. *Stronger the bonding, greater is the absorption shift towards lower wave number than the normal value.* Generally, bands due to intramolecular hydrogen bonds are sharp whereas intermolecular hydrogen bonds give rise to broad bands and depend on concentration.

Theory

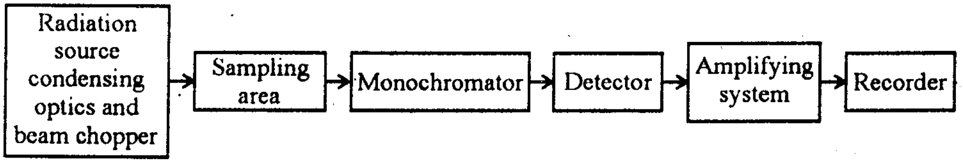
Infrared technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms. The absorption of energy is quantized. Then the molecules of a chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands. Vibrational spectra appear as bands rather than lines because a single vibrational energy change is accompanied by a number of rotational energy changes. Thus **IR** spectrum of a chemical substance is a **finger print** for its identification. Band intensities are expressed either as transmittance *(T)* or absorbance *(A)*. **Transmittance** is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. **Absorbance** is the logarithm, to the base 10, of the reciprocal of the transmittance, $A = \log_{10}(1/T)$.

INSTRUMENTATION

Infrared Spectrophotometer: These are either single beam or double beam. In a single beam spectrophotometer the radiations emitted from the source are passed through a cell containing the sample and through the prism which disperses the light. **Single beam spectrophotometers** are simple, sensitive, accurate, versatile and are used to study fine details. But these instruments have two disadvantages.

1. When the spectra of the solution is to be recorded, the absorption bands due to solvent are also obtained, thus, making the interpretation of the bands and identification of the compounds more difficult.
2. The base line, i.e., the line obtained without the use of the sample in the light path, slopes because the intensity of the source changes continuously with the wavelength.

Flow sheet diagram of Infrared Spectrophotometers is given below:



Double Beam Spectrophotometers: These are so designed that the light from the source is split into two beams of equal intensity, one passing through the sample and the other through the reference (air or solvent) for compensation. The two beams are recombined on to a common axis and are alternately focused on to the entrance slit of the monochromator. This removes the second disadvantage of single beam spectrometers and a horizontal base line is obtained.

Components of Double Beam Infrared Spectrophotometer

The following components of double beam infrared spectrometer are depicted in Fig. 24.5.

1. Radiation source
2. Monochromator and optical material
3. Sampling area
4. Detector
5. Amplifier and Recorder

1. Radiation Source

Infrared radiation is produced by electrically heating a source, usually a Nernst filament or a Globar to 1000-1800° C. The Nernst filament is fabricated from a binder and oxides of thorium, cerium, zirconium and yttrium. The Globar is a small rod of silicon carbide usually 5 cm in length and 0.5 cm in diameter. The maximum radiation for the Globar occurs in the 5500-500 cm^{-1} IR region. Nichrome wire, carbon arc, rhodium wire and tungsten filament lamp are also used as light source.

2. Monochromator and Optical Material

The separation of desired frequencies can be achieved by means of monochromators. Prisms and gratings are used for this purpose. Most IR spectrophotometers use prisms of alkali halides. Prisms of LiF or CaF_2 give more resolution in the region where the significant stretching vibrations are located. However, recent spectrometers are of grating type.

3. Sampling

Compounds may be examined in the vapour phase, as pure liquids, in solution and in solid state.

(a) **Gaseous Samples:** The vapour is introduced into a special cell, usually about 10 cm long that can be placed directly in the path of one of the infrared beams. The cell is usually made of sodium chloride, which is transparent to infrared.

(b) **Liquid Samples:** Liquids are usually handled pure, i.e., without solvent because all solvents have their own absorption spectra. Thin films of liquids are exposed to IR beam to take the spectrum.

(c) **Solid Samples:** A wide variety of techniques is used for measurement of infrared absorption spectra of solid materials. Solid samples may be used in the form of solution, powder, glassy film or pellet.

(i) **Solids in Solution:** If the solid is soluble in some suitable solvent, its solution can be placed in one of the cells for liquids. However, suitable solvents are limited in number and none are totally transparent. Carbon disulphide is transparent below 1330 cm^{-1} while carbon tetrachloride is transparent above 1330 cm^{-1}.

(ii) **Solid Films:** Amorphous solid samples may be cast into films.

(iii) **Mull Technique:** The most convenient and routine method is called mulling. Mulls are prepared by thoroughly grinding 1 mg of a solid in a smooth agate mortar. The powdered sample is mixed with little high boiling petroleum, usually Nujol and mulled to form a past which is then transferred to flat plates of sodium chloride. The oil has a few absorption bands specifically at about 2857, 1449 and 1389 cm^{-1}. Hexachlorobutadiene is also used for mulling.

(iv) **Pressed Pellet Technique:** This technique depends upon the fact that dry, powdered potassium bromide (or KI or CsBr) can be mixed with sample and pressed under high pressure in vacuo to form transparent discs. The resulting transparent discs are inserted into a special holder for taking IR spectrum.

4. Detector

Detector is a device that usually changes the thermal radiant energy into electrical energy. The infrared detectors may be selective or non-selective. The selective detectors are those whose response is markedly dependent upon the wavelength of the incident radiation. Examples of this type are photocells, photographic plates, photoconductive cells etc.

5. Amplifier & Recorder

An alternating current amplification is used. The radiation beam is chopped at a suitable frequency to provide the A.C. signal for the detector and rectified and used to drive the recorder.

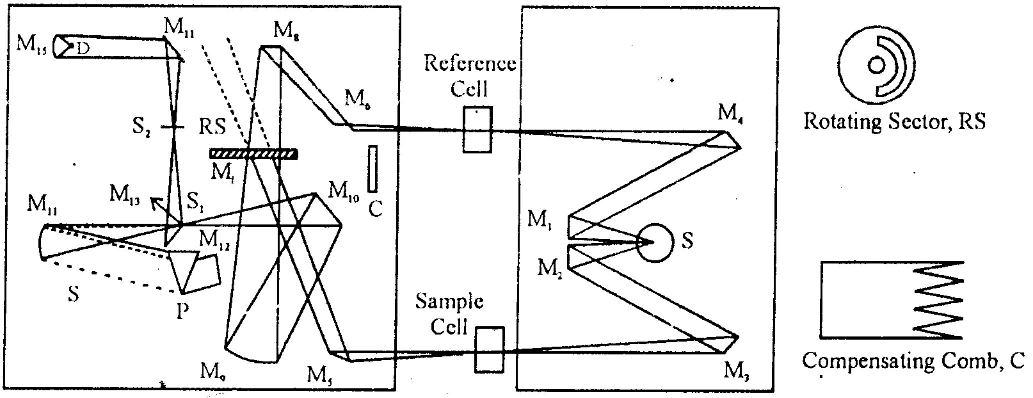


Fig. 24.5 Schematic Diagram of Double Beam Infrared Spectrophotometers.

FOURIER TRANSFORM INFRA RED SPECTROSCOPY (FTIR)

Recently a new method of taking an infrared spectrum involves the use of FTIR or Interferometers. Light is collimated by lens and a beam splitter splits the light into two equal parts.

Either one beam is passed through the sample, or both are passed, but one beam is made to traverse a longer path than the other. Recombination of the two beams produces an interference pattern. By systematically changing the difference in the two paths, the interference patterns change to produce a detected signal varying with optical path difference. This pattern is known as the **interferogram.** However, Fourier transformation of the interferogram using a computer converts it into a plot of absorption against wave number which resembles the usual spectrum obtained by the traditional method. Interferograme can be interpreted well with electronic assistance or digital mini computer.

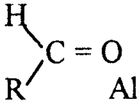
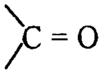
There are several advantages to FTIR over the traditional method.

1. By FTIR, it is possible to measure the whole spectrum in a few seconds, because it is not necessary to scan each wave number successively.
2. Since it is not dependent upon slit and a prism or grating, high resolution in FTIR is easier to obtain without sacrificing sensitivity.
3. FTIR is especially useful for examining small samples.
4. The digital form in which the data are handled in the computer allows the spectrum of a pure compound to be subtracted easily from that of a mixture to reveal the spectrum of other components of the mixture.

The Infrared Spectrum

A molecule can have a large number of vibrational modes. Some of these vibrations are associated with the vibrations of individual bonds or functional groups referred to as localized vibrations and others are based on vibrations of the whole molecule. The localized vibrations are either stretching, bending rocking, twisting or wagging. These localized vibrations are very useful for the identification of functional groups. The vibrations of molecules as a whole give rise to a series of absorption bands at low frequency or wave number below 1500 cm^{-1}, the positions of which are characteristic of the molecule. The IR bands at frequencies less than 1500 cm^{-1} are nor very useful for diagnostic purposes and are called finger print region of the spectrum. The regions in which functional groups absorb are of great significance in infrared spectroscopy. The stretching vibrations of single bonds to hydrogen give rise to the absorption at the high frequencies because of the low mass of hydrogen atom. The stretching frequencies are at higher frequency than double bonds and double bonds at higher frequencies than single bonds. Thus greater the strength of the bond between two similar atoms the higher would be the frequency of the vibrations. Bending vibrations are of much low frequencies usually below 1500 cm^{-1}. Absorption frequencies of single bonds to hydrogen, single and double bonds and various functional groups are given in Table 24.1.

TABLE 24.1

Group	Band Region cm^{-1}	Remarks
$> CH_2$ $- CH_3$	2960 - 2850 (s)	C – H stretching
$> CH$	2890 - 2880 (w)	CH stretching
$- C \equiv CH$	3300	C – H stretching
$- OH$	3650 - 3590 (vs) 1410 - 1260 (s)	O – H stretching O – H bending
$- OH$	3600 - 3200 (s)	O – H due to hydrogen bonding
$> NH$	3500 - 3300 (m)	N – H stretching
$- NH_2$	1650 - 1560 (m)	N – H bending
$- C \equiv C - H$	3300 (m) 2140 - 2100 (w)	C – H stretching $C \equiv C$ stretching
$- C \equiv C -$	2260 - 2150 (vs)	$- C \equiv C -$ stretching
$- C \equiv N$	2260 - 2200 (vs)	$C \equiv N$ stretching
$> C = C <$	1600 - 1700 (s)	$C = C$ stretching
$C = O$	1600 - 1900 (s)	$C = O$ stretching
$- N = N -$	1575 (vs)	$N = N$ stretching
 Aldehyde	1740 - 1720	
Aryl	1715 - 1695	
 Ketone	1725 - 1700	
Ester	1735	
Hydrogen bonding	2800 - 2400	Broad bands
Carbonate	1450 - 1400	
Metal Carbonyls	2050 - 1950	$Cr(CO)_6$ at 2000 $Ni(CO)_4$ at 2046
Sulphate	1130 - 1080	
Nitrate	1390 - 1350	
Nitrite	1250 - 1230	
Phosphate	1100 - 1000	

vs stands for very strong; *s* stands for strong; m stands for medium and w stands for weak.

The regions in which various functional groups absorb are summarized in Fig. 24.6 with reference to IR spectrum of ethyl chloride.

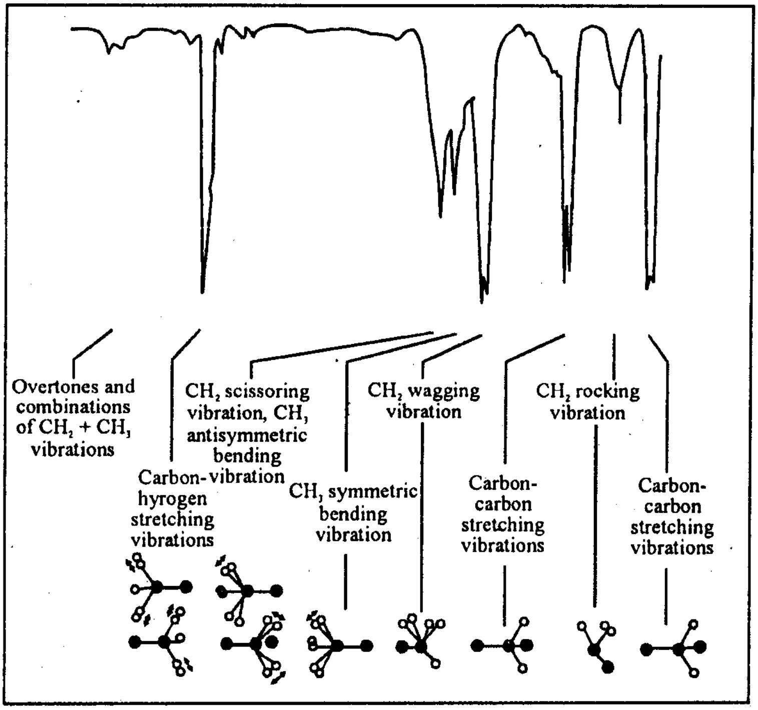
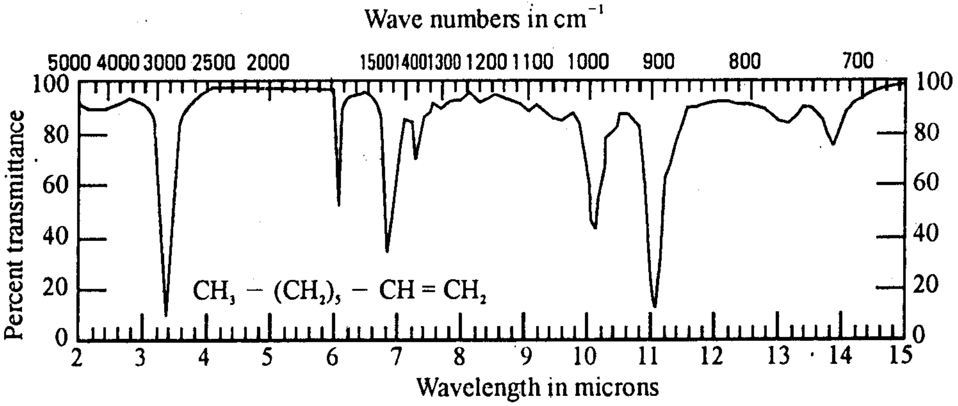


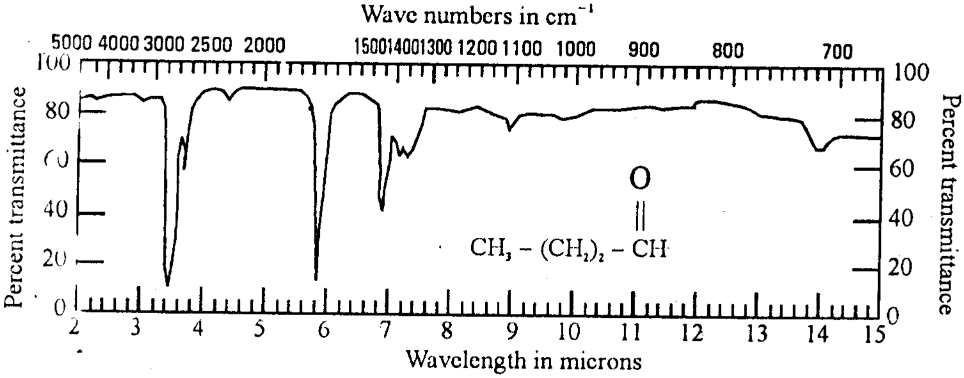
Fig 24.6 Ir spectrum of ethyl chloride from 4000 to 650 cm^{-1} and correlation of virbational modes.

Infrared Spectra:

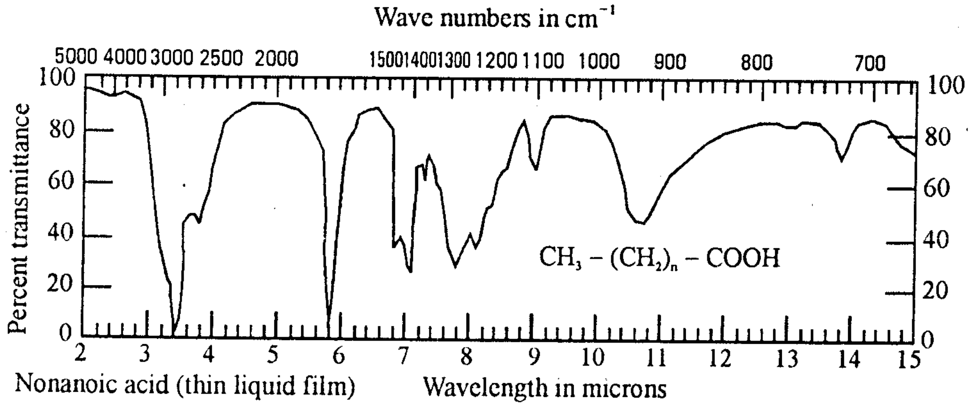
The infrared spectra of some of the commonly available organic compounds are given below. The IR bonds in regions above 1500 cm^{-1} clearly depict the stretching vibrations of the functional groups.



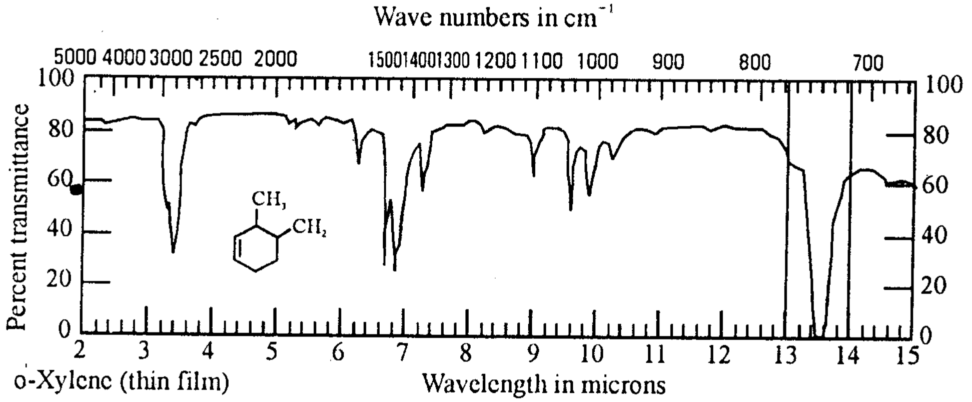
Infrared spectrum of 1-octene.



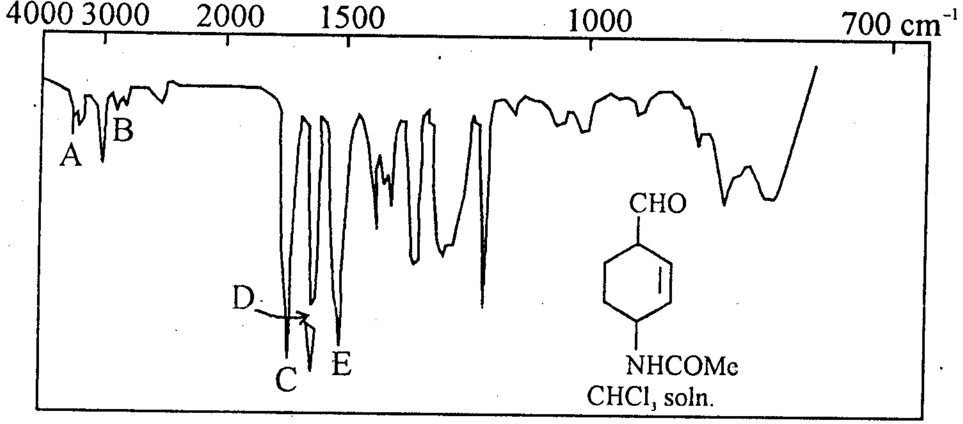
Infrared spectrum of n-undecanal



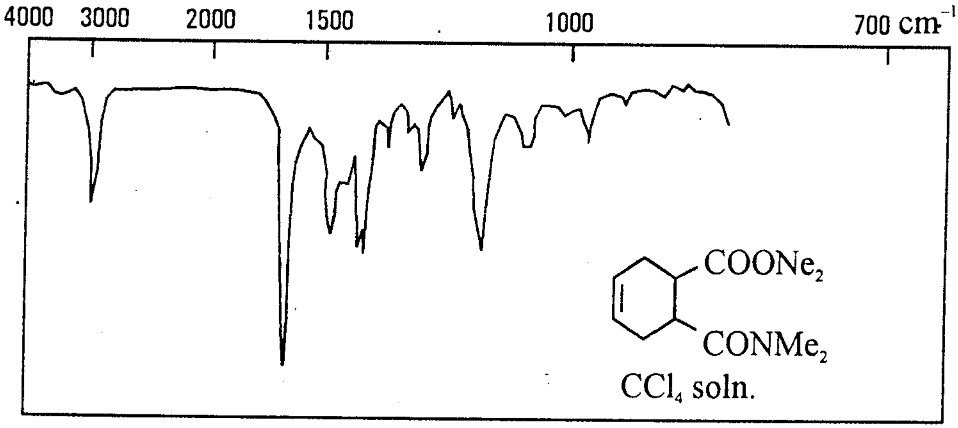
Infrared spectrum of n-nonanoic acid



Infrared spectrum of o-xylene

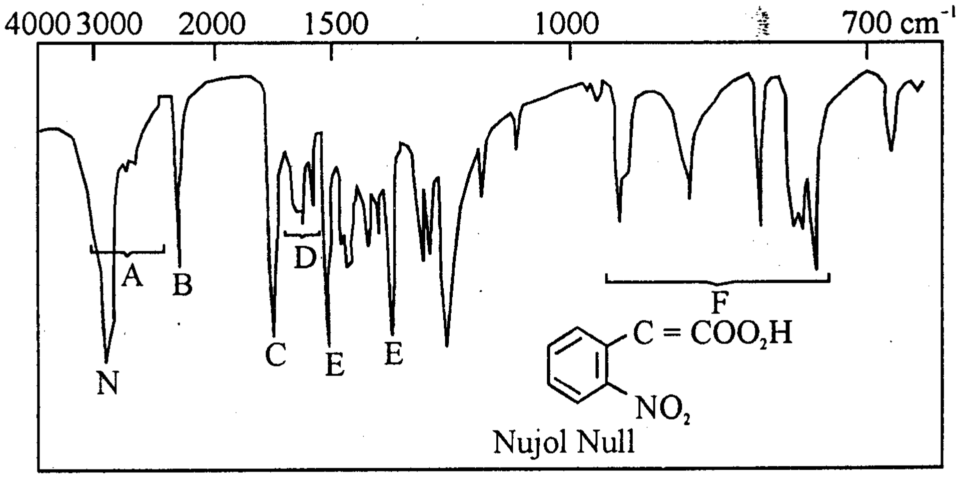


A	3400, 3300 cm^{-1}	Non-cyclic secondary amide NH
B	2810, 2720 cm^{-1}	Aldehyde C – H
C	1700 cm^{-1}	Aldehyde C = 0 and Amide 1
D	1600 cm^{-1}	Benzene ring
E	1515 cm^{-1}	Amide II and benzene ring

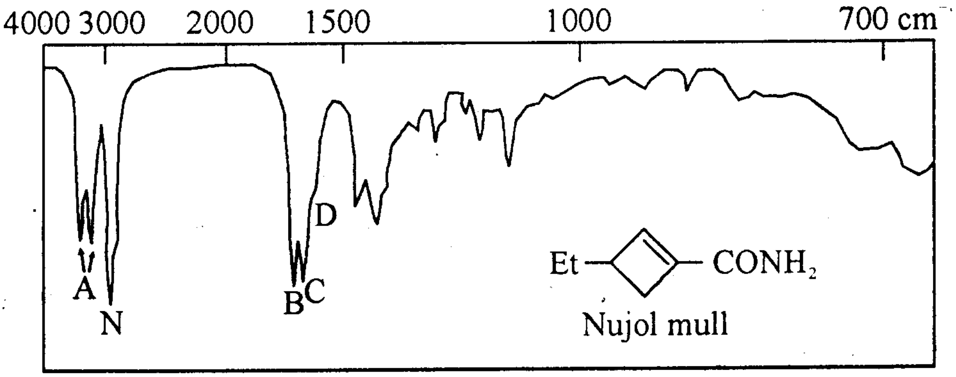


A	3010 cm^{-1}	Olefinic C – H
B	2900 cm^{-1}	Saturated C – H
C	1650 cm^{-1}	Tertiary amide C = O

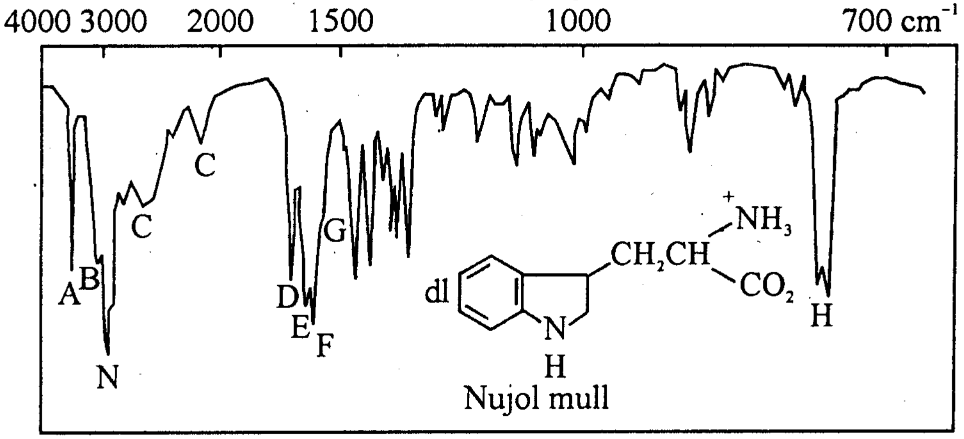
This spectrum shows the absence of N – H, the strong single sharp C = O of a tertiary amide, and because of the symmetry of the molecule, no C = C stretching absorption.



A	3200 – 2600 cm^{-1}	Characteristic strongly H-bonded O – H of carboxylic acid
B	2225 cm^{-1}	Conjugated C ≡ C, hence strong
C	1715 cm^{-1}	Conjugated – CO_2H, the value is higher than usual
D	1605 and 1570 cm^{-1}	Benzene ring, further conjugated. A band near 1600 cm^{-1} is masked
E	1520 and 1340 cm^{-1}	Conjugated nitro group – NO_2
F	900 – 700 cm^{-1}	An example of a substituted ring in which it is not possible to decide with any certainty, due to the large number of bands in the region, in favour of 1, 2-disbustitution. For an example where the assignment can be made with confidence see Fig Nujol peaks.



A	3300 and 3130 cm^{-1}	Tyical amide – NH_2 pair of bands
B	1670 cm^{-1}	Amide I
C	1630 cm^{-1}	Amide II
D	1600 cm^{-1}	Conjugated and strained C = C
N		Nujol peaks



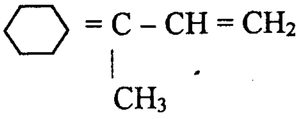
A	3360 cm^{-1}	Indole N – H
B	3030 cm^{-1}	Broad 'ammonium' band due to – $\overset{+}{NH_3}$
C	~ 2500 and ~ 2100 cm^{-1}	Two bands, very common with amino acids; also shown by primary amine salts
D	1665 cm^{-1}	Amino acid I; unusually strong
E	1610 cm^{-1}	Possibly aryl group
F	1590 cm^{-1}	Amino acid II; the ionized carboxylate group – CO_2^-
G	1550 cm^{-1}	– NH_3 deformations
H	760 or 768 cm^{-1}	C – H out-of-plane deformations showing a 1, 2-disubstituted benzene ring
N		Nujol peaks

Questions

1. Define electronic spectroscopy. What is its absorption range?
2. Explain the relationship between wavelength, frequency and wave number.
3. Explain quantization of energy.
4. Describe various types of transitions inorganic compounds.
5. What are the spectral effects of adding chromophores to a molecule.
6. How an ultraviolet spectrum can be scanned for a pure organic compounds?
7. What are absorption bands formed instead of sharp lines in the spectrum?
8. Explain the effect of polar solvents on $n \rightarrow \pi^*$ and $\pi - \pi^*$ transitions.
9. Describe various types of absorption bands which arise as a result of the electronic transitions.
10. Define the term chromophore. How will you detect the presence of carbonyl group in aldehydes and ketones?
11. Which solvents are generally used in ultraviolet spectroscopy and why?
12. Increase in polarity of the solvent shifts band to longer wavelength. Comment.
13. What is spectroscopy? How will you proceed to classify spectra?
14. What is the electromagnetic radiation? Discuss its wave and particle nature.
15. How electromagnetic radiation interacts with matter?
16. Discuss the general principle and instrumentation of Atomic Emission Spectroscopy. What are the applications, advantages and disadvantages of using this technique?
17. What is the principle of flame photometer? Give important applications.
18. What is the principle of Atomic Absorption Spectroscopy? Describe the instrumentation used. Give its significant applications.
19. What is Beer's Law? Discuss various causes of its deviation.
20. What is the basis of visible and ultraviolet spectroscopy? Describe the prerequisites of the spectral measurements.

21. Describe the following terms:
   a. Chromophores
   b. Auxochromes
   c. Bathochromic effect or red shift
   d. Hypsochromic effect or blue shift

22. Calculate λ_{max} for



23. What is the principle of Infrared Spectroscopy? The functional groups of various compounds are identified by IR?

SHORT ANSWER QUESTIONS

1. ***Why a low temperature flame is used for the analysis of alkali and alkaline earth metals?***

Ans. With the increase in temperature, ionization of the atoms of these elements may also occur. This ionization in the hot flames decreases the number of absorbing particles significantly.

2. ***Why the technique of AAS is only limited to metals?***

Ans. In case of non-metals, the resonance lines fall in the far or vacuum ultraviolet region and difficulties arise for the absorption of IR light.

3. ***In atomic absorptions, the elements such as Al, Ti, Mo, Si and V can not be detected. Why?***

Ans. Because these elements give rise to oxides in the flame.

4. ***Indicate the pressure maintained in the hollow cathode lamp.***

Ans. The pressure maintained in the hollow cathode lamp is 1 to 5 torr.

5. *Why a separate lamp is required to determine each element in AAS?*

Ans. AAS is highly specific because each cathode lamp emits the spectrum of that metal which is used in the cathode.

6. ***What is the maximum temperature in flame atomizer?***

Ans. It is 1200°C.

7. ***Why a flame is not preferred in atomizer?***

Ans. Due to interferences and back striking effect.

8. ***Give Examples of multielement lamps.***

Ans. (a) Ca, Mg, Al (b) Fe, Cu, Mn (c) Cr, Co, Cu, Fe, Mn, Ni, (d) Pb, Cu, Zn, Sn are multielement hollow cathodes but they do not give reproducible results.

9. ***Why chopper in interposed between the hollow cathode lamp and flame?***

Ans. Chopper is interposed to break the steady light from the lamp into an intermittent or pulsating light. This gives a pulsating current in the photocell. Only the alternating or pulsating current is amplified and recorded..

10. ***Why is ethanol a good solvent in ultraviolet?***

Ans. Ethanol (95%) is transparent down to 210 nm.

11. ***The wavelength of λ_{max} for methyl chloride is 173 nm while for methyl iodide it is 259 nm. Why?***

Ans. Electrons on iodine atom are loosely bound (I is less electronegative than CI). Hence for CH_3I less energy is required for $n \rightarrow \sigma^*$ transition. Hence CH_3I shows λ_{max} at higher wavelength than CH_3Cl.

12. ***Why hydrogen bonding shifts the absorption to shorter wavelengths in alcohols and amines?***

Ans. Non-bonding n-electrons present in alcohols and amines form **hydrogen bonds** with the solvent molecules. Greater energy is needed for $n \rightarrow \sigma^*$ transition hence the absorption shifts to lower wavelength.

13. ***Amines absorb at higher wavelength than alcohols. Why?***

Ans. Non-bonding electrons on N atom in amines are loosely held compared to electrons on O atom in alcohols owing to lesser electronegativity of N than O.

14. ***The position of absorption of acetone shifts in different solvents are: 279 nm in hexane, 272 nm in ethanol and 264.5 nm in water. Why?***

Ans. The shift towards shorter wavelength is due to hypsochromic or blue shift of transition as the polarity of the solvent increases in the order hexane < ethanol < water.

15. ***The bands due to $n \rightarrow \sigma^*$ transition in amine disappear in acid solution. Why?***

Ans. The bands disappear because of the formation of a bond between an acid proton and n-electrons.

16. ***Which type of transitions is considered to be the origin of charge transfer bands?***

Ans. Promotion of an electron from the ligand to the empty orbitals of the metal ion.

FILL IN THE BLANKS

1. The trans isomer absorbs at .... wavelegth with .... intensity than the cis isomer.
2. Normally the charge transfer transition occurs in which the metal is .... and ligand is ....
3. The spectra of condensed ring systems are useful as Aldehydes absorb at .... nm.
4. Sometimes, the structure of a compound changes with the change in ....
5. If the steric hindrance to coplanarity about a single bond is more, then there is a marked .... in intensity.
6. In AAS, high concentrations of gaseous atoms cause .... of absorption lines.
7. The most widely used fuel is ....
8. In AAS, the relation between .... and .... is nearly linear.
9. AAS technique is .... sensitive than flame emission.
10. Both sensitivity and detection limit very widely with .... and ....

ANSWERS

1. longer, greater **2.** reduced, oxidized **3.** finger print **4.** solvent

5. decrease **6.** broadening **7.** acetylene

8. absorbance, concentration **9.** more

10. flame temperature, spectral band width

TRUE OR FALSE

1. Butadiene absorbs at 217 nm 21000.
2. The wavelength of UV light is shorter than IR radiation.
3. Auxochromic groups do not show characteristic absorption above 200 nm.
4. The $n \rightarrow \pi^*$ transition for carbonyl compounds experiences bathochromic shift when polarity of the solvent is increased.
5. The $n \rightarrow \sigma^*$ transitions are very sensitive to H-bonding.

6. In AAS, the sample container is a flame.
7. Lower excitation temperatures are preferred for alkali metals.
8. On account of their low ionization potential, Na, K, Cs estimated by flame photometry.
9. Radiation from the hollow cathode should be continuous.
10. In case of non-flame atomizers, an electrical heating device is now used.

ANSWERS

1. True
2. True
3. True
4. False
5. True
6. True
7. True
8. True
9. False
10. True

❀ ❀ 24 ❀ ❀

APPENDIX

Table 1: IONIZATION POTENTIALS OF THE ELEMENTS (in electrovolts)†

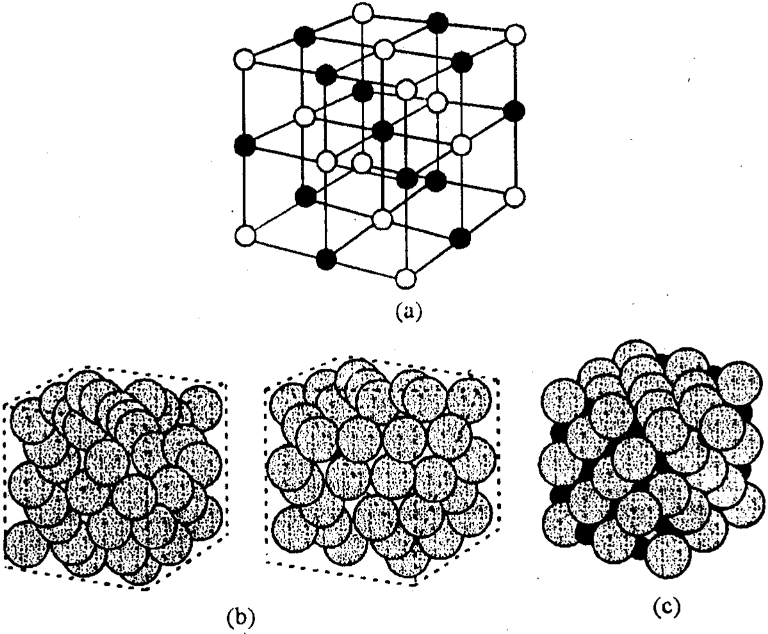
Z	Element	I	II	III	IV	V	VI	VII	VIII
1	H	13.598							
2	He	24.587	54.416						
3	Li	5.392	75.638	122.451					
4	Be	9.322	18.211	153.893	217.713				
5	B	8.298	25.154	37.930	259.368	340.217			
6	C	11.260	24.383	47.887	64.492	392.077	489.981		
7	N	14.534	29.601	47.448	77.472	97.888	552.057	667.029	
8	0	13.618	35.116	54.934	77.412	113.896	138.116	739.315	871.387
9	F	17.422	34.970	62.707	87.138	114.240	157.161	185.182	953.886
10	Ne	21.564	40.962	63.45	97.11	126.21	157.93	207.27	239.09
11	Na	5.139	47.286	71.64	98.91	138.39	172.15	208.47	264.18
12	Mg	7.646	15.035	80.143	109.24	141.26	186.50	224.94	265.90
13	Al	5.986	18.828	28.447	119.99	153.71	190.47	241.43	284.59
14	Si	8.151	16.345	33.492	45.141	166.77	205.05	246.52	303.17
15	P	10.486	19.725	30.18	51.37	65.023	220.43	263.22	309.41
16	S	10.360	23.33	34.83	47.30	72.68	88.049	280.93	328.23
17	Cl	12.967	23.81	39.61	53.46	67.8	97.03	114.193	348.28
18	Ar	15.759	27.629	40.74	59.81	75.02	91.007	124.319	143.456
19	K	4.341	31.625	45.72	60.91	82.66	100.0	117.56	154.86
20	Ca	6.113	11.871	50.908	67.10	84.41	108.78	127.7	147.24
21	Sc	6.54	12.80	24.76	73.47	91.66	111.1	138.0	158.7
22	Ti	6.82	13.58	27.491	43.266	99.22	119.36	140.8	168.5
23	V	6.74	14.65	29.310	46.707	65.23	128.12	150.17	173.7
24	Cr	6.766	16.50	30.96	49.1	69.3	90.56	161.1	184.7
25	Mn	7.435	15.640	33.667	51.2	72.4	95	119.27	196.46

Z	Element	I	II	III	IV	V	VI	VII	VIII
26	Fe	7.870	16.18	30.651	54.8	75.0	99	125	151.06
27	Co	7.86	17.06	33.50	51.3	79.5	102	129	157
28	Ni	7.635	18.168	35.17	54.9	75.5	108	133	162
29	Cu	7.726	20.292	36.83	55.2	79.9	103	139	166
30	Zn	9.394	17.964	39.722	59.4	82.6	108	134	174
31	Ga	5.999	20.51	30.71	64				
32	Ge	7.899	15.934	34.22	45.71	93.5			
33	As	9.81	18.633	28.351	50.13	62.63	127.5		
34	Se	9.752	21.19	30.820	42.944	68.3	81.70	155.4	
35	Br	11.814	21.8	36	47.3	59.7	88.6	103.0	192.8
36	Kr	13.999	24.359	36.95	52.5	64.7	78.5	111.0	126
37	Rb	4.177	27.28	40	52.6	71.0	84.4	99.2	136
38	Sr	5.695	11.030	43.6	57	71.6	90.8	106	122.3
39	Y	6.38	12.24	20.52	61.8	77.0	93.0	116	129
40	Zr	6.84	13.13	22.99	34.34	81.5			
41	Nb	6.88	14.32	25.04	38.3	50.55	102.6	125	
42	Mo	7.099	16.15	27.16	46.4	61.2	68	126.8	153
43	Tc	7.28	15.26	29.54					
44	Ru	7.37	16.76	28.47					
45	Rh	7.46	18.08	31.06					
46	Pd	8.34	19.43	32.93					
47	Ag	7.576	21.49	34.83					
48	Cd	8.993	16.908	37.48					
49	In	5.786	18.869	28.03	54				
50	Sn	7.344	14.632	30.502	40.734	72.28			
51	Sb	8.641	16.53	25.3	44.2	56	108		
52	Te	9.009	18.6	27.96	37.41	58.75	70.7	137	
53	I	10.451	19.131	33					

Z	Element	I	II	III	IV	V	VI	VII	VIII
54	Xe	12.130	21.21	32.1					
55	Cs	3.894	25.1						
56	Ba	5.212	10.004						
57	La	5.577	11.06	19.175					
58	Ce	5.47	10.85	20.20	36.72				
59	Pr	5.42	10.55	21.62	38.95	57.45			
60	Nd	5.49	10.72						
61	Pm	5.55	10.90						
62	Sm	5.63	11.07						
63	Eu	5.67	11.25						
64	Gd	6.14	12.1						
65	Tb	5.85	11.52						
66	Dy	5.93	11.67						
67	Ho	6.02	11.80						
68	Er	6.10	11.93						
69	Tm	6.18	12.05	23.71					
70	Yb	6.254	12.17	25.2					
71	Lu	5.426	13.9						
72	Hf	7.0	14.9	23.3	33.3				
73	Ta	7.89							
74	W	7.98							
75	Re	7.88							
76	Os	8.7							
77	Ir	9.1							
78	Pt	9.0	18.563						
79	Au	9.225	20.5						
80	Hg	10.437	18.756	34.2					
81	Tl	6.108	20.428	29.83					

Z	Element	I	II	III	IV	V	VI	VII	VIII
82	Pb	7.416	15.032	31.937	42.32	68.8	88.3		
83	Bi	7.289	16.69	25.56	45.3	56.0			
84	Po	8.48							
85	At								
86	Rn	10.748							
87	Fr								
88	Ra	5.279	10.147						
89	Ac	6.9	12.1						
90	Th		11.5	20.0	28.8				
91	Pa								
92	U								
93	Np								
94	Pu	5.8							
95	Am	6.0							

† C.E. Moore, "Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra, "NSRDS-NBS 34, National Bureau of Standards, Washington, D.C, 1970.



(a)

(b)

(c)

Fig. 1: Conventional NaCl structure (a), cubic close packing of spheres (b), and anoth representation of the NaCl structure (c). [From W. Barlow, Z. Krist, 29, 433 (1898)]

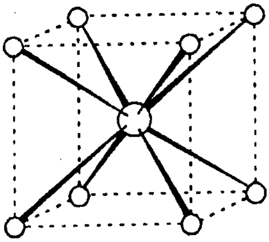


Fig. 2: The CsCl structure.

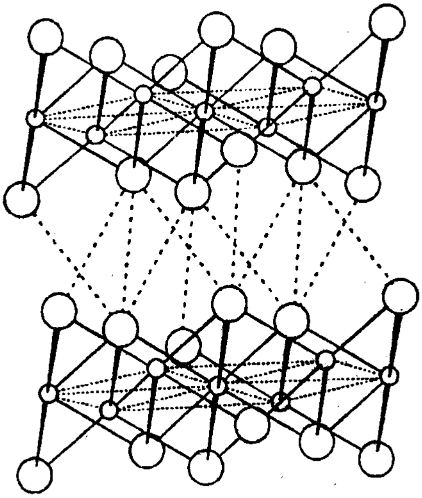
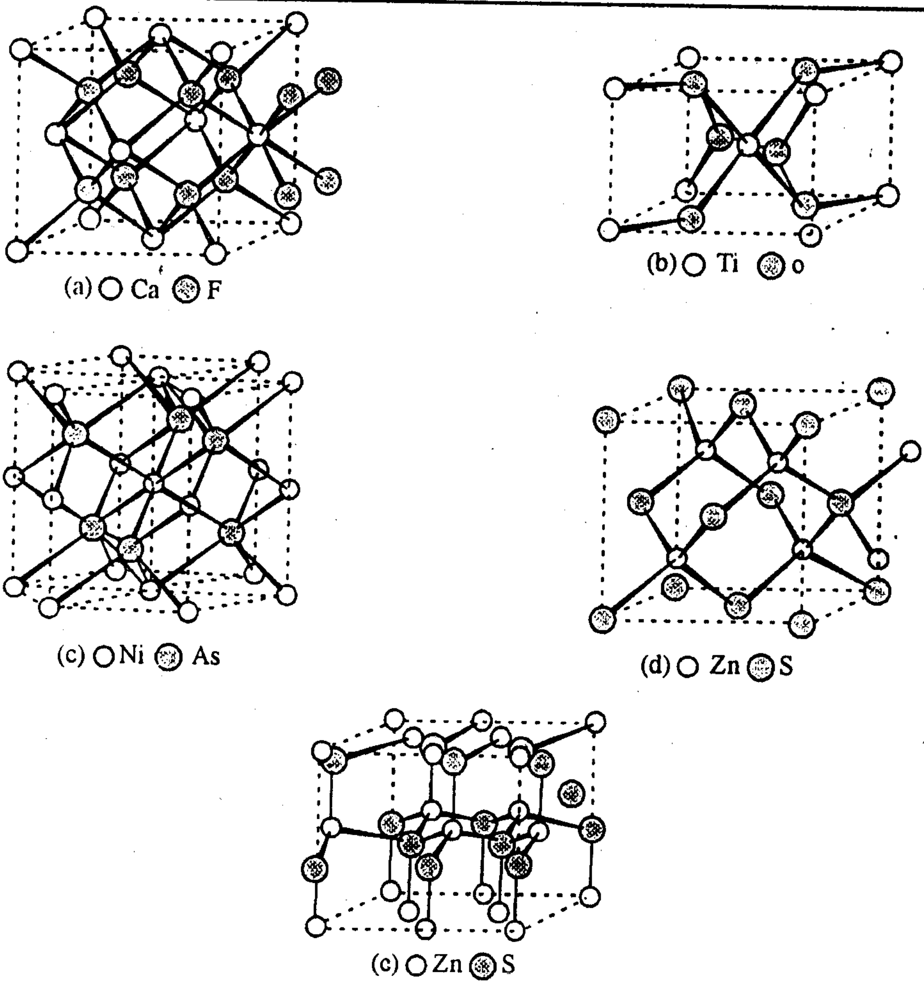


Fig. 3: A portion of the CdI_2 structure. Small spheres represent metal cations.



(a) ○ Ca ● F

(b) ○ Ti ● o

(c) ○ Ni ● As

(d) ○ Zn ● S

(e) ○ Zn ● S

Fig. 4: Structures of (a) fluorite (CaF_2), (b) rutile (TiO_2), (c) nickel arsenide (NiAs), (d) zinc blende (ZnS), and (e) wurtzite (ZnS)

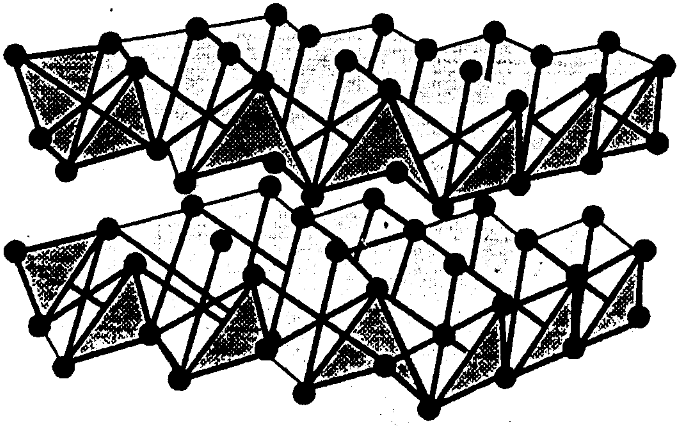


Fig. 5: Structure of tin (IV) sulphide

PAINTS

Products of surface-coating industries are essential for the preservation of all types of architectural structures, including factories, from ordinary attacks of weather. The surface-coating industry is indeed an ancient one. In fact, Noah was told to use pitch within and without the Ark. Surface coatings have been divided into paints (relatively opaque solid coatings applied as thin layers), varnishes (clear coatings), enamels (pigmented varnishes), lacquers (films formed by evaporation), printing inks, polishes etc.

Liquid paint is a dispersion of a finely divided pigment in a liquid composed of a resin or binder and a volatile solvent. The pigment, although usually an inorganic substance, may also be a pure, insoluble organic dye known as a toner, or an organic dye precipitated on an inorganic carrier i.e., aluminum hydroxide, barium sulphate or clay. Pigments should be nontoxic, or at least of very low toxicity, to both painter and the inhabitants. Pigments must get wet by the film-forming constituents and be of low cost.

Drying oils or synthetic resins are commonly used in paints. Styrene-butadiene rubber (SBR) copolymer is used as film-former in latex paint, Polyvinyl acetate (PVA), and acrylics are largely used as film-formers.

Proper paint formulation is specific for particular application. These requirements are hiding power, colour, weather resistance, washability, gloss, metal anticorrosive properties, consistency etc.

Polyvinyl chloride (PVC) is also now commonly used in paints as indicated in the following tabulation with percentage of PVC.

Flat Paints	50-75%	Exterior house paints	28-36%
Semi Gloss Paints	35-45%	Metal primers	25-40%
Gloss Paints	25-35%	Wood primers	35-40%

The various operations needed to mix paints are wholly physical. The ingredients such as resins, oils, pigments and thinners are thoroughly mixed in grinding mills. Centrifuges, screens or pressure filters are used to remove nondispersed pigments. The paint is then poured into cans or drums, labeled, packed and moved to storage.

LITHOPHONE:

Lithophone is a mixed Zinc Sulphate-Barium Sulphate pigment wh contains about 30% Zinc Sulphide. Lithophone is a brilliantly white, extre fine, cheap, white pigment. It is particularly used for interior coatings.

Lithophone is prepared by reducing barite ore ($BaSO_4$) with carbon and leaching the resulting mass.

$$BaSO_4 + 4C \longrightarrow BaS + 4CO$$

Zinc Sulphate is prepared by treating zinc scrap or zinc ore with sulphuric acid.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Zinc Sulphate solution is mixed with Barium Sulphide to get a heavy precipitate of Zinc Sulphide (30%) and Barium Sulphate (70%).

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

The precipitate is filtered, dried, crushed, heated to high temperature and quenched in cold water.

Lithophone is used in water-based paints because of their excellent alkali resistance. It is also used as a whitener and reinforcing agent for rubber and a filler and whitener for paper.