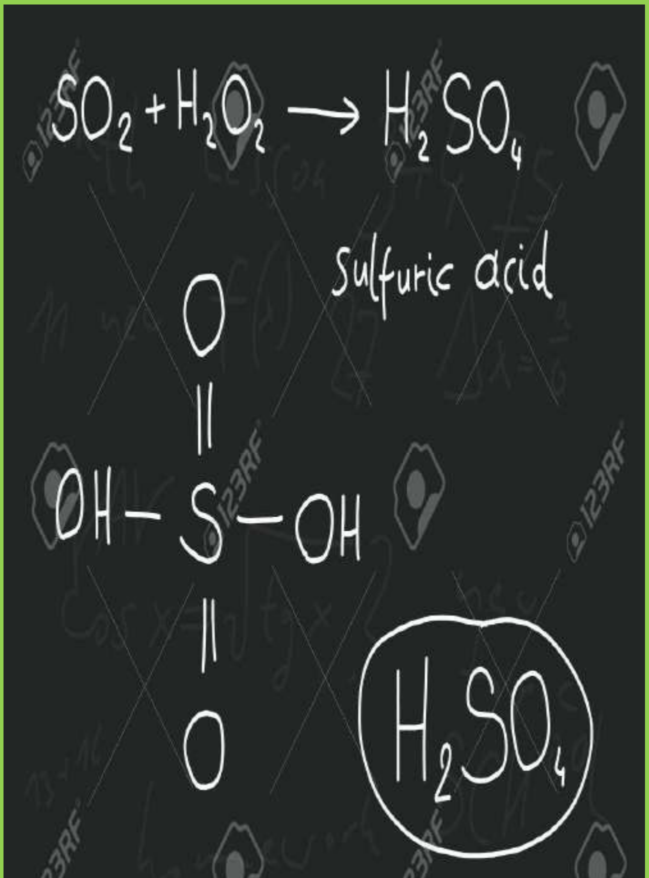
BSCCH- 101

B. Sc. I YEAR

INORGANIC CHEMISTRY-I



SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

BSCCH-101

INORGANIC CHEMISTRY-I

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. mail info@uou.ac.in
htpp://uou.ac.in

Board of Studies

Programme Coordinators

Dr. Charu C. Pant Department of Chemistry School of Sciences, Uttarakhand Open University Haldwani, Nainital	**Dr. Shalini Singh** Department of Chemistry School of Sciences, Uttarakhand Open University Haldwani, Nainital

Unit Written By	Unit No.
1. **Dr. K. S. Dhami (Ret. Proff.)** Department of Chemistry D.S.B. Campus, Kumaun University Nainital	**01, 02, 03, 04, 05, 06, 07, 08, 09, 10 &11**
2. **Dr. Geeta Tiwari** Department of Chemistry D.S.B. Campus, Kumaun University Nainital	**12, 13 & 14**

Course Editor

Dr. A. B. Melkani
Professor & Head
Department of Chemistry
D.S.B. Campus Kumaun University, Nainital

Title	**:**	**Inorganic Chemistry I**
ISBN No.	**:**	**978-93-85740-53-4**
Copyright	**:**	**Uttarakhand Open University**
Edition	**:**	**2017**

Published by : Uttarakhand Open University, Haldwani, Nainital- 263139

UNIT 1: ATOMIC STRUCTURES

CONTENTS:

1.1. OBJECTIVES

The objective of the preparation of the text of this unit is to acquaint the readers with the fascinating and exciting realm of the atoms. Accordingly, an attempt has been made to through light on the arrangement of the internal constituents of the atoms (the subatomic particles), their peculiarities and characteristics along with their behaviour towards their neighbours, i.e. the arrangement of protons and neutrons in the nucleus and the rules governing the arrangement of electrons in the extra nuclear region of an atom and filling of orbitals belonging to higher energy shells prior to the entry of electrons in the orbitals of lower energy shells. At the same time, the problem “what makes the electron cloud to acquire different shapes in three dimensional space around the nucleus?” has been entertained and various other interesting problems have also been taken into account.

1.2. INTRODUCTION

In the beginning of nineteenth century, John Dalton (1766-1844) put forward his atomic theory, he regarded atom as hard and smallest indivisible particle of matter that takes part in chemical reactions; the atoms of one particular element are all identical in mass and atoms of defferent elements differ in mass and other properties.

Later on, various investigators around the end of nineteenth century and beginning of twentieth centurydid several experiments and revealed the presence of much smaller negatively charged particles, named electrons by J.J. Thomson (1897) and positively charged particles, named protons by Rutherford (1911) within an atom. These tiny particles were called subatomic particles. It was also established by Rutherford that the whole positive charge and most of the mass of an atom lies at nucleus. The positive charge on the nucleus was attributed to the presence of protons called the atomic number by Moseley (1912). The electrons were said to be arranged around the nucleus in the extra nuclear region in certain well defined orbits called energy shells and were said to be in constant motion (N. Bohr, 1913). Chadwick’s experiments (1932) also revealed the existence of yet another subatomic particle in the nucleus which did not have any charge and named as neutrons. Further investigations established that there were also present some other subatomic particles in the nucleus in addition to electrons, protons and neutrons. These particles are positrons, neutrinos, antineutrinos, pions (π-mesons) etc. The pions (Yukawa, 1935) are said to be continuously consumed and released by proton-neutron exchange processes.

Thus, it is concluded that the atom no longer is an ultimate and indivisible particle of matter and the outer or valence shell electrons are responsible for chemical activity of the elements.

1.3. DE-BROGLIE’S MATTER WAVES: DUAL NATURE OF MATTER

This is based on wave mechanical concept of an electron in an atom. Albert Einstein proposed dual character of electromagnetic radiation in 1905, *viz*. wave character based on Maxwell’s concept evidenced by diffraction, interference, polarisation kinds of phenomena and particle character based on Planck’s quantum theory witnessed by quantization of energy and hence photoelectric effect, i.e. the ejection of photoelectrons from metal surface on striking electromagnetic radiation.

On the basis of above analogy, French Physicist Louis de Broglie (1924) postulated that not only light but all material objects (both micro and macroscopic) in motion such as electrons, protons, atoms, molecules etc. possess both, wave and the particle propertiesand thus have dual character, i.e. the wave character and particle (corpuscular) character. He called the waves associated with material particles as matter waves which are now named de Broglie’s wave. These waves differ from electromagnetic or light waves in a sensethat these are unable to travel through empty space and their speed is different form light waves.

de Broglie’s relation

de Broglie deduced a fundamental relation between the wave length of moving particle and its momentum by making use of Einstein’s mass energy relationship and Planck’s quantum theory. The material particle as a wave satisfies the Planck’s relation for a photon, i.e.

$$E = h\nu \qquad \text{……….. (1.1)}$$

where h is Planck’s constant and ν is the frequency of the wave. The frequency for light wave, $\nu = \frac{c}{\lambda}$ and for particle wave, $\nu = \frac{v}{\lambda}$ (c = speed of light wave and v = speed of particle wave). At the same time, Einstein’s mass energy relationship is applicable to it, i.e.

$$E = mc^2 \text{ (for a photon)} \qquad \text{……….. (1.2)}$$

or $$E = mv^2 \text{ (for a particle where } v \neq c\text{)} \qquad \text{……….. (1.3)}$$

where m is the mass and v the speed/velocity of the particle. From the equations 1.1 and 1.3, we have

$$h\nu = mv^2 \qquad \text{……… (1.4)}$$

or $$\frac{h\mathrm{v}}{\lambda} = mv^2$$

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

or $$\lambda = \frac{h}{p} \text{ or } \left(\frac{h}{mv}\right) \qquad \text{…… (1.5)}$$

(momentum p = mv, mass x velocity)

Here, λ corresponds to the wave character of matter and p its particle character. This is Known as de Broglie's relation. From this relationship, it is concluded that "the momentum of a moving particle is inversely proportional to the wavelength of the wave associated with it".

It is important to note here from above discussion that de Broglie's relation is applicable to material particles of all sizes and dimensions but the wave character is significant only for micro objects like electrons and is negligible for macro objects hence cannot be measured properly. This infers that de Broglies's relation is more useful for smaller particles.

de Broglie's relation has been applied to a moving electron around a nucleus in a circular path in an atom to justify Bohr's postulate which states that elections can move only in those orbits for which the angular momentum is equal to an integral multiple of $\frac{h}{2\pi}$, i.e.

$$mvr = n\frac{h}{2\pi} \qquad \text{……….(1.6)}$$

This moving electron is considered as a standing wave extended around the nucleus in circular path and not as a mass particle. If the circumference of the orbit is an integral multiple of the wave length, λ,

i.e. $$2\pi\ r = n\ \lambda \qquad \text{………(1.7)}$$

where r is the radius of the orbit and n is the whole number, the wave remains continually in phase, i.e. is a merging wave (Fig. 1.1 a)

From equation 1.5, we have

$$\lambda = \frac{h}{p} = \frac{h}{m\mathrm{v}}$$

Putting the value of λ in equation 1.7, we get

$2\pi r = n \frac{h}{m\mathrm{v}}$ Fig 1.1 (a) merging waves, (b) Crossing waves

or $m\mathrm{v}r = n\frac{h}{2\pi}$ (on rearranging)

………(1.8)

which is the same as equation 1.6, i.e. Bohr's postulate mentioned above. If the circumference of the orbit is bigger or smaller than the value given above, the wave is out of phase, i.e. a crossing wave (Fig. 1.1 b)

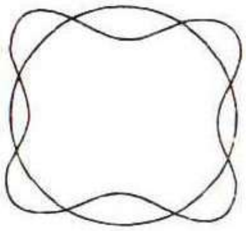


Fig. 1.1 a: in phase

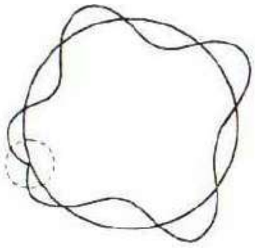


Fig. 1.1 b: out of phase

de Broglie's concept has been experimentally verified by Davisson and Germer, G.P. Thomson and later by Stern independently.

1.4. HEISENBERG'S UNCERTAINTY PRINCIPLE

According to classical mechanics, a moving electron behaves as a particle whose position and momentum could be determined with accuracy. But according to de Broglie, a moving electron has wave as well as particle character whose precise position cannot be located because a wave is not located at a particular point rather, it extends in space. To describe the character of a subatomic particle that behaves like a wave, Werner Heisenberg in 1927 formulated a principle known as Heisenberg's Uncertainty Principle. According to the principle "**it is impossible to determine simultaneously both the position as well as the momentum (or velocity) of a moving particle at the same time with certainty (or accurately)"**

He also proposed a mathematical relationship for the uncertainty principle by relating the uncertainty in position with the uncertainty in momentum which is given below:

$$\Delta x \text{x} \Delta p \geq \frac{h}{4\pi} \qquad \text{...............(1.9)}$$

or Δx x m (Δv) $\geq \frac{h}{4\pi}$ (since $p = m\ v$ and Δp = mxΔv) ……….(1.10)

where $\Delta x$is the uncertainty or error in the position of the particle, Δp and Δv are the uncertainties in it's momentum and velocity and h is Planck's constant.

This equation states that the product of Δx and Δp can either be greater than or equal to (≥) but never smaller than $\frac{h}{4\pi}$, a constant. If Δx is measured more precisely (i.e. Δx is small) then there is large uncertainty or error in the measurement of momentum (Δp is large) and vice versa.

1.5. CONCEPT OF PROBABILITY AND SCHRODINGER'S WAVE EQUATION

From the uncertainty principle, it has been concluded that the exact position and exact momentum or velocity (related to kinetic energy) of a micro particle can be replaced by the concept of probability. For an electron in an atom we can say that there is probability of finding it in a particular region of space and in a particular direction (except for s-electron).

To describe the wave motion of electron in hydrogen atom, Schrodinger in 1927 combined the de Broglie's relation for the wavelength of a particle wave with the well known differential equation for standing waves and proposed a mathematical form called Schrodinger's wave equation. This equation is now widely used to explain the behaviour of atomic and molecular systems. The equation for a single particle in three dimensional space, i.e. along x, y and z directions is given as follows:

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{4\pi^2}{\lambda^2}\psi = o \qquad \ldots\ldots\ldots(1.11)$$

In place of three partial differentials, symbol '∇' (del) can be used, hence the above equation becomes

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \qquad \ldots\ldots\ldots(1.12)$$

where ∇^2 (del square) is equal to $\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}$ and is known as laplacian operator.

Putting the value of λ from de Broglie's relation (i.e. $\lambda = \frac{h}{mv}$), the above equation becomes

$$\nabla^2\psi + \frac{4\pi^2 mv^2}{h^2} = 0 \qquad \ldots\ldots\ldots(1.13)$$

Extracting the value of v from kinetic energy, potential energy and total energy terms i.e. E = K.E+V where K.E. = $\frac{1}{2}mv^2$ and putting in the above equation, we get the final form of the equation as:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots\ldots\ldots(1.14)$$

This equation is known as Schrodinger's wave equation.

1.5.1. Significance of ψ and ψ^2

An electron, from the probability concept, is considered as a three dimensional wave system extended around the nucleus and is represented by the symbol ψ which denotes the wave function of the electron; ψ itself has no physical significance and simply represents the amplitude of electron wave. Schrodinger's equation has several solutions for ψ, both real and imaginary. Some of the real values of ψ are appreciable while others are too small and hence neglected. If the value of ψ obtained as above is continuous, finite, single valued and electron probability in space related to ψ is equal to 1, then ψ is known as eigen function (meaning characteristic), ψ^2 gives the probability of finding an electron of a given energy, E from place to place in a given region around the nucleus. Since, ψ often contains the imaginary quantity, but the probability of an electron in a given volume must be a real quantity, therefore the product $\psi \psi^*$ (ψ star) is used rather than ψ^2 where ψ^* is complex conjugate of ψ. This product will always be real whereas ψ^2 may be real or imaginary. If ψ is real quantity, then ψ and ψ^* both are same and hence ψ^2 is also a real quantity and corresponds to probability density per unit volume.

1.5.2. Radial and angular wave functions:

The radial wave function, R (r)

The value of ψ appearing in Schrodinger's wave equation in polar coordinates, $(r,\theta,\emptyset)$, can be determined only when $\psi$is written in the following form (mention of equation is not required) :

$$\Psi (r,\theta, \phi) = R (r)\, \Theta(\theta)\, \Phi(\phi) \qquad \text{…………..(1.15)}$$

Where $\psi (r,\theta, \phi)$, is known as total wave function, R (r) is the radial wave function and other two are angular wave functions. The radial wave function, R (r) is dependent on r only where r is the distance of electron from the nucleus and is independent of θ and ϕ. Therefore, R (r) deals with the distribution of the electron charge density as a function of distance (r) from the nucleus. R (r) depends on two quantum numbers n and l and can be denoted as $R_{n,l}$ (r) or simply $R_{n,l}$. Both $R_{n,l}$ and $R^2_{n,l}$ are significant only for drawing the probability curves for various orbitals. The radial wave functions for all s-orbitals are spherically symmetrical.

The angular wave function, $\psi (\theta, \phi)$.

The angular wave functions depend on the angles θ and ϕ and are independent of the distance (r). As given above in equation 1.15, these are represented as $\Theta (\theta)$ and $\mathit{\Theta} (\phi)$. Their values depend on the quantum numbers l and m and can be written as $\Theta_{l,m}$ and $\mathit{\Theta}_{m,}$ respectively. Therefore, the equation 1.15 can also be written as

$$\Psi_{n,l,m} = R_{n,l}\, \Theta_{l,m} \Phi_{m} \qquad \text{………….(1.16)}$$

This equation shows that the total wave function besides depending on r, θ, ϕ, also depends on the quantum numbers *viz.*, n, l and m. Each permitted combination of n, l and m gives a distinct wave function and hence a distinct orbital.

The angular wave functions together are used to predict the shapes of the orbitals.

1.5.3. Probability distribution curves:

Before discussing the distribution curves, let us know about the electron probability function. The probability or the chance of finding an electron in three dimensional space round the nucleus is known as electron probability function, D. For an extremely small spherical shell of radius r and thickness dr round the nucleus, the value of D can be given by

$D = \psi^2 \text{ x volume of shell} = \psi^2 \text{ x } 4\pi r^2 \, dr$ ………… (1.17)

and the electron probability between r = o and r = r would be equal to

$\int_{r=0}^{r=r} \psi^2 . 4\pi r^2 \, dr. \ (\psi^2 = R^2(r) \quad \text{or} \quad R^2_{n,l})$

Radial probability distribution curves

The square of the radial wave function multiplied by a volume element, dv, i.e. $R^2(r)$ x dv measures the probability of locating an electron at a distance from the nucleus and within a small radial space. This is same as electron probability function given above in which ψ^2 can be replaced by $R^2_{n,l}$, meaning radial distribution. When R^2 (r). dv or $R^2_{n,l}$. $4\pi r^2$ dr where dv= $4\pi r^2$ dr, is plotted against r, the distance from nucleus, we get radial probability distribution curves. The peak of the curve gives the distance from the nucleus where the probability is maximum and at distances smaller or greater than this, value of probability is less but not zero. Thus, it is observed that electron charge density decreases but volume of shell increases with r. Various such curves are shown below:

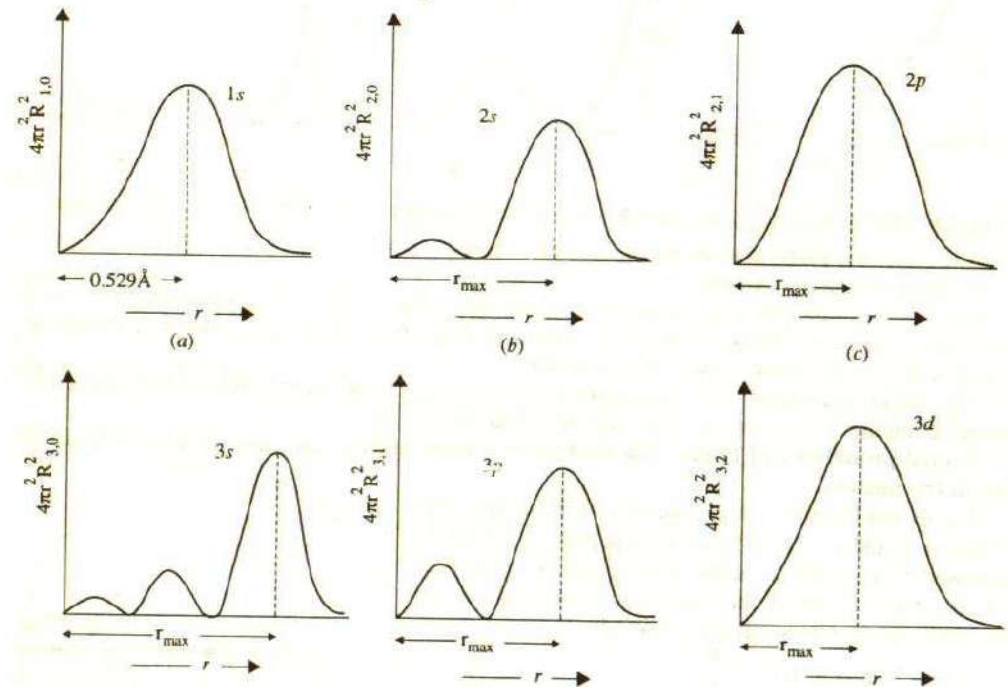


Fig. 1.2 Radial Probability distribution curves for 1s,2s,2p,3s,3p and 3d-orbitals. Simple sketches have been given in which the values of n and l have been shown and d_r has been omitted.

The important features of these curves are;

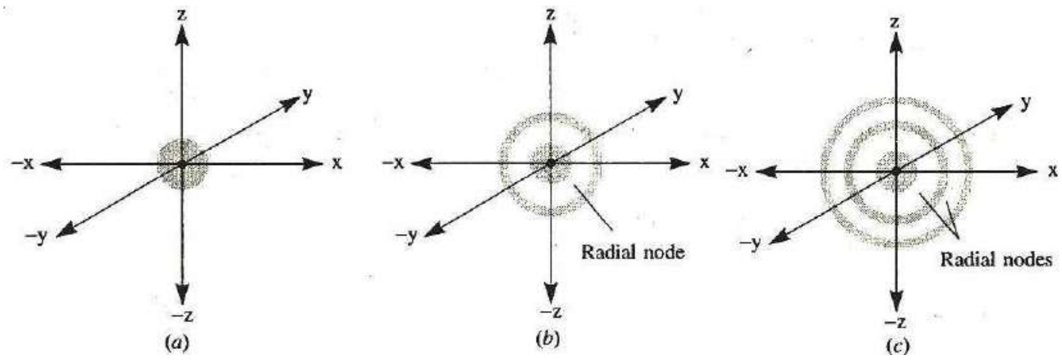
(i). Curves start from the origin and the areas covered by the envelopes of a particular curve for a subshell (orbital) go on increasing from left to right so that the area of the last envelope is maximum.

(ii). The number of minima where density of electronic charge is zero, appearing in a particular curve gives the number of radial nodes or nodal points for the orbital (subshell). The number of nodal points is equal to n-l-1. Thus for the electrons of 1s,2s,2p,3s,3p and 3d orbitals, the number of nodal points is 0,1,0,2,1 and 0, respectively. This is also evident from the curves of these orbitals. Evidently, 3s orbital (nodal points = 2) is bigger in size and more diffused than 1s (nodal point = 0) and 2s orbitals (nodal point = 1) both due to greater number of nodal points in it (see figure 1.2)

1.6. SHAPES OF ATOMIC ORBITALS AND ANGULAR PROBABILITY DISTRIBUTION CURVES

The shapes of atomic orbitals depend θ and ϕ i.e. the product [Θ (θ) x Φ (ϕ)] or $_{l,m}$ x Φ_m is related with the shapes of the orbitals. The values of $\Theta_{l,m}$ x Φ_m for s-orbital (l=0,m=0), p-orbital (l = 1, m = 0, ±1), and d-orbitals (l = 2, m = 0, ±1, ±2) can be obtained and correlated with the shapes of orbitals.

For s-orbitals (l = 0, m = 0), the angular wave function $\Theta_{o,o}$ x Φ_o is independent of the angles Θ and ϕ, i.e. there is no angular wave function and hence orbitals have only one orientation and are spherically symmetrical over all the directions, hence have spherical shape as well as are non-directional. Thus, s-orbitals are usually represented by circles. Greater the value of n and higher the number of nodal points for s-orbital, larger is the size of orbital. The electron density in s-orbitals could be shown by concentric shades as follows:



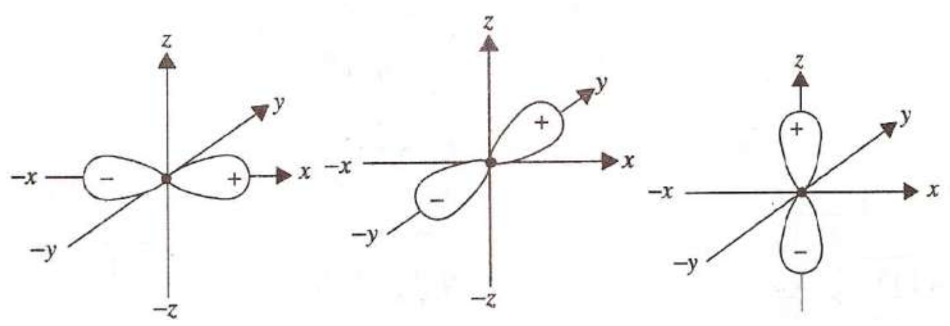
1s-orbital 2s-orbital 3s-orbital

(no nodal point) (1 nodal point) (2 nodal points)

Fig. 1.3 Electron charge density pictures for 1s, 2s and 3s-orbitals. Nucleus has been shown by thick dot.

For **p orbitals** (l = 1, m = 0, ±1), there are three values of m and therefore, there are three orientations of lobes of orbitals along cartesian coordinates *viz.* p_x, p_y and p_z. The subscripts x, y and z indicate the axes along which orbitals are oriented. The three p-orbitals are similar in size, shape and energy but differ in orientation only. The angular wave function for these orientations is the product$\Theta_{,m}$ x $\Phi_{m.}$ For l=1, m =0 orientation, the angular wave function $\Theta_{1,0}$ Φ_0 is a real quantity and corresponds to p_z orbital which is dumb-bell shaped curve along z-axis in three dimensional space (**Fig. 1.4 c**).

For l = 1,m = +1 and l =1, m= -1 orientations, angular wave functions are $\theta_{1,+1}$ x Φ_{+1} and $\theta_{1,-1}$ x Φ_{-1} which have imaginary quantities and are avoided. The real values are obtained by the normalised linear combinations (addition and subtraction) of angular angular wave functions. Thus, addition process, i.e. $\theta_{1,+1}$ x Φ_{+1} + $\theta_{1,-1}$ x Φ_{-1} gives normalised wave function corresponding to p_x orbital. In three dimensional space, this gives dumb-bell shaped curve along x- axis (Fig.1.4a) The subtraction process, i.e. $\theta_{1,+1}$ x Φ_{+1} - $\theta_{1,-1}$ x Φ_{-1} gives normalised wave function corresponding to p_y orbital which is again dumb-bell shaped curve in three – dimensional space along y-axis (**Fig. 1.4b**).



P_x orbital (a)

P_y orbital (b)

p_z orbital (c)

Fig.1.4 The orientation of p- orbitals along x, y and z- axis.

The (+) and (–) signs are algebraic signs of angular wave function and not the charge. The angular part of the wave function ψ (θ, Φ) has (+)sign on one lobe and (–)sign on the opposite lobe although ψ2 (θ, Φ) will be positive on both the lobes. Thus, for p-orbitals, the important points to be noted are:

(i) Since x, y and z axes are perpendicular to each other, the three p-orbitals are also perpendicular to each other.

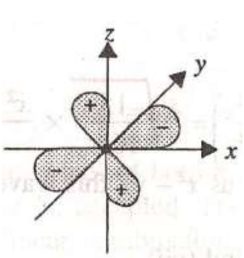
(ii) Each of the three p-orbitals has two lobes on each side of the nucleus which is at the origin of the axes, hence the probability of finding the electron (s) in both lobes is equal. These lobes are separated by nodal planes passing through the nucleus. The electron density on the nodal plane is zero.

(iii) Greater the value of n (principal quantum number or the shell number), larger is the size of p orbital i.e. 3p orbital is larger in size than 2p orbital though the shapes of both the orbitals are the same.

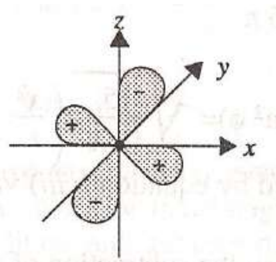
(iv) The energy of the three p-orbitals with the same value of n is same i.e. all the three p-orbitals are degenerate.

For **d-orbitals** (l = 2, m = 0, ±1, ±2), five orientations (or orbitals) are there corresponding to five values of m for l = 2. Depending on the permitted combinations of l and m, values for five d-orbitals, angular wave functions corresponding to different d-orbitals are as follows:

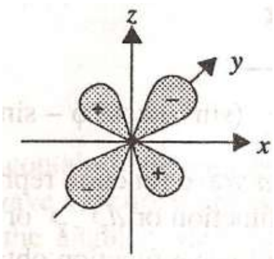
For l = 2 and m=0, the angular wave function $\Theta_{2,0} \text{ x } \Phi_0$ has a real value and corresponds to $d_z{}^2$-orbital. For l =2 and m = ±1, we have two angular wave functions, $\Theta_{2,+1} \text{ x } \Phi_{+1}$ and $\Theta_{2,-1} \text{ x } \Phi_{-1}$. The values of these angular wave functions contain imaginary quantity and hence, these values are not accepted. The real and acceptable values are obtained from these by normalised linear combinations (addition and subtraction) of above functions. The addition process of above angular wave functions, i.e. $\Theta_{2,+1} \text{ x } \Phi_{+1} + \Theta_{2,-1} \text{ x } \Phi_{-1}$ gives the wave function for d_{zx} (or d_{xz}) orbital and subtraction process, i.e. $\Theta_{2,+1} \text{ x } \Phi_{+1} - \Theta_{2,-1} \text{ x } \Phi_{-1}$, gives the wave function for dyz, orbital, for l = 2 and m = ±2, we have two wave functions *viz.* $\Theta_{2,+2} \text{ x } \Phi_{+2}$ and $\Theta_{2,-2} \text{ x } \Phi_{-2}$. Again the values of these wave functions contain imaginary quantity and hence are not accepted. Real and acceptable values are obtained by the nornalised linear comlimation of the two angular wave functions. The addition process of above angular wave functions, i.e., $\Theta_{2,+2} \text{ x } \Phi_{+2} + \Theta_{2,-2} \text{ x } \Phi_{-2}$, gives the wave function for d_{x2-y2} orbital and subtraction process i.e., $\Theta_{2,+2} \text{ x } \Phi_{+2} - \Theta_{2,-2} \text{ x } \Phi_{-2}$, gives the wave subtraction for d_{xy} orbital. When these five angular wave functions for different orbitals obtained above are plotted in three dimensional space, we get the solid curves which give the orientations along the axes or in between the axes as shown below:



d_{xy} orbital



d_{yz} (or d_{xz}) orbital



d_{zx}orbital

d_{x2-y2} orbital d_{z2} orbital

Fig. 1.5 Angular dependence and shapes of d-orbitals.

The probability density is the square of the wave function and is positive everywhere. The lobes on the positive or negative side of both the axes are assigned (+) sign and those on positives side of one axis and negative side of the other or vice versa are assigned (–)sign.

The characteristics of the d-orbitals may be summarised as follows:

(i) d_{xy}, d_{yz} and d_{zx} (or d_{xz}) as well as d_{x2-y2} orbitals are double dumb-bell shaped and contain four lobes. The lobes of the first three orbitals are concentrated between xy, yz and zx planes, respectively and lie between their coordinate axes. The lobes of d_{x2-y2} orbital are concentrated along x and y axes. d_{z2} orbital has a dumb-bell shape with two lobes along z-axis with (+) sign and a concentric collar or ring around the nucleus in xy plane with (–)sign.

(ii) The d-orbitals belonging to same energy shell are degenerate, i.e. have the same energy in a free atom.

(iii)The d-orbitals belonging to all main energy shells have similar shape but their size goes on increasing as the value of n and number of nodal points increase. For example, the size of 5d-orbital (number of nodal points = 5 – 2–1=2) is larger than that of 4d-orbital (number of nodal points = 4 – 2 – 1=1).

N.B. The shapes of f, g etc. orbitals are beyond the scope of the text.

1.7. QUANTUM NUMBERS

These are the integral numbers and most of them (i.e. first three) have been derived from the mathematical solution of Schrodinger’s wave equation for ψ. These numbers serve as the address of the electrons in an atom and hence are also known as **identification numbers.** These describe the energy of an electron in a shell, radius of that shell (i.e. distance of electron from the nucleus), shape and orientation of the electron cloud (or orbital) and the direction of the spinning of the electron on its own axis.

There are four quantum numbers *viz.* principal quantum number (n), azimuthal or subsidiary quantum number (l), magnetic quantum number (m) and spin quantum number (s).

(i) Principal or Radial quantum number

This quantum number represents the number of shell or main energy level to which the electron belongs round the nucleus. It is denoted by the letter n. It arises from the solution of radial part of ψ. This quantum number can have integral values 1,2, 3, 4………..etc. which are designated by the letters K,L,M,N……..etc. as follows (proposed by Bohr):

Value of n	**Designation**
1	K
2	L
3	M
4	N

It can be concluded that the principal quantum number (n) gives an idea of:

(a) The shell or main energy level which the electron belongs to.
(b) The distance (r) of the electron from the nucleus, i.e. the radius of the shell.
(c) The energy associated with the electron.
(d) The maximum number of electrons that may be accommodated in a given shell.

According to Bohr-Berry scheme, the maximum number of electrons in nth shell = $2n^2$. Thus the first shell (n = 1) can accommodate ($2 \times 1^2 = 2$) two elections, second, third and fourth shells with n = 2, 3 and 4 can accommodate eight ($2x2^2 = 8$), eighteen ($2x3^2 = 18$) and thirty-two ($2x4^2 = 32$) electrons, respectively.

(ii) Azimuthal or Subsidiary quantum number (l)

This quantum number is also known as orbital angular momentum quantum number. It is denoted by the letter l and refers to the subshell which the electron belongsto. This quantum number describes the motion of the electron and tells us about the shape of the orbitals of a subshell. The values of l depend on the value of n (the principal quantum number) and may have all possible values from 0 to (n-1), i.e. l = 0,1,2,3………(n-1). Thus, for a given value of n, total number of l values is equal to n, *e.g.* when n = 4, l = 0,1,2,3 (total 4 values of l). For each value of l, separate notation is used which represents a particular subshell as shown below;

Azimuthal quantum number (l)	**0**	**1**	**2**	**3**	**4**	**……**
Notation for the subshell	**s**	**p**	**d**	**f**	**g**	**……**

These notations of subshells have been taken from the characteristics of the spectral lines in atomic spectra. Thus, s stands for sharp, p for principal, d for diffuse and f for fundamental.

The subshells belonging to various shells are given below:

N	**L**	**notation for the subshell**
1	0	1s
2	0 1	2s 2p
3	0 1 2	3s 3p 3d
4	0 1 2 3	4s 4p 4d 4f

The main points to be noted for azimuthal quantum number are;

(a) This gives an idea of the subshell which the electron belongs to.

(b) Total number of subshells in a given shell is equal to the numerical value of n (main shell).

(c) This quantum number corresponds to the orbital angular momentum of the electron.

(d) This gives an idea of the shape of the orbitals of the subshell.

(e) The maximum number of electrons that can be accommodated in a given subshell is equal to 2(2l+1). Thus s, p, d and f- subshells with l = 0, 1, 2 and 3 can have a maximum of 2, 6,10 and 14 electrons, respectively, i.e. s^2,p^6, d^{10} and f^{14}

(iii) Magnetic quantum number (m)

This quantum number determines the direction of angular momentum of the electrons thereby describing the orientation of orbitals of a subshell in space. The value of m depends on the value of l thus showing that each subshell consists of one or more regions in space with maximum probability of finding the electron (i.e. orbitals). The number of such orbitals (or regions) is equal to the number of ways the electrons can orient themselves in space. This number is equal to (2l + 1) and values of m are represented as (+) l to (–) l through 0. Thus, each value of m represents a particular orbital within a subshell and total number of m values gives total number of orbitals in that subshell. For example, for s-subshell, m =0 corresponding to l=0, i.e. m has only one value indicating that s-subshell has only one orbital or one possible orientation of electrons which is spherically symmetrical around the nucleus. When l=1, (i.e. p-subshell), m has three values v*iz.* +1, 0,-1 implying that p-subshell has three orbitals or orientations which are perpendicular to each other and point towards x, y, and z-axes. These are designated as p_x, p_y, and p_z. For l = 2 i.e. d-subshell, m=+2,+1,0,-1,-2,i.e. five values meaning thereby that this subshell has five orbitals or orientations *viz.*, d_{xy}, d_{yz}, d_{zx}, d_{x2-y2} and d_{z2}. On the same grounds it can be shown for f-subshell (l=3) that it has seven orbitals or orientations corresponding to seven values of m *viz.*, +3,+2, +1,0,-1, -2 and -3. For p, d, and f subshells (l=1, 2 and 3) various m values may be summarised as follows:

Subshell	**Value of l**	**Values of m**	**Total m values**
p - subshell	1	+1, 0, -1	3
d – subshell	2	+2,+1,0,-1,-2.	5

f – subshell	3	+3,+2,+1,0,-1, -2, -3	7

The main point to be noted for magnetic quantum number is that it determines the total number of orbitals present in any subshell belonging to preferred orientations of electrons in space.

(iv) Spin quantum number (s)

This quantum number arises from the direction of spinning of electron about its own axis. It is denoted by the letter s which can have only two values shown as (+)$\frac{1}{2}$ and (-)$\frac{1}{2}$ representing clockwise spin(α-spin) or anticlockwise spin (β-spin). These values i.e. (+)$\frac{1}{2}$ and (-)$\frac{1}{2}$ are also represented as ↑ (upward arrow) and ↓ (downward arrow). Being a charged particle, a spinning electron generates a so called spin magnetic moment which can be oriented either up or downward. The value of s for an electron in an orbital does not affect the energy, shape, size or orientation of an orbital but shows only how the electrons are arranged in that orbital.

1.8. PAULI'S EXCLUSION PRINCIPLE

This principle was proposed by Pauli in 1924 and as an important rule, governs the quantum numbers allowed for an electron in an atom and determines the electronic configuration of poly electron atoms. In a general form, this principal states that "In **an atom, any two electrons cannot have the same values of four quantum numbers**". Alternatively, this can be put in the form "**any two electrons in an atom cannot exist in the same quantum state".** Consequently, it can be said that any two electrons in an atom can have same values of any three quantum numbers but the fourth (may be n or l or m or s) will definitely have different values for them. This can be shown as follows;

	Values of quantum numbers			
	n	**l**	**m**	**s**
For any two electrons in an atom	same	same	same	different

or	same	same	different	same
or	same	different	same	same
or	different	same	same	same

Thus the values of all the four quantum numbers for any two electrons residing in the same orbital like s, p_x, p_y, p_z, d_{xy} etc. cannot be the same. For example, in case of 2 electrons in 1s-orbital (i.e. $1s^2$), the values of n, l and m are same for both the electrons but s has different values as shown below:

		n	**l**	**m**	**s**
For $1s^2$ electrons	1st electron	1	0	0	$+\frac{1}{2}$
	2nd electron	1	0	0	$-\frac{1}{2}$

The values of s may also be written in the reverse order but by convention the given order is preferred. The important conclusion drawn from this discussion is that "**an orbital can accommodate only two electrons with opposite spins**"

Application of Pauli's Exclusion Principle

This principle has been used to calculate the maximum number of electrons that can be accommodated in an orbital, a subshell and in a main shell. For example, for K-shell, n=1, l=0 and m=0 and s can have a value equal to either $(+)\frac{1}{2}$ or $(-)\frac{1}{2}$. These values of n, l, m and s give two sets of values of four quantum numbers as gives above. It is concluded that in K-shell,there shall be only one subshellwith one orbital i.e. the s-orbital is present which can contain only two electrons with s = $(+)\frac{1}{2}$ and $(-)\frac{1}{2}$.

For L-shell, n=2, l=0 and 1. The corresponding values of m are 0 (for l=0) and +1, 0, -1 (for l=1). For each value of m, s will have two values, $(+)\frac{1}{2}$ and $(-)\frac{1}{2}$. This leads to eight sets of quantum numbers belonging to eight different electrons. These are shown below:

$$\left.\begin{array}{l} n = 2,\ \ l = 0,\ \ m = 0,\ \ s = +\frac{1}{2} \\ n = 2,\ \ l = 0,\ \ m = 0,\ \ s = -\frac{1}{2} \end{array}\right\} \begin{array}{l} \text{These values correspond to two} \\ \text{elections in 2s – orbital.} \end{array}$$

$$\left.\begin{array}{l} n\ = 2,\ \ l = 1,\ \ m = +1,\ \ s = +\frac{1}{2} \\ n\ = 2,\ \ l = 1,\ \ m = +1,\ \ s = -\frac{1}{2} \end{array}\right\}$$ These values correspond to two elections in $2p_x$ – orbital.

$$\left.\begin{array}{l} n\ = 2,\ \ l = 1,\ \ m = 0,\ \ s = +\frac{1}{2} \\ n\ = 2,\ \ l = 1,\ \ m = 0,\ \ s = -\frac{1}{2} \end{array}\right\}$$ These values correspond to two elections in $2p_y$ – orbital.

$$\left.\begin{array}{l} n\ = 2,\ \ l = 1,\ \ m = -1,\ \ s = +\frac{1}{2} \\ n\ = 2,\ \ l = 1,\ \ m = -1,\ \ s = -\frac{1}{2} \end{array}\right\}$$ These values correspond to two elections in $2p_z$ – orbital.

By convention, the first p-orbital is denoted as p_x, second as p_y and third as p_z-orbital as given above.Therefore, we can say that an orbital can accommodate maximum two electrons. Further, since same values of 1 for a particular value of n corresponds to a particular subshell, total number of electrons in a subshell can be calculated, e.g., s-subshell contains two and p-subshell (l=1) will accommodate six electrons, respectively. Thus total number of electrons in L-shell will be eight (2 in s and 6 in p-subshell). Likewise, one can calculate total number of electrons in M-shell (18) and N- shell (32) etc. as well as d (10) and f (14) subshells.

1.9. HUND'S RULE OF MAXIMUM MULTIPLICITY

This rule states that "**electron pairing in the orbitals of a subshell will not take place until each orbital is filled with single electron**" (due to same energy of orbitals of a subshell). This is because it is easier for an electron to enter an empty orbital than an orbital which already possesses an electron.

If an atom has three electrons in p-subshell, these can be arranged in three p-orbitals as follows:

↓↑ ↑ ↑ ↓ ↑ ↑ ↑ ↑

(**a**) (**b**) (**c**)

Among these arrangements, the option(**c**) is the correct arrangement because this rule can be stated alternatively as "**the most stable arrangement of electrons in the orbitals of a subshell is that with greatest number of parallel spins**". It implies that before pairing starts, all the electrons of the subshell have the same spins (parallel).

This rule serves as a guideline for filling of multi orbital p, d and f subshells, e.g., the electron pairing in p, d and f-subshells will not start until each orbital of the given subshell contains one electron. Thus pairing starts in the three orbitals of p-subshell at fourth electron, in five orbitals of d-subshell at sixth electron and in seven orbitals of f-subshell at eighth electron, respectively. The electronic arrangements (or configurations) for p^4, d^6 and f^8 systems have been illustrated here along with p^3, d^5 and f^7:

P^3 : ↑ ↑ ↑ d^5 : ↑ ↑ ↑ ↑ ↑ f^7 : ↑ ↑ ↑ ↑ ↑ ↑ ↑

P^4 : ↑↓ ↑ ↑ d^6 : ↑↓ ↑ ↑ ↑ ↑ f^8 : ↑↓ ↑ ↑ ↑ ↑ ↑ ↑

Here p^3, d^5 and f^7 provide the examples of maximum multiplicity in the respective subshells and p^4, d^6 and f^8 provide the examples where pairing of electrons in these subshells starts.

1.10. THE AUFBAU PRINCIPLE

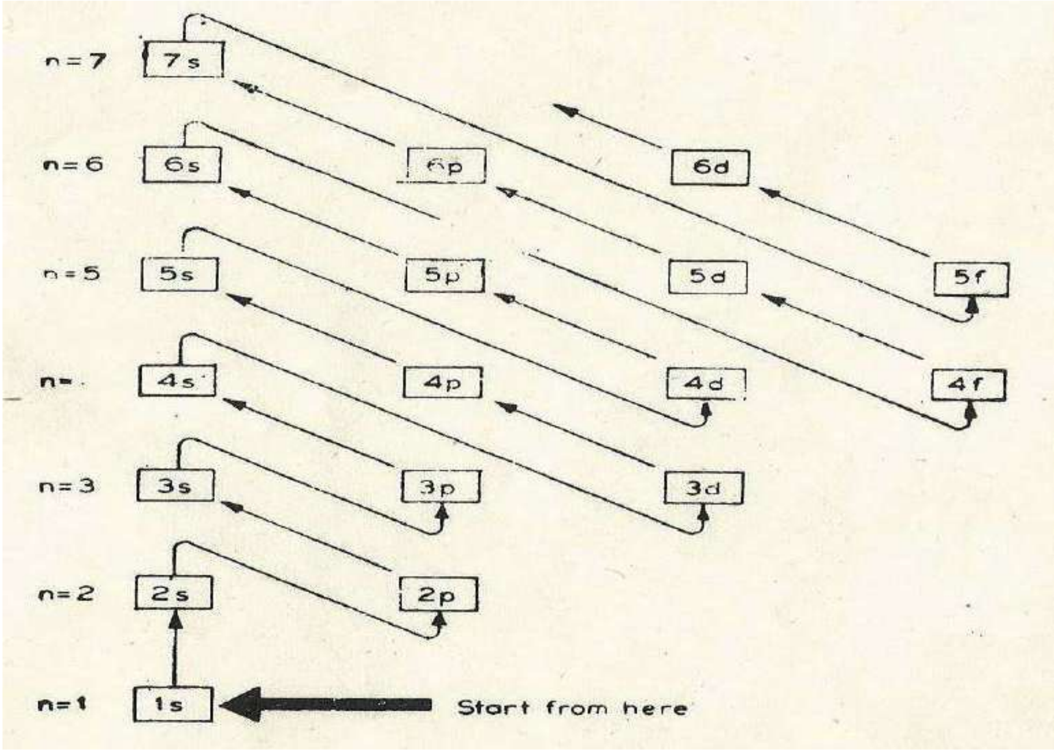
Aufbau is a German word which means building up or construction. The building up of orbitals implies the filling of orbitals with electrons. This principle gives us the sequence in which various orbitals are filled with electrons. The principle can be stated as "**in the ground state of poly electronic atoms, the electrons are filled in various subshells in the increasing order of their energy".** This means the electrons are filled in the subshell of the lowest energy first followed by the higher energy subshells.

There are certain rules which constitute the Aufbau principle:

(i) In general, the subshells with lower n values are filled first followed by those with higher n-values (called lower n rule).

(ii) For any given principal quantum number n, the order of filling up of subshells is s, p, d and f.

(iii) (n +l) Rule; sometime lower (n + l) rule is violated. In such cases (n+l) rule is applicable according to which the subshells are filled in order of increasing (n+l) values, e.g., 4s-subshell [(n+l) = 4+0 equal to 4] is filled before 3d subshell [(n+l) =3+ 2 equal to 5) due to lower (n+l) values. Keeping in mind the above discussion, various subshells can be arranged in the order of increasing energy as follows:



Energy sequence of subshells for electron filling

This relative order of energy of various subshells of an atom may also be given as follows:

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d…

The electrons are filled according to this order only in polyelectron atoms. Configurations of lanthanum (La, Z = 57) and actinium (Ac, Z = 89) are the exceptions where the last electron enters 5d and 6d-subshells instead of 4f and 5f-subshells against the Aufbau's lower (n + l) rule though (n+l) values are same for 4f and 5d as well as 5f and 6d-subshells.

1.11. ELECTRONIC CONFIGURATION OF ELEMENTS

Based on the Pauli's exclusion principle, Hund's maximum multiplicity rule and Aufbau principle, we can formulate a system for electron distribution in atoms and electronic configuration of the elements can be worked out. By electron distribution, we mean arrangement of electrons in various atomic orbitals and subshells.

Looking at the relative energy sequence of subshells of atoms in the elements, it can be concluded that we can work out and write down the electronic configuration of the elements straightaway up to argon (Ar, Z = 18) as follows:

Name of the element	**Symbol with atomic number**	**Electronic configuration**
Hydrogen	H (Z = 1)	$1s^1$
Helium	He (Z = 2)	$1s^2$
Lithium	Li (Z = 3)	[He] $2s^1$
Beryllium	Be (Z = 4)	[He] $2s^2$
Boron	B (Z = 5)	[He] $2s^2\ 2p^1$
Carbon	C (Z = 6)	[He] $2s^2\ 2p^2$
Nitrogen	N (Z = 7)	[He] $2s^2\ 2p^3$
Oxygen	O (Z = 8)	[He] $2s^2\ 2p^4$
Fluorine	F (Z = 9)	[He] $2s^2\ 2p^5$
Neon	Ne (Z = 10)	[He] $2s^2\ 2P^6$
Sodium (Natrium)	Na (Z = 11)	[Ne] $3s^1$
Magnesium	Mg (Z = 12)	[Ne] $3s^2$
Aluminium	Al (Z = 13)	[Ne] $3s^2\ 3p^1$
Silicon	Si (Z = 14)	[Ne] $3s^2\ 3p^2$

Phosphorus	P (Z = 15)	[Ne] $3s^2\ 3p^3$
Sulphur	S (Z =16)	[Ne] $3s^2\ 3p^4$
Chlorine	Cl (Z = 17)	[Ne] $3s^2\ 3p^5$
Argon	Ar (Z = 18)	[Ne] $3s^2\ 3p^6$

If we try to write down the electronic configuration of potassium (Kalium) (K, Z=19) according to above trend, the last electron must go to the 3d subshell, i.e. K_{19} = [Ne] $3s^2\ 3p^6\ 3d^1$ or [Ar] $3d^1$, but this electron is said to enter the 4s–subshell according to lower(n+l)rule of Aufbau principle. This may also be explained on the basis of effective nuclear charge given at the end of this topic. The (n + l) value for 4s = 4+0 is equal to 4 and for 3d, it is 3+2 is equal to5. Hence the electronic configuration of potassium (K, Z =19) is [Ar_{18}] $4s^1$ and that for calcium (Ca, Z = 20), the next higher element, is [Ar] $4s^2$. Again, the last electron in the atom of the next element, Sc, (Z = 21) has the opportunity to occupy either 3d or 4p-subshell because both are available to it. The (n+l) values for 3d (3+2=5) and 4p (4+l = 5) are same and electron prefers to enter that subshell which has lower n value, i.e. 3d-subshell according to lower n rule of Aufbau principle. The filling of 3d-subshell goes on up to zinc (Z = 30).

The electronic configurations of the elements with Z = 21 to 30 are given below:

Name of the Symbol with atomic number	**Electronic Configuration**
Sc (Z = 21)	[Ar] $4s^2\ 3d^1$
Ti (Z = 22)	[Ar] $4s^2\ 3d^2$
V (Z = 23)	[Ar] $4s^2\ 3d^3$
Cr (Z = 24)	[Ar] $4s^1\ 3d^5$
Mn (Z = 25)	[Ar] $4s^2\ 3d^5$
Fe (Z = 26)	[Ar] $4s^2\ 3d^6$

Co (Z = 27)	[Ar] $4s^2\ 3d^7$
Ni (Z = 28)	[Ar] $4s^2\ 3d^8$
Cu (Z = 29)	[Ar] $4s^2\ 3d^{10}$
Zn (Z = 30)	[Ar] $4s^2 3d^{10}$

The next six elements, *viz*. Ga_{31}, to Kr_{36} belong to p-block and the last electron, as is evident, enters the 4p – subshell of the atoms of these elements. The electronic configurations of these elements are as follows:

Gallium	Ga (Z = 31)	[Ar] $4s^2\ 3d^{10}\ 4p^1$
Germanium	Ge (Z = 32)	[Ar] $4s^2\ 3d^{10}\ 4p^2$
Arsenic	As (Z = 33)	[Ar] $4s^2\ 3d^{10}\ 4p^3$
Selenium	Se (Z = 34)	[Ar] $4s^2\ 3d^{10}\ 4p^4$
Bromine	Br (Z = 35)	[Ar] $4s^2\ 3d^{10}\ 4p^5$
Krypton	Kr (Z = 36)	[Ar] $4s^2\ 3d^{10}\ 4p^6$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^2\ 4p^6$

In next two elements of 5th period, the last electron goes to 5s- subshell. (s-block):

Rubedium	Rb (Z = 37)	$[K_r]\ 5s^1$
Strontium	Sr (Z = 38)	$[K_r]\ 5s^2$

Filling of 4d – subshell begins in the next element, yttrium, Y (Z = 39) and ends at cadmium, Cd (Z = 48) {Y: [Kr] $5s^2\ 4d^1$ to Cd: [Kr] $5s^2\ 4d^{10}$} with anomalies in the configurations of ^{42}Mo, ^{46}Pd and ^{47}Ag as shown below. In the next six elements of p-block, electron filling occurs in 5p – subshell, i.e. Indium ^{49}In: [Kr] $5s^2\ 4d^{10} 5p^1$ to Xenon, ^{54}Xe : [Kr] $5s^2\ 4d^{10}\ 5p^6$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^2\ 4p^6\ 4d^{10}\ 5s^2 5p^6$. Next two elements caesium ^{55}Cs and barium, ^{56}Ba are s-block elements and the last electron in these elements enters the 6s-subshell. ^{55}Cs: [Xe] $6s^1$ and ^{56}Ba: [Xe] $6s^2$. Next element lanthanum ^{57}La, belongs to d-block: [Xe] $6s^2\ 5d^1$ and is followed by 14 lanthanides: cerium, ^{58}Ce to lutetium, ^{71}Lu in which electron filling takes place in f-subshell except ^{64}Gd and ^{72}Lu in which the last electron enters d-subshell due to f^7 and f^{14} stable configuration but these show close resemblance with other f-block elements and have been placed with them in the periodic table.

It is observed that in case of chromium (Cr, Z = 24) and copper (Cu, Z = 29), the electronic configurations are against the trend. These configurations have been obtained experimentally by spectroscopic studies. Simple explanation to these anomalies can be given as under. For Cr and Cu, d-electrons being higher in number contribute more towards the stability of the atoms. Because d^5 (just half filled) and d^{10} (completely filled) configurations are more stable compared to d^4 and d^9 configurations, electronic transition occurs from s to d-subshells in these elements (due to exchange energy effect and symmetry of orbitals), i.e. Cr: $4s^23d^4 \rightarrow 4s^13d^5$ and Cu : $4s^2\ 3d^9 \rightarrow 4s^1\ 3d^{10}$. s- electrons being less in number have little effect in this pursuit.

Similar anomalies have also been observed in the higher homologues of these elements, *viz.* ,molybdenum (Mo, Z = 42) : [Kr] $5s^1\ 4d^5$ and silver (Ag, Z = 47) : [Kr] $5s^1\ 4d^{10}$. Palladium (Pd, Z = 46) contains another typical configuration: [Kr] $5s^0\ 4d^{10}$. Also there are anomalies in the configurations of lanthanides and actinides.

The important point to be noted here is that during the filling of electrons, these enter first in ns-subshell and then (n-1) d or (n-2) f-subshell. But during the removal of electron (s), it is first removed from nths orbital rather than (n-1) d or (n-2) f-subshell though $E_{ns} < E_{n-1d} < E_{n-2f}$ and removal of the electron must occur from higher energy subshell. For example, in case of first transition series (3d-series) elements filling and removal of 4-s-electrons occurs first followed by 3d-electrons. This is, perhaps, because after filling of d-subshell, it becomes of lower energy than 4s-subshell.

1.12. EFFECTIVE NUCLEAR CHARGE (Z_{EFF}.)

This term is related with shielding or screening effect. The electrons residing in the innermost shell experience the attraction of full charge of the nucleus (actual charge) but this is not true for the electrons contained in the outer shells. Actually the electrons in the inner shells called intervening electrons, act as a shield or screen between the nucleus and outer shell electrons and thus reduce the force of attraction between them. This is called screening or shielding effect. This effect of inner electrons causes a decrease in the actual charge of the nucleus (atomic number, Z) acting on the outer electrons by a quantity σ (sigma) known as screening or shielding constant. The decreased nuclear charge (Z- σ) is called effective nuclear charge denoted by Z_{eff}.

It is to be noted that only inner electrons cause the shielding of nucleus from outer electrons and outer electrons do not produce any shielding effect on any of the inner electrons in question.

The shielding constant is greater than zero and less than Z_{actual} and is a measure of the degree to which the intervening electrons shield the outer shell electrons from the nuclear pull.

The effective nuclear charge (Z_{eff}.) is defined as "**the difference between actual nuclear charge (Z_{actual}) and the screening constant (σ) produced by the intervening electrons".**

The shielding effect caused by inner electrons varies with the type of subshells to which these electrons belong, e.g. s > p > d > f. This shows that s-electrons cause maximum shielding effect followed by p, d and f-electrons which produce minimum shielding effect due to their arrangement around nucleus. There are certain factors which influence the magnitude of σ and Z_{eff}.

(i) Number of intervening electrons: Greater is the number of intervening electrons, more will be the magnitude of σ and less is the value of Z_{eff}. Down in a group, number of intervening electrons in elements increases and hence value of σ also increases. Consequently, Z_{eff} value goes on decreasing.

(ii) Size of atom: As the size of atoms increases, value of Z_{eff} decreases, e.g. down in a group. Along a period, atomic size decreases and hence Z_{eff} goes on increasing.

Slater's Rules for calculating σ and Z_{eff}.

Slater gave illustrative rules for calculating σ and Z_{eff}. These have been discussed here with illustrations:

(i) The screening constant (**σ**) for an electron contained in ns or any of np orbitals of n^th^ shell of an atom/ion = 0.35 x [number of remaining electrons in n^th^ shell] + 0.85 x [number of electrons in (n-1^th^ shell)] + 1.0 x [number of electrons in farther inner shells].

From this formula, we conclude that;

(a) Each of the remaining electrons in the n^th^ shell contributes 0.35 to the value of σ.

(b) Each of the electrons in (n- l)^th^ shell makes a contribution of 0.85 to the value of σ.

(c) Each of the electrons in the next inner shells makes a contribution of 1.0 to it.

(d) There is no contribution of electrons to the value of σ which are residing in the orbitals having higher value of the principal quantum number than the shell number of the electron in question.

(e) For an s-electron of first shell (n=1), there will be a contribution of 0.30 from other single electron in 1s-orbital.

Some examples may be cited to make the rule clear:

Example 1. Calculate σ and $Z_{eff.}$ values for 4s electron in

(i) cu (Zn = 29) and (ii) Mn (Z = 25) atom.

Solution: (i) for cu (Z = 29), $^{29}Cu = \underbrace{1s^2\ 2s^2\ 2p^6}_{(10)}\ \underbrace{3s^2 3p^6 3d^{10}}_{(18)}\ \underbrace{4s^1}_{(01)}$

σ for $4s^1$ electron in Cu atom = 0.35x0+0.85x18+1.0x10 = 25.30

∴ Z_{eff}. for $4s^1$ electron in Cu atom = $Z_{act.} - σ$ = 29 – 25.30 = 3.70

(ii) For Mn (Z = 25), $^{25}Mn = \underbrace{1s^2\ 2s^2\ 2p^6}_{(10)}\ \underbrace{3s^2 3p^6 3d^5}_{(18)}\ \underbrace{4s^2}_{(1)}$

σ for $4s^1$ electron in Mn-atom = 0.35 x 1+ 85 x 13 + 1.0 x 10 = 21.40

∴ Z_{eff} experienced by a 4s – electron in Mn atom = $Z_{act.} - σ$ = 25 – 21.40 = 3.60

Example 2. Calculate $Z_{eff}$for (i) the last electron in Cl atom (Z=17) and

(ii) 1s electron in N atom (Z = 7).

Solution: (i) for Cl (Z = 17), $^{17}Cl = 1s^2\ \ 2s^2\ \underline{2p^6}\ \ \underline{3s^2 3p^5}\ \ \underline{\qquad}$

(2) (8) (7)

∴ Last shell contains 7 electrons, hence remaining electrons in this shell for the last electron = 7-1 =6

σ for the last electron of Cl-atom = 0.35 x 6 + 0.85 x 8+ 1.0 x 2 = 10.90

∴ Z_{eff} for the last electron of Cl atom = 17-10.90 = 6.10

(ii) For N (Z = 7), $^{7}N = \underbrace{1s^2}_{(2)}\ \ \underbrace{2s^2\,2p^3}_{(5)}$

There will be no contribution of valence shell electrons towards σ of $1s^1$ electron.

∴σ of $1s^1$ electron of N atom = 0x5+0.30x1 = 0.30

and Z_{eff} for this electron = $Z_{act.}$- σ = 6.70

(ii) **σ** for an electron contained in (n-1) d-orbitals of (n-1)th shell of an atom/ion

= 0.35 x [number of electrons in (n-1)d-orbitals]+ 1.0 x [Number of electrons in (n-1)s, (n-1)p-orbitals and inner shells]

From this formula, it is inferred that

(a) These is no contribution of the electrons of ns-orbital to the value of σ.

(b) Each of the remaining electrons in the (n-1)d-orbitals contributes 0.35 to σ.

(c) Each of the electrons in (n-1) s and (n-1)p-orbitals as well as inner shells i.e. n=1 to n (n-2)th shell makes a contribution of 1.0 to the value of σ.

Let us discuss few examples:

Examples 3. Calculate σ and Z_{eff} for 3d-electron in (i) Cr (Z = 24) and (ii) Ni (Z = 28).

Solution. (i) for Cr (Z = 24), $^{24}Cr = \underbrace{1s^2\,2s^2\,2p^6\,3s^2\,3p^6}_{(18)}\ \underbrace{3d^5}_{(5)}\ \underbrace{4s^1}_{(1)}$

(on arranging the configuration according to Slater's rule)

Here $4s^1$ electron does not contribute towards the value of σ.

σ for a 3d-electron in Cr atom = 0.35 x 4+1.0 x 18 = 19.40

(remaining electrons in 3d orbitals = 5-1 = 4)

∴Z_{eff} experienced by a 3d electron in Cr atom = $Z_{act.}$– σ = 24 – 19.40 = 4.60

(ii) For Ni (Z = 28), $^{28}Ni = 1s^2\,2s^2\,2p^6\,3s^2 3p^6\quad 3d^8\quad 4s^2$

(18) (8) (2)

$4s^2$ electrons do not contribute to the value of σ. Remaining electrons in 3d orbitals = 8-1 = 7.

σ for a 3d-elctron in Ni atom = 0.35x7+1.0x18 = 20.45

∴$Z_{eff}$for a 3d-electron in this atom= Z – σ = 28-20.45 = 7.55

(iii) To calculate the Z_{eff} experienced at the periphery of an atom/ion.

This is calculated by subtracting the shielding constant (σ) for all the electrons present in the electronic configuration of the atom/ion from its actual nuclear charge.

For example, suppose we have to calculate the Z_{eff}. at the periphery of Ti (Z = 22) atom, then $^{22}Ti = \underbrace{1s^2\,2s^2\,2p^6}_{(10)}\;\underbrace{3s^2 3p^6 3d^2}_{(10)}\;\underbrace{4s^2}_{(2)}$

σ for all the electrons of Ti atom = 0.35x2+0.85x10+1.0+10 = 19.20

∴ Zeff at the periphery of this atom = $Z_{act.}$– σ = 22- 19.20 = 2.80

Applications of effective nuclear charge and Slater's Rules

The concept of effective nuclear charge in the light of slater's rule has been used to explain; why is 4s-orbital filled in preference to 3d-orbitals in potassium atom (Z =19)?

Argon (Z = 18) with electronic configuration: $1s^2\,2s^2\,2p^6\,3s^2 3p^6$, is the last element of third period in which the 3d-orbitals remain vacant and the last electron goes to 3p-subshell. For the 19th electron of potassium atom, two subshells are theoretically available, v*iz*. 3d and 4s. Under these two possibilities, the electronic configurations of potassium atom are:

K (Z = 19) = $\underbrace{1s^2\,2s^2\,2p^6\,3s^2\,3p^6}_{(18)}\underbrace{3d^1}_{(1)}$

and K (Z = 19) = $\underbrace{1s^2\,2s^2\,2p^6}_{(10)}\;\underbrace{3s^2 3p^6}_{(8)}\underbrace{4s^1}_{(1)}$

The σ (shielding constant) for 4s-electron of K atom

= 0.35x0+0.85x8+1.0x10 = 16.80

∴ Z_{eff} for $4s^1$ electron of K atom = $Z_{act.}$– σ = 19-16.80 = 2.20

Similarly, the Z_{eff}experienced by $3d^1$ electron of K-atom is

19- [0.35x0+1.0x18] = 1.0

Since Z_{eff} for $4s^1$ electron is greater than $3d^1$ electron of K atom, the attractive force between $4s^1$ electron and nuclear charge is greater than that of between $3d^1$ electron and the nucleus of this atom. Hence the configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^1$, would be more stable than that having $3d^1$ electron. This infers that 4s-orbital is filled in preference to 3d-orbitals in K atom. Other applications of the concept will be given in the next units of the text as and when required.

1.13. SUMMARY

This unit contains the text related with the dual nature of matter, the uncertainty principle, probability concept, the wave equation, significance of ψ and ψ^2 and related wave functions as well as probability distribution curves and shapes of atomic orbitals in the simple way. A brief and informative discussion of quantum numbers, the rules governing the filling of atomic orbitals such as Pauli's exclusion principle, Hund's rule and Aufbau principle has been given. The electronic configuration of elements has effectively been discussed with examples and the limitations are also given. At the last, Slater's rules for calculating the effective nuclear charge with examples and applications have been given briefly.

1.14. TERMINAL QUESTIONS

(only some samples have been given)

i) What do you mean by dual nature of matter?

ii) Discuss the meaning and significance of ψ and ψ^2 with reference to the wave equation.

iii) Write a note on radial wave function.

iv) Discuss the angular wave function and correlation between this wave function and shape of p-orbitals.

v) Discuss azimuthal quantum number with suitable examples.

vi) What possible values of n, l, m and s quantum numbers can an electron in a 4f- orbital have?

vii) How many electrons can be contained in fourth hell of an atom and why?

viii) How are the quantum numbersn, l and m related to one another?

ix) What is meant by shielding effect?

x) What quantum numbers would you assign to the last electron of Rb-atom(Z = 37) as well as its 30th electron?

xi) Calculate σ and Z_{eff} for 3d electron in Mn (Z = 25) atom.

xii) Write down the electronic configurations of the elements with Z = 46, and 71.

1.15. ANSWERS

---

i) Please see de Broglie's matter waves.

ii) Please see significance of ψ and ψ^2.

iii) Please see radial wave function.

iv) Please refer to angular wave function and shapes of orbitals.

v) Please see quantum numbers.

vi) An electron in a 4f orbital will have the values: n = 4, l = 3 (n-1 = 4-1),

m = any one of +3,+2,+1,0,-1,-2,-3,s = + $\frac{1}{2}$ or - $\frac{1}{2}$.

vii) According to Bohr – Burry scheme, the maximum number of electrons in nth shall = $2n^2$.

$\therefore$ In fourth shell, maximum number of electrons = $2x4^2$ = 32.

viii) n, l and m are inter related as follows:

l = 0 to n-1, m = +l to – l through 0, n is independent of both l and m.

ix) Please refer to effective nuclear charge and shielding effect.

x) The electronic configuration of Rb (Z = 37) atom is ^{37}Rb = [Kr] $5s^1$ i.e. $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6 5s^1$ (Aufbau principle) The last electron is $5s^1$ electron. Its quantum numbers are n=5, l= 0, m = 0, s = + $\frac{1}{2}$

The 30th electron is the last electron in 3d subshell i.e. the 10th electron.

Its quantum number are: n=3, l= 2, m= -2, s = - $\frac{1}{2}$

xi) $$^{25}Mn = \underbrace{1s^2\,2s^2\,2p^6\,3s^2\,3p^6}_{(18)}\quad \underbrace{3d^{15}}_{(5)}\ \underbrace{4s^2}_{(2)}$$

$4s^2$ electrons do not contribute to the value of σ for 3d electrons.

σ for a 3d-electron in Mn atom = 0.35 x [number of remaining electrons in 3d-orbitals]+ 1.0 x [number of all the electrons in1s ,2s, 2p, 3s,and 3p, orbitals] = 0.35 x 4+ 1.0x 18 = 19.40

$\therefore$ Zeff = Z – σ = 25- 19.40 = 5-60

xii) For this answer, please refer to Aufbau principle:

Z = 46 : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^0\ 4d^{10}$ (observed config.)

Z = 71 : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^1$

1.16. REFERENCES

1. Principles of Inorganic Chemistry: B. R. Puri, L.R. Sharma & K. C. Kalia, Milestone Publishers and Distributers, Daryaganj, Delhi (2013).
2. Selected topics in Inorganic Chemistry: W.U. Malik, G.D. Tuli & R.D. Madan, S. Chand & Co. Ltd., New Delhi (1993).
3. Comprehensive Inorganic Chemistry: Sulekh Chandra, New Age International (Pvt.) Ltd., New Delhi (2004).
4. The Nature of the Chemical Bond: Linus Pauling, 3rd Edn., Cornell University Press, New York (1960).
5. A Simple Guide to Modern Valency Theory: G.I. Brown, Revised Edn., Longmans Green, London (1967).
6. Advanced Inorganic Chemistry: Satya Prakash, G.D. Tuli, S.K. Basu and R.d. Madan, Vol. **I**, 7th Edn., S. Chand & Co. Ltd, New Delhi (1998).
7. Shriver and Atkins' Inorganic Chemistry: Peter Atkins *et. al*., 5th Edn., Oxford University Press, New York (2010).

UNIT 2: THE PERIODIC TABLE

CONTENTS:

2.1 OBJECTIVE

The objective of writing the text of this unit is to give the readers an information about how the elements whose number increased with time, were organised in the tabular form.The systematic classification of these elements with respect to their physical/chemical properties made the readers and the scientists comfortable and predictable in their further study. Till date, this number has gone up to 112 to whom symbols have been assigned and some more elements have been predicted and evidenced by laboratory studies.

2.2 INTRODUCTION

With the rapid advance of chemistry with time, the number of discovered elements increased continuously. These elements exhibited marked difference in their properties. Hence it became more and more difficult and tedious job for the scientists to study each and every element individually for its physical and chemical behaviour. Therefore, many attempts were made to arrange the elements with similar physical and chemical bhaviour, at one place to make their study systematic and easier. This attempt was named **the periodic classification of elements** which means, the ideal arrangement of those elements which are alike in their behavior. It was thought, in the process, that there might be some relation between some fundamental characteristic of an element and its properties. Originally, this characteristic taken into account was the atomic weight, later called atomic mass. Eventually, the atomic mass was replaced by more appropriate basis, the atomic number. At the same time the periodicity in properties of the elements was also taken care of.

2.3 HISTORY OF PERIODIC TABLE

The first important attempt for the arrangement of elements, i.e. their classification, was made by Dobereiner in the beginning of nineteenth century by proposing what is now known as **"Dobereiner's law of triads"**.According to him when various triads (i.e. containing three) of elements with similar properties were arranged in increasing order of their atomic weights, the atomic weight of the middle element of the triad was found approximately equal to the arithmetic mean of the remaining two corner elements. For example:

Li	Na	K
7	23	39
S	Se	Te
32	79	127.6
Cl	Br	I
35.5	80	127

This law of triads was not found useful because triads of all the known elements at that time could not be formed.

In the middle of nineteenth century, scientist **Duma** put forward his idea called **"Duma's homologous series"** in an attempt to classify the elements. He proposed that "the atomic weights of certain elements could be placed in homologous series like organic compounds". For example, the elements of nitrogen family were arranged as follows:

Element	**Atomic Weight**	**Homologous series**
N	14	A
P	31 (14+17)	A+B
As	75 (14+17+44)	A+B+C
Sb	119 (14+17+2x44)	A+B+2C
Bi	207 (14+17+4x44)	A+B+4C

(Here A = 14, B = 17 and C = 44).

This scheme of Duma was also not found useful in the classification of elements.

Further step in this field was takenin 1864 by John Newlands, an English chemist. He tried to correlate the chemical properties of elements with their atomic weights and proposed a law, now known as "**Newlands' law of octaves**". According to this law "**if the elements were arranged in increasing order of their atomic weights, every eighth element was found to have similar properties**". For example, as given below, the eighth element starting from Li is Na which have similar properties. Similarly, Mg is the eighth element from Be and both of them also have similar properties.

Li	Be	B	C	N	O	F
7	9	11	12	14	16	19
Na	Mg	Al	Si	P	S	Cl
23	24	27	28	31	32	35.5

However, this classification proposed by Newlands was limited to 14 elements only (given above) and his work was not accepted by scientific community.

2.4 LAWS OF PERIODIC TABLE

(A) Mendeleev's Periodic law:

Dmitri Mendeleev, a Russian chemist, in 1869 observed that "**when the elements were arranged in the increasing order of their atomic weights, the elements with similar properties recurred (or reappeared) at regular intervals (or periods)"**. From this observation, he put forward a law known as Mendeleev's periodic law. This law states:

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

Working on this law, he arranged the elements, known at his time, in the increasing order of atomic weights and presented them in the form of a table. That was known as **Mendeleev's periodic table (please see table 2.1).**

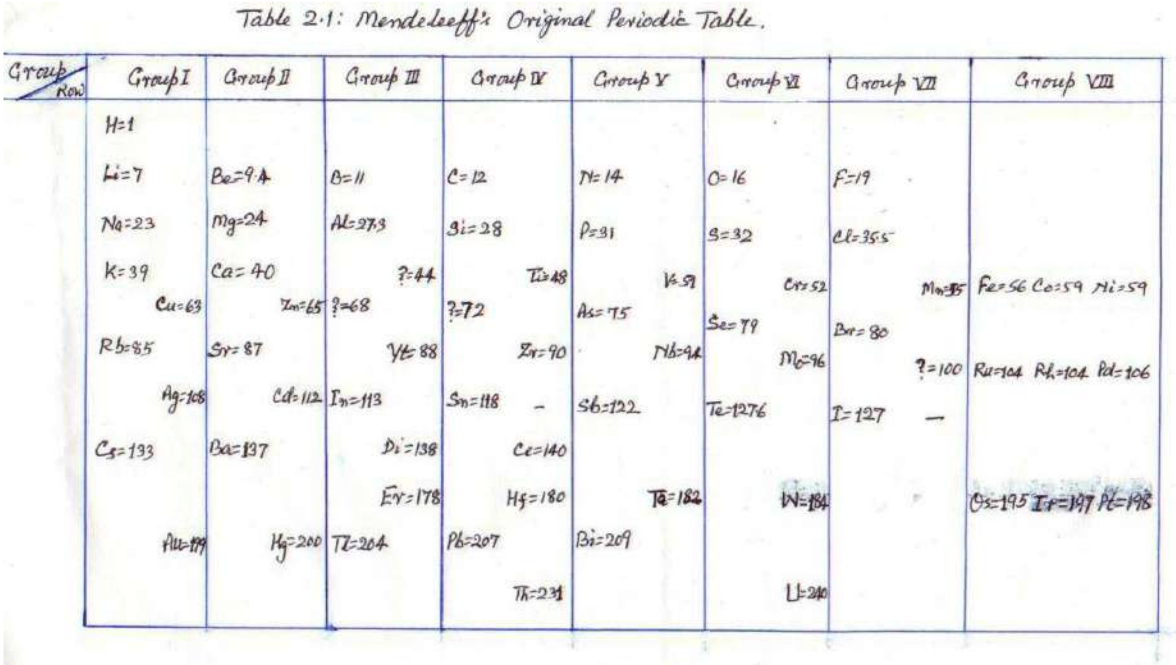


Table 2.1: Mendeleeff's Original Periodic Table.

Group / Row	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	H=1							
	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
	K=39	Ca=40	?=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Co=59 Ni=59
	Cu=63	Zn=65	?=68	?=72	As=75	Se=79	Br=80	
	Rb=85	Sr=87	Yt=88	Zr=90	Nb=94	Mo=96	?=100	Ru=104 Rh=104 Pd=106
	Ag=108	Cd=112	In=113	Sn=118 –	Sb=122	Te=127.6	I=127 —	
	Cs=133	Ba=137	Di=138	Ce=140				
			Er=178	Hf=180	Ta=182	W=184		Os=195 Ir=197 Pt=198
	Au=199	Hg=200	Tl=204	Pb=207	Bi=209			
				Th=231		U=240		

Table 2.1: Mendeleev's original Periodic Table

In that table, the elements were arranged in columns (called groups) and rows (called periods). The original periodic table formed by Mendeleev had following characteristics:

(i) The elements were arranged in the increasing order of their atomic weights.

(ii) The table contained eight vertical columns and seven horizontal rows.

(iii) Every column (group) contained two sub groups (subgroup A and subgroup B) except, the eighthcolumn which contained three series of three elements (triads).

(iv) The columns contained the elements of similar physical and chemicalproperties.

(v) First period (horizontal row) was called very short period, second and third periods were named as short periods, fourth and fifth periods were called long periods and sixth period was named very long period. Seventh period contained only a few elements (and is still incomplete). The elements of 2nd and 3rd periods were called the typical elements by Mendeleev because, these were truely the representatives of their respective groups.

(vi) Mendeleev had left empty spaces for elements unknown at his time, e.g. Sc, Ga, Ge etc. but had predicted their properties. At his time, around 65 elements were known.

Merits of Mendeleev's Periodic Table:

(i) It helped in the study of elements and compounds which has become easy and systematic.

(ii) The empty spaces in the Mendeleev's periodic table encouraged the scientists to work in the field of discovery of new elements since he had predicted the properties of the probable elements.

Defects of the Mendeleev's Periodic Table:

Although Mendeleev's periodic table helped a lot to study the properties of elements and correlate the elements with one another, yet there were some anomalies which existed unanswered in the Mendeleev's table. These were:

(i) The position of hydrogen remained inappropriate because some of its properties resembled with alkali metals and some others with halogens. Hence it might be placed in group I or group VII.

(ii) Dissimilar elements of sub groups were placed together in groups, i.e. alkali metals and coinage metals of 1st group have altogether different properties. Similar is the case with halogens and elements of manganese family in group VII (sub groupA and B elements).

(iii) Certain elements with higher atomic weights were placed before those with lower atomic weights, e.g.

Cobalt	Nickel (elements of group VIII, triad I)
58.93	58.69

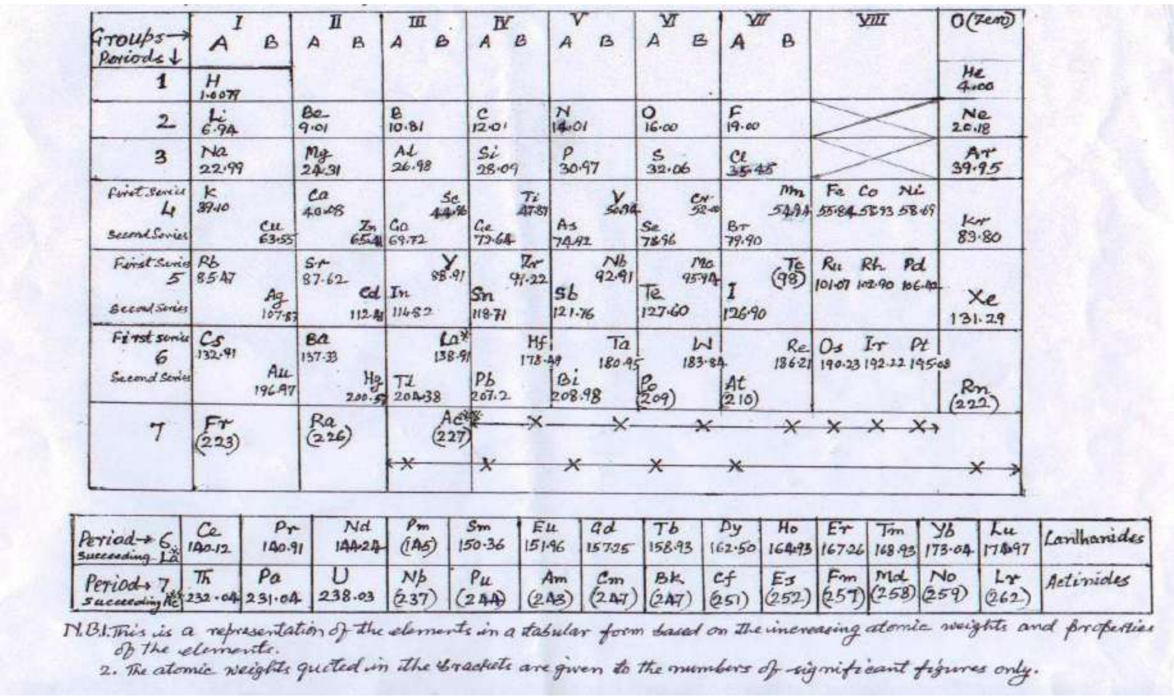
Tellurium	Iodine (elements of group VI and VII)
127.60	126.90

(iv) The Table did not show any correlation between chemical properties and electronic configuration of elements.

(v) No information regarding the position of isotopes and isobars was available from the table.

Modified form of Mendeleev's Periodic Table:

Mendeleev did not imagine the discovery of inert elements, therefore no place was left by him in his periodic table for these elements. After the discovery of inert gases (later called the noble gases),a new group was added to accommodate these elements to his Periodic Table which is called zero group. Similarly, the lanthanides and actinides could not find the proper place in his periodic table. Later including these and other elements which were discovered after Mendeleeff, a modified table was prepared which has been given (**Table 2.2**).



Groups→ Periods↓	I		II		III		IV		V		VI		VII		VIII	0 (Zero)
	A	B	A	B	A	B	A	B	A	B	A	B	A	B		
1	H 1.0079															He 4.00
2	Li 6.94		Be 9.01		B 10.81		C 12.01		N 14.01		O 16.00		F 19.00			Ne 20.18
3	Na 22.99		Mg 24.31		Al 26.98		Si 28.09		P 30.97		S 32.06		Cl 35.45			Ar 39.95
First Series 4	K 39.10		Ca 40.08			Sc 44.96		Ti 47.87		V 50.94		Cr 52.00		Mn 54.94	Fe Co Ni 55.84 58.93 58.69	
Second Series		Cu 63.55		Zn 65.41	Ga 69.72		Ge 72.64		As 74.92		Se 78.96		Br 79.90			Kr 83.80
First Series 5	Rb 85.47		Sr 87.62			Y 88.91		Zr 91.22		Nb 92.91		Mo 95.94		Tc (98)	Ru Rh Pd 101.07 102.90 106.42	
Second Series		Ag 107.87		Cd 112.41	In 114.82		Sn 118.71		Sb 121.76		Te 127.60		I 126.90			Xe 131.29
First series 6	Cs 132.91		Ba 137.33			La* 138.91		Hf 178.49		Ta 180.95		W 183.84		Re 186.21	Os Ir Pt 190.23 192.22 195.08	
Second Series		Au 196.97		Hg 200.59	Tl 204.38		Pb 207.2		Bi 208.98		Po (209)		At (210)			Rn (222)
7	Fr (223)		Ra (226)			Ac** (227)										

Period→6 Succeeding La*	Ce 140.12	Pr 140.91	Nd 144.24	Pm (145)	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97	Lanthanides
Period→7 Succeeding Ac**	Th 232.04	Pa 231.04	U 238.03	Np (237)	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (262)	Actinides

N.B. 1. This is a representation of the elements in a tabular form based on the increasing atomic weights and properties of the elements.
2. The atomic weights quoted in the brackets are given to the numbers of significant figures only.

Table 2.2 Modified form of the Mendeleev periodic table bassed on atomic weight.

This table has following characteristics:

(i) This table contains nine vertical columns or groups including the zero group.

(ii) Except the elements of zero group and eighth group, all the groups have been divided into A and B sub groups. The elements of subgroup A have been kept on left side and those of B on the right side of the group. Elements of a subgroup have more similarities than those placed in the other sub group of the same group. For example, elements of subgroup I A (*viz.*, Li, Na, K, Rb, Cs, etc.) have almost similar properties but differ from subgroup IB elements (*viz.*, Cu, Ag, Au).

(iii) The atomic weights of the elements increase regularly on moving from top to bottom in a column and, in general, in a period with few exceptions.

(iv) The number of horizontal rows has been kept the same but the nomenclature of periods (given in point v of Mendeleev's original periodic table) has been changed in the modified table. The first three periods, in this case, are known as short periods containing 2,8 and 8 elements and the last four are called the long periods though the number of elements is 18 in the fourth and fifth periods and 32 in the sixth period. Seventh period is still incomplete. It may be noted here that there is regular variation in the properties of elements from left to right in a period.

(v) By the year 1900, some 30 more elements had been added to the list of elements. These along with those discovered later have been given in the table.

(B) Lothar Meyer's arrangement:

German chemist Lothar Meger, in 1870 proposed independently a more extensive tabulation of the elements based on regular periodic recurrence of properties. He calculated the atomic volumes of the known elements i.e. volume occupied by one mole of the elements (in cm^3) in the solid state. Thus

Atomic volume $= \frac{\text{mass of one mole}}{\text{density}}$

When he plotted these atomic volumes against the corresponding atomic masses, a curve with sharp peaks and broad minima was obtained. This idea could not get wide acceptance and was not taken for further work by scientific community.

(C) Modern Periodic law (Moseley's Periodic Law).

This is also called Moseley's periodic law. Henry Moseley, a British physicist, in 1911-12, discovered a new property of the elements called **atomic number** which is equal to the total number of protons in the nucleus of the atom of an element (this is also equal to the number of electrons in the atom). He correlated this property with the physical and chemical properties of the elements. This led Moseley to predict that most of the defects of Mendeleeff's periodic table could be removed if the classification of the elements is done on the basis of atomic number rather than the atomic weight. He, thus, modified the periodic law and stated that **"the properties of the elements are the periodic functions of their atomic numbers".** Meanig thereby, if the elements are arranged in the increasing order of their atomic numbers, the recurrence of properties of the elements takes place at regular intervals. The elements with similar properties fall in the same vertical columns (or groups) and are called elements of that family.

Modern or Long form of Periodic Table:

This table is also known as Bohr's periodic table and is based on the atomic number, which is a fundamental property of the elements, and Moseley's periodic law. This table helps us to understand the cause of periodicity of properties, i.e. recurrence of similar properties at certain regular intervals viz., 2,8,18, and 32 which are referred to as magic numbers. This is because the atomic number of elements in a group increases by magic numbers at various steps. This is said to be attributed to the electronic arrangement in the atoms of elements.

The modern periodic table has 18 vertical columns called groups or families and 7 horizontal rows called periods. This has been given in (**table 2.3**).

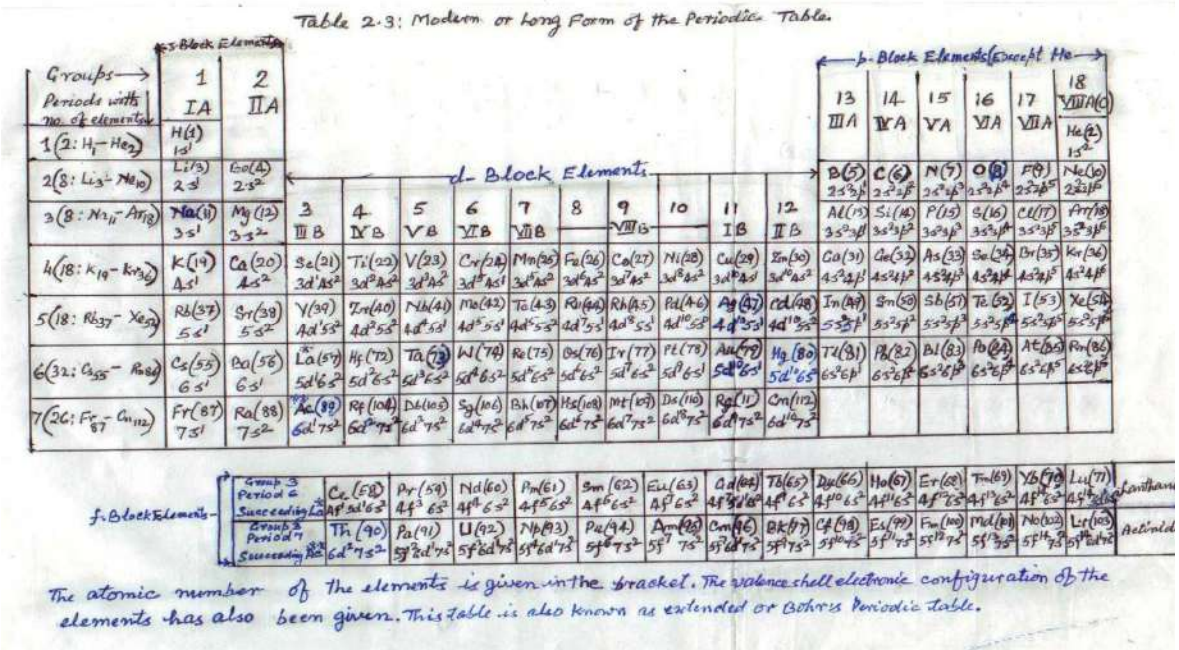


Table 2.3: Modern or Long Form of the Periodic Table.

← s-Block Elements →

← d- Block Elements →

← p- Block Elements (Except He →

Groups → Periods with no. of elements	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA(0)
$1(2: H_1 - He_2)$	H(1) $1s^1$																	He(2) $1s^2$
$2(8: Li_3 - Ne_{10})$	Li(3) $2s^1$	Be(4) $2s^2$											B(5) $2s^2 2p^1$	C(6) $2s^2 2p^2$	N(7) $2s^2 2p^3$	O(8) $2s^2 2p^4$	F(9) $2s^2 2p^5$	Ne(10) $2s^2 2p^6$
$3(8: Na_{11} - Ar_{18})$	Na(11) $3s^1$	Mg(12) $3s^2$											Al(13) $3s^2 3p^1$	Si(14) $3s^2 3p^2$	P(15) $3s^2 3p^3$	S(16) $3s^2 3p^4$	Cl(17) $3s^2 3p^5$	Ar(18) $3s^2 3p^6$
$4(18: K_{19} - Kr_{36})$	K(19) $4s^1$	Ca(20) $4s^2$	Sc(21) $3d^1 4s^2$	Ti(22) $3d^2 4s^2$	V(23) $3d^3 4s^2$	Cr(24) $3d^5 4s^1$	Mn(25) $3d^5 4s^2$	Fe(26) $3d^6 4s^2$	Co(27) $3d^7 4s^2$	Ni(28) $3d^8 4s^2$	Cu(29) $3d^{10} 4s^1$	Zn(30) $3d^{10} 4s^2$	Ga(31) $4s^2 4p^1$	Ge(32) $4s^2 4p^2$	As(33) $4s^2 4p^3$	Se(34) $4s^2 4p^4$	Br(35) $4s^2 4p^5$	Kr(36) $4s^2 4p^6$
$5(18: Rb_{37} - Xe_{54})$	Rb(37) $5s^1$	Sr(38) $5s^2$	Y(39) $4d^1 5s^2$	Zr(40) $4d^2 5s^2$	Nb(41) $4d^4 5s^1$	Mo(42) $4d^5 5s^1$	Tc(43) $4d^5 5s^2$	Ru(44) $4d^7 5s^1$	Rh(45) $4d^8 5s^1$	Pd(46) $4d^{10} 5s^0$	Ag(47) $4d^{10} 5s^1$	Cd(48) $4d^{10} 5s^2$	In(49) $5s^2 5p^1$	Sn(50) $5s^2 5p^2$	Sb(51) $5s^2 5p^3$	Te(52) $5s^2 5p^4$	I(53) $5s^2 5p^5$	Xe(54) $5s^2 5p^6$
$6(32: Cs_{55} - Rn_{86})$	Cs(55) $6s^1$	Ba(56) $6s^1$	*La(57) $5d^1 6s^2$	Hf(72) $5d^2 6s^2$	Ta(73) $5d^3 6s^2$	W(74) $5d^4 6s^2$	Re(75) $5d^5 6s^2$	Os(76) $5d^6 6s^2$	Ir(77) $5d^7 6s^2$	Pt(78) $5d^9 6s^1$	Au(79) $5d^{10} 6s^1$	Hg(80) $5d^{10} 6s^2$	Tl(81) $6s^2 6p^1$	Pb(82) $6s^2 6p^2$	Bi(83) $6s^2 6p^3$	Po(84) $6s^2 6p^4$	At(85) $6s^2 6p^5$	Rn(86) $6s^2 6p^6$
$7(26: Fr_{87} - Cn_{112})$	Fr(87) $7s^1$	Ra(88) $7s^2$	**Ac(89) $6d^1 7s^2$	Rf(104) $6d^2 7s^2$	Db(105) $6d^3 7s^2$	Sg(106) $6d^4 7s^2$	Bh(107) $6d^5 7s^2$	Hs(108) $6d^6 7s^2$	Mt(109) $6d^7 7s^2$	Ds(110) $6d^8 7s^2$	Rg(111) $6d^9 7s^2$	Cn(112) $6d^{10} 7s^2$						

f-Block Elements

Group 3 Period 6 Succeeding La*	Ce(58) $4f^1 5d^1 6s^2$	Pr(59) $4f^3 6s^2$	Nd(60) $4f^4 6s^2$	Pm(61) $4f^5 6s^2$	Sm(62) $4f^6 6s^2$	Eu(63) $4f^7 6s^2$	Gd(64) $4f^7 5d^1 6s^2$	Tb(65) $4f^9 6s^2$	Dy(66) $4f^{10} 6s^2$	Ho(67) $4f^{11} 6s^2$	Er(68) $4f^{12} 6s^2$	Tm(69) $4f^{13} 6s^2$	Yb(70) $4f^{14} 6s^2$	Lu(71) $4f^{14} 5d^1 6s^2$	Lanthan
Group 3 Period 7 Succeeding Ac**	Th(90) $6d^2 7s^2$	Pa(91) $5f^2 6d^1 7s^2$	U(92) $5f^3 6d^1 7s^2$	Np(93) $5f^4 6d^1 7s^2$	Pu(94) $5f^6 7s^2$	Am(95) $5f^7 7s^2$	Cm(96) $5f^7 6d^1 7s^2$	Bk(97) $5f^9 7s^2$	Cf(98) $5f^{10} 7s^2$	Es(99) $5f^{11} 7s^2$	Fm(100) $5f^{12} 7s^2$	Md(101) $5f^{13} 7s^2$	No(102) $5f^{14} 7s^2$	Lr(103) $5f^{14} 6d^1 7s^2$	Actinid

The atomic number of the elements is given in the bracket. The valence shell electronic configuration of the elements has also been given. This table is also known as extended or Bohr's Periodic table.

Table 2.3 Modern or long form of the periodic table.

The detailed discussion of the modern periodic table is given below:

Groups:

In terms of the electronic configuration/arrangement in atoms of the elements, a group consists of elements whose atoms have the same outer most shell electronic configuration (except some of the higher homologues of iron triad). According to IUPAC (International Union of Pure and Applied Chemistry), the groups are numbered as 1,2,3……17,18. Also there is yet another system in practice among the authors in chemistry according to which groups are named as IA, IB, IIA, IIB, IIIA, IIIB. ………..VIIA, VIIB, VIII and zero group in place of numbering the groups from 1 to 18. In the **table 2.3**, both the systems of numbering the groups have been given. At the same time, the elements have been allocated the blocks in the table *viz.,* groups 1 or (IA) and 2 or (IIA) have been placed in s-block, the groups 13 or (IIIA), 14 or (IVA)……….17 or (VIIA) and 18 or (zero group) have been included in p-block. These elements of s and p-block (total 8 columns) are collectively called **main group elements.** The elements placed in s-block and p-block except the elements of groups 18 (zero group) are also known as **representative elements** and zero group elements are called inert or noble gases. The elements of the groups 3 or (IIIB), 4 or (IVB),……..7 or (VIIB), 8 to 10 or (VIII),11 or (IB) and 12 or (IIB) (total ten vertical columns) have been placed in d-block (also called transition elements). There are 28 elements arranged separately in two horizontal rows at the bottom of the main body of the periodic table, each row containing 14 elements. These have been included in f-block also known as innertransition elements or rare earth metals. First row of the elements is called 4f-block elements or lanthanides because they all are having almost similar properties and follow the element lanthanum. The second row is the 5f-block elements or actinides as they fall after actinium and also have almost similar properties.

The transition elements have been placed between s-and p-block elements and inner transition elements within transition elements.

Periods:

The modern periodic table has seven periods. Each period begins with alkali metal (except first one) and ends at a noble gas. The elements in the periods have also been arranged in the increasing order of their atomic numbers and it increases by one unit at each step. The first three periods are known as short periods:

The elements of first period are H_1 and He_2 only (2 elements) The second period contains the elements from Li_3 to Ne_{10} (8 elements) and the third period includes the from Na_{11} to Ar_{18}(8 elements). The next three periods are collectively called long periods and include the elements as follows:

Fourth period: potassium	(K, Z= 19) to krypton (Kr, Z = 36)	(18 elements)
Fifth period: rubidium	(Rb, Z = 37) to xenon (Xe, Z = 54)	(18 elements)
Sixth period: caesium	(Cs, Z = 55) to radon (Rn, Z = 86)	(32 elements).
Seventh period: francium	(Fr, Z = 87) to copernicium (Cn, Z = 112)	(26elements, incomplete)

The seventh period will be completed at Z = 118 (a noble gas) but at present it is in complete. All the elements of this period are radioactive.

The elements of third period except Ar (Na_{11} - Cl_{17}) are called typical elements.

The typical feature of the long form of periodic table is that the elements of 4th, 5th and 6th periods which fall under main group elements are sometimes called the **"normal elements"** because they resemble the elements of 2nd and 3rd periods below which they are placed. The 6th period also includes 14 elements (Z = 58 to 71) which follow lanthanum (La_{57}) and hence are known as lanthanones or lanthanides. The 7th Period contains another series of 14 elements (Z = 90 to 103) following actinium (Ac_{89}), therefore these elements are called actinones or actinides. The elements beyond uranium (U, Z = 92) *viz.*, Z = 93 to 103 (neptunium to lawrencium) are known as trans- uranic elements and have been prepared artificially in the laboratory.

Lanthanides:	Ce_{58}	14 elements	Lu_{71}
Actinides:	Th_{90}	14 elements	Lr_{103}

In general, all the elements of the long form of periodic table have been divided into four categories:

(i) **Representative elements:**

These are the main group elements including the groups 1,2,13…….17 which have either ns^1 or ns^2 and $ns^2\ p^x$ (x = 1-5) outer shell electronic configuration where n is the highest value of principal quantum number. All these elements have been placed in subgroups A of the periodic table.

(ii) **Noble gases:**

These also fall within main group elements and include group 18 (or zero) elements. These all have completely filled s- or s- and p-subshells of outer most or ultimate shell with highest n value, i.e. ns^2 or ns^2p^6 (ns^2 for He). These have also been placed in subgroup A of periodic table.

(iii) **Transition metals:**

These are the elements of groups 3 to 12 and in general have incomplete d-subshell of the penultimate shell and filled s-subshell of ultimate shell with highest n-value. But the elements of some of the groups also have incompletely filled s-subshell of the ultimate shell in addition to incompletely filled d-subshell of the penultimate shell. All these elements have been placed in subgroups B of the periodic table.

(iv) **Innertransition elements:**

These elements are said to belong to group 3 or (IIIB) due to close similarity in their chemical properties with those placed in group 3. These elements genrally have incompletely filled (n-1) d and (n-2) f-subshells.

According to their electronic configuration and the type of subshell to which the last of differentiating electron enters in the atom of the elements, the elements in the modern periodic table have been classified into four blocks i.e. s, p,d and f-block elements.

(i) s-Block elements:

All these elements are metals and solid except H and He which are gases. These are the elements in which the last electron enters the s-subshell. The elements of group 1 (alkali metals, *viz.*, Li, Na, K, Rb, Cs, Fr) and group 2 (alkaline earth metals, *viz.*, Be, Mg, Ca, Sr, Ba, Ra) belong to this block in addition to hydrogen (H) and helium (He). The general valence shell electronic configuration of these elements is ns^x (x = 1 or 2) where n is the number of valence shell or number of period which the element belongs to.

(ii) p-Block elements:

These elements in which the differentiating electron enters the orbitals of p-subshell of the valence or outer most shell are called p-block elements. The elements of groups 13 to 18 (except He with configuration $1s^2$) belong to this block. The group number and the elements contained in them are shown here:

Group 13 : B, Al, Ga, In, Tl
Group 14 : C, Si, Ge, Sn, Pb
Group 15 : N, P, As, Sb, Bi
Group 16 : O, S, Se, Te, Po
Group 17 : F, Cl, Br, I, At
Group 18 : Ne, Ar, Kr, Xe, Rn

The general valence shell electronic configuration of these elements in $ns^2 np^x$ (x=1 to 6) and n is the number of shell. The elements of this block exist in all the three states of matter *viz.* solid, liquid and gas. Most of them are non- metals and the rest are metals and metalloids (or semimetals).

(iii) d-Block elements:

The elements in which the last electron enters the orbitals of (n-1) d subshell, (i.e. the subshell of penultimate shell) and d-orbitals are, thus, being progressively filled are known as d-block elements. These elements are also termed as **transition elements** and have been placed in the middle between s-block and p-block elements in the periodic table. Thus, these elements serve as a bridge or transition between highly electropositive s-block and highly electronegative p-block elements thereby being responsible for gradual change in the properties along a period. Hence the name, transition elements has been given to them. These include the elements of group 3 to group 12 (ten columns). These have further been categorised into 3d, 4d, 5d and 6d series depending on the shell number whose d-orbitals are being filled. Each of these series contains ten elements as given below:

3d series: scandium (Sc, Z = 21) to zinc (Zn, Z = 30)
4d series: yttrium (Y, Z = 39) to cadmium (Cd, Z = 48)
5d series: lanthanum (La, Z = 57), hafnium (Hf, Z = 72) to mercury (Hg, Z = 80)
6d series: actinium (Ac, Z = 89), rutherfordium (Rf, Z = 104) to copernicium (Cn, Z = 112)

The general valence shell electronic configuration of these elements is $(n\text{-}1)\ d^x\ ns^{1 or 2}$ (x = 1 to 10). All these elements are metalsand solid except Hg (a liquid).

(iv)f-Block elements:

In these elements, the last or differentiating electron, in general, enters the orbitals of (n-2) f-subshell, i.e. the subshell of antipenultimate shell. All these elements are metals and solids. These elements are also called **inner transition elements** because they have incomplete f-subshell as well as incomplete d-subshell and fall within d-block elements. These elements have been divided into two series of 14 elements each, as follows:

4f-series elements (lanthanides): cerium (Ce, Z = 58) to lutetium (Lu, Z = 71)

5f- series elements (actinides): thorium (Th, Z = 90) to lawrencium (Lr, Z = 103)

The general valence shell electronic configuration of these elements is $(n-2)\ f^{0-14}\ (n-1)d^{0-2}ns^2$.

It has been noticed that for s and p-block elements, the outermost shell itself is the valence shell. For d-block elements, two subshells *viz.,*(n- 1)d and n-s subshells taken together form the valence shell. For f-block elements, three subshells *viz.,* (n-2)f (n-1)d and n-s subshells jointly form the valence shell. This is due to nearly similar energy of these subshells. A valence shell is that shell of the atoms of the elements, from which the electrons are used for bond formation or chemical combination.

For long form of the periodic table, it may be noted that the s-block elements (group 1and2) have been placed in the extreme left portion of the table and the p-block elements arekept in the extreme right portion. The middle portion includes d-block elements. At the bottom, f-block elements have been placed separately in two series/rows.

Merits and demerits of modern periodic table

By taking the atomic number as the basis for the classification of the elements in the modern periodic table, most of the demerits of Mendeleeff's periodic table have been removed.

(i) The main characteristic of the modern or long form of the periodic table is that the classification of the elements has been made on the basis of their atomic number which gives an information regarding the valence shell electronic configurations of the elements. If we know theelectronic configurationor the atomic number of an element, we can find out its position in the periodic table, i.e. to which group and period that element belongs. For example, for an element the valence-shell electronic configuration is $3s^23p^5$. This gives us the information that 3 is the value of n, i.e. the period and there are 7 electrons in the valence shell, means the elements belongs to VIIA group. Therefore, the element is a member of VIIA group (group 17) and 3rd period.

(ii) The subgroups have been placed separately in the modern periodic table thereby making it easy to have the information regarding the properties of the elements.

(iii)The modern periodic table still has the drawback regarding the position of hydrogen which shows some properties similar to those of the group 1 elements (i.e. alkali metals) and some with the group 17 elements (i.e. halogens). Also the lanthanides and the actinides have not yet been included in the main body of the periodic table.

Nomenclature of the elements with Z = 104 and beyond

A systematic naming scheme was approved by IUPAC in 1977 for the new elments discovered around that period or would be discovered thereafterhaving Z $\geq$ 104. It was decided that a three-letter symbol derived directly from the atomic number would be used by using following numerical roots:

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

These names and symbols can be used for elements with Z = 104 and beyond.These trivial names have been internationally accepted. Hence, the element with Z = 104 is un-nil-quadium (Unq), that with Z = 106 is un-nil-hexium….. and the elements with Z = 109 is un-nil–ennium (Une) etc.

The general names of the elements from Rf (Z = 104) to Cn (Z = 112) are given here:

Symbol	Atomic Number	Name
Rf	104	Rutherforduim
Db	105	Dubnium
Sg	106	Seaborgium
Bh	107	Bohrium
Hs	108	Hassium
Mt	109	Meitnerium
Ds	110	Darmstadtium
Rg	111	Roentgenium
Cn	112	Copernicium.

Earlier, the elements with Z = 104 was named as kurchatovium (Ku) and Z = 105 as hahnium (Ha)

Periodicity of properties

In the modern periodic table, the term periodicity of properties implies that the elements of similar properties reappear at a certain regular intervals of atomic numbers. On examining the properties of elements, it has been found that the elements of the same group have similar properties. These numbers at which this repetition occurs, are 2,8,18 and 32, i.e. we have to pass these numbers to come across an element of similar properties in a group. These numbers are referred to as magic numbers as stated earlier.

Cause of periodicity

When we look into the electronic configuration of the elements, we find that all the elements belonging to a particular group have similar outer or valence shell electronic configuration. For example, elements of group 1 (IA) have ns^1, those of group 3(IIIB) have $(n-1)d^1ns^2$, the elements of group 13 (IIIA) have ns^2p^1 and those of group 17 (VIIA) have ns^2p^5 valence shell electronic configuration. Because of similar valence shell electronic configuration/arrangement, the elements of a particular group have similar properties.

2.5 SUMMARY

This unit contains a comprehensive text on the history of the periodic table i.e. how the historical attempts were taken to develop a classification of elements system in a manner which could facilitate their study, during the time of Dobereiner, Duma and Newlands. The laws of periodic table and on the basis of these laws, the attempts to classify elements have also been exhaustively discussed. In the light of these laws, the elements, arranged in the tabular form, have been given, *viz.* Mendeleeff's pefiodic table, Modified form of Mendeleeff's periodic table (both on the basis of atomic weights) and modern periodic table on the basis of atomic number. In addition to this, the elements have also been classified in the blocks (with general characteristics of each block). A concise description of the periodicity of properties and its cause have been discussed.

2.6 TERMINAL QUESTIONS

i) Write a concise note on Dobereiner's law of triads.
ii) Discuss in short, the Newland's law of octaves.
iii) State the Mendeleeff's periodic law.
iv) Give a brief discussion of Mendeleeff's periodic table.
v) State and explain the merits and demerits of Mendeleff's periodic talbe.
vi) Give a brief account of modern periodic law.
vii) Discuss the main features of modern periodic table.
viii) What are the transition elements and why are they called so?
ix) Write a brief note on inner transition elements.
x) What is the cause of periodicity of properties in the elements in periodic table?
xi) What are the p-block elements?

xii) “The group and the period assigned to the element with $3d^1 4s^2$ valence shell configuration are:

(a) IIIB & 3 (b) IIIB & 4 (c) IIIA & 3 (d) IIIA & 4

xiii) Nepturium (Z = 93) is an elements of

(a) 4f- series (b) 4d- series (c) 5f -series (d) 5d -series.

xiv) Seaborgium (Z = 106) is a member of

(a) 6d- series (b) 5d-series (c) 4d-series (d) 3d-series.

2.7 ANSWERS

i) Please refer to history of periodic table.

ii) Please see the history of periodic table.

iii) Please refer to the laws of periodic table. (A)

iv) Please refer to Mendeleeff’s periodic table.

v) Please see the merits and defects of Mendeleeff’s periodic table.

vi) Please refer to the modern periodic table.

vii) Please refer to the modern or long form of periodic table.

viii) Please refer to the d-block or transition elements.

ix) Please refer to the f block or inner transition elements.

x) Please see the cause of periodicity of properties

xi) Please refer to the p-block elements.

xii) b

xiii) c

xiv) a

2.8 REFERENCES

1. Principles of Inorganic Chemistry: B. R. Puri, L.R. Sharma & K. C. Kalia, Milestone Publishers and Distributers, Daryaganj, Delhi (2013).
2. Selected topics in Inorganic Chemistry: W.U. Malik, G.D. Tuli & R.D. Madan, S. Chand & Co. Ltd., New Delhi (1993).
3. Comprehensive Inorganic chemistry: Sulekh Chandra, New Age International (Pvt.) Ltd., New Delhi (2004).
4. The Nature of the Chemical Bond: Linus Pauling, 3rd Edn., Cornell University Press, New York (1960).
5. A Simple Guide to Modern Valency Theory: G.I. Brown, Revised Edn., Longmans Green, London (1967).

6. Advanced Inorganic Chemistry: Satya Prakash, G.D. Tuli, S.K. Basu and R.d. Madan, Vol. **I**, 7th ed., S. Chand & Co. Ltd, New Delhi (1998).
7. Shriver and Atkins' Inorganic Chemistry: Peter Atkins *et. al*., 5th Edn., Oxford University Press, New York (2010).

UNIT 3: PERIODIC PROPERTIES

CONTENTS:

3.1. OBJECTIVE

The objective of writing the subject matter of this unit is to provide the readers an adequate knowledge of the properties of atoms of the elements which are called atomic or periodic properties. A sincere attempt has been made to provide the information regarding the size of the atoms/ions and their determination, effect of energy supplied to an atom of the elements, the behavior of the atoms towards the electrons trying to enter the region of their influence as well as those lying between the atoms as bonding pairs, variation of atomic properties of elements alongthe periods (horizontal rows) anddown in groups (vertical columns) and some other interesting facts related to these properties.

3.2. INTRODUCTION

According to modern Periodic law, the atomic properties of the elements, *viz.* atomic and ionic radii, atomic volume, ionization potential (or energy), electron affinity or affinity energy and electronegativity and properties associated with them, viz. oxidizing and reducing properties, metallic (or electropositive) and non-metallic (or electronegative) properties are the periodic functions of their atomic number. Hence the term periodic means the recurrence of similar properties of elements after certain regular intervals, also called the periodicity. These properties have been found to depend on the electronic configuration of the elements. It means the cause of periodicity in properties of elements appears to lie in the recurrence of similar valence shell configuration of their atoms at certain regular intervals. Though, these properties apply up to some extent to all the elements of the periodic table, yet special emphasis will be laid down on the main group elements while taking the examples of the applications of the properties.

3.3. PERIODIC PROPERTIES

3.3.1 Atomic and Ionic Radii:

These terms correspond to the size of the atoms and ions which are represented by the magnitude of their radii. Atomic radii, in general, are used for the distance between the nucleus and electron cloud of the outer most shell of the atoms. Since it is impossible to isolated an individual atom or ion and at the same time, the electron cloud, according to wave mechanical concept, is said to come closer to the nucleus at one moment and to go away from it at the other moment, i.e. it does not remain at constant distance from the nucleus, hence it is rather impossible to measure this distance by any means. These quantities are, however, generally derived indirectly from the measured distance between the nuclei of two bonded atoms in a gaseous molecule, generally known as inter nuclear distance (or bond distance) or between the nuclei of two neighbouring ions in crystalline solids called inter ionic distance.

The experimental techniques like Infrared or microwave spectroscopy, X-ray diffraction, electron diffraction etc. are used to determine the internuclear distance in covalent molecules and interionic distance in ionic substances. These determinations become essential to correlate certain physical properties of elements with them because density, melting point, boiling point etc. are related to the size of atoms.

Classification of Atomic Radii

For the purpose of feasibility, the atomic radii of the elements have been explained in three operational categories, as follows:

Atomic redii:

A. Covalent radii

B. Metallic or crystal radii

C. van der Waals' radii

A. Covalent radii

Covalent molecules may be formed by two similar (A_2 type) or two dissimilar atoms (AB type). Hence, covalent radius of an atom is conveniently defined as "**half of the distance between the nuclei of two atoms of the same element bonded together in a molecule by a single covalent bond**". Thus, for the atom A in A_2 type molecule in which two A atoms are linked by a single bond, covalent radius, denoted by r_A, is given as:

$$d_{A-A} = r_A + r_A = 2r_A \qquad \text{.............(3.1)}$$

$$\text{or } r_A = \frac{dA - A}{2} \qquad \text{........... (3.2)}$$

where d_{A-A} is the internuclear distance between two A atoms in A_2 molecules; r_A in equation 3.2 is known as single bond covalent radius of atom A and is used for a gaseous diatomic molecule. For example, internuclear distance (d_{H-H}) in H_2 molecule is 0.74 Å. The covalent radius of H – atom, $r_H = \frac{dH-H}{2} = \frac{74}{2}$ pm = 0.37Å. Similarly, the internuclear distance (d_{Cl-Cl}) atom ($r_{Cl)}$ may be calculated as:

(Å = 10^{-8} cm)

$$r_{Cl} = \frac{dCl-Cl}{2} = \frac{1.98}{2} \text{ pm} = 0.99\text{Å}.$$

For atoms bonded together to form and extensive three dimensional network, atomic radius in simply "**half of the distance between the nuclei of two neighbouring atoms**" i.e.

$$r_{cov} = \frac{\text{inter nuclear distance}}{2}$$

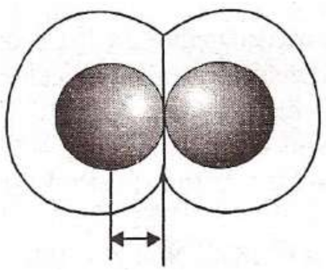


Fig. 3.1 Diatomic molecule (covlalent radius)

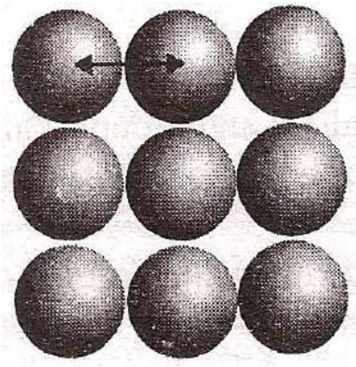


Fig. 3.2 Bulk of atoms (internuclear distance)

In hetero nuclear molecules (e.g. AB type), the single bond covalent radius can be calculated as given below;

(a) When the atoms A and B bonded together by purely covalent bond and the electronegativities of these two atoms are almost same, the internuclear distance is equal to the sum of radii of A and B;

$d_{A\text{-}B} = r_{A} + r_{B}$ (when $\chi_A = \chi_B$) …………………(3.3)

The internuclear distance, $d_{A\text{-}B}$, can be measured by experimental method and if r_A or r_B (any one) is known, the other unknown term (r_A or r_B) can be calculated by using the equation 3.3. The value of r_A or r_B may be obtained from $r_A = \frac{dA-A}{2}$ or $r_B = \frac{dB-B}{2}$.

(b) If the electronegativities of the two combining atoms are not the same ($\chi_A \neq \chi_B$), then the experimental value of $d_{A\text{-}B}$ has been found less than the calculated value obtained as a sum of covalent radii r_A and r_B of the heteroatomic molecule. For example,

(i) in $(CH_3)_3$ N molecule,

$(d_{N\text{-}C})$ exp = 1.47 Å

and $(d_{N\text{-}C})_{cal.} = r_N + r_C = 0.75+0.77 = 1.52$ Å

(ii) In HF molecule,

$(d_{H\text{-}F})_{exp} = 0.92$ Å

and $(d_{H\text{-}F})_{cal.} = r_H + r_F = 0.37+0.72 = 1.09$ Å

This shortening of $d_{A\text{-}B}$ bond length may be due to the following factor:

(a) The higher ionic character of the bond between A and B atoms with larger difference in electronegativities of the hetero atoms. In such a case more electronegative atom attracts the shared pair of electrons towards itself thereby developing slight negative charge on that atom due to accumulation of electrons closer to it and positive charge of equal magnitude on the other atom. This development of opposite charges brings the atoms closer to each other. That is why the experimental value of $d_{A\text{-}B}$ is less than the calculated value. Some correction measures have been suggested in such cases.

In order to compensate this, the following correction has been suggested:

$d_{A\text{-}B} = r_{A} + r_B - 0.09 (\chi_B - \chi_A)$ …….(3.4)

(schoemaker and Stevenson)

Still, if the discrepancy remains, another correction measure may be applied (Porterfield):

$d_{A\text{-}B} = r_{A} + r_B - 0.07 (\chi_B - \chi_A)^2$ …….(3.5)

(b) The other factors in some cases, may be multiplicity of bonds and effective nuclear charge which cause reduction in the length of covalent bonds and as a consequence in covalent radii. For example, it has been found that single bond covalent radius> double bond covalent radius> triple bond covalent radius. This is because the formation of multiple bonds brings the combining atoms closer to each other and the bond length is reduced.

Table 3.1: Covalent radii (single bond radii) for hydrogen and some p-block (non- metallic and metalloid) elements except noble gases (in Å)

s-block **p-block**

Group number	1	2	13	14	15	16	17
Elements with covalent radii	H	-	B	C	N	O	F
	0.37	-	0.82	0.77	0.75	0.73	0.72
	-	-	-	Si	P	S	Cl
			-	1.11	1.06	1.02	0.99
				Ge	As	Se	Br
				1.22	1.20	1.16	1.14
				-	Sb	Te	I
					1.40	1.36	1.33

Among the s-and p-block elements, only the non-metallic elements and metalloids have been taken to tabulate the covalent radii because the formation of covalent bond, in general, is the exclusive property of the non-metals and metalloids. Noble gases have also been excluded from the table because these, except a few, do not participate in covalent bond formation.

Factors affecting the magnitude of covalent radii

There are many factors which influence the magnitude of covalent radii. Some of them are:

(i) **Effective nuclear charge ($Z_{eff.}$)**

As the value of Z_{eff} increases, the force of attraction between the nucleus and outermost shell electrons also increases thereby decreasing the covalent radii of the elements, i.e. $r_{cov.}\ \alpha\ \frac{1}{Zeff}$

(ii) **Principal quantum number (n)**

This gives the number of shells present in the atoms of the elements. As the value of principal quantum number increases the outermost electrons get farther away from the nucleus and covalent radius also increases provided other factors remain the same, i.e. $r_{cov.}\ \alpha\ n$

(iii) **Multiplicity of Bonds**

With the increase in the number of bonds between the atoms, these come closer to each other thereby decreasing the covalent radii i.e. $r_{cov.} \alpha \frac{1}{multiplicity\ of\ bonds}$

B. Metallic or Crystal Radii

These terms are taken synonymous to covalent radii of metal atoms, though metals generally do not form covalent compounds except hydrides and organo- metallic compounds. Further, metals are assumed to be closely packed spheres in the crystals in which their outer boundaries touch one another. Thus metallic or crystal radius may be theoretically defined as **"half of the distance between the nuclei of any two adjacent metal atoms in close-packed metallic crystal"** For example, the internuclear distance between any two adjacent sodium atoms in a crystal of sodium metal in 3.80 Å. Hence crystal or metallic radius of sodium metal is $\frac{3.80}{2}$ = 1.90 Å

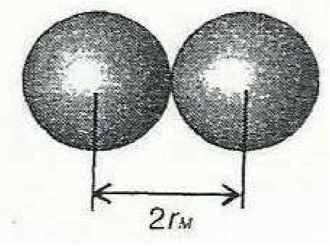


Fig. 3.3 Metallic radius

In practice, in the metallic phase, atomic volumes of metal atoms can be determined from their atomic masses and respective densities. Thus, atomic volume = $\frac{\text{mass}}{density}$. From these data, metallic radii can be obtained. It has been found that the covalent radii of metal atoms determined in metal hydrides and organimatallic compounds and metallic radii determined from atomic volumes in metallic phase have almost similar values though not exactly equal. Hence,the term metallic covalent radii can be used. The metallic radii have slightly higher (10%) value than metallic covalent radii because individual bond in metals is weaker and longer than the covalent bond.

Group number	1	2	13	14	15	16
Elements with metallic radii	Li	Be	-	-	-	-
	1.55	1.12	-	-	-	-
	Na	Mg	Al	-	-	-
	1.90	1.60	1.43	-	-	-
	K	Ca	Ga	-	-	-
	2.35	1.97	1.41	-	-	-
	Rb	Sr	In	Sn	-	-
	2.48	2.15	1.66	1.62	-	-
	Cs	Ba	Tl	Pb	Bi	Po
	2.67	2.22	1.71	1.75	1.70	1.76

Table 3.2 Metallic radii of main group metals (in Å)

C. van der Waals' radii

In solid state, the nonmetallic elements usually exist as aggregations of molecules. Although the bonding within a nonmetal molecule is more or less covalent in character yet the binding force between the molecules is van der Waals'force. Thus each molecule assumes equilibrium position within the crystalline solid. It is to be noted that these forces are absent if the substances are in the gaseous state. van der Waals' radius can be defined as" **half of the distance between the nuclei of two non-bonded but adjacent atoms belonging to two neighbouring molecules**". These radii have higher values by 90-100% in lighter elements and 70-80% in heavier elements than covalent radii because of non-bonded type of binding force between the molecules. The values of van der Waals' radii are obtained from X-ray studies of various non-metallic elements in the solid state. On comparing the covalent radii and van der Waals' radii of the nonmetallic elements, it is noted that the van der Waals' radii have higher values. Please refer to **table 3.2** and **table**

Group number	1	15	16	17	18

Elements with van der Waal's radii	H				He
	1.20				1.20
		N	O	F	Ne
		1.50	1.40	1.35	1.60
		P	S	Cl	Ar
		1.90	1.85	1.80	1.91
		As	Se	Br	Kr
		2.00	2.00	1.95	2.00
		Sb	Te	I	Xe
		2.20	2.20	2.15	2.00

Table 3.3

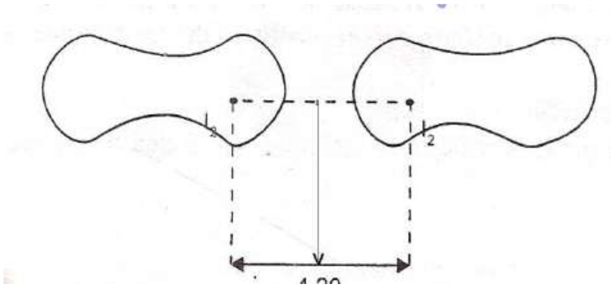


Fig. 3.3 van der Waals' radii

Periodic trends of atomic radii

(a) **Variation in a period**

The atomic radii (*viz.* covalent radii, metallic radii and van der Waals' radii) and hence the atomic size, in general, decrease on moving from left to right in a period. This is because the atomic number in a period increases by one unit at each step but the electrons in all the elements in a period enter the same outer or valence shell. Hence, there operates an increased force for attraction between these outer electrons and the nuclear charge. As a result, the atomic radius or atomic size decreases regularly except the noble gases. For example, we can take the elements of second period and hydrogen. The term covalent radius does not apply to the noble gases. van der Waals’ radii are applicable to all nonmetallic elements including noble gases but the values for noble gases are exceptionally high due to larger repulsion among the monoatomic species with large number of electron.

One Å unit is equal to 10^{-10}m

Elements	H	C	N	O	F	Ne
Covalent radii (in Å)	0.37	0.77	0.75	0.73	0.72	-
van der Waals’ radii (in Å)	1.20	-	1.50	1.40	1.35	1.60

(b) **Variation in a group**

On going down a group, the atomic sizes of elements increase continuously both in metals and non metals as is evident from the table of covalent radii, metallic radii and van der Waals’ radii except the metals of third transition series whose atomic sizes are almost similar to those of second transition series metals. At the same time lanthanide series and actinide series of metals have deceasing trend in their metallic radii.

The regular increasing trend in atomic sizes among the main group elements is due to the introduction of new shell at each step in a group which produces larger effect than that produced by the increase in effective nuclear charge.

Ionic radii

Though, it is very difficult to define ionic radius, yet an approximate definition can be given as “**the effective distance between the nucleus of an ion and the point up to which the nucleus exerts its attractive influence on the electron cloud of the ion**”. Because it is rather impossible to determine the outer boundary of an ion, therefore if the ions in an ionic crystal are taken as spheres whose outer boundaries are touching one another, the interionic distance (or internuclear distance) may be supposed to be the sum of the radii of the two ions (an additive property).

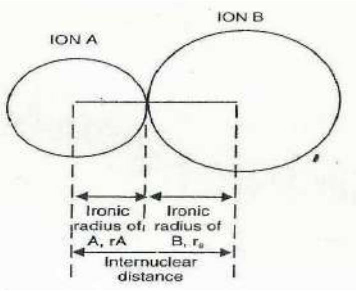


Fig. 3.4 The ionic radius

X-ray analysis of ionic crystals is used for measuring the eqiulibrium distance between the nuclei of the two adjacent ions called interionic distance in taking the ions as spheres. This distance in taken as the sum of the ionic radii of the two ions. e.g.

$d_{C^+-A^-} = r_{C^+} + r_{A^-}$ …….(3.6)

This equation can be used to find out the ionic radius of a cation or an anion. The interionic distance $d_{C^+A^-}$ can be measured by experimental method and if the radius of any one ion is calculated by some other method, the radius of antother ion can be obtained by using the above equation. For example, the inter nuclear distance between sodium and chloride ions ($d_{Na^+Cl^-}$) in NaCl crystal is 2.76Å and radius of sodium ion (r_{Na^+}) is 0.95 Å. From these values we can calculate the radius of chloride ion (r_{Cl}) as follows:

$d_{Na^+Cl^-} = r_{Na^+} + r_{Cl^-}$

Putting the values of $d_{Na^+Cl^-}$ and r_{Na^+}, we get 2.75 Å = 0.95 Å + r_{Cl^-}

$\therefore r_{Cl^-} = 2.76 – 0.95Å = 1.81Å$

Periodic trends of ionic radii

Periodic variation of ionic radii can be easily visualised in main group elements though it is, in general, applied for transition elements.

(a) **Variation in a period**

Since atomic size decreases along a period from left to right, the cationic or anionic size also decreases in the same direction. For transition elements this trend is observed if they are in the same oxidation state.

(b) **Variation in a group**

As we move down a group of main group elements, the cationic or anionic size increases regularly provided the elements are in the same oxidation state. Similar trend, in general, is observed for transition elements though the change in cationic size is very small or negligible between second and third transition series elements. Reverse trend has been observed in case of lanthanides and actinides where ionic size decreases in the series.

Some important facts regarding ionic radii are given below:

(i) **Ionic radii of isoelectronic species**

The isoelectronic species are the cations, anions and atoms of different elements having same number of electrons and same electronic configuration. For example, a common isoelectronic series with ten electrons, i.e. $1s^2\ 2s^2\ 2p^6$ configuration is given here with their radii;

Ion/atom	C^{4-}	N^{3-}	O^{2-}	F^-	Ne	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Atomic numbers	6	7	8	9	10	11	12	13	14
Radius (Å units)	2.60	1.71	1.42	1.36	-	0.95	0.65	0.50	0.41

It is evident from this table that, as the atomic number (or nuclear charge) of the parent atoms from which the ions have been derived, increases the ionic radius decreases. This is because with the increase in the nuclear charge, the attractive force between the nucleus and the outer electrons also increases thereby the electrons come closer to the nucleus and consequently the size of the ions decreases.

(ii) A cation is smaller in size than its parent atom because a cation is formed by the removal of electron (s) from the neutral atom; hence the number of electrons becomes less than the number of protons (nuclear charge). As a result, the electrons are strongly pulled by the nucleus thereby causing a contraction in the size of the cation. Therefore, the cation is smaller in size than its parent atom.

(iii) An anion is larger is size than its parent atom. This is because, an anion is formed by the addition of extra electron (s) in a neutral atom. Thus the number of electrons becomes greater than that of protons (nuclear charge) and the electrons are loosely held by the nucleus. As a result, the anionic size becomes larger than the size of the parent atom.

(iv) For the cations or the anions of the same element in different oxidation states, the cationic size decreases but the anionic size increases with the increasing oxidation states, i.e. for anions: $r_{A^-} < r_{A^{2-}} < r_{A^{3-}} < r_{A^{4-}}$ …….etc. and for cations $r_{C^+} > r_{C^{2+}} > r_{C^{3+}} >$ ……etc. (C = cation, A = anion)

Factors affecting ionic radii

The main factors that affect ionic radii are as follows:

(a) **Crystal coordination number (CCN)**

With the increase in the crystal coordination number, the interionic distance also increases thereby increasing the ionic radii, For example, the radius of Cl^- ion (r_{Cl^-}) in CsCl crystal (C.C.N. = 8) is slightly higher than its radius in NaCl Crystal (CCN =6). This is because with the higher CCN, the number of ions surrounding a particular ion is greater, causing less attraction between the oppositely charged ions than that with lower CCN i.e. $r_{ion} \alpha$ CCN

(b) **Radius ratio (R_r)**

Radius ratio ($R_r = \frac{rc^+}{rA^-}$) also affects the magnitude of ionic radius. If the R_r is larger due to large cation and small anion, the anion-anion repulsion is less and the interionic distance becomes shorter than the sum of the ionic radii (i,e. $d_{C+A-} < r_C + r_{A^-}$) but if R_r is smaller due to small cation and large anion, the anion-anion repulsion is more and interionic distance is greater than the sum of the ionic radii (i.e. . $d_{C^+A^-} > r_C + r_{A^-}$)

(c) **Covalent character of Ionic Bond**

Ionic radii decrease as the covalent character in ionic bond increases. $r_{ion} \alpha \frac{\mathbf{1}}{\mathbf{covalent\ character}}$.

3.3.2 Ionization energy (IE):

This term is related with the removal of electron (s) from the neutral atom and converting it into a positive ion (or cation). If the energy is supplied to an atom, its electron (s) may be promoted to a higher energy level and if this energy is sufficient enough, the electron (s) may completely be removed from it giving a cation. Thus "**the minimum amount of energy required to remove a loosely bound electron from an isolated gaseous atom of an element in its ground state is called its ionization energy**". In the definition, gaseous atoms are specified because an atom in gas phase is uninfluenced by its neighbours and there is no intermolecular forces to take into account while measuring ionization energy. This can be shown as follows:

$$C(g) + (IE)_1 \longrightarrow C^+ (g) + e \text{ (energy absorbed, endothermic process)}$$

In this process, if one electron is removed, it is termed as the first ionization energy, $(IE)_1$. For many electron atom, if more electrons are removed from an atom, the ejection of electrons occurs one by one in steps depending on the amount of energy absorbed/supplied. Thus corresponding to the removal of second electron, the energy is known as second ionization energy, $(IE)_2$ and if third electron is removed, the corresponding energy which has to be supplied is called third ionization energy, $(IE)_3$ and so on. Alternatively, these are also known as successive ionization energies. The sequence of ionization energies in their increasing order may be given as:

$(IE)_1 \ll (IE)_2 \ll (IE)_3$ …………..$(IE)_n$.

This is because when an electron is removed from a neutral atom to give a cation, the number of the remaining electrons of the cation becomes less than the nuclear charge and greater attractive force operates between these electrons and nucleus causing contraction in the size of cation. Therefore, more energy is required to remove another electron from the cation, i.e. $(IE)_1 \ll (IE)_2$. Due to the similar reason, still higher amount of energy is required to remove yet another electron, i.e. $(IE)_2 \ll (IE)_3$ and so on.

An alternative explanation for this observation may be given. Since, the magnitude of ionization energy is a measure of tightness with which an electron is held in the atom, hence higher the ionization energy, more tightly the electron is held in the atom and more difficult it is to remove it. The ionization energy is expressed in the units of kilojoules per mole (kJ/mole) or kilo calories per mole (k Cal/mole)

It has been observed that among the elements of the periodic table, the alkali metals have the least and the noble gases have the highest ionization energy values in the respective periods. Helium has the highest value and caesium possesses the lowest value of first ionization energy among all the main group elements.

Atomic Number (Z)	**Element**	**$(IE)_1$**	**$(IE)_2$**	**$(IE)_3$ ……**
1	H	1312	-	-
2	He	2373	5251	-
3	Li	520	7300	11850
4	Be	899	1757	14850
5	B	801	2430	3660
6	C	1086	2350	4620
7	N	1400	2860	4580
8	O	1314	3390	5300

9	F	1680	3370	6050
10	Ne	2080	3950	6120

Table 3.4: The successive ionization energy values (in kJ/ mole) of the first ten element

Factors affecting the magnitude of ionization energy

(i) **Atomic Size** (or The Principal Quantum Number)

As the principal quantum number for the outer electrons increases, the atomic size also increases and the ionization energy of the elements decreases and vice versa, i.e. IE α $\frac{1}{n\ or\ r\ atom}$. This can be seen in a group.

(ii) **Nuclear charge**

As the nuclear charge increases, other factors remaining the same, more and more attractive force operates between the nucleus and outer electron(s). Thus more energy is required for the removal of electron(s) and as a consequence, the ionization energy goes on increasing. This is observed along the periods, in general, IE α nuclear charge.

(iii) Penetrating power of valence electrons

In a given shell, the penetrating power of the electrons decreases in the order s > p > d >f, therefore, ns electrons are more firmly held by the nucleus (due to highest penetrating power) than np – electrons followed by d and f electrons (due to their scattered orientation). Accordingly, the ionization energy decreases as follows: ns >np >nd >nf i.e. IE α penetrating power.

(iv) **Shielding effect of inner electrons**

In poly electron atom, the valence electrons are attracted by the nucleus and at the same time repelled by the inner shell electrons. As a result, the outer most electron experiences less attraction from the nucleus because inner electrons act as screen or shield between outer electrons and nucleus. This effect produced by inner electrons is called the shielding effect. Within a given shell, this effect decreases in the order: s>p>d>f. Thus, an increase in the number of inner or intervening electrons causes more shielding effect thereby decreasing the attractive force between the nucleus and outer electrons. Consequently the ionization energy also decreases, i.e. IE α $\frac{1}{shielding\ effect}$

(v) **Stable electronic configuration**

According to Hund's rule, half filled (*viz.*ns^1, np^3, nd^5 etc.) or completely filled orbitals (*viz.*ns^2, np^6, nd^{10} etc.) are more stable than the partially filled orbitals. Hence more energy is required to remove the electron (s) from such orbitals. This means that the ionization energy of an atom having half filled or completely filled orbitals in its ground state is relatively higher than expected normally from its position in the periodic table. The relative stablility order of such orbitals has been found as $d^5 < p^3 < d^{10} \ll p^6$. For example, the ionization energies for Be ($2s^2$) and N ($2s^2\,2p^3$) in the second period and Mg and P, the higher homologues of Be an N, in the third period are slighty higher than expected values. This is becauseof the extra stability of the electronic configuration of these elements, High values of ionization energy for noble gas elements is also due to stable $ns^2\ np^6$ (He - ns^2) configuration in the vacance shell, i.e. IE$\propto$ stable configuration.

To gain the necessary energy for the removal of electrons from an atom, a potential difference has to be applied across the sample of element. This potential difference giving the necessary energy is called the ionization potential.

Priodic trends

i) Variation along a period

On going from left to right in a period, there is, in general, an increase in the ionization energy values of the elements due to the effect of reduction in the atomic radii and increase in the nuclear charge by one unit at each step but the outer shell remaining the same (n is constant for the elements of a period). Thus, the electrons in these elements are being successively filled to the same shell. Such electrons shield each other poorly from the increasing nuclear charge. As a result, Z_{eff} increases which cause an increase in ionization energy.

There are some exceptions to this trend. Let us consider the elements of secound period i.e. Li_3 to Ne_{10} for which the expected order of ionization energy is Li< Be < B < C< N< O< F < Ne. The experimental values, however, show that Be and N have higher IEvalues than those of the nextelements, i.e. B and O. This anomaly can be explained on the basis of their stable electronic configurations, i.e. Be (ns^2)> B ($ns^2\ np^1$) and N ($ns^2\ np^3$) > O ($ns^2\ np^4$) (please refer to the IE table of elements). This is evident from the ionization energy values of the above elements that it is easier to remove the last and loosely bound electron from B or O-atoms as compared to that from Be or N-atom and thus elements (B and O) have lower first ionization energy values than Be and N.

The elements of the transition series show irregular trends of ionization energies along their periods due to shielding effects and electronic configurations.

ii) Variation in a group

On going from top to bottom in a group of elements, the nuclear charge increases regularly. This must cause an increase in the IEvalues of the elements. At the same time, the atomic size also increases due to the introduction of a new shell at every next element in the group. This causes a decrease in the IE values of the elements. The effect of increased size is more than that due to increased nuclear charge. The net result is the continuous fall in the values of ionization energy down the group.

Alternatively, this trend may also be explained by the fact given here. As we move down a group, the number of inner shell electrons called intervening electrons increases. As a result there in more shielding effect caused by the inner electrons on the outer electrons. This decreases the ionization energy values of the elements in a group.

There are some exceptions also. The first ionization energy of $Ga_{31,}$ an element of fourth period is slightly higher than that of Al_{13}, the element of third period [$(IE)_1$ of Al = 577.6 kJ/mole and $(IE)_1$ of Ga= 578.8 kJ/mole]This is perhaps due to the poor shielding effect of $3d^{10}$ electrons.

Also, the third row of transition elements shows higher value of ionization energy as compared to second row elements. This is due to the decrease in size of these elements as a result of insertion of lanthanides in 6th period (Lanthenide contraction).

Application of ionization energy

(i) **Prediction of electropositive character**

The electropositive character of the elements is related to the ease with which the electron (s) could be removed from the atom of the elements. More electropositive is the elements, more easily the electron (s) can be removed. As we move down a group, the ionization energy of the elements decreases regularly and hence the electropositive character also increases accordingly. Across a period, the ionization energy of the elements, in general, increases means the electropositive character decreases from left to right. Alkali metals placed at the extreme left portion of the periodic table, are the most electropositive elements with low values of ionization energy.

(ii) **Prediction of metallic and non-metallic character**

The elements with low ionization energy are more metallic in nature because they can lose electrons easily. Hence metallic character increases from top tobottom in the groups and decreases along the period from left to right. The elements showing the opposite trend in ionization energy and periodic variation to that of metals are called the non-metals.

(iii)**Prediction of reducing power of an element**

Lower the value of ionization energy of an element, greater is its reducing power. The alkali metals with the lowest ionization energy values are the strongest reducing agents among all the elements.

3.3.3 Electron affinity (or affinity energy) (EA).

This term is related with the formation of an anion from a neutral atom of an element by the addition of electron (s). Thus, this is the tendency of the atom to gain the additional electron (s). The electron affinity (EA) of an element can be defined as the "**amount of energy released when an electron is added to the outer shell of an isolated gaseous atom of the element to produce the gaseous anion**". This can be shown as: $A\ (g) + e \rightarrow A^{-}(g) - (EA)_1$ (electron affinity energy released). Evidently, this is an exothermic process. The expression actually shows the first electron affinity. Once the uninegative anion has been formed by accepting one electron by the neutral atom, addition of another electron (s) in this ion becomes more difficult due to repulsive force operating between the anion and the incoming electron. To overcome this repulsive force, extra energy has to be supplied to the electron which must actually be more than the energy released during the addition of electron, i.e. the energy supplied to electron > energy released during the addition of electron. The net energy change is the energy absorbed (supplied) by the electron, hence the addition of second or third etc. electron to the anion is an endothermic process:

$$A^{-}\ (g) + e \rightarrow A^{2-}\ (g)\ +\ (EA)_2 \quad \text{(energy supplied)}$$

$$A^{2-}\ (g) + e \rightarrow A^{3-}\ (g)\ +\ (EA)_3 \quad \text{(energy supplied)}$$

The electron affinity values for the elements of second period are given below:

Element	Li	Be	B	C	N	O	F
$(EA)_1$ in kJ/mole	60	≤ 0	27	122	≤ 0	141	328

The electron affinity values of Be and N are shown zero because it is very difficult to add an extra electron to the outer shells of these elements due to extra stability of the electronic configuration.

The electron affinity values of halogens are very high because of the $ns^2\ np^5$ outer shell electronic configuration and very strong tendency to accept the incoming electron thereby getting converted into the negative ions with noble gas configuration, i.e. $ns^2\ np^6$. Though the first element of halogen group, is expected to have the highest value of EA,but its EAvalue is less than that of Cl. This is due to the smaller size and greater electron-electron repulsion in F-atom which opposes the entry of the incoming electron. The EA values of the noble gases are almost zero due to no tendency of accepting the additional electron because of stable ns^2

np^6 configuration. EA values of halogens and noble gas elements are given below (in k J/mole):

Element	F	Cl	Br	I	At	He	Ne	Ar	Kr	Xe	Rn
$(E_A)_1$ value	328	349	325	295	280	≤ 0	≤ 0	≤ 0	≤ 0	≤ 0	≤ 0

Factors affecting the electron affinity

All the factors which affect the ionization energy also affect the electron affinity. The main factors among them are discussed here:

(i) **Atomic size**

Smaller the atomic size, stronger is the attraction of nucleus for the incoming electron and hence greater is its electron affinity and vice versa, i. e. $EA \propto \frac{1}{atomic\ size}$ (as is seen along a period)

(ii) **Effective nuclear charge (Z_{eff})**

Greater is the effective nuclear change of the elements, stronger is the attraction between it and the electron to be added to the atom. Thus with the increase in Z_{eff}, other factors remaining the same, electron affinity of the elements also increases, i.e. $EA \propto Z_{eff}$ (as is seen along a period).

(iii)**Stable electronic configuration**

The atoms of the elements with stable electronic configuration do not show any tendency to accommodate the incoming electron (s). Hence the EA values for such elements is almost zero. For example, the elements of 2nd group with ns^2 outer electronic configuration have zero EA values. The elements of 15th group with ns^2np^3 outer electronic configuration have zero or very low EA values. The noble gases with ns^2np^6 stable configuration in the outer shell also have zero EA values i.e. do not have any affinity for the electron (s) to be added to them.

The electron affinity of an element can be determined by using the Born-Haber cycle.

Periodic trends of electron affinity

(i) **Variation along the periods**

In general, with few exceptions, the electron affinity values of the elements go on increasing on moving from left to right in a period, i.e. from alkali metals to halogens. This is because atomic size decreases and the effective nuclear charge increases along a period. Both these factors increase the force of attraction between the nucleus and the incoming electron which is added easily to the outer shell of the host atom. Exceptions are the elements of 2nd, 15th and 18th groups.

(ii) **Variation in the groups**

The electron affinity values go on decreasing when we move from top to bottom down in a group. On descending a group, the atomic size and the nuclear charge both increase regularly. The increasing atomic size tends to decrease the EAvalues while increasing nuclear charge causes an increase in these values. The net result is that the effect produced by the progressive increase in size more than compensates the effect produced by progressive increase in nuclear charge and hence EA values decrease regularly down the group.

3.3.4 Electronegativity (χ, chi)

In a homoatomic molecule, the bonding pair of electrons lies at the middle of internuclear space. But this is not true for a hetroatomic molecule. As a result polarity is developed on the hetero atoms of the molecule due to the shifting of the bonding pair of electrons towards one particular atom. For example, in H_2 or Cl_2 molecules, the bonded pair of electrons lies at the middle of two nuclei, i.e. is equally attracted by both the atoms. But in HF or like molecules, the bonded pair of electrons is attracted with stronger force by F atom (in HF) and thus, is shifted towards it from its expected middle position. This causes the development of slight negative change on F and equal positive change on H atom, therefore HF is a polar molecule.

This means an atom in a heteroatomic molecule with stronger affinity for bonding electrons is able to pull them towards itself and takes them away from the atom with weaker affinity for them. In the above example *(viz.* HF) F is said to have stronger affinity for bonded electrons as compared to that of hydrogen atom.To explain this tendency in heteroatomic molecules, Linus Pauling, in 1932, introduced the concept of electronegativity. According to him "**electronegativity is the relative tendency or power of an atom of an element in the heteroatomic molecules to attract the shared pair of electrons towards itself**".

Methods of evaluating electronegativity

Various chemists have defined and proposed the methods for evaluating electronegativity. These are known as electronegativity scales.

(i) **Pauling's Scale**

Pauling's definition of electronegativity has been given in the beginning. He used thermodynamic data to calculate the electronegativity of different elements. He considered the formation of AB molecule by the combination of A_2 and B_2 molecules.

$$A_2 + B_2 = 2\,AB$$

$$\text{Or} \quad \frac{1}{2}A_2 + \frac{1}{2}B_2 = AB \qquad \text{………} \ (3.8)$$

This reaction may also be written as

$\frac{1}{2}$ (A-A) + $\frac{1}{2}$ (B –B) = A - B because A_2, B_2 and AB are covalent molecules. This is an exothermic reaction, means the formation of A-B molecules is accompanied by the release of energy, i.e. the bond dissociation energy of A-B covalent bond (E_{A-B}) is always higher than the mean of the bond dissociation energy of

A-A (E_{A-A}) and B-B (E_{B-B}) covalent bonds and $E_{A-B} > \frac{1}{2}(E_{A-A} + E_{B-B})$

Pauling proposed that the difference in the E_{A-B} and mean of E_{A-A} and E_{B-B} is related to the difference in electro negativities of A (χ_A) and B (χ_B)

$$\therefore \Delta = E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) = 23\,(\chi_B - \chi_A)^2 \ (\text{where } \chi_B > \chi_A,) \qquad \text{…….}(3.9)$$

$$\text{Thus,} \ \Delta = 23\,(\chi_B - \chi_A)^2$$

$$\text{Or } \chi_B - \chi_A = 0.208\,\sqrt{\Delta} \qquad \text{……………}(3.10)$$

In place of arithmetic mean, he later used the geometric mean of E_{A-A} and E_{B-B} and expressed the equation as:

$$\Delta' = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = 30(\chi_B - \chi_A)^2 \qquad \text{………}(3.11)$$

$$\therefore \Delta' = 30\,(\chi_B - \chi_A)^2$$

$$\therefore \chi_B - \chi_A = 0.182\,\sqrt{\Delta'} \qquad \text{…………}(3.12)$$

Here χ_A and χ_B are the electronegativities of the atoms A and B. The factors 0.208 and 0.182 arise from the conversion of Δ measured in kCal/ mole into electron volts.

s-block **p-block elements**

1	2	13	14	15	16	17	18
H							He
2.1							0
Li	Be	B	C	N	O	F	Ne

1.0	1.5	2.0	2.5	3.0	3.5	4.0	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.9	1.2	1.5	1.8	2.1	2.5	3.0	0
K	Ca	Ga	Ge	As	Se	Br	Kr
0.8	1.2	1.6	1.8	2.0	2.4	2.8	0
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.7	1.8	1.9	2.1	2.5	0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
0.7	1.9	1.8	1.8	1.9	2.0	2.2	0
Fr	Ra						
0.7	1.9						

Table 3.5: Electronegativity values of s and p-block elements as determined by Pauling (on F = 4.0 scale)

From this table it can be noted that the variation in the values of electronegativity is more pronounced among the non-metals.

(ii) Allred and Rochow's Scale

Allred and Rochow proposed that the electronegativity of an element (say A) can be calculated by using the following equation:

$$(\chi_A)_{AR} = \frac{0.359\, x Zeff}{r^2} + 0.744 \qquad \ldots\ldots\ldots\ldots(3.13)$$

where $(\chi_A)_{AR}$ = electronegativity of the element A on Allred and Rochow's scale, Z_{eff} = effective nuclear charge ($Z - \sigma$) at the periphery of the element A,

r is radius of the atom of element A in Å.

Putting the value of Z_{eff}, the equation can be rewritten as

$$(\chi_A)_{\text{AR}} = \frac{0.359\, x(Z-\sigma)}{r^2} + 0.744 \qquad \text{...........(3.14)}$$

The electronegativity values obtained by this method agree closely to those obtained by Pauling’s approach. These values for the elements of first three periods are given below:

Table 3.6: Electrongativity values of s and p-block elements belonging to first three periods on Allred and Rochow’s scale

Group	1	2	13	14	15	16	17	18
	H 2.20							He 3.2
	Li 0.97	Be 1.47	B 2.01	C 2.50	N 3.07	O 3.50	F 4.10	NA 5.1
	Na 1.01	Mg 1.23	Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83	Ar 3.3
	K 0.91	Ca 1.04	Ca 1.82	Ge 2.02	As 2.20	Se 2.48	Br 2.74	Kr 3.1
	Rb 0.89	Sr 0.99	In 1.78	Sn 1.72	Sb 1.82	Te 2.01	D 2.21	Xe 2.4
	Cs 0.86	Ba 0.97	Tl 1.44	Pb 1.55	Bi 1.67	Po 1.76	At 1.90	Rn -

According to this scale, the inert elements also possess electronegativity. As per the definition given by Pauling, this scale seems to be arbitrary but it has its own importance.

(iii) Mulliken’s scale

It is based on the ionization energy and electron affinity of an atom of an element. According to Mulliken “**the average of ionization energy (IE) and electron affinity (EA) of the atom of an element is a measure of its electronegaivity**”.

Thus, the electronegativity = $\frac{I_E+E_A}{2}$ ………..(3.15)

He proposed two relations for obtaining the electronegativity:

(a) When the energies are measured in electron volts (eV), then

$$\chi_A = 0.374 \frac{(I_E+E_A)}{2} + 0.17$$

$$= 0.187 \frac{(I_E+E_A)}{2} + 0.17 \quad \text{………(3.16)}$$

(b) When the energies are expressed in kJ/mole, then

$$\chi_A = \frac{I_E+E_A}{540} \quad \text{………..(3.17)}$$

All these terms χ_A, IEand EA are for the atom A.

Factors affecting the magnitude of electronegativity

Various factors which affect the magnitude of the electronegativity of an element qualitatively are as follows:

(i) **Atomic size**

It has been observed that the smaller atom has greater tendency to attract the shared pair of electrons towards itself and hence has greater electronegativity. Thus electronegativity α $\frac{1}{Atomicsize}$

(ii) **Charge on the atom** (or oxidation state of the element)

Higher the amount of positive charge on the atom of an element means higher positive oxidation state, smaller is the size and more is the electronegativity, i.e. electronegativity α positive oxidation state (or charge).

(iii) **Effective nuclear charge (Z_{eff})**

With the increase in the magnitude of Z_{eff} of an element, the electronegativity of that element also increases. This factor may effectively be used to explain the variation of electronegativity in a group or along a period. Thus, electronegativity α Z_{eff}.

(iv) **Ionization energy and electron affinity**

According to Mulliken's scale, electronegativity of an element depends on its ionizations energy and electron affinity, Thus, the atoms of the elements which have higher values of ionization energy and electron affinity also have higher values of electronegativity, i.e. electronegativity α IEand EA.

(v) **Type of hybridization of the central atom in a molecule**

It has been observed that electronegativity of an atom having hybrid orbital with greater s-character is high because the electronic charge in hybrid orbitals of an atom in a molecule which has greater s-character remains closer to the nucleus of that atom. For example, the s-character in sp^3, sp^2, and sp hybrid orbitals of CH_4, C_2H_4 andC_2H_2 is 25%, 33% and 50%, respectively. Accordingly, the s-character of hybrid orbitals gives more electronegativity to C atom. Hence the electronegativity of carbon atom in these molecules is in the following increasing order:

$CH_4 < C_2H_4 < C_2H_2$

Periodic trends of electronegativity

(i) **Variation in the groups of main group elements**

On going down a group of main group elements, the electronegativity values go on decreasing due to increasing atomic size and decreasing Z_{eff} of the elements. At the same time, the electropositive character of the elements also increases causing a reduction in electronegativity values of the elements as well as their ionization energies and electron affinities.

(ii) **Variation along a period**

On moving from left to right across a period of main group elements i.e. from alkali metals to halogens, electronegativity values increase with increasing atomic number. This happens secause Z_{eff} increases, electropositive character decreases, atomic size of the elements also decreases thereby increasing electronegativity. Ionization energy and electron affinity, in general, also increase along a period.

Applications of Electronegativity

On the basis of electronegativity, certain facts in chemistry can be explained which are given below:

(i) **To predict the nature of bonds**

With the help of the electronegativity difference $\chi_B - \chi_A$ (where $\chi_B < \chi_A$) between two atoms A and B, we can predict whether A-B bond would be non-polar covalent bond, polar covalent bond or ionic bond. If $\chi_B - \chi_A = 0$, i.e. either the atoms A and B are same or if different have almost similar electronegativity values, the bond is non- polar covalent bond. When $\chi_B - \chi_A$ is relatively small, e.g. O- H, Cl-H etc. the bond formed between the atoms is polar covalent bond. When $\chi_B - \chi_A$ is very large, complete transfer of an electron from atom A to atom B takes place and the resulting bond between the atoms is purely ionic.

The percent ionic character present in the polar covalent bond can be calculated. For a polar covalent molecule A^{S+}-B^{S-}, Pauling has correlated the percent ionic character of a covalent bond with the electronegativity difference between the combining atoms as is given below:

$(\chi_B - \chi_A)$	0.6	1.0	1.7	2	3
Percent ionic character	9	22	51	63	91

He used the equation:

Amount of ionic character in A-B bond = $[1 - e^{0.25(\chi B - \chi A)}]$ % ………(3.18)

Further, Hannay and Smith gave the following equation to calculate the ionic character.

Ionic Character in A - B bond = $[16(\chi_B - \chi_A) + 3.5(\chi_B - \chi_A)^2]$ % $(\chi_B > \chi_A)$….(3.19)

(ii) **To calculate the bond length**

In a heterodiatomic molecule of AB type, the bond length d_{A-B} can be calculated provided the molecule has ionic character and the values of atomic radii r_A and r_B as well as the electronegatitvities χ_A and χ_B are known. This can be done by using the Schoemaker and Stevenson equation, *viz.*

$d_{A-B} = r_A + r_B - 9(\chi_B - \chi_A)$ $(\chi_B > \chi_A)$ …………..(3.20)

(iii) **To predict the trends in acid-base character**

(a) The acidic character of the oxides has been bound to increase from left to right along a period because of decreasing $\chi_0 - \chi_B$ values (χ_0 and χ_B are electro- negativities of oxygen and other atom), e.g.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
χ_B	0.9	1.2	1.5	1.8	2.1	2.5	3
$\chi_0 - \chi_B$	2.6	2.3	2.0	1.7	1.4	1.0	0.5
Nature	strongly basic	basic	ampoteric	weakly acidic	acidic	strongly acidic	strongly acidic

$(\chi_o = 3.5)$

(b) The acidic character of hydrides of the elements of the same period goes on increasing from left to right across a period. For example, the acidic nature of CH_4, NH_3, H_2O and HF molecules, the hydrides of the elements of second period, increases in the order: CH_4, < NH_3, < H_2O < HF because of the increasing electronegativity of the central atom and increasing elelctronegativity difference between the central atom and hydreogen atom i.e.

$\chi_{\text{central atom}} - \chi_H$

(c) The acidic character of oxyacids of the elements of the same group and in the same oxidation state, e.g. $HClO_4$, HB_rO_4 and HIO_4 decreases as the electronegativity of central halogen atom decreases as we move down the group form Cl to I (χ_{Cl} = 3.0) and χ_I = 2.5 on Pauling's scale).

(iv) **To explain the diagonal relationship**

It has been found that the elements of second period of the periodic table show similarities in properties with the elements lying diagonally opposite on right hand side in the third period This property is called diagonal relationship. These elements are shown below:

Elements of 2nd period	Li	Be	B	C	N	O	F	
		↘	↘	↘	↘	↘	↘	
Elements of 3rd period		Na	Mg	Al	Si	P	S	Cl

This similarity in properties can be explained by various facts and one of them is the concept of electronegativity. The electronegativites of the diagonally opposite elements are almost the same and hence show similar properties.

3.4 TRENDS IN PERIODIC TABLE

All the periodic properties, i.e. atomic and ionic radii, ionization energy, electron affinity and electronegativity show variation along the period and down a group. The trends for various properties have been discussed in the respective sections.

3.5 SUMMARY

The text of this unit contains a concise and comprehensive discussion of various periodic properties such as atomic and ionic radii, ionization energy, electron affinity and electronegativity, factors affecting these properties, periodic trends (or variation) of the properties, the methods of their determinations and their applications wherever necessary and available. The periodic properties are the basis of the physical and chemical properties of the elements which can be predicted keeping in view the above propert

3.6 Terminal questions.

i) Arrange the following ions in the increasing of their size

a. Na^+, Mg^{2+}, Al^{3+}, F^-, O^{2-}, N^{3-}

b. C^{4-}, N^{3-}, O^{2-}, F^-

ii) Which atom or ion in the following pairs has smaller size and why ?

a. Na, Na^+

b. Be, Mg

c. Fe^2,Fe^3

iii) Explain giving appropriate reasons:

a. The $Cl^{—}$ ion is larger in size than Cl atom.

b. The atomic radius decreases with the increasing atomic numbers in a period.

iv) Arrange the following in the decreasing order of their ionization energy: Be, B, N, O and F.

v) Arrange the Be, B, N, O and F in the increasing order of their electron affinities.

vi) EA values of the halogens are the highest in each period. Explain.

vii) The noble gases have very high values of ionization energy but their electron affinity values are almost zero. Why?

viii) Which of the following elements has the highest values of electronaffinity and why?

a. Na, Cl, Si, Ar

b. (i)$1s^2$, $2s^2$, $2p^1$ (ii) $1s^2$, $2s^2$, $2p^6$, $3s^1$ (iii) $1s^2$, $2s^2$, $2p^5$ (iv) $1s^2$, $2s^2$, $2p^3$

ix) Distinguish between electron affinity and electronegativity.

x) Which element among the following has the highest value of electro negativity and the highest value of electron affinity? F, Cl, O, Br, and I.

xi) Which one of the following oxides is basic, amphoteric, and acidic in nature?

a. MgO

b. Al_2O_3

c. P_4O_{10}

xii) How does electron affinity depend on effective nuclear charge?

3.7. ANSWERS

i) **a.** $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

d. $F^- < O^{2-} < N^{3-} < C^{4-}$

All of the above are isoelectronic ions whose ionic size decreases with increasing nuclear charge (atomic number) of the parent atom.

ii) a. Na^+ has smaller size because this has been derived from Na atom by removing its outermost electron. This causes greater attraction between the nucleus and the remaining electrons and contraction in the size occurs.

b. Be has smaller size because both Be and Mg belong to the same group. Down a group the size of the atom of the elements increases.

c. Fe^{3+} ion has smaller size because both Fe^{2+} and Fe^{3+} are the ions of Fe. As the oxidation state increases, the ionic size decreases (for the ions of the same element).

iii) a. Please see some important facts regarding ionic radii no. 3.

b. Please see variation of atomic radius in a period.

iv) The decreasing order of the ionization energy is

F > N > O > Be > B.

v) The increasing order of the electron affinity is

Be < N < B < O < F

vi) Please refer to the electron affinity.

vii) Due to the most stable electron configuration, it is very difficult to remove the electron(s) from the noble gases and hence have very high values of ionization energy. Due to the same reason, they do not have the tendency to accommodate the electron(s) in their outer shell, therefore have almost zero electron affinity.

viii) a. Among the given elements Cl with $3s^2$ $3p^5$ outer shell configuration has the greatest tendency to accept the incoming electron and hence has the highest value of electron affinity.

b. (iii) With $2s^2$ $2p^5$ configuration in the outer shell has the highest value of electron affinity among the given elements,

ix) Please refer to the definitions of electron affinity and electornnegativity.

x) Among the given elements F has the highest values of electronegativity. (Pauling's scale) and Cl has the highest value of electron affinity.

xi) Basic oxide: MgO

Amphoteric oxide: Al_2O_3

Acidic oxide: P_4O_{10}

xii) Please refer to the factors affecting the electron affinity.

3.8. REFERENCES

For references please see at the end of Unit 5

UNIT 4: CHEMICAL BONDING- I

CONTENTS:

4.1 OBJECTIVES

The objective of writing the text of this unit is to enable the readers to understand various facts regarding the driving force that makes the isolated atoms to combine to form the polyatomic molecules or ions as well as to find the answers of certain interesting questions such as: What is a chemical bond? What happens to the energy of the atoms and the molecules? What happens in terms of electronic structure, while bond formation takes place?

Why do the group 18 elements, i.e. the noble gases, generally not participate in bond formation and suffer from lack of reactivity while almost all other elements do so? etc.

4.2 INTRODUCTION

The atoms are said to combine together because of the following two main reasons:

(i) Concept of lowering of energy

It has been observed that the aggregate (or the molecules) are lower in energy than the individual atoms from which they have been formed. This means when the individual atoms combine to form molecules through a bond, the potential energy of the combining atoms decreases and the resulting molecules are more stable than the free atoms. This energy difference between the free atoms and bonded atoms (or molecules) is generally 40kJ mol^{-1} or more. It follows from this that the process of bond formationbetween the atoms decreases the energy of the molecule formed from these atoms and forms a system of lower energy and greater stability.

(ii) Electronic theory of valence (the octet rule)

The atoms of the noble gases-helium to radon- do not, except a few cases, react with any other atoms to form the compounds and also they do not react with themselves. Hence they stay in atomic form. These atoms are said to have low energy and cannot be further lowered by forming compounds. This low energy of noble gas atoms is associated with their outer shell electronic configuration, i.e. the stable arrangement of eight electrons (called octet). It has also been established that the two electrons in case of helium atom (called doublet) is as stable as an octet present in other noble gas atoms. The chemical stability of the octet of noble gases led chemists to assume that when atoms of other elements combine to form a molecule, the electrons in their outer shells are arranged between themselves in such a way that they achieve a stable octet of electrons (noble gas configuration) and thus a chemical bond is established between the atoms.

This tendency of the atoms to attain the noble gas configuration of eight electrons in their outer shell is known as octet rule or rule of eight and when the atoms attain the helium configuration, it is called doublet rule or rule of two. This octet rule was later called **“Electronic Theory of Valence”**.

It may be noted here that in the formation of a chemical bond, atoms interact with each other by losing, gaining or sharing of electrons so as to acquire a stable outer shell configuration of eight electrons. This means, an atom with less than eight electrons in the outer shell is chemically active and has a tendency to combine with other atoms. Accordingly, three different types of bonds may exist in the molecules/aggregates.

4.3. COVALENT BOND

A covalent bond is formed between the two combining atoms, generally of the electronegative non-metallic elements by the mutual sharing of one or more electron pairs (from their valence shell). Each of the two combining atoms attains stable noble gas electronic configuration, thereby enhancing the stability of the molecule. If one electron pair is shared between the two atoms, each atom contributes one electron towards the electron pair forming the bond. This electron pair is responsible for the stability of both the atoms. A covalent bond is denoted by the solid line (-) between the atoms. Depending on the number of shared electron pairs i.e. one, two, three etc. electron pairs between the combining atoms, the bond is known as a single, double, triple etc. covalent bond. For example,

H:H H-H

Cl:Cl Cl-Cl **single bond**

H:Cl H-Cl

O::O O=O **double bond**

N:::N N≡N **triple bond** **multiple bond**

In the molecules, the bond strength and bond length has been found in the following order:

Bond strength: triple bond > double bond > single bond

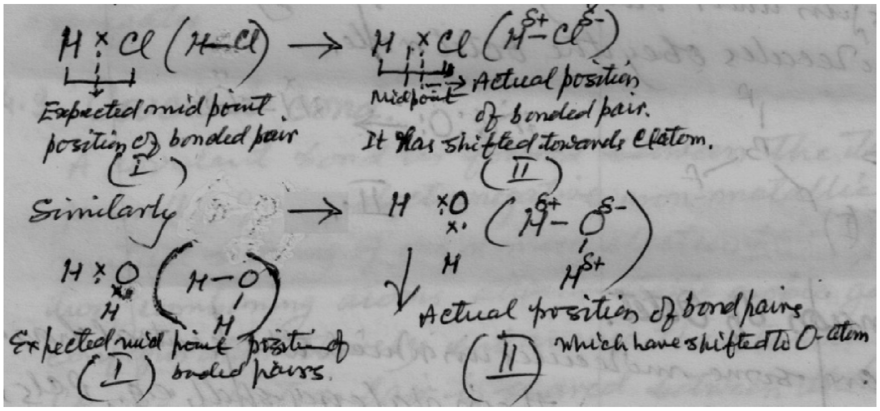
Bond length: triple bond < double bond < single bond

It may be noted that the covalent bond formation between multielectron atoms involves only the valence shell electrons that too, the unpaired electrons. Thus O-atom has two unpaired electrons in its valence shell and N-atom has three unpaired electrons thereby forming two and three bonds with themselves or other atoms.

Polar and non-polar covalent bond

In the examples given above, most of the bonds *viz.* single, double and triple covalent bonds, have been shown to be formed between the like atoms such as H-H, Cl-Cl, O=O and N≡N in H_2, Cl_2, O_2 and N_2, respectively. The bonded atoms in these molecules attract the bonding or shared pair of electrons by equal forces towards themselves due to equal electronegativity of the atoms. Hence the bonding pair of electron lies at the mid point of the internuclear distance (or bond distance). This type of bond is known as the non-polar covalent bond.

But if the covalent bond is formed between two unlike atoms of different elements, e.g. HCl, H_2O, NH_3 etc., the shared pair of electrons will not be equally attracted by the bonded atoms due to electronegativity difference. It shifts towards more electronegative atom and hence moves away from less electronegative atom. This develops small negative charge on more electronegative atom and equal positive charge on less electronegative atom. Such a molecule is called a polar molecule (this is different from ionic bond) and the bond present in such molecules is known as polar covalent bond. For example,



4.3.1. Valence Bond Theory (VBT) and its limitations:

This theory was put forward by Heitler and London in 1927 to explain the nature of covalent bond. They gave a theoretical treatment of the formation of the bond in H_2 molecule and the energy changes taking place therein. Later, it was extended by Pauling and Slater in 1931 to account for the directional characteristics of the covalent bond.

The main points called the postulates of this theory are given below:

(i) The atoms involved in the bond formation maintain their individuality(identity) even after the bond is formed i.e. in the molecule.

(ii) The bond is formed due to the overlapping of half filled atomic orbitals (or the interaction of electron waves) belonging to the valence shell of the combining atoms as these approach each other. Thus the spins of the two electrons get mutually neutralised. The electrons in the orbitals of inner shells remain undisturbed.

(iii) The filled orbitals (i.e. containing two electrons) of the valence shell do not take part in the bond formation. However, if the paired electrons can be unpaired without using much energy, they are first unpaired by promoting to the orbitals of slightly higher energy and then can take part in bonding. For example, N can form NCl_3 only retaining a lone pair while P can form both PCl_3 and PCl_5.

(iv) The electrons forming the bond undergo exchange between the atoms and thus stabilize the bond.

(v) The strength of the covalent bond depends on the extent to which the two atomic orbital overlap in space.

This theory is based on two main theorems which are:

(a) If $\Psi_A(1)$ and $\Psi_B(2)$ are the wave functions of the orbitals containing electrons in two isolated independent atoms A and B with energies E_A and E_B, respectively then the total wave function Ψ of the system can be given as a product of wave functions of two atoms, i.e.

$$\Psi = \Psi_A(1).\ \Psi_B(2) \qquad \ldots\ldots(4.1)$$

and the energy of the system by

$$E = E_A + E_B \qquad \ldots\ldots.(4.2)$$

Where (1) and (2) indicate two electrons belonging to atoms A and B.

(b) If a system can be represented by a number of wave functions such as Ψ_1, Ψ_2, Ψ_3 ……, then the true wave function Ψ can be obtained by the process of linear combination of all these wave functions as:

$$\Psi = N(C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3 + \ldots\ldots) \qquad \ldots..(4.3)$$

Where N is normalization constant and C_1, C_2, C_3…are the coefficients indicating the weight of each of Ψs. They are so adjusted as to give a state of lowest energy. The squares of the coefficients may be taken as the measure of the weight of each wave function to total wave function.

The valance bond theory was first applied to the formation of H_2 molecule. If the two H-atoms, *viz*. H_A and H_B are infinitely apart from each other, there is no interaction at all but if these are brought close together, H_A- H_B covalent bond is formed and the energy of the system is decreased. Now if the orbitals of the two H-atoms are represented in terms of wave functions Ψ_A and Ψ_B, then the wave function for the system $H_A.H_B$ can be written as

$$\Psi = \Psi_A(1).\ \Psi_B(2) \qquad \ldots\ldots(4.1 \text{ as given above})$$

Where electrons belonging to H_A and H_B are 1 and 2.

But once the bond is formed, the electrons 1 and 2 have equal freedom to get associated with either of the H-atoms. Thus due to the exchange of electrons between H-atoms, two possible covalent structures of H_2 molecule may shown as $H_A(1).H_B(2)$ and $H_A(2).H_B(1)$. The wave functions of these structures are $\Psi_A(1).\ \Psi_B(2)$ and $\Psi_A(2).\ \Psi_B(1)$ respectively. Now the true wave function for H_2 molecules can be obtained by linear combination of the wave functions for the two covalent structures. This can be done in two ways:

(i) When the combination of these wave functions takes place in a symmetric way, i.e. by addition process, symmetric wave function Ψ_s is obtained:

$$\Psi_s = \Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_B(1) \qquad \text{……..(4.4)}$$

This is also known as covalent wave function, Ψ cov.

(ii) When the combination of the above wave functions takes place in a asymmetric way i.e. by subtraction process, asymmetric wave function, Ψ_a, is obtained: $\Psi_a = \Psi_A(1).\ \Psi_B(2) - \Psi_A(2).\ \Psi_B(1)$ …….(4.5)

The value of Ψ_s does not change by exchange of electrons 1 and 2 but that of Ψ_a changes in this process. The two situations are presented graphically as follows: ***(Fig 4.1)***

The curve s is for addition process and curve a is for subtraction process of the wave functions. The calculated value of r_o for the minimum energy state i.e. the bonding state is 87 pm against the experimental value of 74 pm.

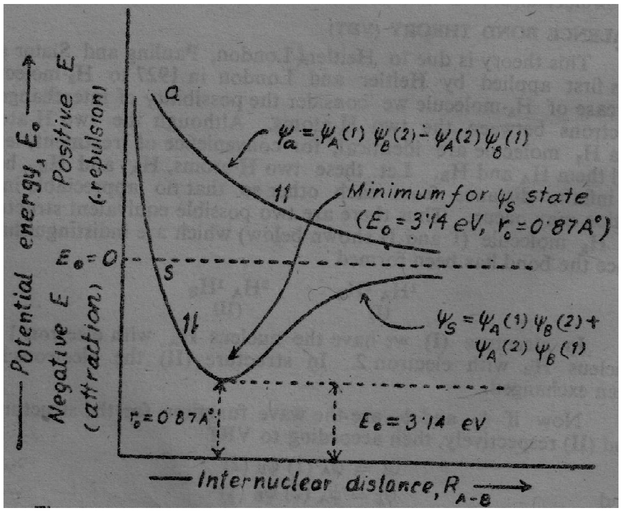


Fig 4.1

Pauling has suggested that the bond between two H-atoms in H_2 molecule is not absolutely covalent, it rather has partial ionic character. He proposed two ionic structures for H_2

molecule in which both the electrons 1and 2 are either attached to H_A or H_B as given below,

$H_A(1,2).\ H^+_B$ $H^+_A.H_B(1,2)$

If the above wave functions for these structures are $\Psi_{(1)}$ and $\Psi_{(2)}$,

then $\Psi_{(1)}= \Psi_A(1).\ \Psi_A(2)$ …..(4.6)

And $\Psi_{(2)}= \Psi_B(1).\ \Psi_B(2)$ ……(4.7)

The consideration of ionic structures as given above of H_2 molecule converts the equation 4.4 to

$\Psi s=[\Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_B(1)] +\lambda\ [\Psi_{(1)}+\Psi_{(2)}]$

or $\Psi s=[\Psi_A(1).\ \Psi_B(2)+ \Psi_A(2).\ \Psi_A(1)] + \lambda[\Psi_A(1).\ \Psi_A(2)+ \Psi_B(1).\ \Psi_B(2)]$ ..(4.8)

or $\Psi s =\Psi cov. + \Psi ionic$ …..(4.9)

the coefficient λis used in equation 4.8 is a measure of the degree to which the ionic forms contribute to the bonding. Thus three important contributions to covalent bonding may be summarized as follows:

(i) Delocalization of electrons over two or more nuclei

(ii) Mutual screening

(iii) Partial ionic character.

Limitations of Valence Bond theory:

i) The formation of coordinate covalent bond (also known as dative bond) cannot be explained on the basis of this theory because according to this theory a covalent bond is formed as a result of overlapping of half filled orbitals of the combining atoms and the paired orbitals of the atoms do not take part in normal covalent bond formation.

ii) The odd electron bond formation between the atoms cannot be explained by this theory because a covalent bond is an electron pair bond means two electrons are required for a bond.

iii) This theory is unable to explain the paramagnetic behaviour of oxygen molecule because paramagnetism is a property caused by the presence of unpaired electrons and in an oxygen molecule, according to VBT, two electron pair bonds are present between the oxygen atoms and hence it should be diamagnetic.

iv) In some molecules, the properties like bond length and bond angles could not be explained by assuming simple overlapping of atomic orbitals of the atoms.

4.3.2 Directional characteristics of covalent bond:

The covalent bonds are directed in space. This fact is evidenced by the stereoisomerism and a wide variety of geometrical shapes shown by the covalent compounds. It is also possible to measure the actual bond angles between covalent bonds in the molecules because of the directional nature of bonds. An important fact about the covalent bonds is that these are formed by the overlapping of pure as well as hybridised atomic orbitals. All these atomic orbitals except the pure s-orbitals, are oriented in the particular directions which determine the direction of covalent bonds i.e. the direction in which the overlapping orbitals have the greatest electron density. From this discussion we can conclude that it is the directional nature of p, d and f orbitals which accounts for the directional nature of the covalent bond. For example, the three p-orbitals are directed along the three axes x,y and z and the bonds formed by their overlapping are also directed towards the three axes. Though the s-orbitals are spherically symmetrical around the nucleus, their overlapping along the molecular axis gives a bond in that direction.

Let us discuss the modes of overlapping of pure and some of the hybridised atomic orbitals:

(i) **s-s overlapping**

This type of overlapping occurs between the s-orbitals of the combining atoms thereby giving the s-s covalent bond. This type of overlapping always occurs in the direction of molecular or internuclear axis.

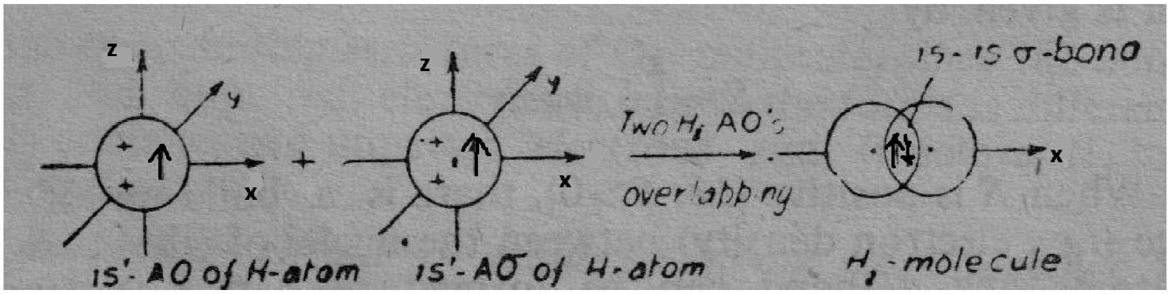


Fig 4.2 ovrelapping of two s-orbitals along molecular axis

(ii) **s-p overlapping**

The overlapping taking place between the s-orbital of one atom and p-orbital of another atom is called s-p overlapping. The resulting bond is the s-p covalent bond formed in the direction of the orientation of p-orbital taking part in overlapping.

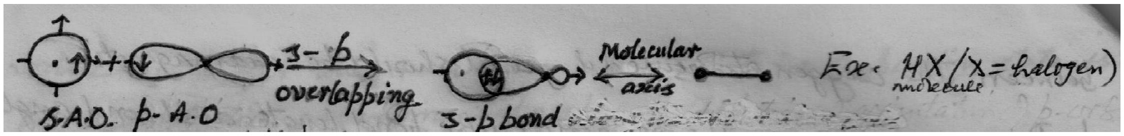


Fig 4.3 *overlapping of s and p orbitals along molecular axis*

(iii) p-p overlapping

When the p-orbital of one atom overlaps with the p-orbital of another atom, this process is called p-p overlapping and the bond so formed is known as p-p covalent bond. The necessary condition for this type of overlapping is that the p-orbitals must be of the same type, i.e. p_x and p_x, p_y and p_y and p_z and p_z. The p_x-p_y or p_x-p_z type of overlapping does not occur.

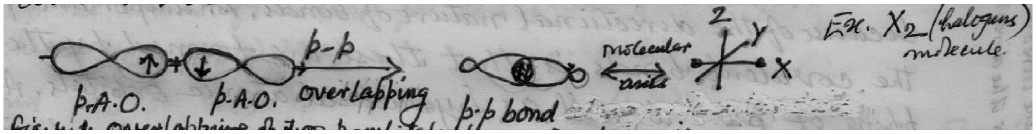


Fig 4.4 *overlapping of two p-orbitals along molecular axis*

If an atom possesses two or three half filled orbitals, they can simultaneously overlap with another similar atom (or other atoms as well) thereby forming multiple bonds (both σ and π), for example oxygen molecule.

Similarly bonding in N_2 can be explained

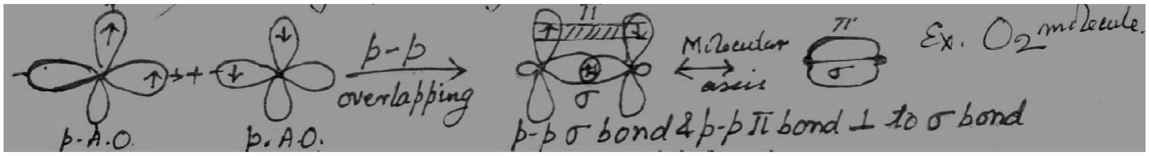


Fig 4.5 *overlapping of orbitals forming σ and πbonds*

(iv) Overlapping of the hybrid orbitals with pure atomic orbitals

The s and p-orbitals may overlap with hybrid orbitals to give the directional covalent bonds such as s-sp(B_eH_2), s-sp^2(BH_3 ,C_2H_4), s-sp^3 (CH_4 and higher alkanes), p-sp (B_eCl_2), p-sp^2 (BCl_3), p-sp^3 (CCl_4), p-sp^3d (PCl_5), p-sp^3d^2 (SF_6) p-sp^3d^3(IF_7) etc. bonds in the directions of hybrid orbitals. d and f - orbitals in non-metallic elements (which mostly form covalent compounds) do not generally take part in overlapping as such to form covalent bonds but d-orbitals may participate in hybridisation, e.g. in PCl_5, SF_6, higher intehalogens etc. and form covalent bonds by the overlapping of hybrid orbitals with atomic orbitals in the directions of hybrid orbitals.

(v) Overlapping of the hybrid orbitals among themselves. This type of overlapping mainly occurs among the organic compounds, e.g. sp-sp(C_2H_2), sp^2-sp^2(C_2H_4), sp^3-sp^3(C_2H_6) etc. Here only the overlapping of hybrid orbitals with themselves has been given.

4.3.3 Sigma (σ) and pi (π) covalent bonds:

σ Covalent bonds

The covalent bond formed between the two atoms by axial or head on overlapping of pure or hybrid atomic orbitals belonging to valence shells of the atoms is called a σ bond. Pure s-orbitals of the atoms on overlapping with s or p atomic orbitals or hybrid orbitals of other atoms always form σ bonds. Pure p-orbitals of the atom when overlap with s and p-orbitals (of the same symmetry) or hybrid orbitals of other atoms also form σ bonds. d and f- orbitals by themselves seldom take part in σ bond formation through the d-orbitals are sometimes involved in hybridisation and thus form a σ bonds, e.g. PCl_5, SF_6, IF_7 etc. The overlapping of hybrid orbitals between two atoms always gives σ bond.

(i) Pure atomic orbital – pure atomic orbital overlapping

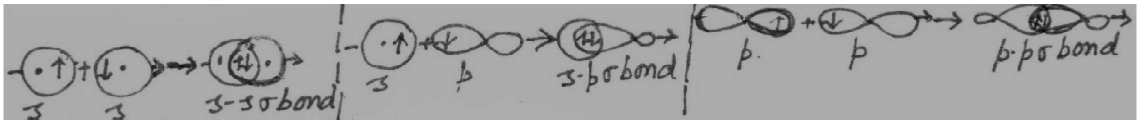
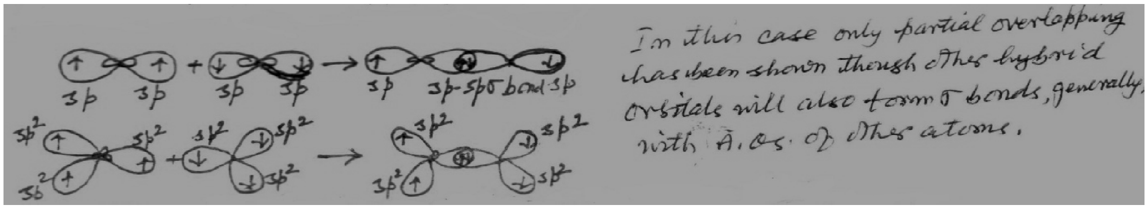


Fig 4.6(a) *formation of σbond by atomic orbitals*

(ii) Hybrid atomic orbital – hybrid atomic orbital overlapping



In this case only partial overlapping has been shown though other hybrid orbitals will also form σ bonds, generally, with A.Os. of other atoms.

Fig 4.6(b) *formation of σbond by hybrid orbitals*

In this case only partial overlapping has been shown though other hybrid orbitals will also form σ bonds, generally with atomic orbitals of other atoms.

Similarly sp^3-sp^3σ bond formation may also be shown.

π (pi) Covalent bond

A covalent bond formed between two atoms by side to side or lateral (perpendicular to the molecular axis) overlapping of only p-atomic orbitals or sometimes p and d- orbitals belonging to the valence shell of the atoms is called a π bond. If in a molecule, a particular atom uses one of its p-orbitals for σbond formation then rest of the two p-orbitals are used to form the πbonds by lateral overlapping. For example, if x axis is taken as the molecular axis, then πbond is formed by p_y - p_y or p_z-p_z overlapping as happens in the oxygen and nitrogen molecules.

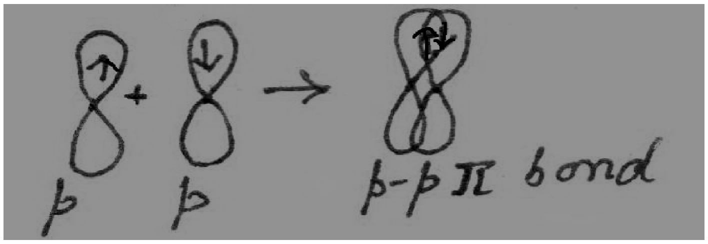


Fig 4.7 *formation of πbond by lateral overlapping of atomic orbitals*

Forσ and πbonds, the following points are important:

(i) A σbond is formed by axial overlapping of either pure or hybrid atomic orbitals of the two combining atoms while a πbond results from the lateral overlapping of the pure atomic orbitals.

(ii) A σbond is stronger than a πbond due to greater extent of overlapping of orbitals along the inter nuclear axis than in lateral overlapping.

(iii) A σbonds determine the direction of the covalent bond and bond length, πbonds have no effect on the direction of the bond. However, their presence shortens the bond length.

(iv) There is free rotation of the atoms about a σbond because the electron cloud overlaps symmetrically along the internuclear axis while this is not possible about a πbond because the electron clouds overlap above and below the plane of the atoms.

(v) A σbond has its free existence between any two atoms in a molecule while πbond is formed between the atoms only when σbond already exists.

The shapes of covalent molecules and ions can be explained by employing (a) the concept of hybridisation and (b) VSEPR Theory.

4.4. HYBRIDISATION OF ATOMIC ORBITALS

It is the theoretical model used to explain the covalent bonding in the molecules and is applied to an atom in the molecule. To explain the anomaly of expected mode of bonding (according to VBT) shown by Be, B and C in their compounds where these elements should be zerovalent, monovalent and bivalent due to the presence of 0,1 and 2 unpaired electrons in their valence shells and the observed bonding exhibited by them, i.e. these are bivalent, trivalent and tetravalent due to the availability of 2,3 and 4 unpaired electrons in their valence shells in those compounds, a hypothetical concept of hybridisation was put forward. According to this concept, before the bonding occurs in the compounds of Be, B and C, one of the 2s electrons gets promoted to the vacant 2p orbital due to the energy available from the heat of reaction when covalent bonds are formed or perhaps due to the field created by the approaching atoms, thereby making 2,3 and 4 unpaired electrons available in the valence shell of the atoms of these elements.

These orbitals having unpaired electrons then mix up together or redistribute their energy to give rise a new set of orbitals equivalent in energy, identical in shape and equal to the number of atomic orbitals mixed together. This process is known as hybridisation, the atomic orbitals are said to be hybridised and the new orbitals formed are called the hybrid orbitals. The hybrid orbitals so formed then overlap with the half filled orbitals of the approaching atoms and form covalent bonds.

Salient features (or the Rules) of hybridisation

i) The atomic orbitals belonging to the valence shell of the central atom/ion of a molecule/ion with almost similar energies mix up together or hybridise to give the hybrid obitals. But the atomic orbitals of the central atom participating in the πbond formation are excluded from the hybridisation process.

ii) The number of hybrid orbitals produced is equal to the number of atomic orbitals undergoing hybridisation. The hybrid orbitals like pure atomic orbitals can accommodate a maximum of two electrons of opposite spins.

iii) If required, electron(s) may be promoted from an orbital in ground state of the central atom to the next empty higher energy orbital provided the value of n does not change as happens in the central atom of $BeCl_2$, BCl_3, CH_4, PCl_5, SF_6etc.

iv) Most of the hybrid orbitals are equivalent in energy, shape and size but may not be identical. They differ from one another in their orientation in space.

v) From the type of hybridisation, the geometry and bond angles of a molecule can be predicted.

vi) In a few cases empty atomic orbitals or those with lone pairs of electrons (i.e. filled atomic orbitals) are also involved in the hybridisation process but in such cases normal covalent bond is not formed rather this process leads to the formation of coordinate covalent bond. Sometimes these filled hybrid orbitals do not form the bonds and the electron pair remains as lone pair on central atom.

vi. The hybrid orbitals are involved in the σbond formation only and π bond is not formed by them at all.

4.4.1. Types of hybridization:

Following are the important types of hybridisation. The central atom in a given molecule/ion can undergo any of the following possible hybridisations.

(i) Sp hybridization:

When one s and one p (oriented along molecular axis) atomic orbitals belonging to the valence shell of the central atom in a given molecule/ion mix up together to give rise two hybrid orbitals, the process is known as sp hybridisation and the new orbitals formed are called sp hybrid orbitals. This process can be shown diagrammatically as follows:

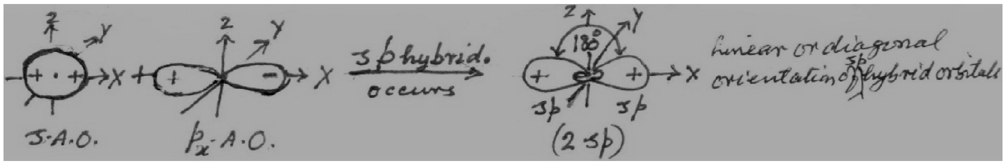


Fig 4.8 (a) *Formation of two collinear sp hybrid orbitals from the mixing of one s and one p atomic orbitals*

Characteristics:

i) These hybrid orbitals are equivalent in energy, shape (oval shaped) and are oriented in the opposite directions at an angle of 180^0 from each other, leading to linear geometry.

ii) Each hybrid orbital has one large lobe and one small lobe. The larger lobe takes part in overlapping process.

iii) These hybrid orbitals possess 50% character of s-orbital (spherical) and 50% that of p-orbital (pear shaped) and hence are oval shaped.

Examples: BeX_2 (X=H,F, Cl). Let us take BeF_2 molecule for illustration.

Be_g: $2s^2p^0$ Be_{ex}: $\longrightarrow \underset{sp}{\underline{2s^1p^1}}$

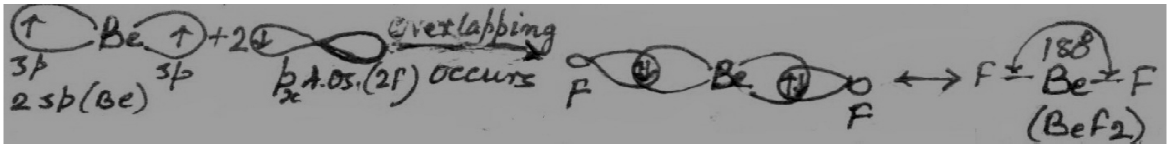


Fig 4.8 (b) *formation of two σcovalent bonds by the overlapping of sp-hybrid orbitals of Be and 2p-orbitals of F-atoms*

(ii) Sp^2 hybridisation:

On mixing together one s and any two p-orbitals belonging to the valence shell of the central atom of a given molecule/ion, a set of three hybrid orbitals is obtained. This process is known as sp^2 hybridisation and the new orbitals formed are termed as sp^2 hybrid orbitals. The process can be shown as given below:

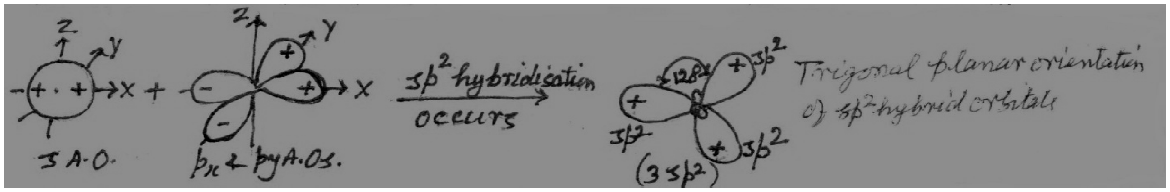


Fig 4.9(a) *Formation of three trigonal planar sp^2 hybrid orbitals from the mixing of one s and two p atomic orbitals*

Characteristics:

i) The sp^2 hybrid orbitals are equivalent in energy and shape and are oriented towards the corners of an equilateral triangle, hence inclined at an angle of 120^{0}with one another, leading to trigonal planar geometry.

ii) They all lie in one plane (i.e. planar).

iii) They possess 33% s- character and 66% p- character and therefore are less oval than sp- hybrid orbitals.

Examples: BX$_3$(X=H, F,Cl) Let us take BF$_3$ molecule for discussion.

B_g :$2s^2\ 2p_x^{\ 1}$ B_{ex}: $\longrightarrow$ $\underbrace{2s^1p_x^{\ 1}p_y^{\ 1}}_{sp^2}$

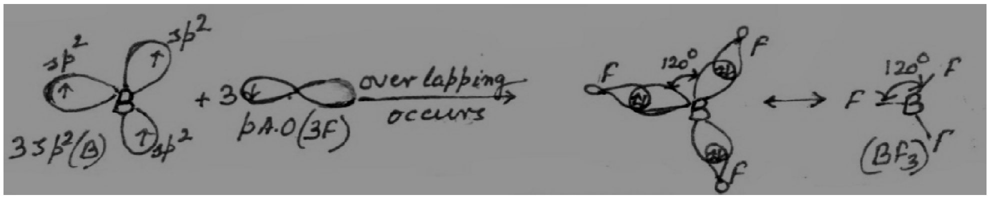


Fig 4.9(b*) formation of three σ covalent bonds by the overlapping of sp^2 hybrid orbitals of B-atoms and 2p-orbitals of 3F-atoms*

(iii) Sp^3 hybridisation:

In this hybridisation, one s and three p-atomic orbitals belonging to the valence shell of the central atom of a given molecule/ion mix up together and form a set of four hybrid orbitals. This mixing process is known as sp^3 hybridisation and the new orbitals formed are called sp^3 hybrid orbitals. This process has been shown below:

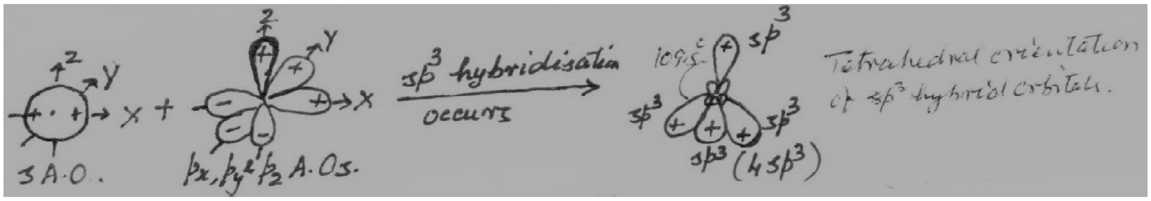


Fig 4.10(a) *formation of four tetrahedral sp^3 hybrid orbitals from the mixing of 1s and 3p atomic orbitals*

Characteristics:

i) These sp^3 hybrid orbitals are equivalent in energy and shape and are oriented along the four corners of a regular tetrahedron. The bond angle between each pair of these orbitals is 109.5^0, called tetrahedral angle.

ii) Each sp^3 hybrid orbital has 25% s- character and 75% p- character, hence their shape is closer to that of p- orbitals i.e. are pear shaped.

Examples: AX_4 where A = C, Si and X = H, F, Cl, Br, I, simplest of these is CH_4. In this molecule, C-atom is the central atom which undergoes sp^3 hybridisation as follows:

$$C_g{:}2s^2\,p_x^1p_y^1p_z^0 \qquad C_{ex}{:} \quad \longrightarrow \quad \underbrace{2s^1p_x^1p_y^1p_z^1}_{sp^3}$$

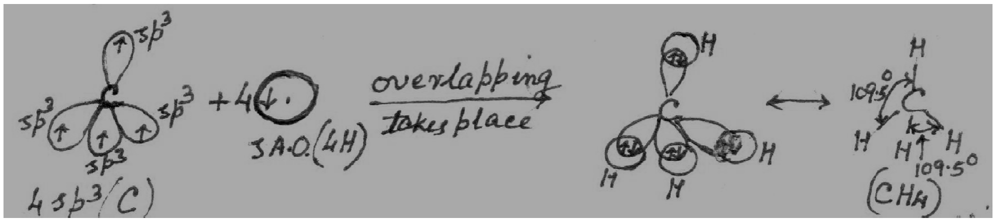


Fig 4.10 (b) *formation of four σcovalent bonds by the overlapping of sp^3 hybrid orbitals of C-atom and 1s orbitals of four H-atoms*

(iv) Sp^{3}d hybridization:

When one s, three p and one d (generally dz^2) atomic orbitals of the valence shell of the central atom of a given molecule/ion mix up together and give rise to the formation of a set of five hybrid orbitals, the process is known as sp^3d hybridisation and the new orbitals formed are called sp^3d hybrid orbitals. The process of this type of hybridisation has been shown here:

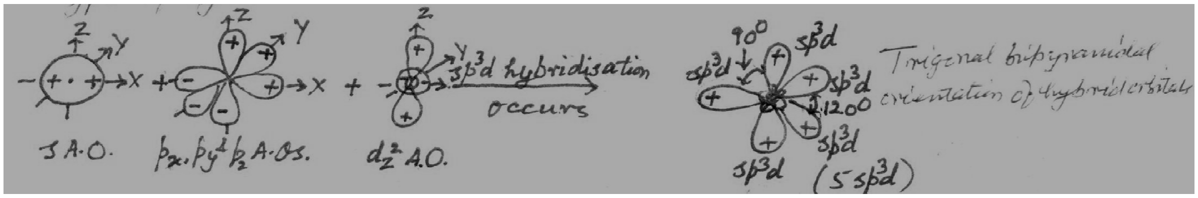


Fig 4.11 (a) *formation of five trigonal tripyramidal sp^3d hybrid orbitals from the mixing of one s, three p and one d (dz^2) atomic orbitals*

Characteristics:

i) The sp^3d hybrid orbitals are equivalent in energy and shape and are oriented towards the five corners of a regular trigonal bipyramid i.e. their spatial arrangement is trigonal bipyramidal.

ii) They do not lie in one plane. Three of the five hybrid orbitals called the basal or equatorial hybrid orbitals are oriented towards the corners of an equilateral triangle forming a triangular plane while the remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of plane. The angle between each adjacent pair of basal hybrid orbitals is 120^0, that between two axial hybrid orbitals is 180^0 and that between the axial and basal hybrid orbitals is 90^0.

Examples: AX_5 molecule (A = P, As, Sb and X = F, Cl, Br). Let us discuss the hybridisation and bonding in PCl_5 molecule.

$$p_g: 3s^2\ p_x^1 p_y^1\ p_z^1 \longrightarrow p_{ex}: \underbrace{3s^1\ p_x^1 p_y^1 p_z^1\ d_{z2}^1}_{sp^3d}$$

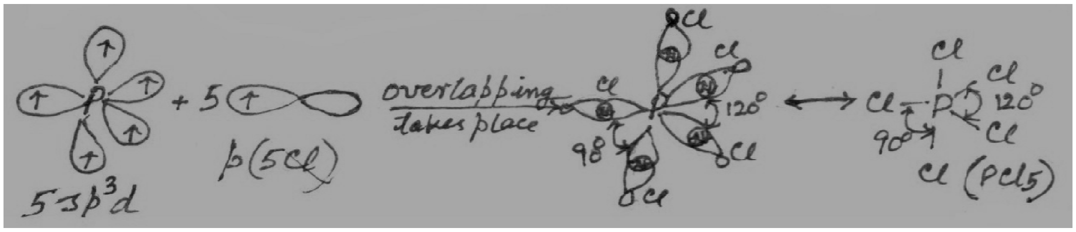


Fig 4.11(b) *Formation of fiveσcovalent bonds by the overlapping of sp^3d hybrid orbitals of P central atom and p-orbitals of five Cl-atoms*

(v) Sp^3d^2 hybridisation:

On mixing one s-orbital, three p-orbitals and two d (generally dx^2-y^2 and dz^2) orbitals of the valence shell of central atom of the given molecule/ion, a set of six hybrid orbitals is formed. This process is known as sp^3d^2 hybridisation and the new orbitals formed are called sp^3d^2 hybrid orbitals. The formation of these orbitals is shown below:

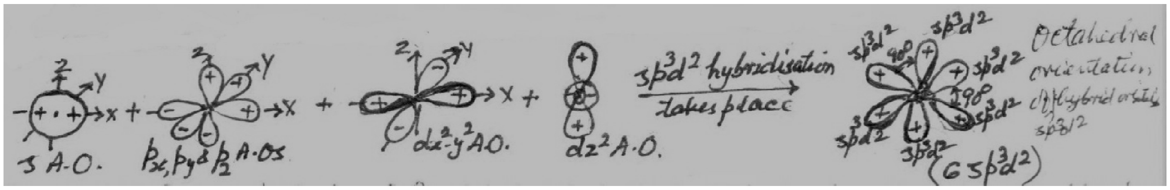


Fig 4.12(a) Formation of six sp^3d^2 hybrid orbitals from the mixing of one s, three p and two d-atomic orbitals

Characteristics:

i) All the six hybrid orbitals formed are equivalent in energy and shape and are oriented along the six corners of a regular octahedron i.e. their arrangement in space is octahedral.

ii) All the orbitals do not lie in a plane. Four hybrid orbitals of the six called basal or equatorial hybrid orbitals are lying in square plane while the remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of the square base. The angles between any adjacent pairs of hybrid orbitals (basal or axial) is 90^0.

Examples: AF_6 type molecule (A=S, Se, Te). Let us see the process of bond formation in SF_6 molecule.

$$S_g: 3s^2p_x{}^2p_y{}^1p_z{}^1 \longrightarrow S_{ex}: \underbrace{s^1p_x{}^1p_y{}^1p_z{}^1\, d^1{}_{z2}d^1{}_{x2\text{-}y2}}_{sp^3d^2}$$

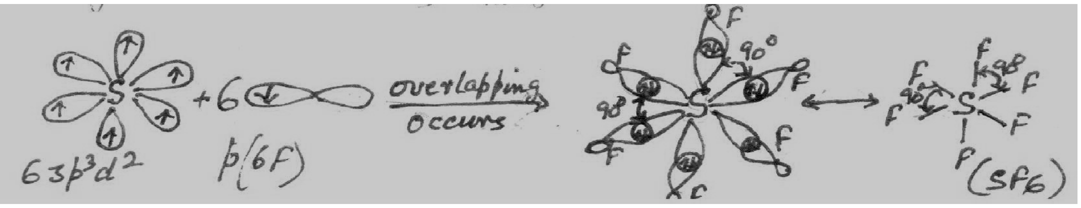


Fig 4.12 (b) *Formation of six σcovalent bonds by the overlapping of sp^3d^2 hybrid orbitals of S central atom with p-orbitals of six F atoms*

(vi) Sp^3d^3 hybridisation:

When one s, three p and three d (generally dxy, dyz, dzx) orbitals of the valence shell of the central atom in a given molecule/ion mix up together, a set of seven new orbitals is formed. This process of mixing is called sp^3d^3 hybridisation and the new orbitals formed are known as sp^3d^3hybrid orbitals. Their formation occurs as follows:

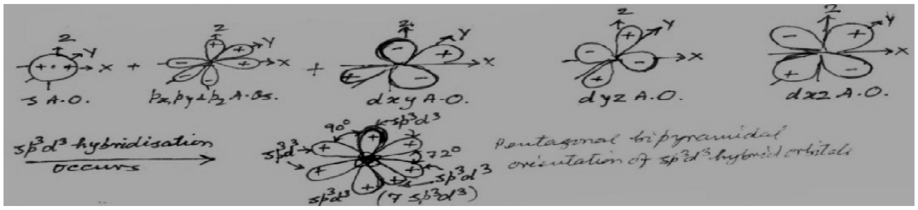


Fig 4.13 (a) *Formation of seven sp^3d^3 hybrid orbitals from the mixing of one s, three p and three d-orbitals of the central atom*

Characteristics:

i) All the seven hybrid orbitals are equivalent in energy and shape and are oriented towards the seven corners of a regular pentagonal bipyramid i.e. their spatial arrangement is pentagonal bipyramidal.

ii) All of them do not lie in one plane. Five of them lie in the pentagonal plane and are called basal or equatorial hybrid orbitals while remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of the pentagonal plane.
iii) The angle between any adjacent pair of basal hybrid orbitals is of 72^0 and that between an axial and a basal hybrid orbital is equal to 90^0.

Example: IF_7 (an interhalogen compound)

$I_g : 5s^2p_x^2p_y^2p_z^1 \longrightarrow I_{ex} : \underbrace{5s^1p_x^1p_y^1p_z^1dxy^1dyz^1dzx^1}_{sp^3d^3}$

The whole act of hybridisation and bond formation in this molecule can be shows as given below:

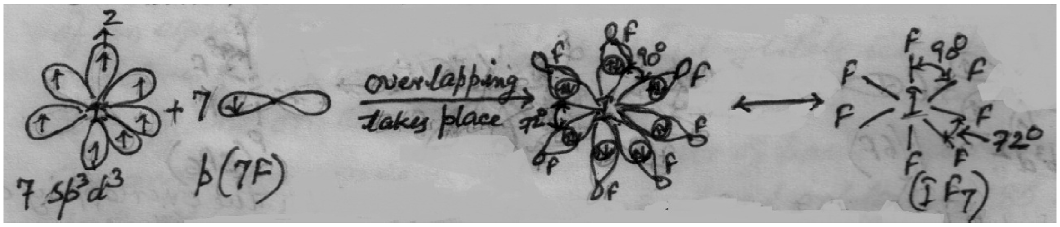


Fig 4.13(b) Formation of seven covalent bonds from the overlapping of sp^3d^3 hybrid orbitals of central I-atom and p-orbitals of seven F-atom

4.4.2 Shape of simple inorganic molecules and ions:

In all the above examples, the central atom uses all of its valence electrons for the bond formation i.e. the hybrid orbitals of the central atom and atomic orbitals (s or p) of the attached atoms are half filled, and after overlapping of the appropriate orbitals, form the normal σcovalent bonds. The molecules so formed have regular geometrical shape i.e. there is no distortion in the shape of the molecule.

However, there are examples in which the central atom of the molecule/ion undergoes a particular type of hybridisation which involves orbital/s with paired electrons as such along with orbitals having unpaired electrons. These hybrid orbitals (with both paired an unpaired electrons) overlap with the orbitals of approaching atoms to give the normal as well as dative σbonds or sometimes the hybrid orbitals with paired electrons do not overlap with the orbitals of approaching atoms and remain attached as such with the central atom in the molecules as lone pairs. The presence of these lone pairs causes distortion in the shape of the molecule/ion. This leads to irregular geometry of the molecule/ion.

The geometrical shapes, and process of hybridisation involved, of some inorganic molecule/ions along with those given under VSEPR Theory in the syllabus will be discussed after the discussion of VSEPR Theory.

4.5. VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The valance bond theory also called the atomic orbital theory can explain the geometrical shape of many molecules/ions of both transition and non-transition elements by employing the concept of hybridisation. But many molecules/ions remain unexplained in terms of their geometry by this method. To overcome this shortcoming, a modification of VBT was developed by Gillespie and Nyholm which can predict the shapes of many species which are left uncovered by the concept of simple hybridisation. According to this theory "The shape or the geometry of a polyatomic molecule/ion of non-transition (mostly non-metallic) element depends upon the number and nature of the electron pairs contained in the valence shell of the central atom." Thus the electrons already present in the valence shell plus the additional electrons acquired by the central atom as a result of bonding with other atoms are called its valence shell electrons. These electrons may be present as bonding or non-bonding electron pairs in the central atom which arrange themselves in such a way that there is a minimum repulsion between them and the molecule has minimum energy and maximum stability. Since there can be only one orientation of orbitals corresponding to minimum energy, hence the molecule attains a definite shape/geometry.

The following rules have been proposed by Gillespie and Nyholm to explain the shape of some inorganic molecule/ions-

i)If the central atom of a molecule/ion contains only the bond pairs of electron in the valence shell, the geometrical shape of the molecule/ion is said to be regular (or undistorted) e.g. linear, trigonal planar, tetrahedral, octahedral etc., respectively. This fact is evidenced by the examples given above in the chapter of hybridisation.

ii) When the valence shell of the central atom in a molecule/ion contains the bonding electron pairs and non-bonded electron pairs (called lone pairs), the molecule/ion has distorted or irregular geometrical shape due to the alteration in bond angles which is caused by the presence of lone pairs on the central atom.

This happens because of the following fact. Since the lone pair of electrons is under the influence of only one nucleus (of central atom), i.e. mono centric, these electrons occupy a broader orbital with a greater electron density radially distributed closer to that nucleus than bonding pair of electrons which is under the influence of two nuclei of bonded atoms i.e. bicentric. Its location between the atoms depends on the electro- negativities of the combining atoms. Thus lone pairs experience more freedom than the bonded pairs and hence exert more repulsion on any adjacent electron pair than a bond pair does on the same adjacent electron pair. The repulsion among the electron pairs follows the sequence as:

$$\underbrace{\text{l.p.-l.p. repulsion}}_{\text{maximum}} > \underbrace{\text{l.p.-b.p. repulsion}}_{\text{intermediate}} > \underbrace{\text{b.p.-b.p. repulsion}}_{\text{minimum}}$$

Because of this fact, if the central atom in a molecule/ion contains both lone pairs (l.ps.) and bonded pairs (b.ps.), there occurs a contraction in the bond angle (which is formed between two adjacent b.ps.). More the number of l.ps. on the central atom, greater is the contraction caused in the bond angle. This statement is supported by the bond angles observed in CH_4, NH_3 and H_2O:

molecules	CH_4	NH_3	H_2O
Type of hybridisation involved	sp^3	sp^3	sp^3
No. of l.ps. on the central atom	0	1	2
Bond angle	109.5^0	107.3^0	104.5^0
Contraction in the bond angle	-	$\approx 2^0$	$\approx 5^0$

iii) $\angle$BAB in AB_2 type molecules decreases with increasing electronegativity of the atom B where A is a central atom. This is because as the electronegativity of the attached atom B increases, the b.p. of electrons moves away from the central atom and experiences less repulsion from its l.ps. and enhanced distance between two bond pairs also causes less repulsion between them resulting in the contraction in bond angle.

For example, (i) $PI_3(\approx 102^0) > PBr_3(\approx 101.5^0) > PCl_3(\approx 100^0)$

(ii) $AsI_3(\approx 101^0) > As\ Br_3(\approx 100.5^0) > AsCl_3(\approx 98.5^0)$

iv) The repulsion between the electron pairs in filled shells is larger than that between electron pairs in incompletely filled shells. As an example, let us compare $\angle$HOH and $\angle$HSH in H_2O and H_2S molecules. It has been observed that $\angle$HOH (104.5^0)>>$\angle$HSH (92.2^0). In both the molecules, the central atoms O and S contain eight electrons in their valence shells, six of their own and two from H-atoms. Thus the valence shell of O-atom (with 2s and 2p orbitals only) is completely filled but that of S-atom is incompletely filled due to the availability of 3d-orbitals (which remain vacant) in addition to 3s and 3p-orbitals. The total capacity of the valence shell of S-atom is to accommodate a maximum of 18 electrons (from $2n^2$ rule).

v)The bond angle involving the multiple bonds are generally larger than those involving only single bonds. However, the geometrical shape of the molecule is not affected by multiple bonds.

Limitations:

The VSEPR Theory suffers from certain limitations which are as follows:

(i) This theory cannot explain the shapes of very polar molecules and those having an inert pair of electrons.

(ii) The shapes of the molecules which have extensive delocalised πelectron systems are not explained by this theory.

(iii) This theory does not cover certain transition metal complexes.

The VSEPR Theory in combination with the concept of hybridisation has been successfully used to discuss and explain the geometrical shapes of most of the covalent inorganic molecules/ions. Here we shall discuss the type of hybridisation and mode of bonding in certain inorganic molecule/ions in addition to those given in the syllabus of VSEPR theory.

A. Shape of $SnCl_2$ molecule (sp^2 hybridisation)

The central atom, Sn, has the ground state valence shell configuration as given below:

Sn_g: $5s^2 5p_x^1 p_y^1 p_z^0 \rightarrow sp^2$ hybridization

This atom undergoes partial hybridisation mixing up together the paired 5s and unpaired $5p_x$ and $5p_y$-orbitals, leaving behind the empty p_z-orbital, to form three sp^2 hybrid orbitals one of which is occupied by the electron pair coming from the 5s-orbital. The process of hybridisation and overlapping of hybrid orbitals with atomic orbitals of Cl-atoms have been shown below:

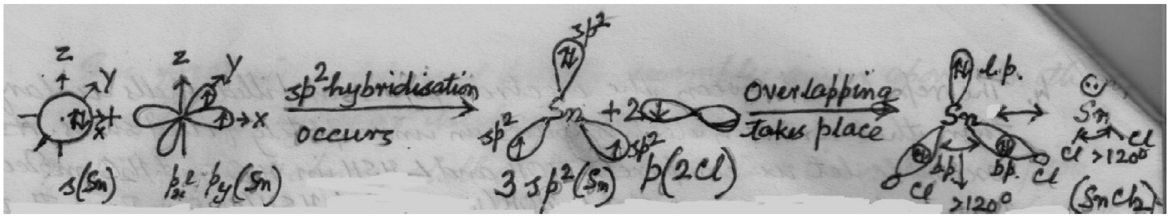


Fig 4.14 Formation of hybrid orbitals and their overlapping with 3p-orbitals of Cl atoms to give $SnCl_2$ molecule

Two unpaired hybrid orbitals of Sn atom overlap with unpaired p-orbitals of approaching Cl-atoms and give $SnCl_2$molecule which contains one lone pair of electrons on Sn-atom. Because of the greater repulsion of lone pair on bond pairs, the ∠Cl SnCl is less than 120^0, the expected angle in case of sp^2 hybridisation. The molecule thus attains angular or bent shape.

B. Shape of NH_3 Molecule (sp^3 hybridisation)

In NH_3 molecule, the central atom N has following ground state valence shell configuration:

N_g : $2s^2 p_x^1 p_y^1 p_z^1 \rightarrow sp^3$ hybridization

All these atomic orbitals participate in hybridisation and give four equivalent sp^3 hybrid orbitals. One of them contains an electron pair (lone pair) and three half filled hybrid orbitals then overlap with 1s orbitals of three H-atoms to form σcovalent bonds (N-H bond).

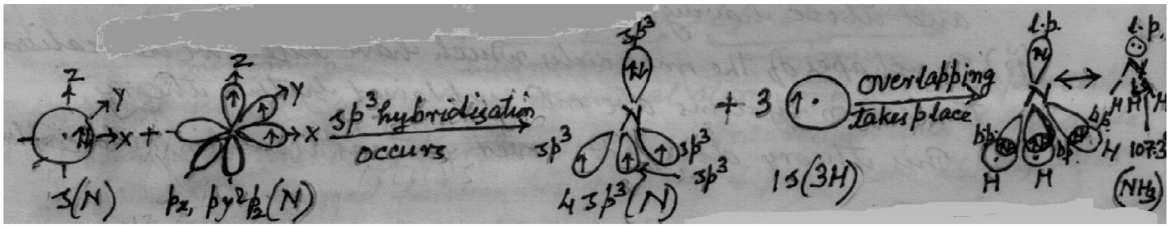


Fig 4.15 *Formation of hybrid orbitals and their overlapping with 1s orbitals of 3H atoms to give NH_3 molecule*

From the figure, it is evident that one lone pair of electrons is present in NH_3 molecule which exerts more repulsion on bonded pairs than that operating between the bonding pairs of electrons. The net result is that the NH_3 molecule attains trigonal pyramidal shape with the bond angle of 107.3^0, a deviation of about 2^0 from the tetrahedral angle of 109.5^0.

C. Shape of H_2O Molecule (sp^3 hybridisation)

The ground state valence shell configuration of the central atom O of H_2O molecule is:

O_g: $2s^2p_x^2p_y^1p_z^1$ → sp^3 hybridization

All these atomic orbitals undergo hybridisation and give rise to four equivalent sp^3 hybrid orbitals. Two of these hybrid orbitals are half filled and remaining two contain lone pairs of electrons. The unpaired hybrid orbitals than overlap with 1s orbitals of two H-atoms to form σcovalent bonds (O-H bonds).

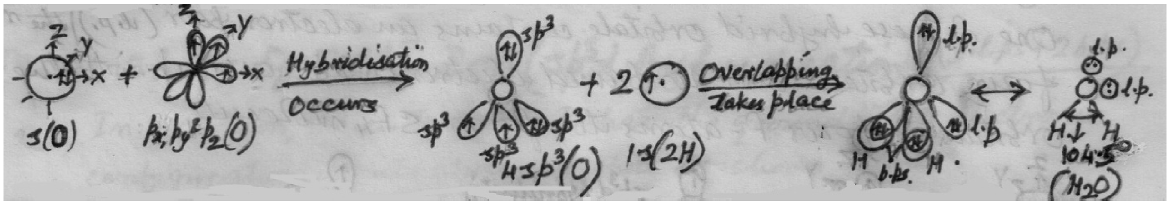


Fig 4.16 *Formation of hybrid orbitals and their overlapping with 1s orbitals of two H-atoms to give H_2O molecule*

There are two lone pairs of electrons present in H_2O molecule which exert strong repulsion on each other and move away towards the bonded pairs of electrons. This brings the bonded pairs closer to each other thereby causing contraction in the bond angle. H_2O molecule thus attains a V-shaped geometry with the bond angle of 104.5^0, a deviation of a bond 5^0 from the tetrahedral angle of 109.5^0

D. Shape of H_3O^+ Ion (sp^3 hybridisation)

Hydronium ion (H_3O^+) is formed by the combination of H_2O molecule and H^+ ion in which H_2O molecule donates one of its lone pairs of electrons to H^+ ion and it accepts that lone pair of electrons in its vacant 1s orbital.

Actually, filled sp^3 hybrid orbital of O-atom in H_2O molecule overlaps with empty s-orbital of H^+ ion as follows thereby forming a coordinate covalent bond:

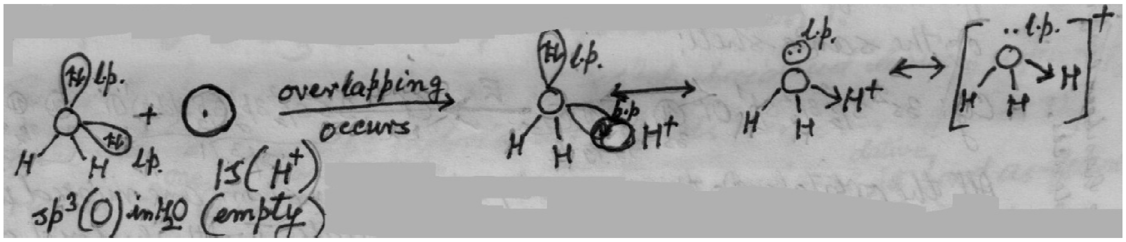


Fig 4.17 *Overlapping of filled sp^3 hybrid orbital of O-atom in H_2O and empty 1s orbital of H^+ ion to form H_3O^+ ion*

This ion has trigonal pyramidal shape like that of NH_3 molecule with one lone pair of electrons on O-atom.

E. Shape of SF_4 molecule (sp^3d hybridisation)

In this molecule the central S-atom is in its first excitation state in which one of its p_x electrons is promoted to the next empty dz^2 orbital. The electronic configuration in the ground and first excited state has been shown below:

S_g: $3s^2p_x^2p_y^1p_z^1$ ⟶ S_{1ex} : $3s^2p_x^1p_y^1p_z^1\,(dz^2)^1$ ⟶ sp^3d

All these atomic orbitals of S_{ex} central atom get hybridised to give five sp^3d hybrid orbitals directed toward the corners of a trigonal bipyramid, one of these hybrid orbitls contains an electron pair (b.p.) and the next four orbitals have unpaired electrons which overlap with the p-orbitals of four F-atom to form SF_4 molecule.

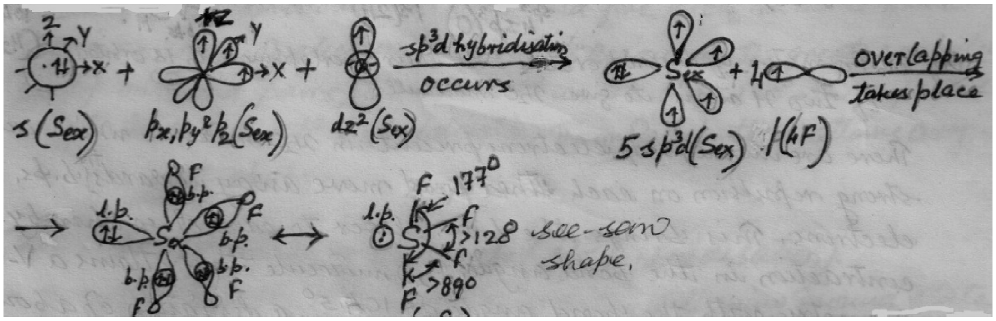


Fig 4.18 Formation of five hybrid orbitals of S_{ex} atom and their overlapping with p-orbitals of four F-atom to give SF_4 molecule

This molecule attains a see-saw shape because of the presence of one lone pair of electron (sometimes also called distorted tetrahedral) and lone pair lies at one of the basal positions (the molecule has 1 lone pair and 4 bonded pairs)

F. Shape of ClF_3 molecule (sp^3d hybridisation)

Cl is the central atom in this molecule with valence shell electronic configuration in ground and first excited state as given below wherein one electron from a filled p-orbital say p_y is promoted to a vacant d-orbital (*viz.* dz^2) of the same shell:

Cl_g: $3s^2p_x{}^2p_y{}^2p_z{}^1$ $\longrightarrow$ $Cl_1{}^{st}{}_{ex}$: $3s^2p_x{}^2p_y{}^1p_z{}^1\,(dz^2)^1$ $\longrightarrow$ sp^3d

All the orbitals of the valence shell of $C_l{}^{st}{}_{ex}$ atom are mixed up together to produce five sp^3d hybrid orbitals. Two of the hybrid orbitals have lone pairs of electrons and three have unpaired electrons which then overlap with unpaired p-orbitals of three F-atoms to form σ covalent bonds. The lone pairs are said to occupy the equilateral positions and the molecule attains T-shaped structure with the bond angle of 87.6^0 instead of 90^0 due to the distortion caused by lone pairs The T-shaped structure has been confirmed by the experimental evidences. The whole act of hybridisation, overlapping and bond formation can be shown as below (molecule has 2 lone pairs and 3 bonded pairs):

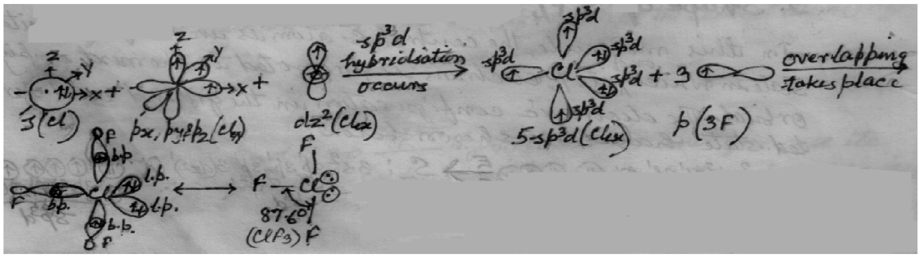


Fig 4.19 *Formation of five hybrid orbitals of $Cl_l{}^{st}{}_{ex}$ atom and their overlapping with p-orbitals of three F-atoms to give ClF_3 molecule*

The mode of hybridisation shape and bonding in BrF_3 and ICl_3 molecules can also be explained on the similar grounds as in the case of ClF_3.

G. Shape of ICl_2^- Ion (sp^3d hybridisation)

In ICl^-_2 ion, the central atom I (iodine) has the ground state electronic configuration in its valence shell as shown below:

I_g: $5s^2p_x{}^2p_y{}^2p_z{}^1\,(d_z{}^2)^0$

All these atomic orbitals including a vacant dz^2 orbital participate in hybridisation to produce five sp^3d hybrid orbitals of which three orbitals contain lone pairs, one hybrid orbital is half filled which overlaps with half filled p-orbitals of Cl-atom to give normal σbond and one hybrid orbital remains vacant and overlaps with the filled orbital of Cl^- ion to give a coordinate covalent σbond (dative bond). The lone pairs occupy the equatorial positions and the bonded pairs are situated in axial positions. The ion has 3 lone pairs and 2 bonded pairs as shown below and has almost linear shape:

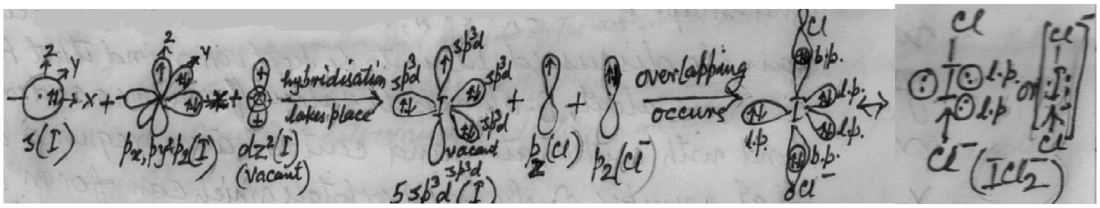


Fig 4.20 *Formation of five sp^3d hybrid orbitals ofcentral atom, I and overlapping of one of these hybrid orbitals with p-orbital of Cl atom and that of filled p-orbital* of *Cl^-ion with vacant* ***hybrid orbital of I atom***

H. Shape of NO_3^- ion (sp^2 hybridisation)

The central N-atom in this ion is sp^2 hybridised leaving a pure p_z orbital behind. These sp^2hybridised orbitals then overlap with the orbitals of one O atom and one O^-ion to form two normal σbonds and one dative σ bond as follows:

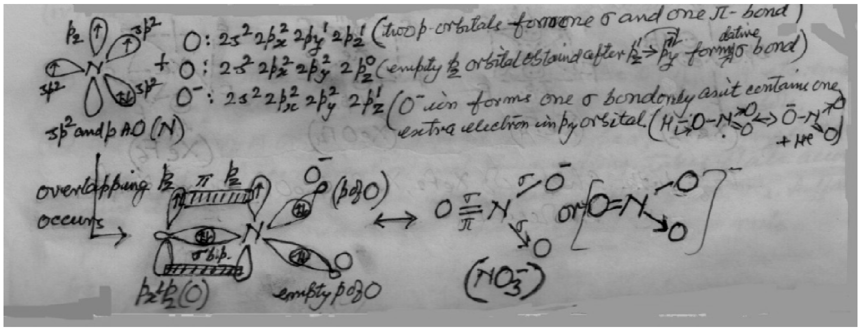
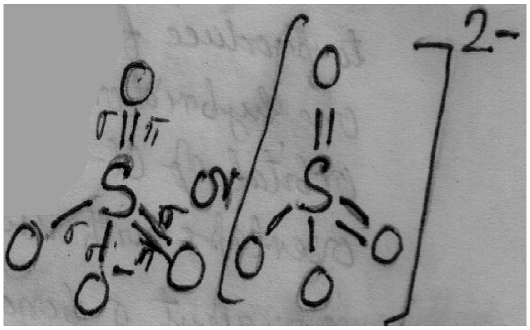


Fig 4.21 *Formation of two normalσbonds, one dative σ bond and one π bond between N central atom and oxygen atoms/ion*

I. Shape of SO_4^{2-} ion (sp^3 hybridisation)

S atom has 6 electron its valence shell and in this ion all the valence electrons of S are present in unpaired state i.e. S_{2ex} state. Out of six, four orbitals are hybridised as follows:

$S_g : 3s^2p_x^2p_y^1p_z^1 \longrightarrow S_{2}{}^{nd}{}_{ex} : 3s^1p_x^1p_y^1p_z^1\ (d_{x2-y2})^1(d_{z2})^1 \longrightarrow sp^3$



The SO_4^{2-} ion can be shown as follows:

For details please refer to sp^3 hybridization & CH_4 molecule.

It has tetradedral shape like CH_4 molecule but has two single and two double bonds (σand π). On the similar grounds the type of hybridisation and shape of XeF_2, XeF_4, $XeOF_4$ and XeF_6 molecules can be discussed. It is to be kept in mind that F-atom is monovalent, O-atom is bivalent (forms one σand one π-bond with central atom) and central atom requires only that number of hybrid orbitals which can form σbonds with approaching atoms and these hybrid orbitals are generally unpaired or half filled. Hence in the above molecules partial hybridisation may take place.

X_eF : sp^3d 3 lone pairs + 2 bonded pairs and linear in shape

X_eF_4: sp^3d^2 2 lone pairs + 4 bonded paires and square planar

X_eOF_4 : sp^3d^2 1 lone pair + 5 bonded pairs +1 πbond and is square pyramidal

X_eF_6 : sp^3d^3 1 lone pair + 6 bonded pairs and pentagonal pyramidal

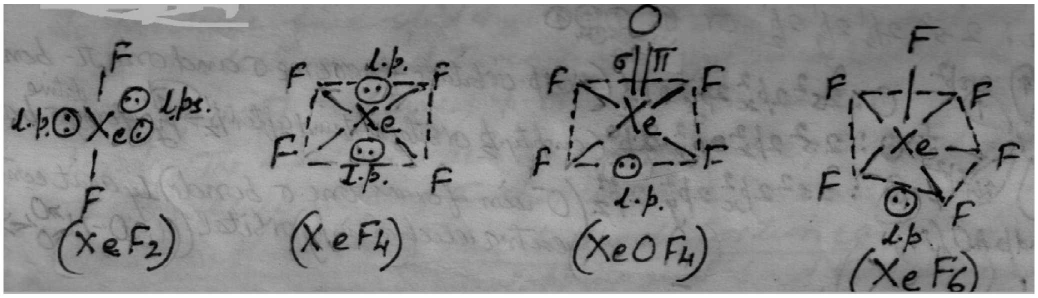


Fig 4.22 *Shapes of XeF_2, XeF_4, $XeOF_4$ and XeF_6 molecules*

4.6 MOLECULAR ORBITAL THEORY (MOT)

To explain the formation of the covalent bond in molecules/ions and their behaviour like relative bond strength, magnetic property etc., a new approach was developed by Hund and Mulliken in 1932 and later by Lennard Jones and Coulson. This approach is known as **Molecular Orbital Theory**. This theory treats the covalent bonds in terms of Molecular

Orbitals (MOs) which are associated with the entire molecule and result from the linear combination of atomic orbitals (LCAOs) of constituent atoms of the molecule/ion. Thus the molecules are supposed to have their own orbitals of varying energy in the same way as the isolated atoms have. The difference between an atomic orbital and a MO is that an electron in an atomic orbital is influenced by one nucleus only i.e. an atomic orbital is monocentric while an electron in a M.O. is under the influence of all the nuclei contained in the molecule/ion, i.e. a M.O. is polycentric.

The atomic orbitals combining linearly to form the MOs must be of the similar energy and same symmetry and may be of the two similar atoms of a homonuclear diatomic molecule/ion (e.g. H_2, H_2^+, N_2, O_2, O_2^{2-} etc.) or may be of two different atoms of a heterodiatomic molecule/ion (e.g. CO, NO, CN^-, NO^+ etc.).

The main characteristics of MOT are as follows:

(i) The atomic orbitals (AOs) combining linearly together to form the moleculer orbitals (MOs) lose their identity and the number of atomic orbitals is equal to the number of moleculer orbitals formed.

(ii) MOs are the energy states of the molecules/ions in which the electrons are filled just like in AOs of the atoms.

(iii) The linear combination of the AOs may occur in two different ways, i.e. the additive combination gives bonding molecular orbitals (BMOs) and the subtractive combination gives antibonding molecular orbitals (ABMOs).

(iv) The bonding MO has lower energy and hence greater stability than the antibonding MO obtained from two AOs.

(v) The bonding MOs are denoted by σ,π,δ,Ψetc. symbols while the antibonding MOs by $\sigma^*,\pi^*,\delta^*,\Psi^*$ etc. symbols.

(vi) The shapes of MOs formed depend on the type of combining AOs and mode of combination and their filling takes place according to the rules which are applicable for AOs, *viz*. Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Formation of MOs LCAO approximation

Suppose Ψ_A and Ψ_B represent the wave function of the electrons in the A.Os. of the atoms A and B respectively. Then linear combination of these A.Os. may be done in two ways:

i) $\Psi^b = \Psi_A + \Psi_B$ (++ combination) ……… (4.10)

This additive combination of AOs gives bonding molecular orbital for which the wave function is denoted by Ψ^b. This is also called constructive interaction. Further, from the above equation, we have

$(\Psi^b)^2 = (\Psi_A+\Psi_B)^2 = \Psi_A^2+\Psi_B^2+2\Psi_A\Psi_B$ -………. (4.11)

Or $(\Psi^b)^2 > \Psi_A^2+\Psi_B^2$ by a factor $2\Psi_A\Psi_B$ where squares of respective Ψs give the probability of locating the electrons in the different orbitals. From this we infer that electrons prefer to reside in the BMO rather than the AOs and placing electrons in BMO yields a stable covalent bond. In this MO the electron density is greater between the nuclei of bonding atoms.

ii) Ψ^* (or Ψ^a) = $\Psi_A-\Psi_B$ (+- (plus minus combination) ….. (4.12)

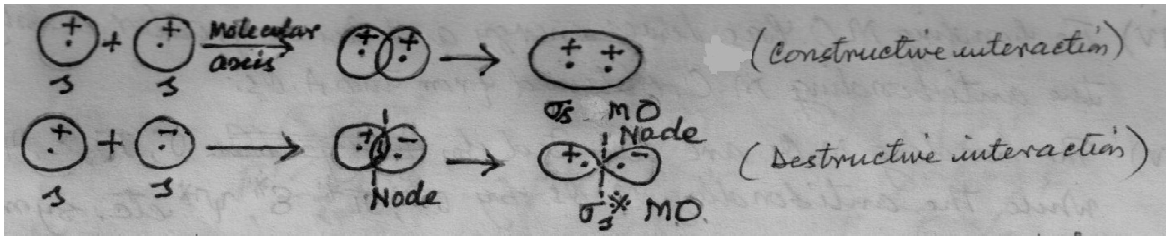
This subtractive combination of AOs gives the antibonding molecular orbital, the wave function for which is represented by Ψ^* (psi star). This is also called destructive interaction. From this equation, we have

$(\Psi^*)^2 = (\Psi_A-\Psi_B)^2 = \Psi_A^2+\Psi_B^2 - 2\Psi_A\Psi_B$ … (4.13)

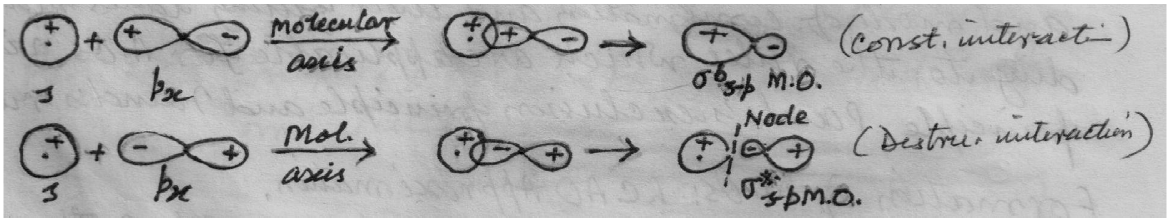
Or $(\Psi^*)^2 < \Psi_A^2+\Psi_B^2$ by a factor $2\Psi_A\Psi_B$. From this relation it can be concluded that electrons prefer to occupy the AOs rather than the ABMO and placing electrons in this MO opposes the bond formation. The electron density in this MO, decreases to zero between the nuclei.

The pictorial representation of the formation of BMOs and ABMOs form AOs is shown below:

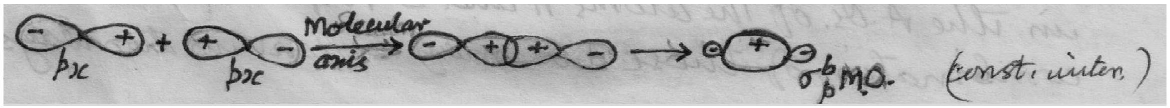
s-orbitals: combination of s-orbitals gives only σMOs (both bonding and antibonding)

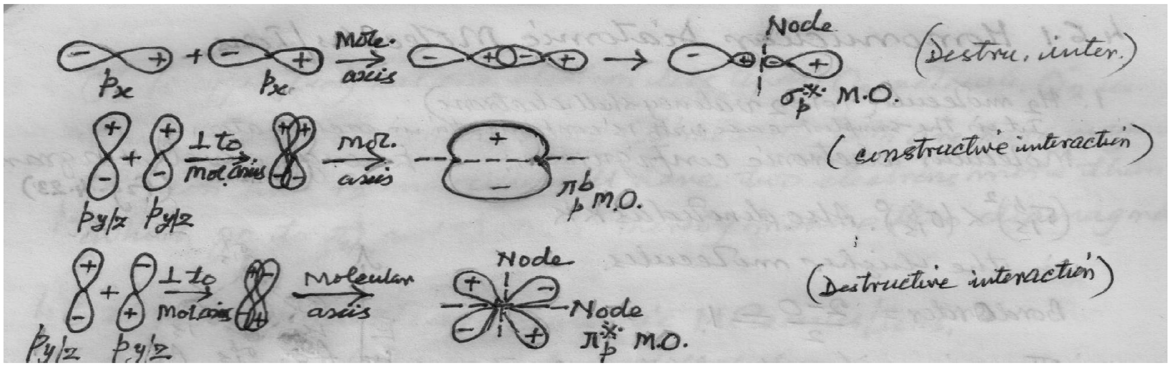


s and p-orbitals: This combination also gives only σM.Os. This is possible only along molecular axis i.e. orientation of p-orbital is along molecular axis.



p-orbitals: The linear combination of p-orbitals may give σas well as π MOs (b and * both).





It is to be noted that the interaction of AOs occurs to form the MOs only if the symmetry consideration are taken care of, e.g. s-p_x combination is allowed but s-p_y and s-Thep_z combination is disallowed if p_x lies along the molecular axis. Similarly, p_x-p_y, p_x-p_z and p_y-p_z combinations are disallowed. p_y-p_y and p_z-p_z combination will produce πM.Os. if X- axis is the molecular axis. Theπ^b_{py} and π^b_{pz} as well as π_{py}^* and π_{pz}^* MOs have the same energy, i.e. these are degenerate orbitals.

Energy level diagrams of the molecules/ions

The MOs of the molecules/ions if arranged in the increasing order of their energy, we get the so called energy level diagrams for them in which the MOs are taken as energy levels.

The electron are filled in these energy levels (MOs) from the lowest energy MO to higher energy MOs according to Aufbau principle. The degenerate MOs are filled according to Hund's rule, i.e. first singly and then in pairs. This condition is applicable to both homonuclear and heteronuclear diatomic molecules/ions.

At the same time if these MOs are written is a sequence using their symbols along with the number of electrons contained in them, then we get the molecular electronic configuration in the same way as the electronic configuration of atoms. This sequence according to increasing energy is:

$$\sigma^b_{1s} < \sigma^*_{1s} < \sigma^b_{2s} < \sigma^*_{2s} < \sigma^b_{2p_x} < \pi^b_{2p_y} = \pi^b_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

This sequence has been found to hold for O_2, F_2 etc. but for hypothetical B_2, C_2, N_2 etc. σ^b2px is of slightly higher energy than $\pi^b 2p_{y/z}$ MOs due to certain well established reasons and hence the sequence becomes (taking x axis as the molecular axis).

$$\sigma^b_{1s} < \sigma^*_{1s} < \sigma^b_{2s} < \sigma^*_{2s} < \pi^b_{2p_y} = \pi^b_{2p_z} < \sigma^b_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Bond order: The bond order is the number of bonds in the molecular species and is given as:

Bond Order $= (N_a – N_b)/2$, N_a= number of antibonding electrons, N_b=number of bonding electrons

4.6.1. Homonuclear diatomic molecules/ions:

i) H_2 molecule (i.e. 1+1=2 valence shell electrons) It is simplest case with $1s^1$ configuration in each H-atom. Molecular electronic configuration:

$(\sigma^{b}_{1s})^2 < (\sigma^{*}_{1s})^0$. Also denoted as KK in the higher molecules.

Bond Order = (2–0)/2=1

.: There is single bond between H-atoms in H_2 molecule (H-H).

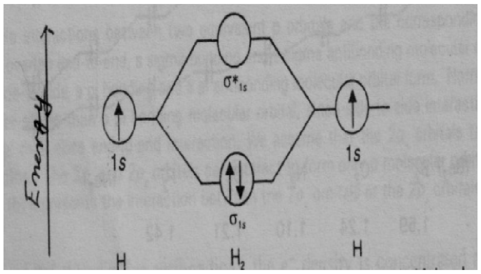


Fig 4.23) Energy level diagram of H_2

ii) N_2 molecule (5+5=10 valence shell electrons)

Each N-atom has $2s^22p^3$ electronic configuration in the valence shell. Thus Molecular electronic configuration of N_2 is:

$$(KK)^4 < (\sigma^{b}_{2s})^2 < (\sigma^{*}_{2s})^2 < (\pi^{b}_{2p_y} = \pi^{b}_{2p_z})^4 < (\sigma^{b}_{2p_x})^2$$

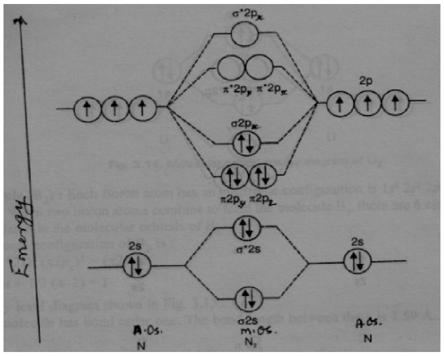


Fig 4.24 Energy level diagram of N_2

Bond order= 8-2=6/2=3. Hence there is a triple bond between N atoms in N_2 molecule. KK are non bonding orbitals.

iii) O_2 molecule (6 + 6 = 12 valence shell electrons)

Each O-atom has $2s^22p^4$ valence shell electronic configuration. $1s^2$ electrons of both O atoms belonging to KK MOs. are non-bonding.

.: Electronic configuration of O_2 molecule is**:**

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^{*}_{2s})^2 < (\sigma^b_{2p_x})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\pi^{*}_{2p_y})^1 = (\pi^{*}_{2p_z})^1$$

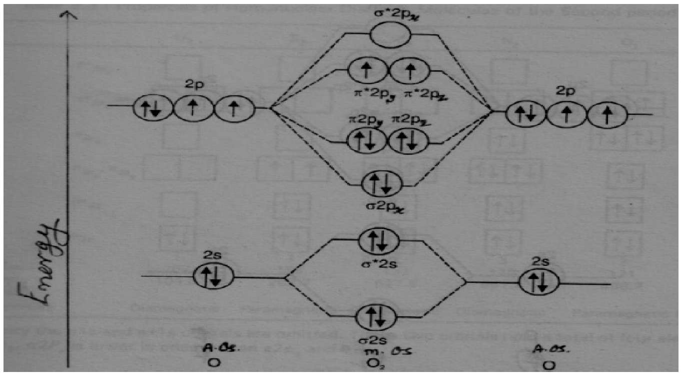


Fig 4.25 eneregy level diagrm of O2

Because of the presence of two unpaired electrons
in ABMOs, O_2 molecule is paramagnetic in nature.

Bond order = (8-4)/2 = 2, There is a double bond between O-atoms in O_2 molecule (O=O)

Similarly we can write down the electronic configuration and draw the energy level diagrams for O_2^+, O_2^- (super oxide ion), O_2^{2-} (peroxide ion) and F_2 molecule.O_2^+ (oxygenyl ion) has one electron less than O_2 molecule. O_2^- ion will have one electron more than O_2 molecule. Both are paramagnetic. O_2^{2-} ion and F_2 molecule will have two electrons more than O_2 which go to π_2p_{y*} and π_2p_{z*} MOs thereby making them diamagnetic.

4.6.2. Heteronuclear diatomic molecules/ions:

i) CO molecule (4+6=10 valence shell electron).

This molecule is isoelectronic with N_2 molecule and has similar molecular electronic configuration and energy level diagram to that of N_2 molecule. There is only a minor difference in electronic distribution in A.Os. as given below:

C : $2s^2 2p^2$; O : $2s^2\ 2p^4$

Electronic configuration of CO molecule is (the M.O. energy level sequence is like that of N_2):

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^*_{2s})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\sigma^b_{2p_x})^2$$

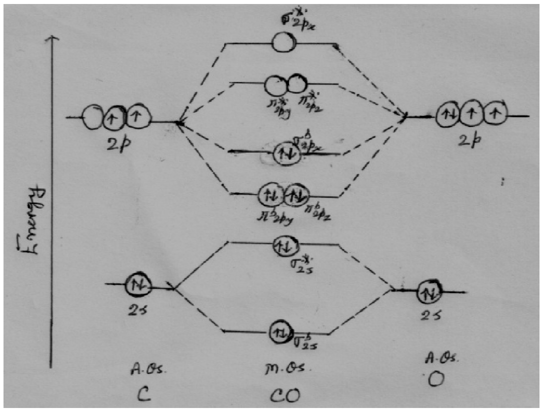


Fig 4.26 Energy level diagram of CO

Bond order =8-2/2=3 (triple bond)

ii) NO molecule (5+6=11 valence shell electron)

N: $2s^2 2p^3$ and O: $2s^2 2p^4$

The electronic configuration of NO molecule is (the M.O. energy level sequence is like that of O_2) but electron distribution is slightly different.

It is paramagnetic due to the presence of one unpaired electron. The bond between N and O is 2½ times as strong as a normal covalent bond.

Similarly, we can write down the electronic configuration and draw energy level diagram for NO^+ (one electron less than NO) ion which is diamagnetic and has only paired electrons upto $\pi^{b}{}_{z}p_{x}$ M.Os. and $\pi^{z}p^{*}{}_{y}$ M.O. is vacant.

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^*_{2s})^2 < (\sigma^b_{2p_x})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\pi^*_{2p_y})^1 = (\pi^*_{2p_z})^0$$

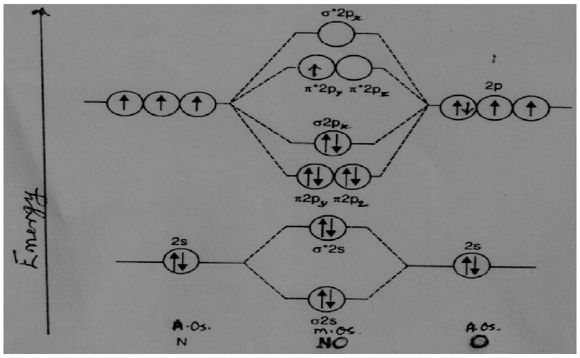


Fig. 4.27 Energy level diagram of NO

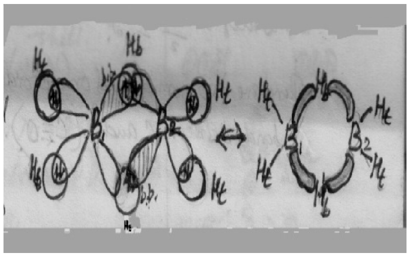
4.7. MULTICENTRE BONDING IN ELECTRON DEFICIENT MOLECULES

In the covalent compounds, in general, an electron pair bond holds two atoms together but there are a number of compounds in which an electron pair holds several atoms together. In these cases, it is said that multicentre or delocalized bond exists. The best known molecule which displays multicentre bonding is B_2H_6, diborane.

A number of evidences showthat the B_2H_6 molecule has hydrogen bridged structure in which four H-atoms are terminal hydrogen atoms (H_t) and the remaining two H-atoms are the bridging hydrogen atoms (H_b). The four H_t atoms are bonded with B-atoms by the normal electron pair bonds (two H-atoms are attached to each B-atom) and H_b-atoms form a multicentre (3c-2e) bond with each B-atom.

Boron has valence shell configuration: B_g: $2s^2p^1$ $\rightarrow B_{ex}$: $s^1p_x^1p_y^1p_z^0$ $\rightarrow sp^3$ hybridization

Thus a maximum of three unpaired orbitals are available in B-atom to form three electron pair bonds with H-atoms to give BH_3. But the given molecule is B_2H_6, it means $H_3B?BH_3$ type situation must be there and there are no electrons available to form the B-B bond in this molecule. This anomaly has been explained as follows:



Each B-atom undergoes sp^3 hybridisation. Two of the hybrid orbitals (half filled) form two σbonds with two H_t atoms in each B-atom. Now one half filled (shaded) orbital of say $B_1$and empty hybrid orbital of B_2 overlap jointly with half filled 1s orbital of H_b atom to give $B_1H_bB_2$ type multicentre bond. Similarly, another 3c-2e bond is formed by the overlapping of empty hybrid orbital of B_1, half filled hybrid orbital (shaded) of B_2 and half filled 1s-orbital of another H_b-atom. These 3c-2e bonds are banana shaped. Therefore, this structure of B_2H_6 is also known as banana structure. Thus the H_b atoms in this molecule may be said to show bivalence which is possible only when the two H_b atoms are bonded with both the B-atoms forming two BHB bridging or 3c-2e bonds.

Another example of multicentre bonding is H_2^+ (hydrogen molecule ion) which contains a 2c-1e bond.

4.8. BOND STRENGTH

By bond strength we mean how strong is the bond between the atoms in a molecule. Bond length, bond multiplicity and extent of overlapping of atomic orbitals in addition to bond energy are the factors which determine the bond strength.

It has been observed that as the bond multiplicity increases, the bond length decreases thereby increasing the bond strength. Similarly, as the extent of overlapping between the atomic orbitals increases, the bond formed becomes stronger. That is why a σbond is stronger than a πbond. Another important factor influencing the bond strength is the bond energy(bond strength ά bond energy).

4.8.1 Bond energy:

The bond energy can be explained in two ways:

(i) Bond formation energy (ii) bond dissociation energy

(i) Bond Formation Energy:

The bond formation energy of a covalent bond A-A or A-B in a diatomic molecule A_2 or AB is the amount of energy released during the formation of these molecules from the atoms A and B.

A+A $\longrightarrow$ A-A + Energy released, $-E_{A-A}$ these are the exothermic
atoms molecule processes, hence the
A+B $\longrightarrow$ A-B + Energy released,- E_{A-B} energy is shown with
atoms molecule negative sign

This can be defined as **"the amount of energy released when one mole (Avogadro's number) of bonds are formed between the constituent atoms in gaseous state of a molecule of A_2 or AB type".** This energy is expressed in kJ mol^{-1}.

(ii) Bond dissociation energy

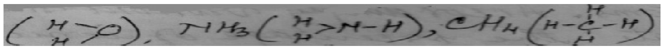
It is the energy required to break the A-A bond in A_2 or A-B bond in A-B molecule into the constituent atoms, i.e.

$$\left.\begin{array}{l} \underset{\text{molecule}}{\text{A-A}} + \text{Energy required}, + E_{A-A} \longrightarrow \underset{\text{atoms}}{\text{A+A}} \\ \underset{\text{molecule}}{\text{A-B}} + \text{Energy required}, + E_{A-B} \longrightarrow \underset{\text{atoms}}{\text{A+B}} \end{array}\right\}$$

these are the endothermic processes and hence the energy is shown with positive sign

This can be defined as **"the amount of energy required to break one mole of bonds in gaseous state of a molecule of A_2 or AB type into the constituent atoms."**

Evidently both the bond formation energy and bond dissociation energy for **A-A or A-B bonds** in A_2 or AB diatomic molecule are equal in magnitude but are associated with opposite processes.

In polyatomic molecules of AB_n type, n numbers of A-B covalent bonds are present e.g. H_2O etc. 

molecules have two, three and four bonds respectively and equal number of bond dissociation energies are there. Each bond requires 1/n bond dissociation energy in these molecules to break up that bond.

In such cases the bond energy is actually an average bond energy. For example, there are two bonds in H_2O molecule:

$$\left.\begin{array}{lll} H_2O \quad OH+H,\ D_{HO-H} \longrightarrow & = 496\ \text{KJ} \\ \text{and } OH \longrightarrow \quad O+H,\ D_{O-H} & = 426.5\ \text{KJ} \end{array}\right\}$$

Total bond dissociation energy of two covalent bond in H_2O molecule

= 496+426.5 =922.5 J mol^{-1}

The average bond energy for O-H bond in water is 461.2 kJ mol^{-1}. Thus, it can be generalized as:

Average bond dissociation energy of A-B bond in AB_n gaseous molecule

$$= \frac{\text{sum of successive A-B bond dissociation energires}}{\text{Total number of A-B bonds in } AB_n \text{ molecule (n)}}$$

4.8.2 Measurement of bond energy:

i) In diatomic molecules

The determination of bond energy in a diatomic molecule containing a covalent bond involves the measurement of heat of formation of the molecule from its free atoms. But normally this cannot be measured directly because a compound is formed from molecules and not from free atom as well as a compound on dissociation splits up into molecules and not into free atoms of its component elements. Further, a molecule cannot be completely dissociated into its free atoms merely by heating. This can, however, be obtained from heat of reaction which, in turn, is measured from the change in the degree of dissociation with temperature and from heat of sublimation.

ii) In polyatomic molecule

The average bond energy in a polyatomic molecule can be obtained from measured heats of formation and heats of atomisation. For example, to obtain the average bond energy for the C-H bond in methane, it require measurement of the heats of combustion of methane, graphite and hydrogen gas together with the heats of atomization of graphite and hydrogen gas.

4.9. PERCENTAGE OF IONIC CHARACTER

The percentage of ionic character of a polar covalent bond (also called polarity) depends on two factors: (i) dipole moment and (ii) electronegativity difference between the combining atoms. Accordingly, various methods are employed to calculate the percentage of ionic character of a covalent bond.

i) Dipole moment (dpm) method

A polar molecule acts as a dipole i.e. $A^{\delta+}$ - $B^{\delta-}$ ($\chi_A < \chi_B$) because of the electronegativity difference between the combining atoms. The degree of polarity in the molecule is given by the dipole moment (μ) which is the product of the magnitude of the charge at each centre (this is equal and of opposite in nature at the two centres) and the distance separating the two centres, i.e. positive and negative.

Thus, $\mu = q x d$, where q is magnitude of change at each centre and d is distance between the two poles. The measured (or experimental) dipole moment (μ_{exp}) of a molecule can be used to evaluate the ionic character in a bond.

$$\% \text{ ionic character} = \frac{\text{Experimental or measured dipole moment}}{\text{calculated dipole moment (assuming 100\% ionic character}} \times 100$$

$$= \frac{\mu_{exp}}{\mu_{cal}} x100$$

$$= \frac{\mu_{exp}}{d_{A-B} \text{ x electronic charge}} x100$$

where d_{A-B} is internuclear distance between A and B atoms in AB molecule. For example, the experimental or observed dpm of HF is 1.98D and the internuclear distance (d_{H-F}) is 0.91Å. If the bond is taken 100% ionic in the molecule, then calculated dpm (μ_{cal}) is electronic charge X internuclear distance = $4.8x10^{-10}$ esu x $0.91x10^{-8}$ cm = 4.37×10^{-18} esu cm = 4.37 D (Å=10^{-8}cm and D stands for Debye)

.: % ionic character = 1.98/4.37 x100=45.3%

ii) Electronegativity difference method

In the polar molecule AB, polar covalent bond is present, the polarity or % ionic character which depends on the electronegativity difference between the linked atoms and can be evaluated by using various empirical equations.

(a) Pauling's equation

According to Pauling, the amount of ionic character in the A-B bond is:

% ionic character = 1- $e^{1/4(\chi_B - \chi_A)}$ ($\chi_B > \chi_A$)

With the help of this equation Pauling established the following relation:

$\chi_B - \chi_A$	1.0	1.7	2.0	3.0
% ionic character	~22	~ 51	~ 63	~ 91

This shows that when $\chi_B - \chi_A = 1.7$, A-B bond has 50% ionic character and 50% covalent character. When $\chi_B - \chi_A > 1.7$, the bond has more ionic character than the covalent character and when $\chi_B - \chi_A < 1.7$, the bond has more covalent character than ionic character.

(b) Hannay and Smith equation

These two workers proposed a more simplified equation for calculation the % ionic character in a polar covalent bond.

% ionic character = $[16 (\chi_B - \chi_A) + 3.5(\chi_B - \chi_A)^2]$ ($\chi B > \chi A$)

Using the electronegativity values as calculated by using Pauling's scale and this equation, the percent ionic character of hydrogen halide (gaseous) molecules are as follows:

HF 43%, HCl 17%, HBr 13% and HI 12%

These values reveal that the hydrogen halide molecules in gaseous state, are only partially ionic and mainly covalent.

4.10. SUMMARY

This unit of the study material consists of a concise discussion of covalent bond based on the octet rule and deviation from the octet rule. A brief account of polar and non-polar nature of covalent bond has been given. The valence bond theory and its limitations, directional nature of covalent bond as well as pictorial representation along with the formation of sigma and pi bonds have also been discussed. The concept of hybridisation has been fruitfully discussed with examples as well as shapes of inorganic molecules and ions based on hybridisation and valence shell electron pair repulsion theory have been given in the simple way.Molecular orbital theory, the energy level diagrams of the molecules/ions, multicentre bond, bond strength, bond energy and percentage of ionic character in polar covalent bonds have also been discussed and explained.

4.11. TERMINAL QUESTIONS

i) The d-orbital involved in sp^3d hybridisation is

(a) $d_z{}^2$ (b) dx^2y^2 (c) d_{xy} (d) d_{zx}

ii) Which of the following compounds contains covalent bond?

(a) NaOH (b) HCl (c) K_2S(d) LiH

iii) Which of the following compounds has the least tendency to form hydrogen bond?

(a) HF (b) NH_3 (c) HCl (d) H_2O

iv) Nitrogen atom in NH_3 molecule is sp^3 hybridised. NH_3 contains a lone pair of electron on N-atom. What is the shape of this molecule?

(a) Tetrahedral (b) square plannar

(c) Trigonal plannar (d) Trigonal pyramidal

v) Discuss the difference between a polar and a non-polar covalent bond with examples.

vi) What do you understand by directional nature of covalent bond?

vii) What is a multicentre bond. Explain with example.

viii) Discuss the shape of H_3O^+.

ix) Write down theMOelectronic configuration of O_2, $O_2{}^+$ and $O^-{}_2$and predict the bond order and magnetic behaviour.

x) Write down Hannay and Smith equation for calculating the percent ionic character of a polar covalent bond. With its help, evaluate percent ionic character present in HCl molecule (χ_H= 2.1, χ_{Cl}=3.0).

xi) Draw molecular orbital energy level diagram for NO^+ ion and predict its magnetic behaviour.

xii) XeF_2 molecule is linear though Xe atom in this molecule undergoes sp^3d hybridisation. Explain.

4.12. ANSWERS

i) (a)

ii) (b)

iii) (c)

iv) (d)

v) Please see polar and non-polar covalent bonds

vi) Please refer to directional characteristics of covalent bond

vii) Please refer to multicentre bonding

viii) Please see the VSEPR Theory

ix) Please see the MO theory

x) please refer to % ionic character of polar bond

xi) Please see the MO theory

xii) Please refer to shapes of inorganic molecules

4.13 . REFERENCES

For references and list of books consulted kindly see at the end of Unit 5.

UNIT 5 : CHEMICAL BONDING II

CONTENTS:

5.1. OBJECTIVE

The objective of writing the study material of this unit is to make the readers comfortable with electrostatic attraction forces and to acquaint them with the exciting world of the ionic crystals. An attempt has been made to through light on the type of force that holds an extremely large number of ions together forming a bulk or cluster of ions which exists in solid state only. At the same time the text gives an idea about why are the ions in an ionic crystal arranged in a regular manner and have a definite ratio. It has also been tried to give a brief account of lattice defects and semi conductors which are of immense importance industrially. The readers must also have an idea of the covalent character of ionic bond and weak interactions which has been taken care of.

5.2. INTRODUCTION

The solids have been classified in two different ways:

A. First kind of Classification

This classification gives two categories of solids, *viz.* true solids and pseudosolids.

(i) True solids-These have definite shape and volume which are retained even on long standing. These are rigid and hence cannot be distorted. These solids have sharp melting points. Examples are NaCl, KCl, Fe, Cu, S etc.

(ii) Pseudo solids-These do not have definite shape and volume and lose them on long standing. These are less rigid and hence can easily be distorted. These solids melt over a range of temperature. Examples are glass and pitch.

B. Second kind of classification

This classification is more appropriate and gives three categories of solids, *viz.* crystalline solids, non-crystalline or amorphous solids and polycrystalline solids.

(i) Crystalline solids- The constituent particles (atoms, ions or molecules) of these solids are arranged in a regular and definite manner in three dimensional space. These are said to have long range order. They have sharp melting points and can be broken into pieces, e.g. NaCl, sugar, diamond, graphite, sulphur etc.

(ii) Amorphous solids- The constituent particles of these solids are not arranged in a regular manner and hence have short range order. These do not have sharp melting points, i.e. they first soften and then change to liquid state on heating. Example are glass, rubber, plastics, silica etc.

(iii) Polycrystalline solids- These solids occur as powder and resemble amorphous solids but their individual particles have all the characteristics of crystalline solids.

Based on the nature of bonding forces existing between the constituent particles of crystalline solids, these have further been categorised into five classes, *viz.* ionic crystals, covalent crystals, molecular (van der Waals') crystals, metallic crystals and hydrogen bonded crystals.

Lattice points and crystal lattice

It has been mentioned above that the constituent particles of a crystalline solid are arranged in a regular order. The position of these particles relative to one another in the solid is represented by points (·) which are called lattice points or lattice sites and the orderly arrangement of these infinite lattice points is called a crystal lattice or space lattice.

Unit cell is a small unit of lattice points which on repeating infinitely in three dimensions gives a crystal lattice. This small unit is called a unit cell of the lattice. This shows all the properties of the crystal lattice.

5.3 IONIC SOLIDS

In these solids, the constituent particles are the ions, both positive and negative, which are held together by strong electrostatic force of attraction. There operates a repulsive force between the ions of same charge if these are adjacent to each other, therefore, the ions of similar charge move away from one another and those of opposite charge come closer together. These ions are arranged in the crystal lattice in regular pattern where the positive ions are surrounded by a definite number of negative ions and the negative ions, in turn, are surrounded by a certain number of positive ions. The attractive forces are maximum when each ion is surrounded by the greatest possible number of the oppositely charged ions. The positive and negative ions are present in the crystal lattice in a simple whole number ratio, i.e. 1:1, 1:2, 2:1 etc. The ionic solids along with other crystalline solids have been assigned seven basic crystal systems. These systems along with types of space lattices present in the crystal system and examples have been given below (**Table 5.1**):

Table. 5.1 The seven crystal systems

S. No.	**Name of the crystal system**	**Type of space lattices present in the crystal system**	**Examples**
1	Cubic	(i) Simple cubic (SC) (ii) Body-centred cubic (BCC) (iii) Face- centred cubic	NaCl, KCl, CaF_2, $NaClO_2$ ZnS, Cu_2O, alums, diamond Pb, Au, Ag, Hg

		(FCC)	
2	Orthorhombic	(i) Simple orthorhombic (ii) Body centred orthorhombic (iii) End – centred orthorhombic	KNO_3, K_2SO_4, $BaSO_4$, $MgSO_4$ Mg_2SiO_4 Pb CO_3, α–sulphur.
3	Tetragonal	Simple tetragonal Body centred tetragonal	$NiSO_4$, SnO_2, TiO_2 $ZrSiO_4$, KH_2PO_4, $PbWO_4$
4	Monoclinic	Simple monoclinic End-centred monoclinic	Na_2 SO_4. 10 H_2O FeO_4, $CuSO_4$. $2H_2O$, $Na_2B_4O_7$. $10H_2O$
5	Triclinic	Simple triclinic	$CuSO_4.5H_2O$, $K_2Cr_7O_7$, H_3BO_3
6	Hexagonal	Simple hexagonal	AgI, ZnO, CdS, HgS, PbI_2, quartz, Mg, Cd, Zn.
7	Rhombohedral	Simple	$NaNO_3$, calcite, magnesite, Sb, Bi.

The ions in a given ionic crystal are arranged (or packed) in different ways which are given below:

(i) **Hexagonal close-packed** (hcp) **structure,** i.e. AB AB ………packing of spheres.
This structure has the packing sequence of different layers of spheres as AB AB….. In this structure, each sphere is surrounded by 12 other nearest spheres and hence the coordination number (CN) of each spheres is 12.

(ii) **Cubic close-packed** (ccp) **or face-centred cubic** (fcc) **structure,** i.e. ABC ABC……packing of spheres.

This structure has the packing sequence of different layers of spheres is ABC ABC………This structure has cubic symmetry. Each sphere is surrounded by 12 other nearest spheres in this arrangement and hence the coordination number of each sphere is 12.

In both of the above structures, the coordination number of each sphere is 12 since each sphere is surrounded by six nearest spheres lying in the same layer, three spheres lying in the layer just above it and three spheres lying in the layer just below it. Both types of the above structures have the same packing efficiency which is 74 %, i.e. 74 % of the total volume of the unit cell is occupied by the spheres.

(iii)**Body-centred cubic** (bcc) **structure-**In this arrangement, there are 8 spheres at eight corners of a cube and one sphere at the centre of the cube. Each sphere is in contact with 8 other spheres in this structure and hence the coordination number of each sphere is 8.

Interstitial sites (holes or voids) **in ionic crystals**

In an ionic crystal, the bigger ions (i.e. anions) have close packed structure which may be either hexagonal close packed or cubic close packed type. In this close-packed structure, there is some vacant space between the anions which is called interstitial site (or hole or void). These sites or voids are occupied by smaller ions, i.e. cations.

Depending on the number of anions and the pattern in which they surround a cation in a given ionic crystal, there are four types of interstitial sites, *viz.* trigonal (C.N. = 3), tetrahedral (C.N. =4), octahedral (C.N. =6) and cubic (C.N. =8), respectively.

5.3.1 Characteristics of ionic solids:

Following are the main characteristics of ionic solids:

(i) The constituent particles of these solids are the cations and the anions which are held together by strong electrostatic force of attraction known as ionic bond and these exist as crystalline solids.

(ii) The ionic bond in ionic crystals is not rigid and nondirectional, i.e. it extends equally in all directions. Hence the ionic solids neither have any definite geometry nor show stereoisomerism like covalent molecules.

(iii)Since the anions are generally larger in size than the cations, the anions have closest packing arrangement in ionic solids in which there are left some empty spaces called interstitial sites or voids. These sites may be tetrahedral, octahedral or cubic type which are occupied by the cations.

(iv) Each ionic solid is formed from a small unit called a unit cell which contains a definite number of cations and anions. This unit cell in electrically neutral.

(v) The ionic solids are poor or bad conductors of electricity because in solid state the ions are fixed in their position and cannot move even if an external electric field is applied on them. However, in fused state or in aqueous solution they conduct electricity because under these conditions the ions are free to move. Also, the ionic solids having defects can conduct electricity due to the movement of ions from the lattice sites to the vacancies or that of free electrons present in them.

(vi) These solids are very hard and brittle due to the movement of one layer over the other along a plane on applying external force.

(vii) These have lattice energy and high melting points and boiling points.

(viii) These solids are generally soluble in water or polar solvents due to ionization and undergo ionic reactions in that medium.

5.3.2 Crystal coordination number (CCN):

We have learnt above that in ionic crystals the positive ions are surrounded by a definite number of negative ions and vice versa. The number of ions of opposite charge surrounding an ion in the ionic crystal is called the crystal coordination number or simply coordination number (C.N.)

In case of ionic crystals of AB type (e.g. NaCl, CsCl, Zns etc.) in which the number of both kind of ions is same, the C.N. of cation is equal to the C.N. of the negative ion, e.g. in NaCl crystal each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion, in turn, is surrounded by six equidistant Na^+ ions. Hence the coordination number of both Na^+ and Cl^- ions is 6. In CsCl, the C.N. of Cs^+ ion and Cl^- ion, both is 8 (due to different type of packing of ions than in NaCl).

In ionic crystals of the type AB_2 or A_2B (e.g. CaF_2, Na_2S etc.) in which the cation-anion ratio is 1:2 or 2:1, the two types of ions have different coordination numbers. For example, in Ca F_2, the C.N. of F^- ions is half to that of Ca^{2+} ions. The X-ray study has shown that C.N. of Ca^{2+} ions is 8 and that of F^- ions is 4.

5.3.3 Radius ratio (R_r):

In an ionic crystal, the arrangement of ions (packing) and their coordination number depend on the relative size of ions or the ratio of radii of the ions which is known as radius ratio. Thus the radius ratio (R_r) is defined as "**the ratio of the radius of cation (r_{C+}) to that of anion (r_{A}-) in an ionic crystal**". This can also be shown as

$R_r = \frac{r_{C+}}{r_{A-}}$ Where $r_{C+}$is the radiusof cation and r_A-is the radius of anion, R_r is radius ratio.

The radius ratio plays an important role in determining the structure of ionic solids and predicting the coordination number of the cation or the anion.

Radius ratio effect

The effect of radius ratio in determining the coordination number and the arrangement of ions (structure or packing) in an ionic crystal is known as radius ratio effect. As the cation becomes larger with respect to the anion, i.e. R_r increases, higher number of anions can fit around the cation and hence the coordination number of the cation increases. Which C.N. will give the most stable arrangement of ions is dependent on radius ratio.

The relationship between the various ionic arrangements and the radius ratios is given below:

Limiting value of $\frac{r_{c+}}{r_{A-}}$	Coordination number	Arrangement of ions
< 0.155	2	Linear
0.155-0.225	3	Trigonal planar (B_2O_3)
0.225-0.414	4	Tetrahedral (ZnS)
0.414-0.732	4	Square planar
0.414-0.732	6	Octahedral (NaCl)
0.732-0.999	8	Body centred cubic (CsCl, CaF_2)

The R_r value can be used for predicting the ionic arrangement and C.N. in the ionic crystals as already mentioned. For example, the radius ratio for NaCl crystal is r_{Na+}/r_{Cl}-= 0.95Å/1.81Å = 0.525. This value lies between 0.414 and 0.732. Thus the C.N. should be either 4 or 6 and the arrangement should be square planar or octahedral. The X- ray study of NaCl crystal has revealed that the crystal has octahedral arrangement of ions, i.e. each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion has six equidistant Na^+ ions. The cation-anion stoichiometry is 1:1 and the C.N. is 6 for both the ions. Similarly, it can be shown for CsCl (R_r = 169/181 = 0.93) that the C.N. is 8 for both the ions and arrangement of ions in the crystal is cubic.

Let us now consider the effect of R_r on the C.N. of the ionic crystal:

(i) If the value of R_r decreases due to decreasing size of cation or increasing size of anion, the crystal will become unstable. In this arrangement all the anions will not be able to touch the outer surface of cation. To do so, anions will move closer to each other and repulsion between them will increase. This repulsion pushes away one or more anions so that remaining anions fit around the cation giving more stable arrangement and coordination number may decrease from 8 to 6 or from 6 to 4.

(ii) It R_r increases either by increasing cationic size or decreasing anionic size, the arrangement will not be stable. In such a case the outer surfaces of the anions will not touch each other. On further increasing the R_r value, anions move far apart from each other and more anions may be accommodated in the packing arrangement. As a result, the coordination number may increase from 4 to 6 or from 6 to 8 This happens with Cl^- ion in NaCl (C.N. 6) and CsCl (C.N. 8).

5.3.4 Limitations of R_r rule:

Though the radius ratio rule is applicable to a majority number of ionic crystals, yet there are exceptions also. Following are some limitations of this rule:

(i) The ionic radii measured are not accurate or reliable because the radius of an ion is not constant but changes depending on its environment. It has been observed that the radius of an ion increase about 3% when C.N. changes from 6 to 8 and decreases about 6% when C.N. changes from 6 to 4. In such cases the radius ratio rule does not apply.

(ii) The R_r rule is valid to the packing of hard spheres of known size only. The anions are not hard due to their large size and are polarisable under the influence of cations thereby forming covalent bonds which are directional in nature and may prefer other orientations.

(iii) This rule does not explain the octahedral lattice arrangement of oxides of large divalent cations such as Pb^{2+}, Sr^{2+},Ba^{2+} etc. through they are expected to have this arrangement (structure).

(iv) Rb halides (RbX,X = Cl, Br, I) show C.N. 6 at ordinary conditions but adopt the CsCl structure at high pressure. Rr rule is unable to explain this observation.

(v) According to this rule, Li-halides should adopt 4-coordination structure but they crystallize in octahedral lattice thus violating the R_r rule. It may be due to covalent character of halides of lithium.

5.4 LATTICE DEFECTS

The packing of ions (or structure) in the ionic solids given above relate to ideal crystals. An ideal crystal is that which has the same unit cells containing the same lattice points throughout the whole of the crystal.

At absolute zero, most of the ionic crystals show well-ordered arrangement of ions and there are no defects, if the crystals are ideal. With rise in temperature, however, there is a chance that one or more of the lattice sites may remain unoccupied due to the migration of ions from their positions to the interstitial sites or out of the surface of the crystal. This constitutes a defect called lattice or point defect. The lattice defects in the ionic crystals are of three types:

(i) Stoichiometric defects
(ii) Non-stoichiometric defects
(iii) Impurity defects

(i) Stoichiometric defects

In the stoichiometric crystals of the compounds, the ratio of different atoms or ions is exactly the same as indicated by the chemical formulae of the compounds. These compounds obey the law of constant composition. If there is deviation from this ideal or perfect crystal structure, the crystal is said to have the defect or imperfection which arises due to the presence of cationic or anionic vacancies or dislocation of ions in the lattice structure. Accordingly, these defects are of two types:

(A) Schottky defects

If equal number of cations and anions are missing from their lattice sites in an ionic crystal of the type A^+B^- and the electrical neutrality of the crystal is maintained, the resulting defect is called the Schottky defect. This consists of pair (s) of holes in the crystal lattice due to missing cation (s) and anion (s).

This type of defect occurs mainly in the highly ionic compounds where

(i) The cations and anions are of similar sizes

(ii) C. N. of the ions is high, i.e. 6 or 8

Examples: NaCl, KCl, CsCl etc.

The presence of this defect decreases the density of the crystal due to missing ions.

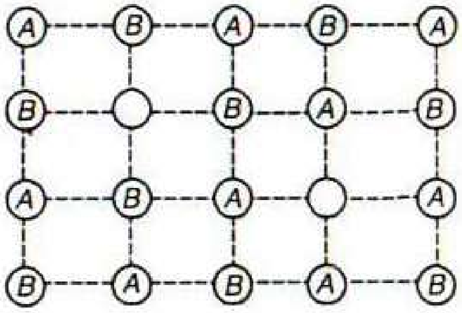


Fig. 5.1 Schottky defect showing one cation and one anion missing

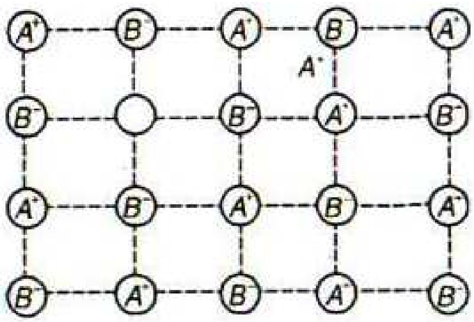


Fig. 5.2 Frenkel defect showing migration of cation to interstitial site

(B) Frenkel defects

This type of defect arises in the ionic crystals due to the departure (or migration) of an ion, usually cation due to its smaller size, from its regular position in the lattice to the vacant interstitial site between the lattice points. This creates a hole in the lattice. The electrical neutrality and the stoichiometry of the crystal are maintained even after this defect is created. This defect occurs mainly in the compounds where;

(i) There is large difference in the cationic and anionic sizes, i.e. an ions are much larger in size than cations (R_r is low)

(ii) The C.N. of the ions is low, i.e. 4 or 6

Examples: ZnS, AgCl, AgBr, AgI etc.

Lattice vacancies (or holes) occur in almost all the ionic solids. However, Schotlky defect occurs more often than Frenkel defect. The reason being much less energy required to form a Schottky defect than needed to create a Frenkel defect. X-ray diffraction of Nacl crystal has shown that at room temp., this substance has one defect for 10^{15} lattice sites but at 500^0C 10^9 defects and at 800^0C, 10^{11} defects have been observed for the same number of lattice sites.

Consequences of the stoichiometric defects

(i) Crystalline solids having these defects are able to conduct electricity to a small extent when an electric field is applied on them. This happens through an ionic mechanism, i.e. a nearby ion under the influence of electric field moves from its lattice site to occupy the vacancy present in the crystal and creates a new hole. Another nearby ion moves to occupy this vacancy. The process in repeated many times thereby causing a hole to migrate across the crystal which is equivalent to moving a charge in the opposite direction. In alkali halides, the migration of cation only has been detected below 500^0c but both ions migrate at higher temperature thereby increasing the conduction.

(ii) The presence of holes lowers the lattice energy and hence the stability of the crystal. If too many holes are present, then it may cause a partial collapse of the lattice.

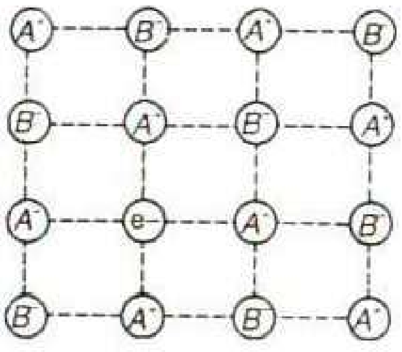
(iii)The closeness of similar charges brought about by the Frenkel defect tends to increase the dielectric constant of the crystals.

(ii) Non-stoichiomstric defects

In the non-stoichiometric crystals, the ratio of different atoms or ions present in the compound differs from that which is required by ideal chemical formula of the compound. These compounds do not obey the law of constant composition. In such cases, there is either an excess of metal ions or deficiency of metal ions (or excess of anions) which creates non-stoichiometric defect. The crystal as a whole is neutral but the crystal structure becomes irregular. These defects can exist in a crystal in addition to the stoichiometric defects. These defects are of two types:

(a) Metal excess defects

In these defects the positive ions are in excess. These may arise due to either the absence of anions, i.e. the anions are missing from the lattice sites leaving the vacancies which are occupied by extra electrons to maintain the electrical neutrality or due to the presence of extra cations occupying the vacant interstitial sites in the lattice which are counter balanced by extra electrons also present in interstitial space.



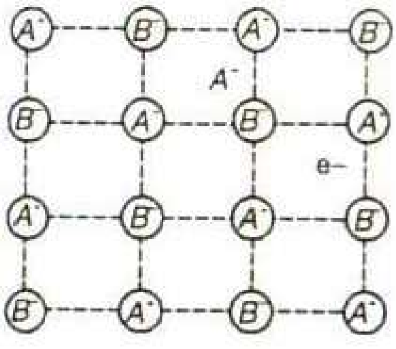


Fig. 5.3 (a) Metal excess defect due to missing of anion

Fig. 5.3 (b) Metal exess defect due to interstitial cation

The anion sites occupied by electrons are called F-centres which are responsible for the colour of the compounds and their paramagnetic behaviour. The first type of metal excess defect is produced by heating the compound with excess of metal vapours. Examples: NaCl, KCl etc. The second type defect is observed in ZnO, CdO, Fe_2O_3, Cr_2O_3 etc.

(b) Metal deficiency defects

These defects occur in the compounds where the metal ion exhibits variable oxidation state, i.e. the compounds of transition elements. The defect is caused either due to missing cations from the regular positions in the lattice thus creating cation vacancies and to maintain the electrical neutrality, the nearby cations acquire extra positive charge (examples FeS, FeO, NiO etc.) or the defect may also be produced by the presence of extra anions in the interstitial sites. The extra negative charge is balanced by extrapositive charge on some of the cations. However, due to the larger size of anions, these can hardly be adjusted in the interstitial sites. Therefore, the examples of this type of defect are rare and the defect remains merely a theoretical possibility.

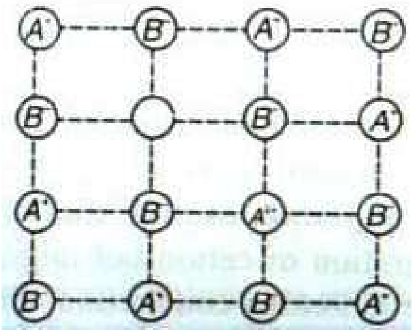


Fig. 5.4 (a) Metal deficiency defect due to missing cation

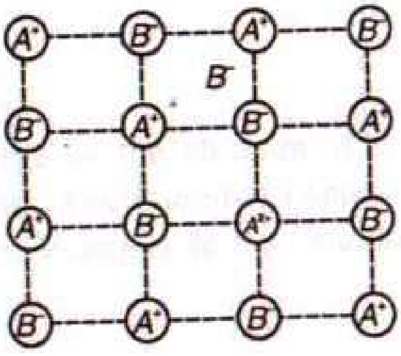


Fig. 5.4 (b) Metal deficiency defect due to an interstitial anion

Consequences of non-stoichiomtiric defects

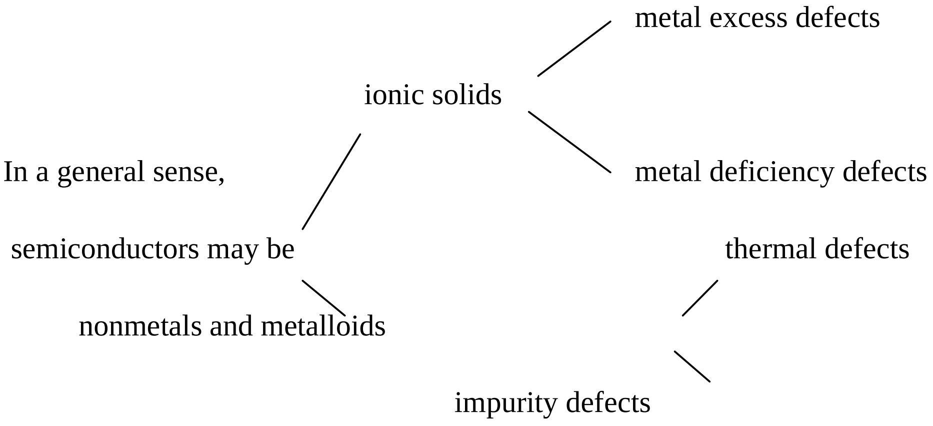
Due to the metal excess defects the compounds show electrical conductivity because free electrons present in the crystals can migrate easily under the electric field. Since the number of defects and hence the number of electrons is small, so such compounds show lesser conductance than metals, fused salts or dissolved salts. These compounds, therefore, are termed as semiconductors. These electrons may also be excited to higher energy levels by absorption of certain wavelengths from the white light (visible range) and are responsible for colour of the compounds.

The crystals of the compounds with metal deficiency defects can also act as semiconductors due to the movement of electrons from one ion of normal oxidation state to that of higher oxidation state to create another higher oxidation at its position. This type of movement of electrons between the ions appears as an apparent movement of positive holes thereby making the crystal a semiconductor.

5.5 SEMICONDUCTORS (THERMAL DEFECTS AND IMPURITY DEFECTS)

Semiconductors are the materials which have electrical conductivity at normal temperature which isintermediate between a conductor (like metals) and an insulator. Thus, the semiconductors allow only a portion of the applied electric field to flow through them. According to the band theory which differentiates among conductors, semiconductors and insulators, the semiconductors are the solids which have only a small difference of energy between the filled valence band of electrons and an empty conduction band. This is called band gap. If this band gap can be overcome by any means, *viz.* thermal energy or impurity addition, the electrons from the filled band may go to higher energy empty conduction band in a limited number thereby making the material to conduct electric current.

This is evident from the fact that there are some materials which may be insulators at low temperature, (i.e. absolute zero) but become conductors at elevated temperatures (thermal defects) or on adding certain impurities (impurity defects). These are called semiconductors, e.g. crystals of silicon (Si) and germanium (Ge).



The conductivity of the semiconductors arises in the following two ways:

(i) **Intrinsic semiconductors (thermal defects)**

A semiconductor which is obtained by heating an insulator is called intrinsic semiconductor, i.e. the defect in the crystal is produced by thermal energy. Pure silicon, pure germanium or pure grey tin are some examples of materials which act as semiconductors. Actually at elevated temperatures, sufficient amount of energy is available to break the covalent bonds in the crystal to make some electrons free. These electrons can migrate through the crystal leaving behind positive holes at the site of missing bonds. We can thus conclude that the heat energy promotes some electrons from the filled band into the next higher energy conduction band across the small energy gap and the material becomes conductor. With the rise in temperature the conductivity of semiconductors, therefore, increases.

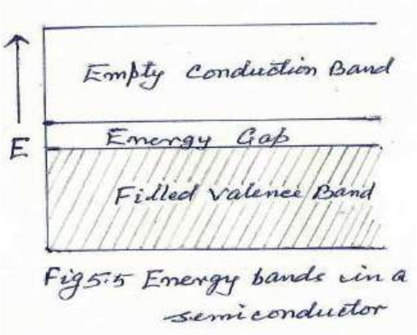


Fig. 5.5 Energy bands in semiconductor

(ii) **Extrinsic semiconductors (impurity defects); n-type and p-type semiconductors**

Certain defects in crystals arise from the presence of chemical impurities called impurity defects. Thus the materials obtained by adding impurity atoms to the insulators and making them conductors are called extrinsic semiconductors which are said to have impurity defects. For example, the addition of phosphorus, arsenic, boron or gallium atoms to silicon or germanium crystals makes them semiconductors. These are of two types:

(a) **n- type semiconductors (n = normal)**

If a very small amount of (say) arsenic, the element of group 15th,is added as impurity to the pure crystal of silicon, the element of group 14, by a suitable means, the process is called doping and we get the so called arsenic dopedsilicon. During the process of doping, a minute proposition of Si atoms is randomly replaced by arsenic atoms with one extra electron in their outer shell because only four outer electrons of As are required to form bonds with neighbouring Si atoms in the lattice (Si, ns^2p^2& As: ns^2p^3, i.e. Si has 4 and As has 5 valence electrons). At low temp., like absolute zero, these free electrons are located at the As atoms but at normal or elevated temperatures, these free electrons migrate through the crystal lattice to conduct the electricity in the normal way as happens in the metallic conductors. Hence this is called n-type semiconduction and the material so obtained in known as n-type extrinsic semiconductor. In these materials, the impurity atoms act as charge carriers.

(b) **p-type semiconductors (p-positive hole)**

Here the pure crystal of Si is doped with a minute quantity of gallium, an element of group 13 (Ga: ns^2p^1, i.e. 3 electrons in the valence shell) in which some of the Si atoms are substituted by Ga atoms. Each Ga atom forms three electron pair bonds with neighbouring Si atoms. Fourth neighbouring Si atom forms a weak one electron bond with Ga atom which behaves as free electron at Si atom. This creates electron deficiency or positive hole in the lattice site from where the electron is missing. There are as many positive holes as the number of Ga atoms. At absolute zero, the positive hole is located at Ga atom and free electron at Si atom. At elevated or normal temperature, these free electrons move through the crystal from one vacancy site to another thereby leaving new vacancies or positive holes behind. Thus, it appears that the positive holes are moving though actually it is the flow of electrons that takes place to conduct electric current through the crystal on applying the electric field. The flow of electrons and the movement of positive holes occurs in opposite directions. This process is, therefore, called p-type semi conduction and the material so produced in known as p-type extrinsic semiconductor.

5.6 LATTICE ENERGY OF IONIC CRYSTALS

An ionic crystal lattice consists of a large number of cations and anions which are considered to be hard spheres. These ions arrange themselves in a regular pattern to attain a close packed structure. The system gets stabilized by releasing energy during the packing process, i.e. the potential energy of the system is decreased. This released energy is called the lattice energy of the ionic crystal lattice. Similarly, if the ionic lattice has to be broken down into the constituent ions, the energy required is also known as the lattice energy of the ionic crystal. Thus, the lattice energy of an ionic crystal may be defined in two ways depending on the process of packing of ions or their separation from the crystal-

(a) **"The amount of energy released when one mole of gaseous cations and one mole of gaseous anions are brought closer together to their equilibrium position in the stable lattice, from an infinite distance, to form one mole of ionic crystal".** It is denoted by the letter U.

e.g. $C^+(g) + A^-(g) \longrightarrow C^+A^-(s)$ + Energy released (-U, exothermic process) (s = ionic solid) ……….. (5.1)

(b) **"The amount of energy required to remove the constituent ions of one mole of a solid ionic crystal from their equilibrium position in the crystal to infinite distance".**

e.g. C^+A^- (s) + Energy released (+ U, endothermic process) $\longrightarrow$ C^+(g) + A^- (g)

(s = ionic solid) ……….. (5.2)

In both the processes, the magnitude of the energy is same, i.e., energy released = energy required (absorbed) but the symbol of lattice energy is associated with opposite signs. The lattice energy is a quantitative measure of the stability of any ionic solid.

Factors affecting the magnitude of lattice energy

The lattice energy of ionic crystals depends on the following factors:

(i) Charge on the two ions or the product of charges α lattice energy.Greater the charge on the cation or the anion or greater the product of charges on the ions, greater is the magnitude of lattice energy, U. Thus, the lattice energy of ionic crystals containing polyvalent ions is more than those containing monovalent ions, e.g.

Ionic solids	Na^+F^- <	$Mg^{2+}F_2$ <	$Mg^2 O^{2-}$
lattice energy (kJ mol^-).	914	2882	3895

and Li^+Cl^- (845 kJ mol^{-1}) < $Ca^{2+}O^{2-}$ (3460 kJ mol^1)

(ii) Interionic distance (r) between the ions or ionic size α $\frac{1}{lattice\ energy}$

Lattice energy is inversely proportional to the interionic distance (r) between the ions. Since r = r_{C+} - r_{A}-, smaller the size of ions, smaller will be the value of r and higher will be value of lattice energy. For example, in case of alkali metal fluorides, the r_{M+} increases from Li^+ to Cs^+ hence energy of these compounds decreases from LiF to CsF:

Ionic solid	Li F >	NaF >	KF >	RbF >	CsF
Lattice energy (kJ mol^-)	1034	914	812	780	744

(iii) Electronic configuration of the cation

Pure ionic crystals are generally formed by the cations having inert gas configuration in their outershell, i.e. ns^2p^6 type. If the cation has non-inert gas/pseudo inert gas configuration in the outer shell, i.e. ns^2p^6 d^{10} type, this involves covalent character in the ionic bond of the crystal thereby increasing the lattice energy of the crystal. For example, AgCl(904kJ mol^{-1}) has larger value of lattice energy than that of NaCl (788kJ mol^{-1}). AgCl has significant covalent character while NaCl is essentially ionic because Ag^+ has $ns^2p^6d^{10}$ outer shell configuration and Na^+ has ns^2p^6 type configuration.

Effect of lattice energy on crystals

(i) **Solubility**- For an ionic solid to be dissolved in a solvent, the strong forces of attraction between its ions (i.e. lattice energy) must over come by the ion-solvent interaction energy called solvation energy (which is released during this interaction). For non-polar solvents, solvation energy is small so ionic solids do not dissolve in them because lattice energy > solvation energy. In a polar solvent like water, generally, ionic solids dissolve because the solvation energy> lattice energy and thus ion-solvent interaction breaks the ionic solid into constituent ions which are solvated and go into the solution.

There are some ionic solids which do not dissolve in polar solvents, *viz*. water. For example, AgCl in insoluble in water. This is due to greater cohesive forces in AgCl resulting from covalent character of ionic bond. $BaSO_4$, $SrSO_4$, $PbSO_4$ etc. are also insoluble in water due to very high lattice energy of these crystals.

(ii) **Melting point** - As the lattice energy increases, the melting point also increases.

5.7 BORN-HABER CYCLE: EXPERIMENTAL DETERMINATION OF LATTICE ENERGY OF AN IONIC SOLID

Since direct experimental determination of lattice energies are not easy, there are determined by indirect method using a thermo-chemical cyclic process known as Born-Haber cycle. To illustrate this, we take example of formation of compound MX(s) from M(s) and X_2(g). The different steps involved in the formation of MX(s) in crystalline state are as given below;

(i) Sublimation of M (s) to M (g). In this step 1 mole of solid M absorbs energy equal to its sublimation energy, $(\Delta H_{sub})_M$ and is converted to gaseous state, M(g), this is an endothermic process. (Energy is absorbed)

$$\underset{(1mole)}{M\,(s)} + (\Delta H_{sub})_M \longrightarrow \underset{(1mole)}{M\,(g)} \quad \ldots..(5.3)$$

(ii) Dissociation of $\frac{1}{2}X_2$ (g) to X (g). In this step half mole of X_2 (g) absorbs energy equal to half of the dissociation energy X_2 (g), $\frac{1}{2}(\Delta H_{diss.})_{X_2}$ and is converted to X (g). It is an endothermic process. (Energy is absorbed):

$$\underset{(1mole)}{\tfrac{1}{2}X_2\,(g)} + \tfrac{1}{2}(\Delta\ H_{diss.})_{X_2} \longrightarrow X\,(g) \quad \ldots\ldots\ldots\ldots(5.4)$$

(iii) Ionisation of M (g) to M^+ (g). Each M (g) atom absorbs energy equal to its ionisation energy $(IE)_M$ and loses its outermost electron to form M^+(g). It is an endothermic process. (Energy is absorbed):

$$\underset{\text{(1mole)}}{M\,(g)} + (IE)_M \longrightarrow \underset{\text{(1mole)}}{M^+\,(g)} + e^- \quad \ldots\ldots\ldots\ldots..(5.5)$$

(iv) Conversion of X(g) into X^- (g). The X (g) atom gains electron given by M(g) above to its outer shell to form X^- (g). In this process X(g) releases energy equal to its electron affinity or affinity energy $(EA)_X$. This is an exothermic process (Energy is released):

$$\underset{\text{(1mole)}}{X\,(g)} + e^- \longrightarrow \underset{\text{(1mole)}}{X^-\,(g)} - (EA)_X \quad \ldots\ldots\ldots\ldots(5.6)$$

(v) Combination of M^+ (g) and X^- (g) to form MX (solid). This is the final step in which M^+ (g) and X^- (g) formed as above combine together to form MX(s). In this process energy equal to lattice energy of MX, $(U)_{MX}$ is released. This is also an exothermic process and energy is released:

$$\underset{\text{(1mole)}}{M^+\,(g)} + \underset{\text{(1mole)}}{X^-\,(g)} \longrightarrow \underset{\text{(1mole)}}{MX\,(s)} - (U)_{MX} \quad \ldots\ldots\ldots\ldots(5.7)$$

The overall change as illustrated above may be represented in one direct step, as;

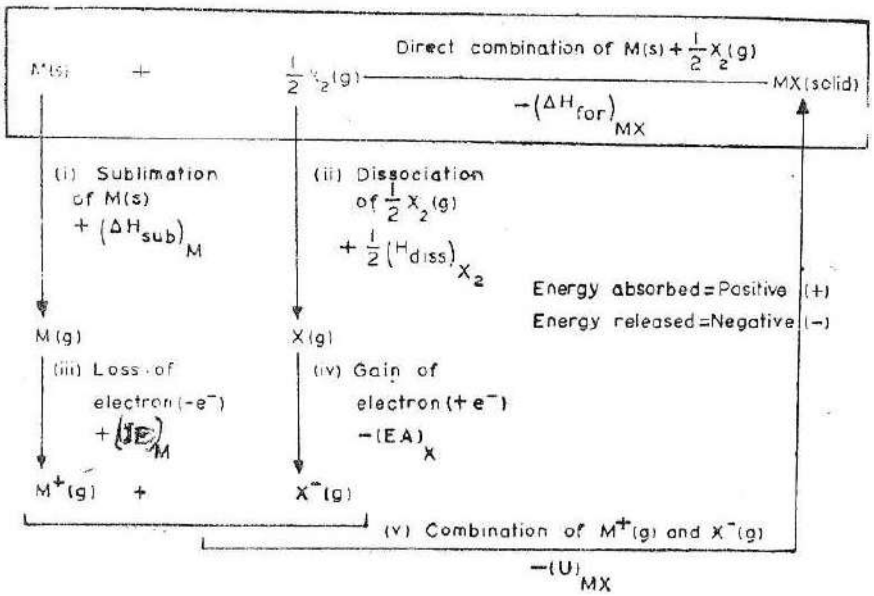
$$M\,(s) + \tfrac{1}{2}\,X_2\,(g) \longrightarrow MX\,(crystal) - (\Delta H_{for})_{MX}\ \text{(exothermic process)}\ \ldots..(5.8)$$

According to Hess's Law, the heat of formation (total enthalpy change) of MX, $(\Delta H_{for})_{MX}$ must be same irrespective of the fact weather it takes place directly in one step or through a number of steps as illustrated above. Hence,

$$-(\Delta\, H_{for})_{MX} = (\Delta\, H_{sub})_M + \tfrac{1}{2}(\Delta\, H_{diss})x_2 + (I_E)_M - (E_A)_X - (U)_{MX} \quad \ldots\ldots\ldots(5.9)$$

Here energy terms of endothermic processes are associated with positive sign and those of exothermic processes with negative sign. With the help of the above final equation we can determine the value of $(U)_{MX}$ if the quantitative values of other energy terms are known and placing these values in the equation along with their algebraic signs. NaCl may be taken as an example.

The whole act of above processes can also be given diagrammatically as shown below:



Applications of Born-Haber Cycle:

(i) Born-Haber cycle can be used to obtain any one of the six energy values for the six appropriate equations given above. In particular, the value of electron affinity of the non-metals which is most difficult to determine experimentally can be obtained by this method.

(ii) This cycle is useful in establishing the stability of ionic compounds. It is generally observed that the lattice energy for a compound is known but standard enthalpy of formation is not. So standard enthalpy of formation can be obtained with the help of Born-Haber cycle.

(iii) This cycle helps to understand the disproportionation reactions from lower to higher oxidation states in metal salts, i.e. most metals fail to form stable ionic compounds in low oxidation states such as MnCl, CaCl, AlO etc, If Born – Haber cycle is compared for MCl and MCl_2 (M = Mg, Ca etc). it can be shown that the formation of MCl_2 in favoured over that of MCl. The much higher lattice energy of MCl_2 over that of MCl is the answer to this question.

5.8 FAJAN'S RULES; POLARISATION OF IONS

In an ionic solid, both cation and anion are maintained at an equilibrium distance but when a cation approaches an anion closely, the net positive charge on the cation attracts the electron cloud of anion and at the same time the cation also repels the positive nucleus of anion. The combined effect of these two forces, attractive and repulsive, is that the electron cloud of anion (being larger in size) no longer remains symmetrical but is shifted towards the cation.

This is called distortion or polarization of the anion by the cation and anion is said to be polarised. The ability of cation to polarise a nearby anion is called its polarising power.

Unpolarised anion

Polarised anion

Fig. 5.6 Polarisation of anion

The anion also polarises a cation but due to the larger size of anion, it polarises a cation to a lesser extent (or almost negligible) while the polarisation of anion by a cation is appreciable, i, e. the anions are more susceptible to get polarised. Thus, in general, the cations have high polarising power and anions have more polarisability, i.e. the tendency to get polarised.

Due to the polarisation of anion by the cation, the electron cloud of anion is concentrated between the nuclei of two ions and behaves as if it is being shared by the two ions. Because of this tendency, the ionic bond in the compound passes to the covalent bond, i.e. has covalent character. There are certain factors which affect the polarisation of the ions, These are known as Fajan's rules.

Fajan's Rules: These rules are as follows:

(i) **Charge on the cation or the anion**

Generally the polarising power of a cation increases with increasing positive charge on it. This is because a cation having higher charge can attract electrons effectively. This can be seen in the anhydrous chlorides, *viz.* NaCl, $MgCl_2$ and $AlCl_3$. With increasing polarising power of cation, the covalent character of the bond between the cation and the anion also increases. Because the covalent compounds have lower melting points, therefore in the above chlorides the polarising power increases in the order: $Na^+ < Mg^{2+} < Al^{3+}$ and accordingly the melting points decrease from NaCl to $AlCl_3$ as given below:

Compound : Nacl $< MgCl_2 < AlCl_3$ (covalent character increases)

Melting point (^{0}C) : $800 > 712 > 575$

Similarly, the polarisability of an anion increases with increasing negative charge on it because the outer electron cloud is loosely held by the nucleus of the anion and also the anion can repel its outer electrons more effectively. Thus the oxide ions, O^{2-} in the oxides of metals are more polarised than (say) F^-ions in the fluorides of the same metals and hence the oxides are more covalent than fluorides having lower melting points.

(ii) **Size of the cation (cationic radii)**

Smaller the cationic size, closer it can go to the anion and more is its polarising power. Thus, with increasing cationic size, the power of cation to polarise an anion decreases which decreases the covalent character of the bond between the ions. This increases the melting points of the compounds. Let us take anhydrous chlorides of group 2nd elements, *viz*. $Becl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $RaCl_2$. The cationic size and melting points of these chlorides are given below:

Metal chloride	$BeCl_2$		$MgCl_2$		$CaCl_2$		$SrCl_2$		$BaCl_2$		$RaCl_2$
Cation present	Be^{2+}		Mg^{2+}		Ca^{2+}		Sr^{2+}		Ba^{2+}		Ra^{2+}
Cationic size (Å)	0.31	<	0.65	<	0.99	<	1.13	<	1.35	<	1.40
Melting point (^0C)	405	<	712	<	772	<	872	<	960	<	1000

The covalent character decreases with increasing cationic size and melting point of the compound and hence ionic character increases.

(iii)**Size of the anion (anionic radii)**

Larger the anionic size, more is its polarisalility, i.e. the tendency to get polarsed. With increasing anionic size, the polarisalility also increases thereby increasing the covalent character in the bond and consequently decreasing the melting point of the compounds. Calcium halides may be taken as examples.

Calcium halide	CaF_2		$CaCl_2$		$CaBr_2$		CaI_2	The covalent character of
Anion present	F^-		Cl^-		Br^-		I^-	the halides increases.
Anionic size (Å)	1.36	<	1.81	<	1.95	<	2.16	
Melting point (^0C)	1392	>	772	>	730	>	575	

(iv) **Electronic configuration of the cation**

A Cation with pseudo inert gas electronic configuration (i.e. $ns^2p^6d^{10}$) in its outer most shell (18 electrons) has greater polarising power, due to greater Zeff, to polorise an anion than a cation with inert gas configuration (i.e. ns^2p^6) in its outer shell (8 electrons) even if both type of cations have the same size and charge. Thus the first type of cation will polarise the anion to a greater extent thereby resulting in a more covalent bond with lower melting point of the compound. Let us look at two chlorides, *viz.* AgCl and KCl, Ag^+ ion has $4s^2p^6d^{10}$ outer shell electronic configuration and gives more covalent AgCl (m.p. 455^0C) than KCl (m.p. 776^0C) which has K^+ ion with $3s^2p^6$ outer shell configuration.

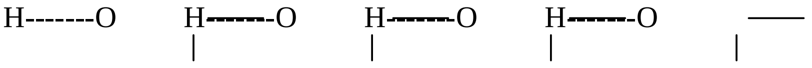
5.9 WEAK INTERACTIONS

The force that holds the atoms together in a molecule is called a chemical bond. These bonds *viz.* ionic bond, covalent bond and coordinate covalent bond are formed due to strong attraction tendency between the species. The resulting products, i.e. the molecules or their aggregates (sometimes) are stable species. But there are instances where only weak bonds exist between/amongst different species, for example within molecules. In these cases, we say that molecular forces are present between the molecules. Such species are said to have formed by weak interactions. Hydrogen bonding and van der waals' forces are common examples of such molecular forces causing weak interactions.

5.9.1 Hydrogen Bonding:

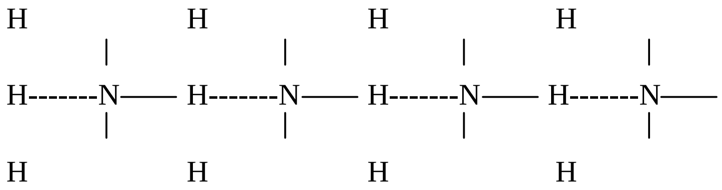
This is a peculiar type of bonding which has been named after an element, hydrogen and operates between the molecules containing hydrogen and an atom of the electronegative elements. It is defined as "**the electrostatic force of attraction between H-atom linked covalently to an atom of highly electronegative element like F, O, N etc. in a molecule and another atom of a highly electronegative elements of the same or different molecule**". Thus hydrogen bond may be formed either between the molecules of same substance or between the molecules of different substances. It is a weak bond formed by the weak interaction and is represented by dotted line (……).

The common examples in which hydrogen bonding exists are:



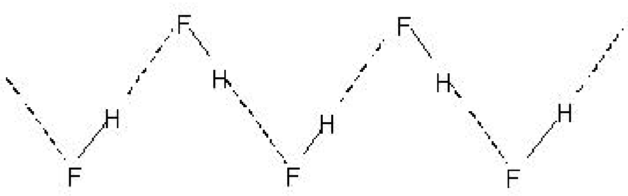
H H H H

$(H_2O)_x$ Cluster

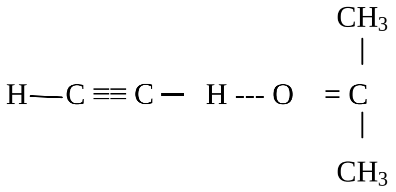


$$H\text{-------}\underset{H}{\overset{H}{N}}\text{——}H\text{-------}\underset{H}{\overset{H}{N}}\text{——}H\text{-------}\underset{H}{\overset{H}{N}}\text{——}H\text{-------}\underset{H}{\overset{H}{N}}\text{——}$$

$(NH_3)_x$ cluster



$(HF)_x$ cluster



$$H—C\equiv C-H\text{ --- }O=\underset{CH_3}{\overset{CH_3}{C}}$$

Hydrogen bonding taking place between the molecules of same substance or different substances.

Cause of hydrogen bond formation

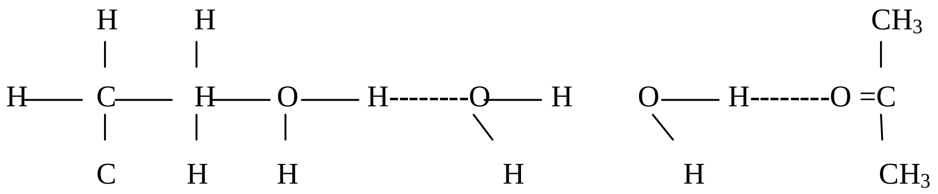
When H-atom is linked with an atom of highly electronegative element (say) A atom (Amay be F, O, N etc.) to form a polar covalent molecule HA, the molecule develops polarity like $H^{\delta+}$-$A^{\delta-}$ due to electronegativity difference between H and A-atoms. If this molecule comes closer to another such molecule, e.g. $H^{\delta+}$-$A^{\delta-}$ or $H^{\delta+}$-$B^{\delta-}$ (B may also be F, O, N etc.), the two dipoles will be linked together by a special type of bond through hydrogen atom, called hydrogen bond: A^{δ} -$H^{\delta+}$----- B^{δ} -$H^{\delta+}$ Here H-atom acts as a bridge between electronegative atoms A and B. This process may be repeated for several molecules to give a cluster of molecules where H– bond is formed between any two adjacent molecules of the aggregate or cluster.

Types of Hydrogen bonding

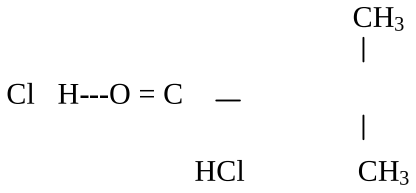
The hydrogen bonding in the compounds has been found of two types:

(i) **Intermolecular hydrogen bonding (molecular association)**

This type of H-bonding takes place between several molecules of the same substance or different substances. The molecules get associated as a result of H-bonding to give a large cluster. This process is known as association. The examples of this type of H-bonding are H_2O, NH_3, HF etc. which have been shown above in the beginning of this topic where association of similar type of molecules occurs. Association of C_2H_2 (acetylene)and CH_3COCH_3(acetone) has also been shown above. Other examples of intermolecular H-bonding are given below between the molecules of different substances:



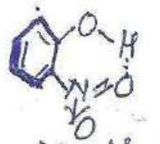
Alcohol water Acetone



Acetone

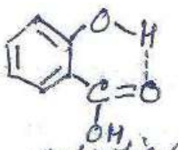
(ii) **Intramolecular hydrogen bonding (**Chelating)

This type of hydrogen bond is formed between the two atoms of the same molecule, one of the atoms being H-atom. It may lead to the linking of two groups of a molecule to form a ring structure, the ring being generally, a five-membered or a six–membered chelate ring (meaning claw). The examples in which intramolecular hydrogen bonding occurs are aromatic organic molecules *viz.* o-nitrophenol, o-chlorophenol, salicylic acid, salicylaldehyde etc.



O-nitro phenol

O-chlorophenol



Salisilic acid,

Strength of H-bond

As has been stated above that this bond is a weak bond since it is merely an electrostatic force of attraction and not a chemical bond. The strength of H-bond increases with increasing electronegativity of the atom attached with H-atom by a covalent bond, i.e. N, O, and F. This bond is much stronger than van der Waals' force but about ten times weaker than a covalent bond. The order of the strength may be given as: van der Waals' forces < H-bond < covalent bond < ionicbond.

Consequences of hydreogen bonding

Hydrogen bonding largely affects a number of physical properties of H-bonded compounds. Some of them are given below:

(i) Melting and boiling points of hydrides of group 15,16 and 17 elements; the hydrides of N, O and F among those of other elements of these groups show abnormal melting and boiling points. This is attribute to the association of molecules caused by the formation of hydrogen bonds. Let us take hydrides of group 16 elements, *viz*. H_2O, H_2S, H2Se & H_2Te. The melting and boiling points of H_2O are exceptionally high in comparison to those of other hydrides which show the increasing trends in these properties, i.e. $H_2O >> H_2S > H_2Se > H_2Te$ (both m.p. and b.p.)

(ii) Density of ice and water; like every solid crystal, ice has definite lattice structure in which water molecules are arranged in such a way that every water molecule is surrounded by four other water molecules in tetrahedral fashion. The central H_2O molecule is linked to four other H_2O molecules by hydrogen bonding (See Fig. 5.7). Because H-bonds are weaker and longer than covalent bonds, this arrangement gives a three dimensional open cage like structure with large empty space within the structure. This increases the volume and decreases the density of ice. That is way ice floats on water surface.

In liquid form water molecules lie closer together hence the same mass of water has smaller volume and its density is more than that of ice.

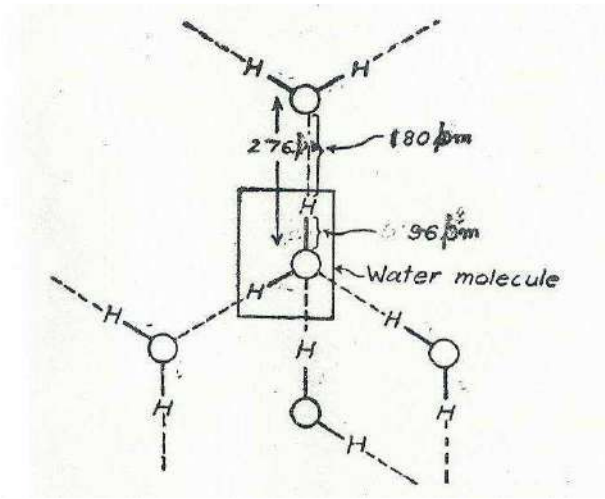


Fig. 5.7 Open cage like crystal structure of ice

(iii) Density of water is maximum a 4^0C; When ice melts, the cage like structure breaks down and the molecules of water are packed closely together, thereby decreasing the volume. The breaking of structure (i.e. hydrogen bonds) is not completed until the temperature reaches 4^0C. Above 4^0C, expansion commences thereby increasing the volume. Thus, the volume of water is minimum and density is maximum (density = $\frac{mass}{volume}$) at 4^0c.

5.9.2 van der Waals' Forces (or Intermolecular forces):

The weak attractive forces between the uncharged atoms or molecules of polar as well as non-polar substances are collectively referred to as van der Waals' forces. The magnitude of these forces is maximum for solids and decreases for liquids and minimum for gases. The crystals whose constituent particles are held together in position by these forces are called molecular crystals. These forces arise from the electrostatic attraction of the nuclei of one molecule for the electrons of a different molecule. The repulsions between the electrons of the two molecules and the nuclei of the two molecules try to counter balance the electrostatic attractions but there is always a small net attractive force. Van der Waals' forces are short range forces. These forces are due to different type of interactions which are given below:

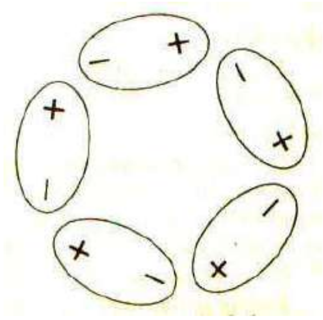


Fig. 5.8 Dipole-dipole interaction (head to tail arrangement)

(i) **Dipole-dipole interaction**

These interactions are present in polar molecules like NH_3, $SO_{2,}$ HCl etc. (all gases). Although these molecules are neutral, they have permanent dipole moments and behave as dipoles. Larger the dipole moment of a molecule, greater is the dipole-dipole attractive force between the molecules. Actually in the dipoles, the van der Waals' forces are due to the electrostatic interactions between the positive end of one dipole and the negative end of the other dipole.

(ii) **Ion-dipole interaction**

If a charged particle such as an ion is introduced into the neighbourhood of an uncharged nonpolar molecule (e.g. an atom of a noble gas), it will distort the electron cloud of the atom or molecule in the same way as a cation does on a large anion (polarisation). The polarisation of neutral species depends on its inherent polarisability and polarising field afforded by the charged ion (±). Such interactions occur only in solution of ionic compounds in non-polar solvents.

(iii) **Dipole- induced dipole interaction**

A dipole can induce an uncharged non-polar species into a dipole as does an ion in ion dipole interaction. Then there occurs dipole induced dipole interaction. These are important only in solution of polar compounds in non-polar solvents.

(iv) **London or dispersion forces** (instantaneous dipole-induced dipole interactions)

These interactions are present in non-polar molecules like N_2, O_2, $Cl_{2,}$ CH_4 etc. and mono atomic molecules like He, Ne, Ar etc. These molecules do not have permanent dipole moment. The average electronic distribution in a non-polar molecule is symmetric but because of continuous motion of the electrons, at any given instant, the centres of negative and positive charges may not coincide. This causes a momentary distortion of the electronic charge cloud which results in an instantaneous temporary polarity. Then this instantaneous dipole may induce polarity in another non-polar atom/molecule. These two dipoles attract each other by electrostatic forces called London forces.

Since van der Waals' forces are weak and may be easily overcome, the condensed gas readily vapourises and molecular crystals are soft and have low melting points.

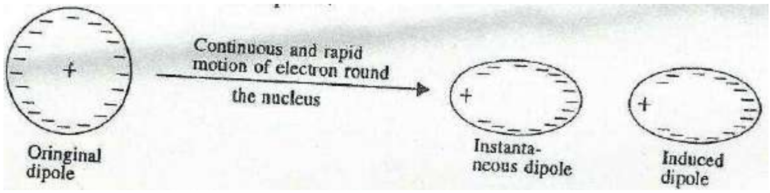


Fig. 5.9 Instantarery dipole dipole induced dipole interaction between non-polar

5.10 SUMMARY

This unit consists of a brief discussion of ionic solids, their characteristics, the interesting topic of radius ratio and its effect, crystal coordination number and limitations of radius ratio rule. The lattice defects have been fruitfully discussed and an elaborate account of semiconductors has been given. A concise account of lattice energy, the factors affecting its magnitude and its experimental determination has been discussed. The rules governing the covalent character of ionic bond, a brief discussion of H-bond and van der Waals' forces have also been taken care offor the readers.

5.11 TERMINAL QUESTIONS

i. The coordiniation number of Cl^- ion in NaCl crystal is:

(a) 4 (b) 6 (c) 8 (d) 12

ii. CsCl crystal has the packing pattern of ions:

(a) Cubic (b) Tetrahedral (c) Octahedral (d) Square planar

iii. If one cation and one anion are missing from their positions in a crystal lattice, the defect produced is:

(a) Schottky defect (b) Frenkal defect (c) n-type defect (d) p-type defect

iv. Which one of the following will have covalent character?

(a) LiCl (b) NaCl (c) KCl (d) CsCl

v. How do the ionic crystals behave towards the electric field applied on them in solid state, fused state and in solution?

vi. Give a brief account of n-type semi conductors.

vii. How is lattice energy of an ionic compound related with its solubility in polar solvent?

viii. What is polarization of ions?

ix. What is the cause of H-bonding in the compounds?

x. We have two cations. One of them has pseudo inert gas outer shell electronic configuration and the other has inert gas configuration in the outer shell. Which of these will cause more polarisation of an anion?

xi. Give a brief account of London forces.

5.12 ANSWERS

i. (b)

ii. (a)

iii. (a)

iv. (a)

v. Please refer to characteristics of ionic compounds.

vi. Please see semiconductors.

vii. Please refer to the effect of lattice energy on crystals.

viii. Please refer to polarisation and Fajan's rules.

ix. Please see H-bonding.

x. Please refer to Fajan's rules.

xi. Please see van der Waals' forces.

5.13 REFERENCES: LIST OF BOOKS CONSULTED

8. Principles of Inorganic Chemistry: B. R. Puri, L.R. Sharma & K. C. Kalia,
   Milestone Publishers and Distributers, Daryaganj, Delhi (2013).
9. Selected topics in Inorganic Chemistry: W.U. Malik, G.D. Tuli & R.D. Madan, S. Chand & Co. Ltd., New Delhi (1993).
10. Comprehensive Inorganic chemistry: Sulekh Chandra, New Age International (Pvt.) Ltd., New Delhi (2004).
11. The Nature of the Chemical Bond: Linus Pauling, 3rd Edn., Cornell University Press, New York (1960).
12. A Simple Guide to Modern Valency Theory: G.I. Brown, Revised Edn., Longmans Green, London (1967).

13. Advanced Inorganic Chemistry: Satya Prakash, G.D. Tuli, S.K. Basu and R.d. Madan, Vol. **I**, 7th Edn., S. Chand & Co. Ltd, New Delhi (1998).
14. Shriver and Atkins' Inorganic Chemistry: Peter Atkins *et. al*., 5th Edn., Oxford University Press, New York (2010).

UNIT6: HYDROGEN

CONTENTS:

6.1. OBJECTIVE

The objective of writing the course material of this unit, i.e. on hydrogen, the first and the lightest element of the periodic table, is to make it easy for the readers to understand its various aspects such as its isotopes and their nature, its isomers, its oxides, *viz.* heavy water and hydrogen peroxide and its compounds with various elements called hydrides etc.

6.2. INTRODUCTION

Cavendish in 1766 while studying the comparative effect of dilute acids on metals like zinc, tin and iron discovered that a similar gas was liberated in each case and named that gas a **inflammable air** because it burnt on ignition. This gas was given the name hydrogen (from hydra, a Greek term meaning water forming) by Lavoisier who noticed that on burning in air, the gas produced water. Hydrogen occurs free in nature only in traces, about 1part in1.5 million parts of air and in volcanic regions. The sun’s atmosphere is said to contain appreciable amounts of hydrogen as revealed by solar spectra. It occurs most commonly in combination with oxygen as water and to a much smaller extent in combination with carbon, sulphur, nitrogen and halogens. All organic matter contains hydrogen combined with carbon, nitrogen and oxygen.

Hydrogen shows the unique property of the existence of a typical bonding called after its name, the hydrogen bonding present in the biomolecules (RNA, DNA etc.) or in other simple molecules. Hydrogen also exhibits the prevalent nuclear spin isomerism (i.e. ortho and para forms). Because of its dual behaviour, i.e. resemblance with alkali metals in some properties and halogens in some other aspects, it can be placed in Group 1(of alkali metals) or Group17 (of halogens) of the periodic table.

6.3. ISOTOPES OF HYDROGEN

It has been established by mass spectrometry that hydrogen has three isotopes each with atomic number 1 and mass numbers 1, 2 and 3, respectively. They differ to a great extent in their physical properties as there is comparatively a large difference in their atomic masses. Because of the similar electronic configuration, they have similar chemical properties. Their names, symbols, mass numbers and relative abundance are summarized in **Table 6.1.**

Table 6.1 Isotopes of Hydrogen

Name	Symbol	Atomic Number	Mass Number	Percentage abundance
Protium or ordinary hydrogen	${}_1H^1$	1	1 (1 proton only)	99.984
Deuterium or heavy hydrogen	${}_1H^2$	1	2 (1Proton+1 neutron)	0.016
Tritium or Radioactive hydrogen	${}_1H^3$	1	3 (1proton+ 2 neutron)	10^{-15}

(i) Protium or ordinary hydrogen (${}_1H^1$):

It is the most common isotope of hydrogen and constitutes 99.984 percent of total hydrogen available in nature. Its nucleus consists of one proton only, that is why its mass number is 1.

(ii) Deuterium or heavy hydrogen (${}_1H^2$ or ${}_1D^2$)

This isotope of hydrogen called deuterium occurs in nature only in traces, i.e. about 1 part in 6000 parts of hydrogen or about 0.016 percent. Its main source is heavy water (D_2O) from which it is separated mainly by electrolysis. Its nucleus consists of 1 proton and 1 neutron (mass number 2). Generally, this isotope is represented by the symbol D and referred to as heavy hydrogen.

(iii) Tritium or radioactive hydrogen ($_1H^3$ or $_1T^3$):

Hydrogen's this isotope is formed in the upper atmosphere only by certain nuclear reactions induced by cosmic rays. It constitutes only $1x10^{-15}$ percent of total natural hydrogen i.e. 1 molecule in 10^{17} molecules of H_2. Its nucleus consists of 1proton and 2 neutrons (mass number 3). Unlike deuterium, it is radioactive with a half- life of 12.4 years and hence is present in nature only in traces. Generally, this isotope is given by the symbol T and is referred to as radioactive hydrogen.

It is to be noted that since the quantities of D_2 and T_2 present in natural hydrogen are exceedingly small, the properties of natural hydrogen are substantially those of protium.

Isotope effect:

Because of similar electronic configuration ($1s^1$) all the three isotopes are chemically identical. But these isotopes show a quantitative difference in their reaction rates i.e. for heavy isotopes reaction rates are slower and equilibrium constants, e.g. the dissociation constant (K) for heavy water is significantly smaller than that for ordinary water:

$$H_2O \rightleftharpoons H^+ + OH^- ; \quad K = 1 \times 10^{-14}$$

$$D_2O \rightleftharpoons D^+ + OD^- ; \quad K = 0.3 \times 10^{-14}$$

The mass difference of isotopes of hydrogen has marked effect on the rates of chemical reactions, e.g.

(i) A bond to a protium atom can be broken as much as 18 times faster than that to a deuterium atom. Thus protium has been found to react with Cl_2 about 13.5 times faster than deuterium does.

(ii) The addition of H_2 to ethylenic compounds takes place about two times faster than that of D_2 at the same temperature.

(iii) Protium has been found to adsorb more rapidly over the solid surfaces than deuterium.

These examples show that reactions with deuterium are slower than those with protium.

Such differences in properties which arise due to the difference in masses of the isotopes are termed as isotopic effect.

Now let us discuss the isotopes one by one

A. Protium or ordinary hydrogen ($_1H^1$):

This isotope does not need to be discussed in detail, hence discarded.

B. Deuterium or heavy hydrogen ($_1D^2$ or $_1H^2$):

The presence of very small amount of heavy hydrogen with mass 2 in the ordinary hydrogen was indicated by various workers. On the basis of these clues, Urey and coworkers worked further and showed that a residue obtained by fractional evaporation of liquid hydrogen at reduced pressure when examined spectroscopically, was found to contain an isotope of mass number 2. This isotope was called heavy hydrogen and named deuterium by Urey. It was assigned the symbol D.

Preparation:

Deuterium has been obtained either from ordinary hydrogen or from heavy water.

(i) From ordinary hydrogen (or Protium):

Ordinary hydrogen contains deuterium, though small (0.016 percent) and hence can be used as the source of deuterium. From ordinary hydrogen deuterium has been separated by employing various techniques which are discussed below:

(a) By diffusion process:

Deuterium can be isolated directly from ordinary hydrogen gas by taking the advantage of different rates of diffusion of the two isotopes. The process is carried out in a series of porous diffusion chambers called Hertz diffusion units, each unit consisting of porous membrane.

When ordinary hydrogen gas is led into diffusion units under reduced pressure with the help of mercury diffusion units, protium being lighter, diffuses more readily than deuterium which diffuses at slower rate and is left behind. The process is repeated several times till, protium is collected in the reservoir on the right and deuterium is collected in the another reservoir on the left side. The efficiency of the process is increased by carrying out the diffusion at reduced pressure and increasing the number of units. The apparatus used for this process is shown in Fig. 6.1

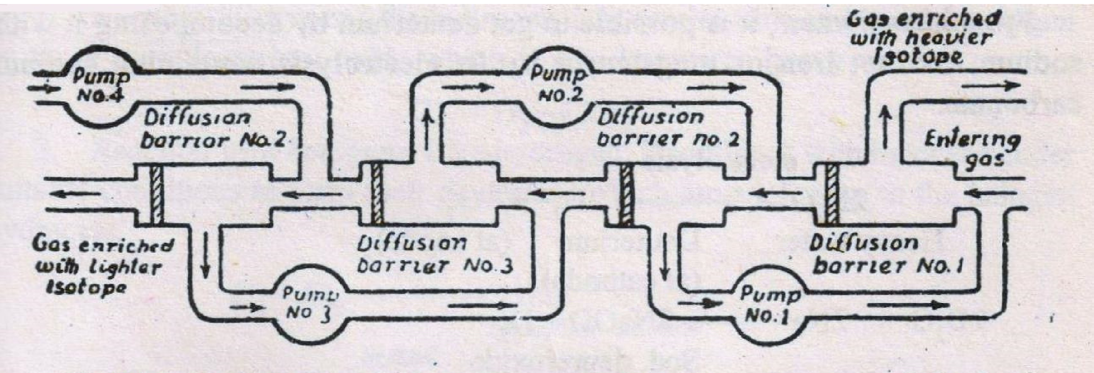


Fig. 6.1 Hertz diffusion units for th separation of deuterium from ordinary hydrogen.

Although this process is slow and tedious, yet it gives absolutely pure deuterium such that the spectrum of deuterium so obtained shows no traces of ordinary hydrogen.

(b) By fractional distillation of liquid hydrogen:

Deuterium can also be separated from ordinary hydrogen by yet another process, i.e. fractional distillation of liquid hydrogen. The boiling point of protium is lower (-)252.8^{0}C than that of deuterium (-249.5^{0}C). Hence the fractionation process results in the enrichment of later fractions in deuterium. From the deuterium enriched fractions, it can be recovered by the diffusion process as given above.

(c) By adsorption on charcoal:

It has been observed that charcoal has different adsorption power for the two isotopes of hydrogen, i.e. $_1H^1$ and $_1H^2$. Protium is adsorbed more readily and strongly on its surface than deuterium. The difference in adsorption of these isotopes can be used for their separation. The mixture of two isotopes is passed over charcoal kept at liquid air temperature, when most of the protium gets adsorbed while most of the deuterium passes out unadsorbed. By repeating the process, a deuterium enriched fraction is obtained from which deuterium can be isolated from protium by the usual diffusion process.

(ii) From heavy water:

Ordinary water contains 1 part in about 6000 parts of heavy water (D_2O) and is the important source of it. Heavy water can be separated from ordinary water by employing various physical methods such as multi- stage electrolysis, fractional distillation, fractional freezing, preferential adsorption etc. as well as chemical methods such as exchange reactions etc. (The details of these methods will be discussed ahead in the chapter under heavy water.). From heavy water, deuterium can be obtained by any of the following methods:

(a) By decomposition of D_2O:

This can be done with sodium metal, Mg – shavings at high temperature, red hot iron, heated W – filament, heated zinc turnings or uranium.

(i) $2Na\ (\text{metal}) + D_2O \longrightarrow 2NaOD + D_2\uparrow$

This method is used when small quantity of D_2 has to be prepared.

(ii) $Mg\ (\text{savings}) + D_2O\ (\text{vapours}) \longrightarrow \overset{\Delta}{MgO} + D_2\uparrow$

When a large quantity of D_2O is required, this method is used.

(iii) $3Fe\ (\text{red hot}) + 4D_2O\ (\text{steam}) \xrightarrow{\Delta} Fe_3O_4 + 4D_2\uparrow$

$\uparrow 2W\ (\text{heated}) + D_2O\ (\text{vapors}) \xrightarrow{\Delta} W_2O + D_2\uparrow$

$Zn\ (\text{turnings}) + D_2O\ (\text{vapour}) \longrightarrow ZnO + D_2\uparrow$

(iv) $U + 2\ D_2O \longrightarrow UO_2 + 2D_2\uparrow$ (pure D_2)

$2U + 3D_2 \longrightarrow 2UD_3 \xrightarrow{\Delta} 2U + 3D_2\uparrow$

The last method using uranium (U) gives pure D_2. It can also be stored as UD_3 for the production of D_2 when required.

(b) By electrolysis of D_2O:

D_2 can also be obtained from pure D_2O by the electrolysis of acidified heavy water in an evacuated all glass apparatus using Pt-electrodes when D_2 is liberated at cathode.

$$2D_2O \xrightarrow{\text{electrolysis}} \underset{\text{Cathode}}{2D_2\uparrow} + \underset{\text{Anode}}{O_2\uparrow}$$

D_2 obtained by this method may contain O_2 and D_2O vapours. When it is heated over platinised asbestos and dried at liquid air temperature, both O_2 and D_2O vapours are removed.

Physical Properties:

The properties of deuterium (D_2) are slightly different from ordinary hydrogen (H_2). It also exists as a diatomic molecule and is insoluble in water and bad conductor of heat and electricity. Its melting and boiling points are slightly higher than those of ordinary hydrogen due to its higher mass number, e.g.

	H_2	D_2
Melting point (^{0}C)	(-)259.2	(-)254.5
Boiling point (^{0}C)	(-)252.8	(-)249.3

Chemical properties:

The chemical properties of deuterium are similar to those of hydrogen, the only difference is that deuterium reacts at slower rate than hydrogen.

i) Burning in oxygen:

It is combustible like hydrogen and burns in oxygen or air at elevated temperature to give its oxide (heavy water).

$$2D_2 + O_2 \xrightarrow{\triangle} 2D_2O$$

ii) Reaction with halogens:

It combines with halogens under suitable conditions to form deuterium halides, e.g.

$$D_2 + Cl_2 \xrightarrow{\text{in light}} 2DCl$$

$$D_2 + Br_2 \xrightarrow{\text{on heating}} 2DBr$$

$$D_2 + F_2 \xrightarrow[\text{cold}]{\text{in dark and}} 2DF$$

iii) Reaction with nitrogen:

In presence of a catalyst, it combines with nitrogen to form deutero – ammonia (or deuterium nitride).

$$3D_2 + N_2 \xrightarrow{\text{cata.}} 2ND_3$$

iv) Reaction with metals:

It combines with alkali metals at high temperature to form deuterides which resemble with alkali metal hydrides.

$$2Na + D_2 \xrightarrow{\triangle} 2NaD$$

These deuterides are hydrolysed easily to give deutero hydrides

$$NaD + H_2O \longrightarrow NaOH + DH \text{ (or HD)}$$

v) Addition reactions:

Like hydrogen, it gives addition reactions with unsaturated hydrocarbons in presence of catalyst and at high temperature but at slower rate.

$$CH_2 = CH_2 + D_2 \xrightarrow[260^0C]{Ni} CH_2D \quad CH_2D \text{ (deutero ethane)}$$

vi) Exchange reactions:

Deuterium and hydrogen atoms undergo ready exchange under suitable conditions, e.g. at high temperature it reacts with H_2, NH_3, CH_4 etc. and slowly exchanges their hydrogen partially or completely.

$$H_2 + D_2 \rightleftharpoons 2HD$$
$$2NH_3 + 3D_2 \rightleftharpoons 2ND_3 + 3H_2$$
$$CH_4 + 2D_2 \rightleftharpoons CD_4 + 2H_2$$

Some exchange reactions can be catalysed by finely divided nickel, chromium, palladium or Pt- black, e.g.

$$C_6H_6 + 3D_2 \xrightarrow{\text{Pt-black}} C_6D_6 + 3H_2$$
$$H_2O + D_2 \xrightarrow{\text{cata.}} D_2O + H_2$$

Acetylene, acetone and acetyl acetone undergo ready xchange reactions in alkaline solution.

$$C_2H_2 + D_2 \longrightarrow \underset{\text{Deutero acetylene}}{C_2D_2} + H_2$$

This reaction is due to the weakly acidic character of C- H bond in acetylene.

vii) Reducing Property:

It reduces certain halides at high temperature, e.g. when D_2 is passed through the suspension of AgCl at very high temperature of about 700^0C, AgCl is reduced to metallic Ag.

$$D_2 + 2AgCl \xrightarrow{\triangle} 2Ag + 2DCl$$

Uses of D_2:

(i) Accelerated deuterons (deuterium nuclei) are employed for bombarding atoms in the nuclear transformation of elements and artificial radioactivity.

(ii) Its oxide, D_2O, known as heavy water, is used as a moderator in the nuclear reactors for slowing down the speed of the fast moving neutrons.

(iii) Deuterium and its compounds are used as tracers in the study of mechanism of various chemical and metabolic reactions taking place in the body because deuterium with higher mass number increases the density of the compound.

C. Tritium or radioactive hydrogen ($_1H^3$ or $_1T^3$):

Tritium is a rare isotope of hydrogen and its oxide, T_2O, is present in water in extremely minute quantities. Though this is present in atmosphere only in traces, yet is produced continuously in upper atmosphere by the reaction of neutrons on atmospheric nitrogen. These neutrons are generated by the action of cosmic radiations on the atmospheric gases.

$$\text{Atmospheric gases + cosmic rays} \longrightarrow {}_0n^1$$

$$_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{12} + {}_1T^3 \text{ (or } {}_1H^3\text{)}$$

Production of Tritium:

Tritium has been obtained, in small quantities, by the certain nuclear reactions given below:

(a) Bombardment of deuterium compounds *viz*. D_3PO_4, ND_4Cl etc. with high energy deuterons.

$$_1D^2 + {}_1D^2 \longrightarrow {}_1T^3 + {}_1H^1$$

(b) Deuterium induced reactions, e.g.

$$_4Be^9 + {}_1D^2 \longrightarrow {}_4Be^8 + {}_1T^3$$

$$_3Li^7 + {}_1D^2 \longrightarrow {}_3Li^6 + {}_1T^3$$

(c) Neutron induced reactions

$$_5B^{10} + {}_0n^1 \longrightarrow {}_5B^{11} \longrightarrow {}_1T^3 + 2\,{}_2He^4$$

$$_3Li^6 + {}_0n^1{}_1 \longrightarrow T^3 + {}_2He^4$$

The last one is the best method of obtaining tritium.

Properties:

Because of the unfavourable neutron to proton ratio, tritium is radioactive (unstable) isotope of hydrogen with a half life of ~12.4 years. It decays emitting low energy β- particles and is transformed into a lighter isotope of helium, $_2He^3$.

$$_1T^3 \longrightarrow {}_2He^3 + {}_{-1}e^0 \text{ (β- particle)}$$

Because of this decay, traces of $_2He^3$ are present in the atmosphere. Its melting point is

(-)252.4^{0}C and boiling point is (-)248.1^{0}C. Being an isotope of hydrogen, it shows similar chemical properties to that of hydrogen and deuterium but reacts at much slower rate, even slower than those of deuterium.

For example,

(i) On burning in O_2 or air, it gives T_2O

$$2T_2 + O_2 \longrightarrow 2T_2O$$

(ii) It combines with H_2, on heating to 300 to 400^{0}C, forming tritium hydride.

$$H_2 + T_2 \longrightarrow 2HT \text{ (or TH)}$$

HT reacts with HCl to give tritium chloride

$$HT + HCl \longrightarrow TCl + H_2$$

Uses:

(i) It is used as a radioactive tracer in chemistry, biology and medicine.

(ii) It is also used in nuclear fusion reactions such as

$$_{1}D^{2} + {}_{1}T^{3} \longrightarrow {}_{2}He^{4} + {}_{O}n^{1} + \text{Energy}$$

In the fusion reaction huge amount of energy is released which is used in hydrogen bomb (Thermonuclear process).

(iii) It is used as the source of tritons which are employed in several nuclear transformations.

(iv) TH is an important compound for the preparation of a number of organic compounds containing this radioactive isotope.

6.3.1 Isomers of hydrogen:

Hydrogen exists in two isomeric forms, first revealed in 1929 by Bonhoeffer and Harteck from spectral studies, known as ortho and para hydrogen. These two forms are isomeric and differ apparently only in their nuclear spins. That is why hydrogen is said to exhibit **nuclear spin isomerism** and the two forms are called nuclear spin isomers.

It has been observed that the nucleus of hydrogen atom spins about its own axis like a top as does an electron. Because the hydrogen molecule is composed of two hydrogen atoms containing, as is well known, a proton in the nucleus and an electron revolving around it. When two hydrogen atoms combine to form the molecule, two types of hydrogen molecules should be formed, one having the spins of the two nuclei parallel or aligned (i.e. in the same direction) and the other having the nuclear spins antiparallel or opposed (i.e. in the opposite direction). The former variety is known as ortho hydrogen and the latter as para hydrogen, respectively.

The two types of hydrogen molecules have been discussed below:

(i) Ortho hydrogen molecule:

The hydrogen molecule in which the nuclei (protons) of both the combining hydrogen atoms spin in the same (i.e. parallel) direction is termed as ortho hydrogen (Fig 6.2a). In this form the resultant nuclear spin is one (i.e.$+\frac{1}{2}+ \; +\frac{1}{2} = 1$).

(ii) Para hydrogen molecule:

The hydrogen molecule in which the nuclei (protons) of both the constituent hydrogen atoms spin in the opposite (antiparallel) direction is called para hydrogen. (Fig 6.2b). In this form the resultant nuclear spin is zero (i.e. $+\frac{1}{2}+ -\frac{1}{2} = 0$).

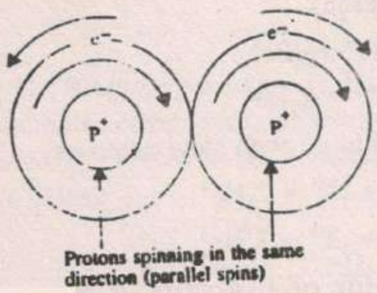


Fig. 6.2(a) Orthohydrogen molecule

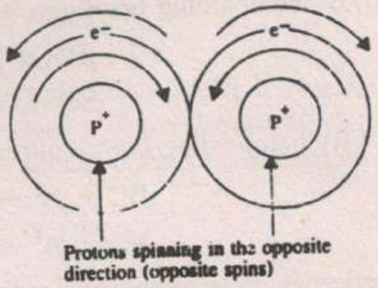


Fig. 6.2 (b) Parahydrogen molecule

It is to be noted that the two electrons in both the ortho and para forms of hydrogen molecules always spin in the opposite directions to result in the stable molecular structure.

Difference between ortho and para hydrogen molecules

(i) Internal molecular energy:

The two forms of hydrogen differ in their internal molecular energy which is attributed to the fact that in case of ortho hydrogen molecule, the spins of the two nuclei (protons), being in the same direction, increase the molecular energy of this form.

On the other hand, in para hydrogen molecule, the spins of the two nuclei (protons) being in the opposite direction, neutralise (or cancel) each other. The neutralisation of spins decreases the molecular energy of para hydrogen molecule. Thus the para form has lower internal energy than the ortho form.

(ii) Physical properties:

The physical properties such as melting point, boiling point, thermal conductivity and specific heat of both the forms are different from each other. Some physical constants of para form are given below whereas those of ortho form have been left blank because the ortho from is difficult to be obtained in a pure state.

	Ortho form	Para form
Melting point (^{0}C)	-	(-)259.17^{0}C

Boiling point (^{0}C) (at 760 mm)	-	(-)252.74^{0}C
Vapour pressure(mm) at (-)253 to (-)243^{0}C	751	737

The magnetic moment of parahydrogen is zero because of the neutralisation of nuclear spins while that of ortho form obtained from the data for known ortho-para mixture is approximately twice the moment of a proton.

The appreciable difference in the thermal conductivities of the two forms is used to estimate the percentage of ortho and para forms in a given sample of hydrogen.

(iii) The ortho form is more stable than the para form and hence the latter (i.e. para form) has a tendency to change into the ortho form.

(iv) Effect of temperature on the relative proportions of the two forms in ordinary hydrogen.

Ordinary hydrogen gas (H_2) is an equilibrium mixture of ortho and para hydrogens, Ortho $H_2 \rightleftharpoons$ Para H_2 and their relative proportion (i.e. ortho-para ratio) in the gas is dependent on temperature. It has been shown that at absolute zero molecular hydrogen consists mainly of the para form and the ratio of para to ortho forms is 1:0 (approximately). As the temperature increases, the proportion of ortho form gets increased and that of para form decreases. At the temp. of liquefaction of air, the ratio of ortho to para forms has been found ot be 1:1 and at room temperature, 27^{0}C, this ratio is 3:1 and remains constant thereafter. This means that it is rather impossible to get pure ortho hydrogen at any temperature, i.e. the above equilibrium cannot be shifted entirely in favour of ortho H_2.

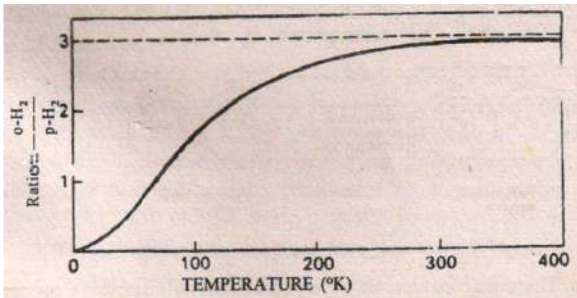


Fig. 6.3 Variation of ortho/parahydrogen with temperature.

However, this equilibrium shifts towards the right, i.e. para H_2, on decreasing the temperature up to near absolute zero when the sample of molecular hydrogen has mainly para hydrogen. This situation has been shown by graphical representation as below in Fig 6.3.

(v) Both the forms have different band spectra and this fact was used to demonstrate the existence of ortho and para hydrogens.

Separation of pure para form of H_2 from ordinary hydrogen:

In order to separate almost pure para form from ordinary hydrogen, the latter is passed through a tube packed with activated charcoal and cooled in liquid air or liquid hydrogen for about four hours. The para form thus obtained is pumped off and is about 99.5% pure. The para hydrogen can be stored in glass vessels at room temperature for about a week with appreciable change into ortho form.

Conversion of para hydrogen into ortho form:

Since ortho form of hydrogen is more stable, it can be easily transformed into the para form. However, the process $P \rightarrow O$ hydrogen is accelerated by the following methods:

(i) by passing an electric discharge through it

(ii) by heating it to high temperature of about 800^0C and above.

(iii) with the help of catalysts like platinised asbestos.

(iv) by mixing it with paramagnetic molecules, *viz.* O_2, NO_2, NO in gas phase or ions like Mn^{2+}, Co^{2+}, Ni^{2+} etc. in solution.

6.4 HYDRIDES

The binary compounds of hydrogen with other elements whose electronegativity is lower than that of hydrogen (i.e. 2.1 on Pauling's scale) are generally called hydrides. This definition excludes the binary compounds of hydrogen with non-metallic elements like H_2O, NH_3, PH_3, H_2S, HF, HCl, HBr, HI etc. But on the basis of type and nature of bonding in the compounds of hydrogen, Gibb (1941) has classified them into the following types:

(a) Ionic or salt like hydrides
(b) Covalent or molecular hydrides
(c) Metallic or interstitial (alloy type) hydrides
(d) Complex hydrides
(e) Borderline hydrides

(a) Ionic or salt like hydrides

The hydrides of the elements of groups IA, IIA (e.g. LiH, CaH_2 etc.) and some highly electropositive lanthanides and actinides are called ionic hydrides (Fr of group IA and Be and Mg of group IIA are the exceptions).

Preparation

These hydrides can be prepared by any of the following methods:

(i) **By heating the metals in a current of H_2**

Alkali and alkaline earth metals when heated at different temperatures in a current of H_2 give ionic hydrides.

$$2M + H_2 \xrightarrow{400^0C} 2MH \quad (M= Na, K\ etc.)$$

$$M + H_2 \xrightarrow{152\text{-}300^0C} MH_2 \quad (M= Ca, Sr, Ba)$$

Li kept in a hard glass tube in an iron boat combines with H_2 at 600^0C to give LiH

$$2Li + H_2 \xrightarrow{\Delta} 2LiH$$

(ii) **By heating carbonates in a current of H_2**

Certain alkali metal carbonates when heated in a current of H_2 at high temperature of about 620 - 650^0C and in the presence of Mg give hydrides, e.g. RbH, CsH etc.

$$Rb_2CO_3 + 2H_2 \xrightarrow[Mg]{\Delta} 2RbH + CO_2 + H_2O$$

(iii) **By heating metal nitride with H_2 gas.**

LiH is prepared by this method.

$$2Li_3N + 3H_2 \xrightarrow{\Delta} 6LiH + N_2$$

(iv) CaH_2 may be prepared by heating CaO with metallic Mg in a current of H_2 at high temp. and optimum pressure:

$$CaO + Mg + H_2 \xrightarrow[\sim 50\ cm]{250^0C} Ca\ H_2 + MgO$$

This is a quick method and the yield is high (99.2%).

Properties

These hydrides are crystalline compounds with ionic lattices, hydrogen acting as electronegative element. These have high melting and boiling points and conduct electricity when fused. The crystals of hydrides are somewhat denser than the parent metal itself because of strong polar bonds existing in the lattice. Except LiH, they decompose on fusion. All these hydrides are stoichiometric compounds.

(i) Thermal stability and order of reactivity

The hydrides of Li, Ca and Sr are stable while others decompose above 400^0C. In a particular group their thermal stability decreases with increasing size of the cation, i.e. down the group:

$LiH > NaH > KH > RbH > C_sH$

$CaH_2 > SrH_2 > BaH_2$

This has been supported by the decreasing values of heats of formation of these hydrides. Hence the relative order of the reactivity is as: $LiH < NaH < KH < RbH < C_sH$.

(ii) Electrolysis: Presence of hydride ion

When these hydrides are electrolysed in their fused states, they liberate hydrogen at the anode showing the presence of H^- ions in them.

(iii) Action of protonic solvents

They all react vigorously with protonic solvents such as H_2O, NH_3, C_2H_5OH etc. forming a base and liberating hydrogen.

$$MH \longrightarrow M^+ + H^-$$

$$H^- + H_2O \longrightarrow OH^- + H_2$$

$$H^- + NH_3 \longrightarrow NH_2^- + H_2$$

$$H^- + C_2H_5OH \longrightarrow C_2H_5O^- + H_2$$

(iv) Reducing property

All these hydrides show reducing property at high temperature which is attributed to the formation of atomic hydrogen. They reduce refractory metal oxides to free metal, chlorides of some semimetals to hydrides, sulphates to sulphides etc.

$$4NaH + Fe_3O_4 \longrightarrow 3Fe + 4NaOH$$

$$4NaH + SiCl_4 \longrightarrow SiH_4 + 4NaCl$$

$$2CaH_2 + PbSO_4 \longrightarrow PbS + 2Ca(OH)_2$$

(v) The alkali metal hydrides possess face-centred cubic lattice while alkaline earth metal hydrides have orthorhombic lattice.

(vi) Reaction with Nitrogen

The hydrides are converted to the nitrides on treating with Nitrogen

$$6LiH + N_2 \longrightarrow 2Li_3N + 3H_2$$

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + 3H_2$$

(vii) Complex hydride formation

Only LiH reacts with $AlCl_3$ in ether forming $LiAlH_4$ which is an important reducing agent.

$$4LiH + AlCl_3 \text{ (in ether)} \longrightarrow LiAlH_4 + 3\ LiCl$$

Uses

These hydrides are used as condensing agents in organic chemistry. Because these are hydrolysed by water giving large quantities of H_2, they are used as reducing agents. LiH and CaH_2 are used as the source of hydrogen for balloons. LiH, NaH and CaH_2 are the important members of such hydrides.

(b) Covalent or molecular hydrides

These hydrides are formed by most of the p-block elements, may these be metals, metalloids or non-metals. The binary compounds with non-metals are excluded from the class of hydrides and those of metalloids and metals (both p-block) are included. The elements, e.g. Sn, Pb, Sb, Bi, Te, Po etc, give only mononuclear hydrides while the elements like B, Al, Ga, In, Si etc. give mono nuclear as well as polynuclear (or polymeric) hydrides as follows:

B $\longrightarrow$ B_2H_6, B_4H_{10}, B_5H_9 etc

Al $\longrightarrow$ AlH_3, $(AlH_3)_n$

Ga $\longrightarrow$ Ga_2H_6, Ga_3H_8 etc.

In $\longrightarrow$ $(In\ H_3)_n$

Si $\longrightarrow$ SiH_4, Si_2H_6, Si_3H_8 etc.

Preparation

(i) By the hydrolysis of compounds

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$

$$Zn_3As_2 + 6HCl\ _3 \longrightarrow ZnCl_2 + 2AsH_3$$

(iii) By the reducition of anhydrous chlorides with $LiAlH_4$

$$MCl_4 + Li\ AlH_4 \longrightarrow MH_4 + LiCl + AlCl_3$$

Properties

In these hydrides H-atom forms covalent bond with central atoms. They exist as discrete molecules held together (in polymeric compounds) by weak van der Waals' forces or hydrogen bonds. Hence these are gases, liquids or solids (with low melting and boiling points).

(i) Thermal stability

In a group, thermal stability decreases with increasing atomic number or metallic character of the elements forming hydride, e.g. $AsH_3 > SbH_3 > BiH_3$. Thus the hydrides of predominantly metallic elements (e.g. PbH_2 and BiH_3) are unstable.

(ii) Property of behaving as Lewis base or Lewis acid

Electron rich hydrides show this property which decreases down a particular group, e.g. $AsH_3 > SbH_3$. Some hydrides, *viz.* B_2H_6, $(AlH_3)_n$ are electron deficient and hence behave as Lewis acids.

$$B_2H_6 + 2 : PF_3 \longrightarrow 2[BH_3 : PF_3]$$

$$(AlH_3)n + n{:}NR_3 \longrightarrow n[AlH_3 : NR_3]$$

(iii) Formation of complex hydrides

Some covalent hydrides react with ionic hydrides to form complex hydrides, e.g.

$$B_2H_6 + 2MH \longrightarrow 2M\,[BH_4] \qquad (M=Li \text{ or } Na)$$

Borohydride

$$AlH_3 + LiH \longrightarrow Li\,(AlH_4)$$

Li- Al hydride

Uses

Boron hydrides are used as fuels and fuel additives. Silane (SiH_4) is used as a source of pure Si employed in transistors.

Hydrides of Boron: Boranes

These will be discussed in Unit 9 ahead.

Hydrides of Silicon: Silanes

These are represented by the general formula Si_nH_{2n+2} like alkanes. Members of this series up to n = 6 are definitely known. In addition, silico ethylene, $(Si_2H_4)_n$ and silico acelyline, $(Si_2H_2)_2$ are also known.

Preparations

When Mg_2Si (obtained by heating a mixture of Mg and SiO_2 in absence of air) is treated with 20% HCl in an atmosphere of H_2, a mixture of silanes is obtained containing varying proportions of different members. These can be separated by fractional distillation of the mixture obtained in liquid form by cooling at liquid N_2 temperature.

$$Mg_2Si + 4HCl \longrightarrow MgCl_2 + SiH_4\uparrow + \text{other silanes}$$

$$2\,Mg_2Si + 8HCl \longrightarrow 4MgCl_2 + Si_2H_6\uparrow + H_2\uparrow$$

Properties

These hydrides are analogous to alkanes. Their thermal stability decreases with increasing molecular weight SiH_4 and Si_2H_6 are colourless gases at room temperature and higher members are liquids. These are poisonous. Chemically these are very reactive and burn spontaneously in oxygen to give SiO_2.

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

$$Si_4H_{10} + 13/2\ O_2 \longrightarrow 4SiO_2 + 5H_2O$$

They form silicates in alkaline water:

$$SiH_4 + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 4H_2\uparrow$$

$$Si_2H_6 + 4NaOH + 2H_2O \longrightarrow 2Na_2SiO_3 + 7H_2\uparrow$$

Structure

As these are analogous to alkanes, hence have the structures similar to those of alkanes.

(c) Metallic or interstitial hydrides

Many of the d-block elements like Ti, Zr, V, Nb, Pd etc., lanthanides and actinides, e.g. La, Ce, Pr etc. absorb hydrogen into the holes or the interstices existing between the atoms in the metallic lattice at elevated temperature without changing the original crystal structure of the metal and thus give the metallic hydrides. The interstitial combination of hydrogen and metal atoms takes place during the process, hence these are also called interstitial hydrides. These may or may not be stoichiometric e.g.

Non – stoichiometric : $Ti\ H_{1.73}$, $Pd\ H_{0.6}$, $NbH_{0.86}$ etc.

Stoichiometric : NiH_2, CoH_2, FeH_2, CrH_3 etc. (typical metallic hydrides)

Mostly these are non-stoichiometric with lower densities than the parent metals (due to expansion of lattice).

(d) Complex hydrides

These hydrides may be regarded as the combined hydrides of the elements, e.g. $LiBH_4$, $NaBH_4$, $Be(BH_4)_2$, $LiAlH_4$ etc. Here hydrogen is covalently linked with trivalent element to form a complex anion which is bonded to the monovalent metal ion through ionic bond, i.e. $LiAlH_4$ ionises to Li^+ and AlH_4^- ions. Such hydrides can be obtained by the action of an excess of alkali metal hydride on an appropriate halide, e.g.

$$4Na\ H + BF_4 \xrightarrow{\text{Ethers}} NaBH_4 + 3NaF$$

$$4LiH + AlCl_3 \xrightarrow{\text{Ethers}} LiAlH_4 + 3LiCl$$

$LiAlH_4$

It is an import complex hydride. It is best prepared by the above reaction from LiH and $AlCl_3$. $LiAlH_4$ remains in solution. On evaporating ether, $LiAlH_4$ is obtained.

(i) It is decomposed by water liberating H_2

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

(ii) It is an import reducing agent and reduces many halides and other compounds to hydrides, e.g.

$$3Li\ AlH_4 + 4BCl_3\ \text{Ether} \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

$$LiAlH_4 + SiCl_4 \xrightarrow{\text{Ether}} SiH_4 + LiCl + AlCl_3$$

$$LiAl\ H_4 + SnCl_4 \xrightarrow{\text{Ether}} SnH_4 + LiCl + AlCl_3$$

$$LiAlH_4 + Zn(CH_3)_2 \longrightarrow ZnH_2 + Li[AlH_2\ (CH_3)_2]$$

$$4RCHO + LiAlH_4 \longrightarrow [R\text{-}CH_2O)_4\ LiAl \xrightarrow{4H_2O} 4RCH_2OH + LiOH + Al(OH)_3$$

Uses

(i) It is used for reducing almost all the compounds containing a carbonyl group, >c=0 like ketones, aldehydes, carboxylic acids etc. to alcohols.

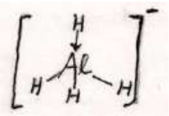
(ii) It is also used for the preparation of hydrides of Si, B, Al etc. from their chlorides.

Structure

The complex ion, $[AlH_4]^-$ like other $[M^{III} H_4]^-$ ions, is tetrahedral involving sp^3 hybridisation in the central atom. Three of these sp^3 hybrid orbitals of Al or M^{III} atom overlap with three unpaired orbitals of H-atoms to form 3 normal σ bonds and fourth vacant sp^3 hybrid orbital overlaps with filled orbital of H^- ion to give coordinate σ bond as follows:

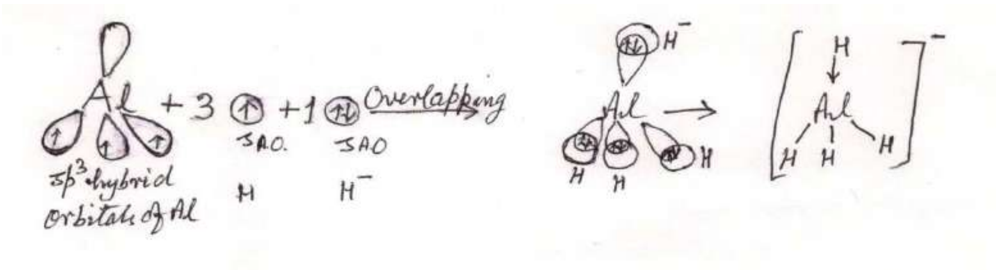
$LiH \longrightarrow Li^+ + H^-$

$H^- + AlH_3 \longrightarrow [AlH_4]^- \longrightarrow$



Al atom in ground state $3s^2\ 3p^1 \longrightarrow$

Al atom in excited state $3s^1\ 3p_x^1\ \underbrace{3p_y^1\ 3p_z^0}$



sp^3

(e) Borderline hydrides

These hydrides do not belong to any type given above and are not easily formed from the elements, e.g. BeH_2, MgH_2, ZnH_2, CdH_2 etc. These are prepared by special methods. Generally these have the properties of both ionic and covalent hydrides or sometimes of metallic hydrides also. These are less known hydrides.

6.5 Oxides of hydrogen

Hydrogen forms four oxides, *viz.* H_2O, D_2O, T_2O and H_2O_2. H_2O and T_2O have not been discussed here. Only D_2O and H_2O_2 will be discussed in detail.

6.5.1 Heavy water, D_2O

It is an oxide of heavy hydrogen, discovered by Urey in 1932 and is an important compound.

Preparation of D_2O.

It occurs in ordinary water in traces which is the chief source of D_2O. Heavy water is prepared by the following methods:

(A) Prolonged (or multistage) electrolysis of ordinary water

Heavy water is largely prepared by the continuous electrolysis of ordinary water in presence of small quantity of NaOH (~3%). The electrolysis is carried out in a steel cell (shown in Fig. 6.4) which itself acts as a cathode and a perforated cylindrical sheet of nickel acts as anode. In actual practice, a large number of such cells are used for each stage and the electrolysis is carried out in many stages usually five to seven. The gases H_2 and D_2, obtained from each stage (second onwards) are burnt and water so formed is returned to the previous stage. Thus by continuous and prolonged electrolysis of ordinary water in several stages, the concentration of heavy water goes on increasing gradually in the residual water left behind at the end of each stage which is taken to the next stage cells. At the end about 99% pure D_2O is obtained which is distilled and the distillate so obtained is again electrolysed to get pure deuterium. This deuterium is burnt in oxygen to get 100% pure D_2O. This technique is used in heavy water plant at Nangal (Punjab) for manufacturing D_2O used in the atomic plants in the country.

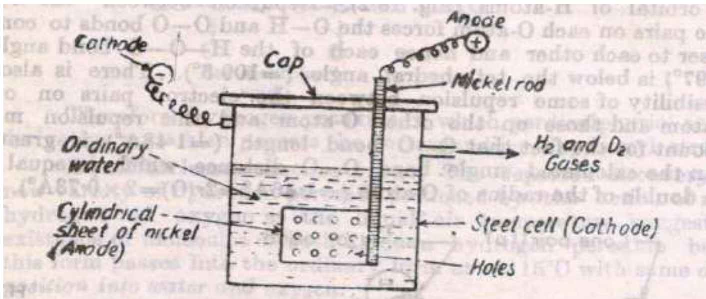


Fig. 6.4 Electrolytic cell used for the preparation of heavy water.

(B) Fractional distillation of ordinary water

Taking the advantage of the difference in the boiling points of H_2O (100^0C) and heavy water (101.42^0C), latter can be separated from ordinary water using long fractionating column and repeating the process several times. The lighter fraction (i.e. H_2O) having lower boiling point is distilled first while the heavier fraction (i.e. D_2O) with higher boiling point is left behind at the end of the repeated process.

(C) Fractional freezing of water

Since the freezing point of ordinary water 0^0C and that of D_2O is 3.82^0C, the two oxides of the isotopes of hydrogen can be separated which is completed in several cycles.

(D) Preferential adsorption

The vapours of D_2O are adsorbed more rapidly on charcoal than H_2O vapours and can be separated by preferential adsorption.

(E) Preparation of pure D_2O

Pure D_2O can be prepared by the action of D_2 gas on O_2 gas

$$2D_2 + O_2 \longrightarrow 2D_2O$$

Properties

Some of the physical properties of H_2O and D_2O are similar like odour, colour, taste etc. but many properties, e.g., density, melting and boiling points etc. are different.

i) Action on metals and their oxides

Like H_2O, D_2O reacts with alkali and alkaline earth metals to liberate D_2 and with basic oxide to give heavy alkalies.

$2Na + 2D_2O \longrightarrow 2NaOD + D_2\uparrow$

$Ca + 2D_2O \longrightarrow Ca(OD)_2 + D_2\uparrow$

$Na_2O + D_2O \longrightarrow 2NaOD$

$CaO + D_2O \longrightarrow Ca(OD)_2$

Heavy alkalies

ii) Action on non-metallic oxides

With non-metallic oxides (acidic), it gives deutero acids.

$N_2O_5 + D_2O \longrightarrow 2DNO_3$ (Deutero nitric acid)

$P_2O_5 + 3D_2O \longrightarrow 2D_3PO_4$ (Deutero phosphoric acid)

$SO_3 + D_2O \longrightarrow 2D_2SO_4$ (Deutero sulphuric acid)

iii) Action on nitrides, phosphides etc.

D_2O, like water, decomposes metallic nitrides, phosphides, arsenides and carbides etc. to give deutero compounds.

$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$ (deutero ammonia)

$Ca_3P_2 + 6D_2O \longrightarrow 3Ca(OD)_2 + 2PD_3$ (deutero phosphine)

$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$ (deutero acetylene)

$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 2CD_4$ (deutero methane)

iv) Formation of deuterates

Heavy water also gets associated with salts like water to form deuterates or deutero-hydrates, e.g.

$CuSO_4 .5H_2O + 5D_2O \longrightarrow CuSO_4 .5D_2O + 5H_2O$

Other examples are: $BeCl_2.4D_2O$, $CoCl_2.6D_2O$, $NiCl_2. 6D_2O$, $MgSO_4\ 7\ D_2O$ etc.

v) Exchange reactions

With a number of compounds containing labile hydrogen atoms, it undergoes exchange reactions in which H-atoms are partially or completely replaced by D-atoms.

$NaOH + D_2O \rightleftharpoons NaOD + HOD$

$HCl + D2O \rightleftharpoons DCl + HOD$

$NH_4Cl + D_2O \rightleftharpoons ND_4Cl + 4HOD$

The last exchange reaction occurs in steps replacing H-atoms one by one in each step.

$C_6H_6 + 3D_2O \rightleftharpoons C_6D_6 + 3H_2O$

deutero benzene

vi) Deutrolysis

These reactions are similar to hydrolysis reactions in which certain inorganic chlorides and other salts are involved. The process is called deutorolysis.

$$AlCl_3 + 3D_2O \longrightarrow Al(OD)_3 + 3DCl$$

$$BiCl_3 + D_2O \longrightarrow BiOCl + 2DCl$$

$$SiCl_4 + 4D_2O \longrightarrow D_4SiO_4 + 4DCl$$

Uses

(i) It is used as a moderator of neutrons in nuclear reactors.

(ii) It is also used for the preparation of D_2 either by electrolysis or by the action of Na-metal on it.

(iii) It is sometimes used as a tracer compound particularly in organic chemistry.

6.5.2 Hydrogen Peroxide (H_2O_2)

(a) Laboratory preparation of H_2O_2

(i) H_2O_2 is generally prepared in the laboratory by the action of cold dilute sulphuric acid on hydrated barium peroxide which is readily decomposed to give H_2O_2 solution while anhydrous barium peroxide gets a protective coating of $BaSO_4$ hence not used.

$$BaO_2.8H_2O + H_2SO_4 \text{ (cold dilute)} \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$$

$BaSO_4$ is filtered off to get the solution of H_2O_2.

Hydrated BaO_2 is obtained by slowly adding anhyd.BaO_2 to a cold conc.HCl (1 part HCl + 1 part H_2O) until it is neutralised.

$$BaO_2 + 2HCl \longrightarrow BaCl_2 + H_2O_2$$

After filtering the impurities, if present, the filtrate is treated with saturated $Ba(OH)_2$ solution and precipitate of $BaO_2.8H_2O$ is filtered off.

$$H_2O_2 + Ba(OH)_2 + 6\,H_2O \longrightarrow BaO_2.8H_2O \text{ (precipitate)}$$

.

(ii) It may also be prepared in the laboratory by adding small quantities of sodium peroxide to ice-cold water.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

(b) Manufacture of H_2O_2

(i) Electrolytic process

On a large scale, H_2O_2 is prepared either by the electrolysis of 50% sulphuric acid followed by distillation in vacuum. Perdisulphuric acid so obtained reacts with water during distillation to give H_2O_2.

$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$ (anode)

$2HSO4^- \longrightarrow H_2S_2O_8 + 2e^-$ (at anode)

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

Or an aq. solution of ammonium sulphate and sulphuric acid in molecular proportion, at low temperature, using pt-anode and graphite cathode separated by a porous diaphram.

$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow 2NH_4HSO_4$

$NH_4HSO_4 \rightleftharpoons H^+ + NH_4SO_4^-$ (anode)

$2[NH_4SO_4]^- \ -2e^- \longrightarrow (NH_4)_2S_2O_8$

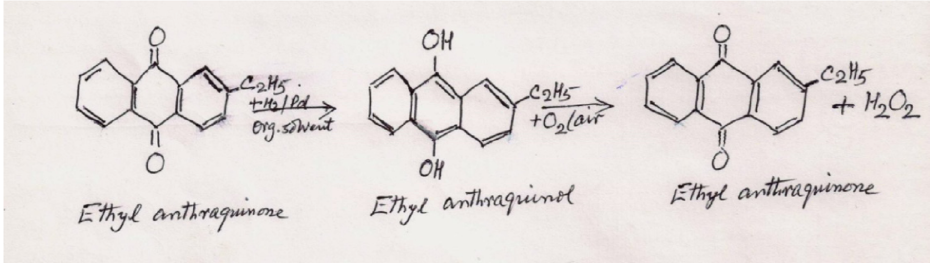
$(NH_4)2\ S_2O_8$ is distilled with H_2SO_4 under reduced pressure and $H_2S_2O_8$ obtained is converted to H_2O_2.

$(NH4)_2\ S_2O_8 + H_2SO_4 \longrightarrow H_2S_2O_8 + (NH4)_2SO_4$

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

(c) Auto-oxidation process

This is a recent process in which ethyl anthraquinone is reduced to ethyl anthraquinol by passing H_2 through its solution in an organic solvent in presence of Pd-catalyst. On frothing the product with air, about 20% solution of H_2O_2 is obtained and ethyl anthraquinone is regenerated.



Concentration of H_2O_2 solution

H_2O_2 obtained by above methods is always in the form of dilute solutions. It can be concentrated as follows:

Careful evaporation of the solution

Dilute solution of H_2O_2 is carefully heated on a water bath preferably under reduced pressure at 60-70^{0}C using a fractionating column. Water being more volatile distils over to increase the concentration of H_2O_2 to 20-25%.

The above solution is heated in a distillation flask upto 45^0C at low pressure (15mm). Initially, water distils over and at ~70^0C H_2O_2 begins to distil over. For most commercial purposes, concentration is carried out upto 55-60% only.

Further concentration of H_2O_2 is possible by using H_2O_2 along with solid CO_2 and ether. The whole mass of CO_2 and ether freezes and if little of frozen solid is dropped in a conc. solution of H_2O_2, needle-shaped crystals of almost 100% pure H_2O_2 separate out.

Properties

Anhyd. H_2O_2 is a colourless syrupy liquid, produces blisters in skin, boils at 112^0C (at 68 mm pressure) and freezes at ~(-)271^0C.

(i) Decomposition

Pure H_2O_2 is unstable and decomposes by itself to give O_2 on standing or on heating.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The decomposition is accelerated in the presence of alkalies, MnO_2, finely divided metals, e.g. Pt, Ag, Cu, Co, Fe etc.

The addition of small quantities of alcohol, acetanilide or glycerol inhibits the decomposition. H_2O_2 is stored in paraffin wax coated bottles and not in glass bottles to avoid its decomposition by alkali oxides present in glass.

(ii) Oxidising and bleaching properties

H_2O_2 is a strong oxidising agent in acidic as well as alkaline solutions because of its tendency to lose oxygen.

$$H_2O_2 \longrightarrow H_2O + O$$

It oxidises Fe^{2+} to Fe^{3+} ions, I^- ions to I_2, sulphides and sulphites to sulphates, nitrite ions to nitrate, arsenites to arsenates, ferrocyanides to ferricyanides, formaldehyde to formic acid etc. Some of these reactions are given here:

$$2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$$

$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$$

$$S^{2-} + 4H_2O_2 \longrightarrow SO_4^{2-} + 4H_2O$$

$$SO_3^{2-} + H_2O_2 \longrightarrow SO_4^{2-} + H_2O$$

$$NO_2^- + H_2O_2 \longrightarrow NO_3^- + H_2O$$

$$AsO_3^{3-} + H_2O_2 \longrightarrow AsO_4^{3-} + H_2O$$

$$2[Fe(CN)_6]^{4-} + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2OH^-$$

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$

The bleaching of silk, hair, ivory and wool is carried out with H_2O_2. This is because of oxidising properties of H_2O_2.

(iii) Reducing properties

H_2O_2 also acts as reducing agent in presence of strong oxidising agents. It reduces $MnO4^-$ ion to Mn^{2+} ion, X_2 to HX, Ag-oxide to Ag metal, MnO_2 to Mn^{2+} ion etc.

$$2MnO4^- + 5\,H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$X_2 + H_2O_2 \longrightarrow 2HX + O_2 \text{ (X=halogen)}$$

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

$$MnO_2 + 2H^+ + H_2O_2 \longrightarrow Mn^{2+} + 2H_2O + O_2$$

It is noted that in all its reducing reactions O_2 gas is liberated.

(iv) Addition reaction

It is capable of adding itself to ethylenic linkages:

$$CH_2{=}CH_2 + H_2O_2 \longrightarrow CH_2OH - CH_2OH \text{ (ethylene glycol)}$$

Strength (or concentration) of H_2O_2 solution

The strength (or concentration) of H_2O_2 solution may be expressed in terms of

(i) Volume of O_2 gas

(ii) Weight of pure H_2O_2 in a given solution of H_2O_2

(iii) Normality

Let us discuss the first type: The volume of O_2 gas obtained at N.T.P. by heating one volume of H_2O_2 solution is called the concentration of H_2O_2 solution, e.g. 1 ml. of a 10 volume of H_2O_2 solution, on heating, will give 10 ml. of O_2 gas.

Uses

(i) It is used in medicine as antiseptic for washing wounds, teeth and ears.

(ii) It finds use as an oxidising agent in the laboratory.

(iii) Used for bleaching materials.

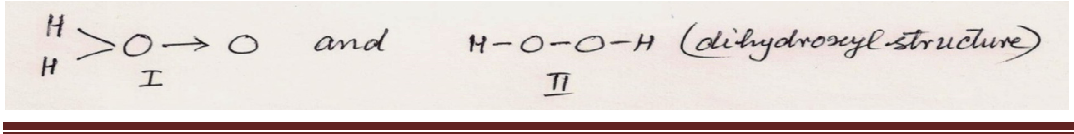
(iv) For restoring the colour of blackened lead paints,

$$\underset{\text{Black}}{PbS} + 4H_2O_2 \longrightarrow \underset{\text{white}}{PbSO_4} + 4H_2O$$

(v) As a propellent or fuel in submarines and rockets.

Structure of hydrogen peroxide

The empirical formula of H_2O_2 has been proposed as HO and molecular formula H_2O_2. Thus



two formulae were suggested for it as:

Structure I is supported by its unstable nature giving oxygen.

$$H_2O_2 \longrightarrow H_2O + O$$

and structure II is evidenced by the formation of two-series of salts, e.g. Na-O-O-H and Na-O-O-Na as well as by its reaction with diethyl sulphate and subsequent reduction of the product to ethyl alcohol:

$$H\text{-}O\text{-}O\text{-}H + (C_2H_5)_2SO_4 \longrightarrow C_2H_5O\text{-}O\ C_2H_5 + H_2SO_4$$

$$C_2H_5O\text{-}O\ C_2H_5 + 2H \xrightarrow{Zn/CH_3COOH} 2C_2H_5OH$$

Similar reaction with structure I would have given diethyl ether. But actually ethyl alcohol is obtained. This is in favour of structure II which is further supported by X-ray analysis of $K_2S_2O_8$ crystals obtained from H_2O_2 and chlorosulphonic acid and subsequent treatment with potassium salts.

Non- planner and non-linear structure

Its dipole moment value (2.1D) indicates its non-planner and non-linear structure confirmed by X-ray analysis of solid H_2O_2 molecule in which the two O-H bonds are asymmetrically distributed and all the four atoms are not lying in the same plane. The position of the atoms, bond angles and bond lengths as determined by experimental methods are shown in the figure (Fig 6.5).

6.6. SUMMARY

This unit on hydrogen and its compounds contains a detailed discussion on isotopes of hydrogen and its isomeric forms, hydrides and oxides along with their preparation, properties and uses wherever necessary. The structure of H_2O_2 has also been given.

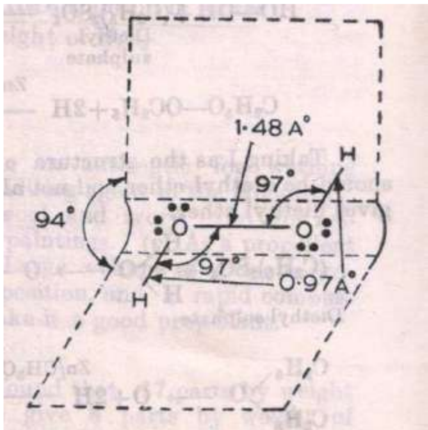


Fig. 6.5 Non-linear and non-planar structure of H_2O_2 molecule.

6.7. TERMINAL QUESTIONS

i. Heavy hydrogen has in its nucleus

(a) 1 neutron

(b) 2 neutrons

(c) 3 neutrons

(d) no neutrons

ii. At 300K, the ratio of O to PH_2 is

(a) 1:1

(b) 1:2

(c) 3:1

(d) 3:2

iii. Silicon hydrides are

(a) Ionic hydrides

(b) Covalent hydrides

(c) Metallic hydrides

(d) complex hydrides.

iv. The boiling point of heavy water is

(a) Higher

(b) Lower

(c) Equal

(d) Much lower than that of ordinary water.

6.8 ANSWERS

i. (a)
ii. (c)
iii. (b)
iv. (a)

UNIT 7: THE ALKALI METALS

CONTENTS:

7.1. OBJECTIVE

The objective of preparing the course material of this unit, i.e. on the alkali metals (the elements of Group 1) is to give a summary of the general properties and their trends in the group. That is to acquaint the readers with general characteristics of these metals along with their flame colouration and their uses, the nature and behaviour of their oxides and hydroxides, solubility behaviour of their salts and hydration, and complexation of alkali metal ions. The anomalous behaviour of lithium, its dissimilarity with other alkali metals and similarity with Mg, the element of next group and next period, called diagonal relationship shall be discussed.

7.2. INTRODUCTION

The six elements of Group 1(or IA) of the periodic table, *viz.* lithium (Li_3), sodium (Na_{11}), potassium (K_{19}), rubedium (Rb_{37}), caesium (Cs_{55}) and francium (Fr_{87}) are collectively called the alkali metals. This name alkali has been derived from arabic which means ash because the ashes of plants contain the compounds of Na and K in large quantities. In addition to this, these elements form strongly alkaline oxides and hydroxides. The individual elements were named on the basis of their use, origin in plants and spectral characteristics, i.e. colours of spectral lines. The last but radioactive element francium was named after the name of the country where M. Curie worked (France) on her persistence, though she was born in Warsaw (Poland).

All these elements belong to s-block of theperiodic table because in the atoms of these elements the last or differentiating electron enters the s-subshell of the valence shell. These occupy their position at the extreme left portion of the periodic table. Every period of the periodic table commences with an alkali metal.

The alkali metals, due to their reducing nature and their oxides being too reactive to occur in nature, are generally found as cations combined with anions of the most electronegative elements. The less electropositive element (*viz.* Li) is present in nature as silicate minerals and more electropositive elements are found as chlorides. The elements are obtained from the minerals/ores by the electrolysis of their fused salts.

All these elements are metals and have less gradation in their characteristic properties.

7.3. GENERAL CHARACTERISTICS OF ALKALI METALS AND THEIR USES

(i) Electronic configuration

The valence (or ultimate) shell electronic configuration of these elements is invariably ns^1 where n denotes the principal quantum number of the valence or outer shell and s is the subshell that receives the solitary differentiating electron while the penultimate shell contains, in general, eight $[(n-1)s^2P^6]$ electrons (Li is an exception with two electrons in its penultimate shell). On losing the solitary valence electron, the alkali metal atoms are converted into M^+ ions having inert gas configuration in the outer shell. These ions are colourless and diamagnetic in nature. The similarity in the electronic configuration of these elements is responsible for their similar physical and chemical properties. These are all monovalent elements and give colourless ionic salts.

(ii) Physical state, hardness and density

The alkali metals, except lithium, are extremely soft solids to be cut by knife and can be readily fused. This is because of the weak metallic bonding among the atoms of the metallic crystals. They are also highly malleable and ductile, freshly cut metals have a bright lustre which is quickly tarnished as soon as the metal comes in contact with atmospheric air. In general, these metals have high density due to the close packing of atoms in the metallic crystals but lithium has low density due to low atomic weight. The density increases down the group because atomic weight increases.

(iii) Atomic and ionic radii (atomic volume)

Both the atomic and ionic radii (of M^+ ions) increase from the first (i.e. Li) to the last (i.e. Fr) element on moving down the group due to the inclusion of an extra shell of electrons at each step, i.e. in the next element. But the ionic radii are smaller than the atomic radii of the corresponding elements due to the elimination of the outer shell and greater attractive pull of nuclear charge on the outer electrons of the ions. The above statement is evidenced by the values of atomic and ionic radii for the alkali metals given below:

Elements	Li	Na	K	Rb	Cs
Atomic (i.e. metallic radii (Å)	1.55	1.90	2.35	2.48	2.67
Ionic (or Crystal) radii (Å)	0.60	0.95	1.33	1.48	1.69

(for M^+ ions)

The group trend of the atomic volume is the same as that for atomic radius due to the similar reason as given above. These elements have the largest atomic radii, ionic radii and atomic volumes among the elements of the respective periods.

(iv) Melting points, boiling points and heats of atomization

Alkali metals have low melting and boiling points because of weak inter- atomic bonds in the crystal lattice which decrease further down the group due to increasing atomic size.

These metals also have low heats of atomization and have the same trends as the melting and boiling points due to the same reason as discussed above though the change is sharp at the beginning and a small change is observed in the higher members.

(v) Ionization energies, electron affinities and electronegativities

Alkali metal atoms can lose their solitary electrons from the respective outer shells (i.e. ns^1) with relative ease because the electron in each atom in held weakly with nucleus due to the larger size of the atom. These metals, therefore, have low ionization energies. Further, the ionization energy values decrease on moving down the group from Li to Fr as shown below:

Elements	Li	Na	K	Rb	Cs
Ionisation energy ($kJmol^{-1}$)	520	496	419	403	376

The electron affinity and electronegativity values are also very low for these metals as these have no or very low tendency to attract or accommodate the electrons. The values of these properties decrease down the group though the change is small.

(vi) Electropositive (or Metallic) character and reducing properties

The electropositive character of the elements depends on the ease with which the atoms of the elements lose their outermost electrons. Because of their low ionization energy values, the alkali metals have the highest electropositive character among all the elements of the periodic table. With decreasing ionization energy values, the electropositive character also increases down the group for alkali metals, i.e. Li metal is the least electropositive due to highest ionization energy and Cs, the most electropositive with the least ionization energy value among the alkali metals. The last element, Fr has been excluded because all its isotopes are radioactive with very short half life periods to be available for their detailed study.

According to the trend of electropositive character of alkali metals, their reducing property must also increase down the group, i.e. from Li to Cs but the reverse trend is observed in the reducing properties though the basic nature of their oxides increases from the first to the last element in accordance with the electropositive character. Li has maximum reducing power and Cs has minimum reducing tendency. The anomalous trend in the reducing properties can be explained as follows:

The standard electrode potential is taken as the measure of the reducing properties of these elements. More negative is the standard reduction potential or more positive is the standard oxidation potential of the metal, greater is its tendency to lose electron (s) and stronger is its reducing power.

It has been found that Li has the highest standard oxidation potential (+3.05V) or highest negative standard reduction potential value (-3.05V) thereby making it the strongest reducing agent among all the alkali metals as it can lose the ns^1 electron most readily in aqueous condition.

Actually the conversion of an alkali metal in the solid state, M (s), in contact with water into M^+ (aq.) represents the reducing power of M in aqueous medium which takes place in three steps, i.e. sublimation, M (s) ---- →M (g) requiring sublimation energy, S, which is slightly higher for Li metal than for others, ionization, M (g) $\longrightarrow$ M^+ (g), absorbing ionization energy, I, again which is maximum for Li atom and hydration of the cation, $M^+(g) + nH_2O$ M^+ (aq), liberating hydration energy, H. Anhydrous Li^+ ion, being the smallest in size, gets hydrated to the maximum extent releasing the highest hydration energy content.

The standard oxidation potential (E^0_{ox}) and other energy terms are related as $E^0 = H – I – S$

The hydration energy of lithium being very high, enough to compensates the values of I and S and consequently results in high electrode potential value making it the strongest reducing agent in contact with water though the reducing power of alkali metals in the dry or anhydrous conditions depends on their ionization energy values.

(vii) Photoelectric effect (effect of light)

The outermost ns^1 electron in the atoms of alkali metals is so loosely held with the nucleus that even the low energy photons (i.e. light) can eject this electron from the surface of these metals. This property of emitting the electron from the metal surface even on the exposure of light is called **Photoelectric effect** and permits the application of these metals (especially K and Cs) in the photoelectric cells which are sensitive particularly to blue light. Li metal with the highest ionization energy does not show this effect.

(viii) Flame colouration and use

The alkali metals give characteristic colour in Bunsen flame, i.e. Li- crimson red, Na- yellow, K-violet, Rb and Cs – also violet.

The reason for this flame colouration being when an alkali metal or its any compound is heated in the flame, the outer electron can be excited to higher energy levels by absorbing some energy from the flame. When the excited electron returns back to the ground or original level, the absorbed excitation energy is released in the form of light in the visible region of the electromagnetic spectrum and colour is imparted by the metal to the flame. Since for the same excitation energy, the electrons of the atoms of different alkali metals are excited to different higher energy levels depending on the tightness with which the nuclear charge holds the outer electron (s) with itself. Thus in Li, electrons are excited up to lower levels and in other metals up to higher levels and the released energy as a consequence goes on increasing from Li to Cs and accordingly the colours are observed for them, i.e. for Li crimson- red(due to lower energy) and for Cs, violet(due to higher released energy).

This property of alkali metals to impart colouration in the Bunsen flame has been used to detect their presence in the salts by the so called flame test and to estimate Na and K quantitatively in plant samples.

(ix) Polarizing power of alkali metal ions

On approaching nearer to an anion, the alkali metal cations attract the anionic charge and repel the nuclei of anions thereby distorting or polarizing the anion. This results in the passage of ionic bond in the compound to covalent bond. This effect has been found to be more pronounced in smaller alkali metal cations, i.e. Li^+ ion (all alkali metal cations have the same charge). That is why Li salts are covalent in nature and insoluble in water but soluble in organic solvents. While others form ionic compounds which are freely soluble in water.

(x) Action of liquid ammonia

The alkali metals dissolve in liq. NH_3 without the evolution of H_2 to give blue colour in dilute solutions. This is due to the excitation of free electrons to higher energy level to give an absorption band in visible range of the spectrum and therefore, the solution looks blue due to transmitted light. The concentrated solutions are good conductors of electricity due to the presence of ammoniated electrons, $[e(NH_3)]^-$ and are bronze coloured.

Uses of alkali metals

(a) The most important use of lithium is in making alloys, e.g. on adding to the alloys of magnesium, it improves their tensile strength and resistance to corrosion.
(b) Lithium is also used as deoxidizer in the purification of nickel and copper.

(c) It is an ingredient of high energy fuels employed for the propulsion of intercontinental rockets (i.e. thermonuclear energy).

(d) Compounds of lithium are used in glass and pottery industry to increase the strength and resistance of glass and to prevent the surface cracking of pottery.

(e) Li-citrate and salicylate are used in medicine for gout.

(f) LiOH is used in making high quality lubricating greases which can withstand extreme temperature variations.

(g) Sodium is used in the laboratory as a reducing agent in the form of sodium amalgam and it is also used for detecting N, S and halogens (Cl, Br, I) in organic compounds.

(h) In metallurgy, this metal is employed for the extraction of many elements like Si, B, Mg etc.

(i) It is largely used in industry for the production of artificial rubber, dyes and drugs.

(j) Its compound, $Na_2 CO_3$, is used as a laboratory reagent, for laundry works and as domestic cleansing agent as well as in softening of hard water.

(k) $NaHCO_3$, another compound of Na, is used in medicine (as soda bicarb) to neutralize the acidity in the stomach and as baking soda.

(l) Potassium and caesium metals are used in photoelectric cells.

(m) The sodium-potassium alloy is used in the special thermometers employed for measuring high temperature.

(n) $KClO_3$, an important compound of potassium is used as oxidizing agent in the laboratory in fireworks as well as match industry.

7.4. OXIDES AND HYDROXIDES OF ALKALI METALS

Oxides:

Alkali metals react with oxygen or air rapidly and get tarnished due to the formation of their oxides on the surface of the metals. That is why alkali metals are stored in kerosene or paraffin oil.

When these metals are burnt in oxygen or air, they yield either of the three types of oxides: monoxide (M_2O) or peroxide (M_2O_2) (Na, K, Rb, Cs) or super oxide MO_2 (K, Rb, Cs) depending on the nature of the metal. The oxides of these metals can also be obtained by dissolving the metal in ammonia and treating the solution with the required amount of oxygen. Lithium does not form higher oxides because Li^+ ion is too small and has much stronger positive field around it than other alkali metal ions. This strong positive field near one oxygen anion restricts the spread of negative charge towards another oxygen atom making the formation of higher oxide difficult.

Generally under normal conditions, following oxides of different metals can be obtained:

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (Monoxide only)}$$

$$4Na + O_2 \longrightarrow 2\,Na_2O \quad \text{and}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \text{ (monoxide and peroxide both)}$$

$$M + O_2 \longrightarrow MO_2 \text{ (M = K, Rb, Cs; superoxide, generally)}$$

Since the normal oxide of alkali metals other than that of Li are not formed by the direct reaction between the metal and O_2 or air, they are obtained by indirect methods, e.g.

$$2Na_2O_2 + 4Na \rightleftharpoons 4\,Na_2O \text{ (reversible reaction)}$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2\uparrow$$

The normal monoxides are strongly basic and highly soluble in water giving alkaline solutions by proton exchange $O^{2-} + H_2O \rightleftharpoons OH^- + OH^-$ (hydrolysis of oxide ion to hydroxide) and disproportionate to peroxide and metal vapours when heated

$$2Na_2O \xrightarrow{\Delta} Na_2O_2 + 2Na \text{ (vapours)}$$

The peroxide of sodium yields H_2O_2 on treatment with dilute acids in cold and superoxide (NaO_2) by heating with O_2.

$$Na_2O_2 + 2H^+ \longrightarrow H_2O_2 + 2Na^+$$

$$Na_2O_2 + O_2 \longrightarrow 2NaO_2$$

In general alkali metal peroxides and super oxides are strongly oxidizing agents and react with water and dilute acids to H_2O_2 and O_2 :

$$O_2^{2-} + 2H_2O \longrightarrow 2OH^- + H_2O_2$$

$$O_2^{2-} + H_2SO_4 \longrightarrow SO^{2-}_4 + H_2O_2$$

` $2O_2- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$

$4O_2^- + 2H_2SO_4 \longrightarrow 2SO_4^{2-} + 2H_2O + 3O_2$

Hydroxides:

All alkali metals form ionic hydroxides with the general formula MOH and can be prepared by treating the monoxides or metals with water:

$2M + 2H_2O \longrightarrow 2MOH + H_2$

$M_2O + H_2O \longrightarrow 2MOH$ (M = alkali metals)

The reaction between water and the metal, except Li, is highly explosive hence this method is not generally used for the preparation of hydroxides. These are obtained by the electrolysis of aqueous solutions of the chlorides.

These hydroxides are highly soluble in water and alcohol and ionize to yield OH^- ions and thus behave as strong bases or alkalies in solution. The solubility increases and the hydroxides become more and more basic on moving down the group, i.e. from Li to Cs due to an increasing trend in electropositive character. LiOH is less basic and less soluble in water.

The hydroxides other than LiOH are thermally stable even at very high temperature:

$$2\,LiOH \xrightleftharpoons{780^0C} Li_2O + H_2O\uparrow$$

$$2NaOH \xrightarrow{1300^0C} \text{stable but sublimes}$$

The alkali metal hydroxides are strong bases and react with acids, acidic oxides and amphoteric oxides to form salts:

$2MOH + H_2SO_4 \longrightarrow M_2SO_4 + 2H_2O$

$2MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$

$2MOH + Al_2O_3 \longrightarrow 2MAlO_2 + H_2O$

The hydroxides absorb CO_2, even in traces, from the air to form carbonates:

$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

7.5. SOLUBILITY AND HYDRATION OF ALKALI METAL COMPOUNDS (IONIC HYDRATION)

The terms, solubility and hydration of compounds are related with the lattice energies and hydration energies of the compounds. The lattice energy is a direct and quantitative measure of ionic bond strength of any compound. When an ionic compound is placed in water (or any polar solvent), the ionic charges of the compound attract the polar molecules (called dipoles). The ions of the compound after separation combine with water (solvent) molecules. This process is called hydration (solvation). For example, when NaCl is placed in water the positively charged Na^+ ions attract the partially negatively charged oxygen atoms ($O^{\partial-}$) and the negatively charged Cl^- ions attract the partially positively charged hydrogen atoms ($H^{\partial+}$) of water molecules. Energy is released in this process which is known as hydration energy. If the hydration energy is more than the lattice energy of the compound, the ionic bonds will be broken and the solid compound dissolves, i.e. the ions go into solution as hydrated ions. But if the hydration energy is less than the lattice energy of the compound, the ionic compounds remain insoluble. It may be concluded that the solubility of ionic compounds depends on the difference between their lattice energies and hydration energies. The large lattice energy of LiF makes it insoluble in water. Thus it can be said that lattice energy and ionic hydration are intimately related with each other. The alkali metal ions are hydrated to different extents, e.g. anhydrous Li^+ ion being smallest in size is hydrated to the maximum extent and anhydrous Cs^+ ion is hydrated to the minimum extent due to its largest size among these ions. After hydration $Li\ (aq)^+$ ion is the largest and $Cs\ (aq)^+$ ion is the smallest in size.

7.6. COMPLEXATION OF ALKALI METAL IONS

The alkali metal ions have the least tendency of complexation with normal ligands among the elements of the periodic table. This is mainly due to:

(i) Relatively larger ionic size of the alkali metal ions
(ii) Low charge densities (charge/size) of the ions
(iii) Non-availability of the vacant d-orbitals of right energy to accept lone pairs from the ligands
(iv) Very high basicity of the metals and
(v) Non-availability of variable oxidation states in the ions.

However, a few complexes of these elements have been formed but the complex forming ability decreases down the group from lithium to caesium. Alkali metals form complexes with oxygen containing multidentate chelating ligands such as salicylaldehyde, acetylacetone etc. (**Fig. 7.1**) given below:

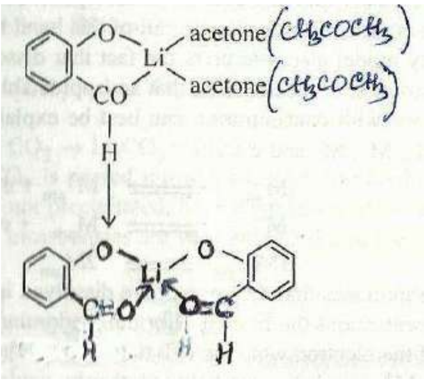


Figure 7.1

An important class of complexing agent, the crown ether, has been synthesized known as dibenzo-18-crown-6 containing two benzene rings and 18 atoms making a crown-shaped ring, six of them being oxygen atoms. These six oxygens may form complexes with a metal ion, even with a large alkali metal ion. The bonding of the metal ion to the polyether is largely electrostatic. Polyethers having different sizes are known. The size of the metal ion and that of the hole in the centre of Polyethers must be comparable for close fitting of the metal ion in the ring.

Benzo-12-crown-4 has a ring of 12 atoms, four of which are oxygens. A crown-4 polyether forms stable complex with Li^+ or Na^+ ion where as a crown-6 polyether prefers K^+ ion with unusual coordination number.

The polyethers act as ion carriers inside living cells to transport ions across cell membranes and thus maintain the balance between Na^+ and K^+ ions inside and outside cells.

The crown ethers also form some unusual complexes called electrides. These are paramagnetic such as Cs^+ (crown ether)e-. Because of very large size and hydrophobic character of the complexed cation, crown ether complexing can lead to salts becoming soluble in organic solvents containing no donor atoms, e.g. [K(crown-6)]OH and K (crown-6)]MnO_4 in benzene and toluene, respectively.

Three dimensional equivalents of crown ethers contain nitrogen atoms to obtain branching and to provide extra donor sites. They are called cryptands as they hide the cation. A typical cryptand-222 has been shown in (**Fig.7.2**) below. All the N and O atoms of this compound act as donors, the conformations at the nitrogen atoms being the ends, i.e. the lone pairs inwards cryptands shield the cations such that they are complexed more effectively than crown ethers. The cryptands-221 and -222 form their more stable alkali metal complexes with Li^+, Na^+ and K^+ respectively in terms of enthalpy.

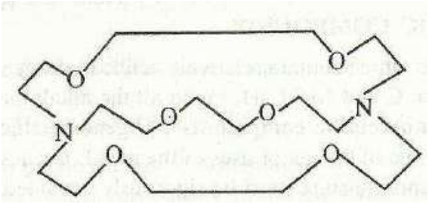


Fig. 7.2 . Cryptand-222

The action of cryptand-222 on sodium in ethylamine solution produces [Na (cryptand-222)]$^+$ Na^-, a golden yellow solid. This shows the striking application of cryptand-222 in shifting the disproportionation equilibrium to the right hand side:

$$2Na \rightleftharpoons Na^+ + Na^-$$

Also the salts containing the ions K^-, Rb^- and Cs^- have also been prepared.

7.7 ANOMALOUS BEHAVIOUR OF LITHIUM

Lithium, the first element of the alkali metal series, though shows most of the characteristic properties of the alkali metals (Group IA) as has been discussed above yet it also differs from them in many respects. This anomalous behaviour of lithium may be attributed to the following points:

(i) Very small size of Li and Li^+ ion as compared to those of others.
(ii) High charge density (charge/size) and high polarizing power of Li^+ ion.
(iii) Higher electronegativity and ionization energy of Li than other alkali metals and less electropositive character.

The main points of difference are summarized below:

i. Lithium is harder and more ductile metal than the other alkali metals with higher melting and boiling points.

ii. Chemically it is less reactive than other alkali metals. Thus it is attacked by water only slowly even at 27^0C while other metals react instantly and vigorously even at lower temperature. Also, Li is not attacked by air easily and does not lose its lustre even on melting.

iii. Li is the only alkali metal which forms nitride (Li_3N) by the reaction with nitrogen. Other alkali metals do not react with N_2.

iv. On burning with O_2 or air, Li gives only monoxide (Li_2O) while other alkali metals generally give peroxides or superoxides, i.e. M_2O_2 and MO_2.

v. Lithium halides, being covalent in nature, are soluble in organic solvents while other alkali metal halides are not.

vi. Li_2O is much less basic (almost amphoteric) in nature while monoxides, M_2O, of other alkali metals are highly basic. Therefore, LiOH is a weak base, MOH of other alkali metals are strong bases.

vii. Most of the lithium salts are only sparingly soluble in water while the corresponding salts of other alkali metals are freely soluble. This is either because of high lattice energy or covalent nature of Li-salts.

viii. The carbonate and hydroxide of lithium are thermally less stable and decompose to give Li_2O:

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

The same salts of other alkali metals are stable to heat and do not decompose.

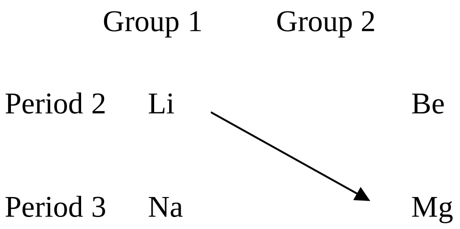
ix. Li- nitrate on heating decomposes easily to evolve NO_2 and O_2 but other metal nitrates are converted to nitrites and O_2:

$$4\,Li\,NO_3 \xrightarrow{\Delta} 2\,Li_2O + 4NO_2\uparrow + O_2\uparrow$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$$

Diagonal relationship of Li with Mg

Though lithium, the first element of alkali metal series and the member of Group 1 and period 2, shows a number of dissimilarities from other alkali metals yet it exhibits close resemblance with Mg, the element of the next higher group (Group 2) and the next higher period (Period 3) located diagonally opposite to it in the periodic table, in many respects. This sort of relationship between the two elements in the periodic table is called diagonal relationship:



The resemblance between these diagonal neighbours is because of:

(i). Close similarity in atomic and ionic sizes, i.e.

r (Li) = 1.34Å, r (Mg) = 1.36Å

r (Li^+) = 0.60Å, r (Mg^{2+}) = 0.65Å

(ii). On moving down the group, the periodic properties, *viz*. ioniziation energy and electronegativity decease and electropositive character increases from Li to Na But the same properties have the reverse trend on moving across the period from Na to Mg, i.e. the first two properties increase and the last one decreases. The net effect is that both Li and Mg have almost the same values of these parameters.

Some points of similarity between Li and Mg are as follows:

a. Both the elements have almost similar polarizing power due to small size and high charge density of the ions.

b. Both Li and Mg decompose water only slowly liberating H_2.

c. Both the elements combine with nitrogen to give nitrides:

$$6Li + N_2 \longrightarrow 2\,Li_3N$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

d. The chlorides of both these elements are deliquescent and are separated from aqueous solutions as hydrated crystals, i.e. $LiCl.\ 2H_2O$ and $MgCl_2\ 6H_2O$

These chlorides are also hydrolyzed in the similar way in water unlike those of other alkali metals.

e. The nitrates, carbonates and hydroxides of both Li and Mg decompose on heating to evolve O_2 & NO_2 (nitrates), CO_2 (carbonates) and H_2O vapours (hydroxides):

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2\uparrow + O_2\uparrow$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2\uparrow$$

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$$

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

7.8. SUMMARY

The course material of this unit deals with the general characteristics of the alkali metals such as their electronic configuration, physical state, density, hardness, atomic and ionic radii along with their atomic volume, their melting and boiling points as well as heats of atomization, ionization energies, electron affinities and electronegativity, their electropositive or metallic character and reducing properties, the photo electric effect and flame colouration along with its use in qualitative and qualitative analysis. A brief account of their polarizing power and the uses of alkali metals and their compounds have also been taken care of. The general discussion of oxides and hydroxides of alkali metals with their preparation and properties has been given in short. An account of the cause of solubility of alkali metal compounds and its connection with hydration has also been given. The complexation of alkali metal cations, anomalous behaviour of lithium and its diagonal relationship with magnesium have been discussed with appropriate reasoning.

7.9. Terminal questions.

i. The element used in photoelectric cells is ?

(a) Li (b) Na (c) Mg (d) Cs

ii. Which one of the following has maximum reducing power in aqueous solution ?

(a) Li (b) Na (c) K (d) Cr

iii. The element imparting crimson red to Bunsen flame is ?

(a) Li (b) Na (c) K (d) Rb

iv. The least stable among the following is ?

(a) $RbNO_3$ (b) KNO_3 c) $NaNo_3$ (d) $LiNO_3$

v. Write a note on reducing property of alkali metals ?

vi. What is photo electric effect ?

vi. How does the electropositive character of the alkali metals vary in the group and why ?

viii. Li gives only monoxide but not higher oxides Explain?

ix. What happens when alkali metal nitrates are heated?

x. Differentiate between lattice energy and hydration energy?

xi. How does Li_2CO_3 differ from K_2CO_3?

xii. Salts of lithium, in general, are covalent while those of other alkali metals are ionic. Explain.

7.10. Answers.

i. (d)
ii. (a)
iii. (a)
iv. (d)
v. Please refer to reducing properties.
vi. Kindly see the photoelectric effect.
vii. Please see the electropositive character.
viii. Please refer to oxides.

ix. Kindly refer to the anomalous behaviour of lithium.

x. Kindly refer to solubility and hydration of alkali inetal compounds.

xi. Please see the anomalous behaviour of Li

xii. Please refer to the polarizing power of alkali metal ions.

UNIT 8: THE ALKALINE EARTH METALS

8.1. OBJECTIVES

The course material of this unit, i.e. on the alkaline earth metals, has been written to give a summarized view of the general characteristics and their gradation in the group and to acquaint the readers about the properties as well as the uses of these metals and their salts in the light of the said properties, the preparation and properties of the halides and hydrides of beryllium, the complexation behaviour of alkaline earth metal ions along with the anomalous behaviour of beryllium in contrast to other group members.

8.2. INTRODUCTION

The alkaline earth metals, the members of Group 2 (or IIA) of the modern periodic table, consist of the six elements, *viz.* beryllium (Be_4), magnesium (Mg_{12}), calcium (Ca_{20}), strontium (Sr_{38}), barium (Ba_{56}) and radium (Ra_{88}). The name alkaline earth metals was taken from the fact that in old days the word ‘earth’ was applied for the metallic oxides and the oxides of three of these metals, *viz.* calcium, strontium and barium were known much earlier than the metals themselves and occurred in nature as lime (CaO), strontia (SrO) and baryta (BaO). These oxides were called alkaline earths since they were alkaline in nature and produced alkaline solution in water as well as they existed in nature as the earths (oxides). Later when these elements were discovered, they were named as alkaline earth metals. After the discovery of other members of this group, v*iz*. Be, Mg and Ra, this term was used to include all the elements of the group (Group 2).

However, because radium corresponds to the alkaline earth metals in its chemical properties but it is a radioactive element, therefore, it is studied separately along with other radioactive elements.

These elements are also said to belong to s-block of the elements because in the atoms of these elements too, like group IA elements (or alkali metals), the differentiating or last electron enters the s-subshell of the ultimate shell. These elements are also placed at the extreme left portion of the periodic table after the alkali metals.

These metals are never found free (in metallic form) in nature because of their active reducing behaviour like alkali metals and react readily with a variety of non-metals. Magnesium is the second most abundant metallic element in the sea water and also occurs in a variety of silicate minerals. Beryllium occurs as beryl minerals. Calcium is found abundantly as carbonate in marble, lime stone and chalk. Strontium and barium are found most frequently as the sulphates. Radium is a member of decay chain of U^{238}. All these metals can be prepared by the electrolysis of their halides or by the reduction of their oxides with the available strong reducing agents.

8.3. GENERAL CHARACTERISTICS OF ALKALINE EARTH METALS AND THEIR USES

The general characteristics of alkaline earth metals can be summarized as follows:

(i) Electronic configuration:

The valence (or ultimate) shell electronic configuration of the metals of the group IIA is invariably ns^2 where n is the principal quantum number or the shell number of the ultimate shell and s denotes the subshell which receives the last electron. The penultimate shell, like alkali metals, except Be has eight, i.e. $(n\text{-}1)s^2p^6$, electrons in these elements. Be has two electrons i.e. $(n\text{-}1)s^2$ in the penultimate shell. If the valence electrons are ejected from the metal atoms of these elements, they are converted to M^{2+} ions having the inert gas configuration in the outer shell. These ions are colourless and diamagnetic in nature, i.e. the elements form colourless ionic salts and are bivalent. Due to their alike electronic structure, these elements resemble closely in their physical and particularly in chemical properties.

(ii) Physical state, hardness and density:

All these metals are silvery white solids exhibiting grayish white metallic lustre when freshly cut but tarnish soon after their exposure to air. They are also malleable and ductile but less than alkali metals and are harder than alkali metals. This is because of stronger metallic bonding in the crystal lattice. The hardness of these metals increases with increasing atomic number. They have high electrical as well as thermal conductivity because the two valence electrons can move easily through the crystal lattice.

These metals have higher density than alkali metals because they can be packed more tightly due to greater charge and smaller radius. The density first decreases up to calcium and then increases, i.e. there is irregular trend due to different crystal structures of the metals.

(iii) Atomic and ionic radii and atomic volume:

The atomic radii of these elements, though large enough, are smaller than those of the neighbouring alkali metals in the same period due to higher nuclear charge of the atoms which tends to draw the valence electrons inwards. The atomic radii increase down the group from Be to Ra due to the inclusion of an extra shell of electrons at each step.

The ionic radii of M^{2+} ions of these elements are smaller than those of the alkali metal ions and larger than those of other elements of the respective periods (with the same charge). These radii also have the increasing trend as that of atomic radii down the group. This is clear from both atomic and ionic for these elements as given below:

Elements	Be	Mg	Ca	Sr	Ba	Ra
Atomic radii (Å)	1.12	1.60	1.97	2.15	2.22	----
Ionic radii (Å) (of M^{2+} type ions)	0.31	0.65	0.99	1.13	1.35	1.40

The atomic volume of these elements has been found to increase on moving down the group from Be to Ra as happens in the case of atomic radii.

(iv) Melting and boiling points and heat of atomization:

Both the melting and boiling points do not show regular trend. These are, however, higher than those of the neighbouring alkali metals due to smaller size as compared to those elements and much stronger bonds in solid state due to the presence of two electrons in the valence shell.

Heat of atomization decreases from Be to Ra. Though it falls considerably from Be to Mg but the difference is small in the subsequent elements. This reveals that the metallic bond strength is maximum in the case of beryllium among all the alkaline earth metals.

(v) Ionization energies and oxidation states:

These elements have higher ionization energy values (1st ionization potential) than those of the neighbouring alkali metals. This is due to the smaller size and greater nuclear charge of the atoms of these elements as compared to alkali metals which exert stronger pull on outer electrons. The outer ns^2 electrons of these elements are removed from their atoms one by one in steps on supplying energy and thus two ionization energy values are observed for each element. The first as well as the second ionization energy values of these elements decrease on going down the group from Be to Ba as expected because of increasing atomic size in the group. However, The ionization energies of Ra are slightly higher than those of Ba but no satisfactory explanation is available for this anomaly. Thus beryllium has the highest values and barium has the lowest values of ionization energies among these elements. It has been noticed that the second ionization energy is approximately double to the first ionization energy for each element as is evident from the following table:

Table 8.1 First and Second Ionization Energies of Alkaline Earth Metals

Elements		Be	Mg	Ca	Sr	Ba	Ra
Ionization Energies ($kJmol^{-1}$)	$IE_{(1)}$	899.5	738	590	549.5	503	509.5
	$IE_{(2)}$	1757	1451	1145.5	1064	965	979

It is interesting to note that in view of the much higher second ionization energy values of these elements than the first ionization energy values, it appears that these metals would prefer to form M^+ ions rather than M^{2+} ions. However, in actual practice, these metals form only M^{2+} ions, *viz*, Be^{2+}, Mg^{2+} etc. If ionization energy were the only factor involved, they would have formed only M^+ ions rather than M^{2+} ions but actually they only form M^{2+} ions. This anomaly has been explained by the fact that the M^{2+} ions are excessively hydrated and a large amount of energy known as energy or enthalpy of hydration is released in the process which more than counterbalances the higher value of the second ionization energy in each case. The hydration energy values have been given below and could be compared with IInd I.E. values of the elements:

Elements	Be	Mg	Ca	Sr	Ba	Ra
Enthalpy of hydration (kJ mol^{-1})	-2455	-1900	-1565	-1415	-1275	-

(vi) Electropositive character and reducing property:

Because of their large size and having comparatively low ionization energies, the alkaline earth metals are strongly electropositive elements as the change $M \rightarrow M^{2+} + 2e^-$ can be brought about fairly readily. However, these are less electropositive than group IA elements of their respective periods. That is why these metals do not show photoelectric effect on exposure to light.

Among these elements beryllium has the least electropositive character and hence also has least tendency to form Be^{2+} ions. That is why its compounds with nitrogen, oxygen, sulphur and halogens are covalent whereas the corresponding compounds of other members of this group are ionic. Also the hydroxides of these elements become more and more basic as we move from Be to Ba.

The reducing properties (based on values of standard electrode potential) are also high for these elements which increase down the group from Be to Ba though this property is lower than that exhibited by alkali metals. This infers that these metals are less electropositive and weaker reducing agents than the alkali metals of the corresponding periods inspite of high enthalpy of hydration because of their higher sublimation and ionization energies.

(vii) Flame colouration:

The alkaline earth metals and their salts impart characteristic colours to the Bunsen flame, *viz.* calcium-brick red, strontium-crimson red, barium-apple green and radium-crimson red.

The reason for this is that when energy is supplied to these elements or their compounds by putting them in the flame, their outer electrons are excited to higher energy levels by absorbing energy. On returning back to the ground or original level, the electrons emit or release the absorbed energy in the form of visible light of a particular wavelength which appears in the form of characteristic colours as given above.

In the atoms of Be and Mg elements and their salts because of their smaller size and stronger force of attraction between the outer electrons and the nuclear charge, these electrons are not excited to the higher levels by the energy of the flame which is unable to overcome the attractive force. Therefore, they do not give any colour to the Bunsen flame.

(viii) Polarizing power of alkaline earth metal ions:

The polarizing power of bivalent cations of the group IIA metals for a given anion goes on decreasing from Be^{2+} to Ra^{2+} due to increasing ionic size. This results in the formation of covalent compounds by smaller cations, as expected, with an anion. This is the reason why most of the Be-compounds are covalent in nature.

(ix) Hydration of alkaline earth metal ions:

The M^{2+} ions of alkaline earth metals are extensively hydrated to form the hydrated cation, $[M(H_2O)x]^{2+}$ and in this process a large amount of energy called energy or enthalpy of hydration is released as has already been discussed (see subsection **v**). The hydration energy values and extent of hydration of the cations decrease with increasing ionic radii of anhydrous M^{2+} ions, i.e. Be^{2+} to Ba^{2+} ion.

The hydration energy values for alkaline earth metals are higher than those of the alkali metals in the respective periods and hence the alkaline earth metal compounds are hydrated to the larger extent. For example, magnesium and calcum chlorides exist as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$, respectively while NaCl and KCl do not form hydrates.

(x) Solubility in liquid ammonia:

Like alkali metals, alkaline earth metals also dissolve in liquid ammonia yielding coloured solutions. On evaporation, the metal-ammonia solutions give hexa-ammoniates, $[M(NH_3)_6]$. These ammoniates are good conductors of electricity and decompose at high temperature.

The tendency of ammoniate formation is decreased with increasing size of metal atom, i.e. down the group.

Uses of alkaline earth metals:

(a) Beryllium (pure) is used in the nuclear reactors as the source of neutrons.
(b) Due to high permeability to X-rays, Be-sheets are used for windows of X-ray tubes. It is also used for imparting hardness to alloys, e.g. Cu-Be alloy.
(c) Mg is used as a structural metal because of its lightness and alloying property with other metals.
(d) Being a powerful reducing agent, Ca is used in the extraction of Be, Cr and Th metals from their oxides which are otherwise difficult to be reduced by carbon.
(e) When alloyed with lead, Ca is used as cable covering.
(f) Since, Ca and Ba have great affinity for oxygen and nitrogen, these are used for removing air from vacuum tubes and as deoxidizer in the manufacture of steel.
(g) Sr and Ba are also used as scavengers for removing last traces of air in steel production and from vacuum tubes.
(h) Various Ca-salts are used industrially as follows:
(i) CaO: manufacture of bleaching powder, calcium carbide and as basic lining in furnaces.
(ii) Ca $(OH)_2$: preparation of sodalime $[Ca(OH)_2 + NaOH]$ which is a good adsorbent for a number of gases and as a decarboxylating agent in organic chemistry.
(iii) Gypsum : manufacture of plaster of paris.
(iv) $CaCO_3$: manufacture of cement.
(i) Ba salt, $BaSO_4$ is used to prepare white pigment-lithopone $(BaSO_4 + ZnS)$
(j) Ra-salts are used in radiotherapy for the treatment of cancer and in luminous paints.

8.4. HALIDES AND HYDRIDE OF BERYLLIUM

8.4.1 Preparation and properties of Be-halides:

Beryllium reacts directly with halogens at appropriate elevated temperatures to form halides, Be X_2:

$$Be + X_2 \xrightarrow{\Delta} Be\,X_2$$

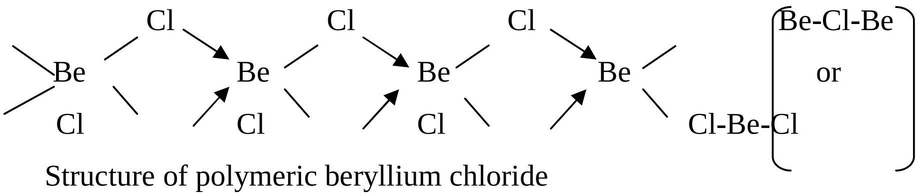
BeF_2, though covalent, yet is more soluble in water than other alkaline earth fluorides.

Anhydrous $BeCl_2$ is made by the action of carbon tetra chloride on BeO at high temperature of about 800^0C (This is a standard method for preparing metal chlorides).

$BeCl_2$ has lower melting and boiling points as well as much lower electrical conductivity in the fused state than other alkaline earth metal chlorides because of its covalent nature (due to high polarization power of Be^{2+} ions). This is hygroscopic and fumes in air, is soluble in some organic solvents. $BeCl_2$ is hydrolysed in aqueous solution and makes it an acidic solution.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

In the gas phase, $BeCl_2$ is a linear symmetric molecule which is consistent with a description of the bonding in terms of sp-hyprid orbitals around the Be-atom. In the solid state, beryllium chloride displays the Be-Cl-Be bridged structure in which each Be atom is tetrahedrally surrounded by four Cl-atoms through covalent bonds as shown below:



Structure of polymeric beryllium chloride

The two Be-Cl covalent bonds in the polymeric solid $BeCl_2$ are normal covalent bond and rest two bonds are coordinate covalent bonds with each chlorine donating a lone pair of electrons to the Be-atom (2c-2e bonds). This compound sometimes taken as a polymer involving a three centre-two electron (3c-2e) or multicentre bonds formed by the overlapping of an unpaired sp-hybrid orbital of one Be, unpaired atomic orbital of Cl-atom and an empty atomic orbital of another Be-atom.

$BeCl_2$ is sometimes used as a Friedel –Crafts catalyst.

8.4.2 Preparation and properties of Be-hydride (BeH_2):

Beryllium shows only a slight tendeny to react with hydrogen, hence BeH_2 cannot be prepared by direct combination of Be and H_2. Therefore, this is prepared by reducing $BeCl_2$ with LiH or $LiAlH_4$ in ethereal medium.

$$BeCl_2 + 2\,LiH \xrightarrow{\text{Ether}} BeH_2 + 2\,LiCl$$

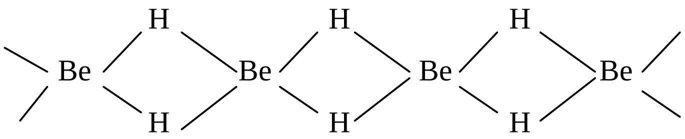
Ether

$$2\ BeCl_2 + LiAlH_4 \longrightarrow 2\ BeH_2 + LiCl + AlCl_3$$

Beryllium hydride is a covalent compound and reacts very slowly with water liberating hydrogen, hence used as reducing agent.

$$BeH_2 + 2H_2O \longrightarrow Be(OH)_2 + 2H_2\uparrow$$

It is a polymeric hydride $(BeH_2)_n$ and exists as a solid. It contains hydrogen bridges between Be-atoms forming three centre-two electron (3c-2e) bonds in which a banana shaped molecular orbital covers three atoms i.e., Be-----H----Be and contains two electrons.



Structure of polymeric beryllium hydride

The formation of three centre two electron or multicentre bonds in this polymeric hydride can be explained in the similar way as has been done for the polymeric $BeCl_2$. The only difference being H atom in place of Cl- atom (see above). There is no possibility of the existence of a coordinate bond as in case of $BeCl_2$.

8.5. COMPLEXATION BEHAVIOUR OF ALKALINE EARTH METALS

The complex formation by a metal is favoured mainly by the small size, highly charged ion and availability of suitable empty orbitals. The cations of group IIA elements do not possess these characteristics, hence are not having a significant tendency to form complexes, however the tendency is more than those of alkali metals by virtue of their higher charge density.

However, Be forms a number of complexes with many oxygen and nitrogen containing organic compounds. It also gives stable complexes with F^- ion due to its small size, e.g. $[BeF_3]^-$, $[BeF_4]^{2-}$ etc. in which Be F_2 accepts electron pairs from F^- ions:

$$BeF_2 + F^- \longrightarrow [BeF_3]^-$$

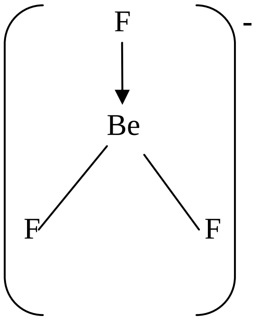
(Be is sp^2 hybridised and contains two normal covalent bonds and one coordinate bond.)

$$BeF_2 + 2F^- \longrightarrow [BeF_4]^{2-}$$

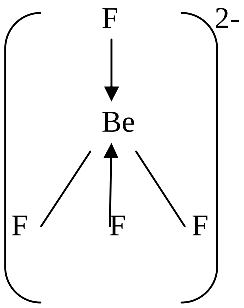
(Be is sp^3 hybridised and contains two normal and two coordinate bonds: $F^- \longrightarrow BeF_2$)

Be^{2+} ion also gives $[Be(H_2O)_4]^{2+}$ complex with four coordinate bonds of $H_2O \longrightarrow Be$ type and $[Be(oxalate)_2]^{2-}$ type complex with oxalic acid.

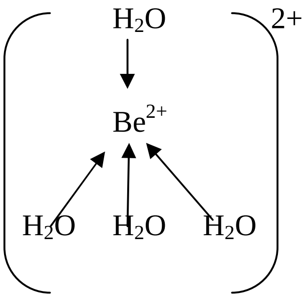
It gives $M^I_2[BeCl_4]$ with alkali metal chlorides which are decomposed by water. In aqueous medium, Be forms stronger complex with fluoride than chloride ions. The fluoride, aquo and oxalate complexes may be shown as:



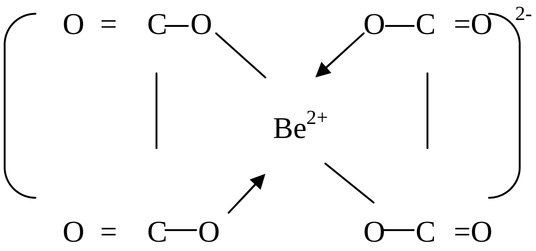
trigonal



tetrahedral

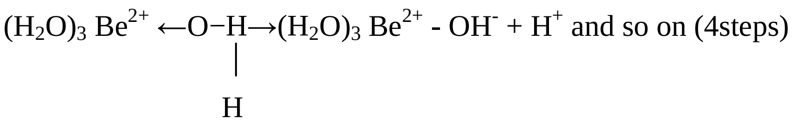


tetrahedral



Tetrahedral

In $[Be(H_2O)_4]^{2+}$ complex, Be^{2+} ion withdraws electronic charge from oxygen atoms of water towards itself and facilitates the removal of protons forming $[Be(OH)_4]^{2-}$ complex ion.



$$(H_2O)_3\, Be^{2+} \leftarrow \underset{\displaystyle H}{\underset{|}{O}}-H \rightarrow (H_2O)_3\, Be^{2+} - OH^- + H^+ \text{ and so on (4steps)}$$

Thus $[Be\ (H_2O)_4]^{2+}$ is an acid and $[Be(OH)_4]^{2-}$ is a base.

Be has been found to have a unique property of forming a series of stable and volatile molecular oxide-carboxylate complexes of general formula $[OBe_4(RCOO)_6]$ where R = H, Me, Et, Pr, Ph etc. These are white crystalline compounds readily soluble in organic solvents but are insoluble in water or lower alcohols.

Basic beryllium acetate, R = CH_3, is a common and typical example. They are best prepared by refluxing the oxide or hydroxide with the carboxylic acid. Mixed oxide carboxylates can be prepared by reacting a given compound with another organic acid or acid chloride. The structure of the acetate complex (**Fig. 8.1**) features a central oxygen atom surrounded tetrahedrally by four Be-atoms. The six edges of the tetrahedron so formed are bridged by the six acetate groups in such a way that each Be atom at the corner of tetrahedron is also coordinated tetrahedrally by four oxygen atoms.

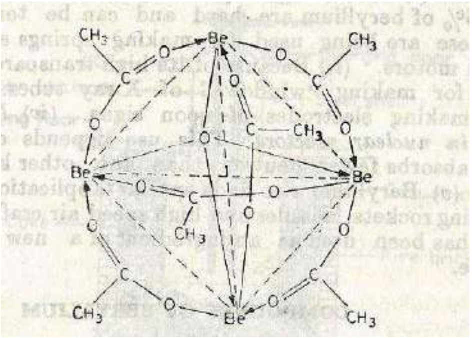


Fig. 8.1 Structure of basic beryllium acetate

Be also forms numerous chelating and bridge complxes with ligands such as the oxalate ion given earlier, alkoxides, β-diketonates and 1,3- diketonates.

The tendency to form complexes goes on decreasing when we move down the group which is attributed to increasing size of the metal ions. However, Mg^{2+} and Ca^{2+} form complexes with multidentate, ethylene diammine tetra acetate ion and Mg^{2+} alone with 8-hydroxy guinoline (oxine) etc. This property is used in quantitative analysis for the estimation of these metal ions.

8.7 Anomalous behaviour of beryllium

Beryllium, the first element of the alkaline earth metals, though shows various chemical similarities with other group members, yet also differs from them in many respects. This anomaly has been attributed to its small size, high charge density (charge/size) and high electronegativity as compared to other members of the group. The main points of difference are as follows:

(i) Beryllium is the hardest metal of all the elements of the group with the highest melting and boiling points.

(ii) It has the tendency to form covalent compounds with anions due to its high polarizing power and high electronegativity. At the same time its highest ionization energy among the group IIA elements does not allow it to form Be^{2+} ions easily to give the ionic compounds.

(iii) It does not react with water even at high temperatures. Other alkaline earth metals decompose water to liberate H_2 as given below:

$$M + H_2O \longrightarrow MO + H_2 \quad \text{(M = alkaline earth metals except Be)}$$

(iv) Beryllium has the lowest standard oxidation potential among all the group members and hence has the least electropositive character. This is evident from the nature of its oxide and hydroxide which are amphoteric, i.e. they dissolve both in acids and alkalies to form salts and beryllates respectively:

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

The corresponding compounds of other alkali earth metals are basic in nature, the basicity increasing down the group.

(v) BeO is covalent and has 4:4 types ZnS (wurtzite) structure but other elements give (MO type) oxides with 6:6 type NaCl structure and are ionic.

(vi) Beryllium does not react directly with hydrogen while other elements of the group IIA do so easily. Further, BeH_2 and MgH_2 are covalent but other elements give MH_2 compounds which are electrovalent.

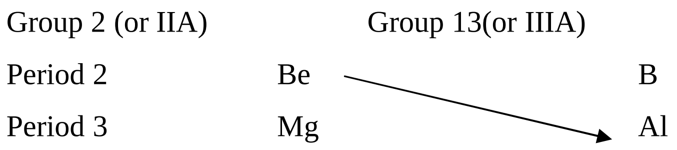
(vii) Beryllium on heating with carbon forms Be_2C type carbide which when treated with water evolves methane. The other members of the family form ionic carbides of the type MC_2 if the metals or their oxides are heated with carbon. These ionic carbides when treated with water evolve acetylene.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4\uparrow$$

$$CaC_2 + H_2O \longrightarrow CaO + C_2H_2\uparrow$$

8.6. ANOMALOUS BEHAVIOR OF BERYLLIUM (SIMILARITIES BETWEEN Be AND Al)

Be shows similarities in some of its properties with aluminum, the element of Group 13 (or IIIA) and period 3 situated diagonally opposite to it. This is called diagonal relationship.



The main points of similarities are given as follows:

(i) Both the elements (Be and Al) have strong tendency to form covalent compounds due to high polarizing power which is based on the small size and high charge density of the metal ions (charge/radius ratio: Be^{2+} = 6.45 and Al^{3+} = 6.0).

(ii) Both of them have the same value of electronegativity (1.5).

(iii)Both have almost similar values of standard oxidation potential:

Be = + 1.70 V, Al = + 1.67V

(iv)The oxides of both the elements are amphoteric in nature, i.e. dissolve in acids as well as alkalies.

$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$

$BeO + 2Na\,OH \longrightarrow Na_2BeO_2 + H_2O$

$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

(v) The Carbides of both Be and Al evolve methane (CH_4) on treatment with water.

$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4 \uparrow$

$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4 \uparrow$

(vi) Both the metals on reacting with dilute mineral acids or caustic alkalies liberate hydrogen gas.

$Be + 2HCl \longrightarrow BeCl_2 + H_2\uparrow$

$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2 \uparrow$

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$

$2Al + 2NaOH + 2H_2 \longrightarrow 2NaAlO_2 + 3H_2\uparrow$

(vii) Both Be and Al are rendered passive on treating with conc. HNO_3 due to the formation of protective oxide coating on the metal surface.

8.7. SUMMARY

In the text of this unit, a detailed description of the general characteristics such as their electronic configuration, hardness, density, atomic and ionic radii, ionization energies, reducing property and electropositive character, melting and boiling points, flame colouration, polarizing power, hydration property and solubility in ammonia along with the uses of alkaline earth metals and their salts has been given. A detailed account of the halides and hydride of beryllium has also been given in the light of their preparation, properties and structural details. The complexation behaviour of the alkaline earth metals in general and that of beryllium in particular has been discussed with example. The anomalous behaviour of beryllium and its diagonal relationship with aluminum, the element of the next higher group and period has also been taken care of.

8.8. Terminal questions.

i. Which one of the following is more basic ?

(a) $Be(OH)_2$

(b) $Mg(OH)_2$

(c) $Ba(OH)_2$

(d) $Ca(OH)_2$

ii. Which oxide of the following is amphoteric ?

(a) BaO

(b) SrO

(c) CaO

(d) BeO

iii. The metal used in nuclear reactors is

(a) Be

(b) Ca

(c) Ba

(d) Ra

iv. The alkaline earth metal having the lowest ionization energy value is

(a) Be

(b) Ca

(c) Ba

(d) Ra

v. The two alkaline earth metals imparting crimson red flame colouration are

(a) Be and Mg

(b) Mg and Ca

(c) Ca and Sr

(d) Sr and Ra

vi. Though the alkaline earth metals have two ionization energy values, yet in aqueous solution they exhibit only + 2 Oxidation state. Explain.

vii. why do Be and Mg not give any colour in the Bunsen flame?

viii. Why are these metals used as deoxidizers?

ix. Discuss briefly the bonding in BeH_2.

x. Discuss the structural aspects of basic beryllium acetate.

xi. How do Be and Al react with acids and alkalis?

xii. What factors are responsible for anomalous behaviour of Be in contrast other group members?

8.9 ANSWERS

i. (c)

ii. (d)

iii. (a)

iv. (c)

v. (d)

vi. Please see ionization energies and oxidation state.

vii. Please refer to flame colouration.

viii. Due to their high affinity for oxygen and air.

ix. Please refer to hydrides of Be.

x. Please see the complexation behavior of group IIA elements.

xi. Please see the diagonal relationship.

xii. Please refer to anomalous behaviour of Be.

UNIT 9: ELEMENTS OF GROUP -13

CONTENTS:

9.1 OBJECTIVES

The text of the study material of this unit, i.e. on the elements of Group 13 or group IIIA, has been prepared to throw light on the general characteristics and uses of the elements of boron family, to make the readers understand the interesting and important aspects of hydrides of boron particularly diborane and borazine in terms of their preparation and properties as well as their structure, the halides of boron and aluminium and oxides of boron and borates. The readers have to be well acquainted with anomalous behaviour of boron in contrast to other family members of this group.

9.2 INTRODUCTION

Group 13 (or group IIIA) of the long form of periodic table contains five elements, namely boron (B_5), aluminium (Al_{13}), gallium (Ga_{31}), indium (In_{49}) and thallium (Tl_{81}). This group is also known as boron group. All these elements are said to belong to the p-block of elements as the differentiating electron in the atoms of these elements enters the p-subshell of the outermost or the valence shell. The first element boron is semimetal while other members of this group are metals as is indicated by their properties, i.e. boron is closer to non-metals is its properties but the rest of the members show metallic properties.

Boron occurs rather sparsely, aluminium is the third most abundant element found in earth's crust, i.e. it is the most abundant element of these all, gallium, indium and thallium are not found in concentrated deposits and do not find much of commercial applications.

9.3 GENERAL CHARACTERISTICS

The inclusion of these elements in the same group of the periodic table is justified by the following general characteristics of these elements but these have been found to show a wider range of variations and also notable contrast in their properties.

(i) Electronic configuration:

These elements are characterized by three electrons in the valence shell, two of which are s-electrons and one a p-electron, i.e. the valence shell configuration of the atoms of these elements is ns^2np^1, n being the principal quantum number, the ultimate shell which varies from 2 for boron to 6 for thallium. Unlike the s-block elements, the electronic configuration of the penultimate shell of the atoms of these elements varies from inert gas to pseudo inert gas type. Boron has helium configuration (i.e.$1s^2$), aluminium has octet ($2s^2p^6$) and rest of the elements have $(n\text{-}1)s^2p^6d^{10}$ type configuration (i.e. n-1 = 3 for Ga, 4 for In and 5 for Tl) in the penultimate shell. This difference in the electronic configuration in the penultimate shell, though the valence shell has the same configuration, is responsible for the abrupt variation in the properties of these elements.

(ii) Density, melting and boiling points and heat of sublimation:

The density, in general, increases on moving down the group, however, Al has exceptionally low density. Melting point decreases considerably from B to Ga and then increases up to Tl but boiling point shows a regular decreasing trend down the group. Similar trend is observed in heats of sublimation also indicating that the atoms of the elements are held less and less closely as we move down the group. Very low melting point of Ga (30^0C) which is about ten times less than that of Tl and about seventy times less than that of B is explained on the basis that its structure contains Ga_2 molecules.

(iii) Ionization energy:

The first ionization energy of these elements corresponds to the removal of np^1 electron which is invariably held with nucleus less tightly and has low value. Its value decreases, as expected from B to Al because Al has larger size but then increases slightly in Ga. This is because from Al to Ga though atomic size increases but d-electron in the penultimate shell (with $s^2p^6d^{10}$ configuration) in Ga not able to shield the nuclear charge effectively and the valence electrons in this element are more firmly held to the nucleus thereby having slightly higher ionisation energy value. Thallium has unexpectedly higher ionisaton energy due to the inclusion of f-electrons as well as d-electrons in the inner shells and their low shielding effect.

These elements have been assigned three successive ionization energies (i.e. I_1, I_2 and I_3), the first belonging to the removal of p-electron and last two to the ejection of s-electrons one by one for each elements $I_3 > I_2 > I_1$. Boron has the highest values of all the three ionisation energies among these elements. Though the nuclear charge of these elements is larger and their size is smaller than those of Group 2 elements, yet their first ionisation energies are unexpectedly lower than those of the alkaline earth elements in the respective periods. This is due to the fact that the p-electrons are less penetrating and lie at larger distance from the nucleus than the s-electrons and hence can be removed more easily.

(iv) Oxidation state:

Boron gives mainly covalent compounds and has least tendency to from B^{3+} ion which is unstable because of very small size and very high ionization energy of its atoms but it may be arbitrarily assigned +3 oxidation state in its compounds with more electronegative elements. Aluminium has high charge density due to small size and high charge of Al^{3+} ion, hence its compounds, in general, are ionic in solution (having high hydration energy) and are covalent in gaseous phase. In solid state, its compounds have high lattice energy. In general sense it can be assigned + 3 oxidation state.

The higher elements exhibit both +1 and +3 oxidation states, +1 state becoming more and more stable down the group from Ga to Tl. Thus in Ga, +3 state has been found more stable than +1 state but in Tl, +1 state is more stable. This peculiar property of these elements is due to the **inert pair effect** which increases from Ga to Tl down the group. In the compounds of Ga, In and Tl with +1 oxidation state, the np^1 electron only takes part in combination and ns^2 electron pair remains inert due to its penetration in the inner shell and strong attractive force operating between nucleus and ns^2 electrons.

The relative stability of +1 and +3 oxidation states in the last three elements can be shown as follows:

$$Ga^{3+} > In^{3+} > Tl^{3+} \quad \text{and } Ga^{+} < In^{+} < Tl^{+}$$

(v) Electropositive character:

The electropositive or metallic character of these elements increases form B to Tl down the group. Boron is a semi-metal and all the other elements are distinctly metallic and good conductors of electricity having almost equal electropositive character as well as close ionisation energy values.

(vi) Tendency to form ionic or covalent compounds:

From the electronic configuration of these elements, all of them would be expected to form M^{3+} type ions and the compounds would be ionic. However, the second and third ionisation energies of boron are so high that it has little tendency to form B^{3+} ion and other elements have higher tendency to form such ions under suitable conditions due to lower ionisation energies. Thus these elements form ionic compounds.

Further if trivalent ions are formed, the smaller ions will have more polarising power and will tend to give covalent compounds. This tendency goes on decreasing down the group. That is why B gives covalent compounds, Al forms both covalent and ionic compounds and the higher members result mainly in ionic compound formation.

(vii) Oxidation potential:

With the exception of B, the standard oxidation potential values for the elements corresponding to the conversion; $M \longrightarrow [M (aq)]^{3+} + 3e^-$, are quite high because of large quantity of hydration energy associated with the $[M_{aq}]^{3+}$ ions in solution inspite of their large values of ionization energies. These high potential values for these elements may be attributed to the high charge and small radii of M^{3+} ions (i.e. high charge density).

(viii) Gradation in chemical properties:

Some chemical properties of these elements along with their gradation in the group are discussed below:

(a) Action of air and water:

Boron is almost unreactive at ordinary temperature but when heated it reacts with air (O_2). It does not react with water but is attacked by hot conc. acids, e.g. H_2SO_4.

Aluminium readily reacts with air even at ordinary temperature to form a protective layer of the oxide which protects it from further action of air. It decomposes cold water.

Galium and Indium do not react with water in absence of O_2. Thallium forms an oxide coating on the surface when treated with air.

(b) Nature of oxides and hydroxides:

All the elements form oxides and hydroxides. B_2O_3 and $B(OH)_3$ both are acidic. This is because hypothetical B^{3+} ion, being very small, has very high positive charge density. Hence when placed in water, it tends to pull off electrons from water molecule towards itself sufficiently strongly by rupturing the O-H bond in water molecule. This results in the rapid hydrolysis of hypothetical B^{3+} ion by H_2O releasing H^+ ions. $B(OH)_3$ dissolves in strong alkalies to form metaborates, e.g.

$$B(OH)_3 + NaOH \longrightarrow NaBO_2 + 2H_2O$$

The Trivalent Al^{3+} and Ga^{3+} ions, being relatively larger have smaller capacity to rupture the O-H bond in H_2O molecule by pulling off electrons. Consequently they are hydrolysed to a smaller extent than the hypothetical B^{3+} ion. Hence the oxides and hydroxides of Al and Ga are amphoteric. The In^{3+} and Tl^{3+} ions are very large and their interaction with water is very slow. The O-H bond in water is hardly affected by these ions. This makes the oxides and hydroxides of In and Tl distinctly basic. It can be concluded from above that on moving down the group of these elements, the oxides and hydroxides change from acidic through amphoteric to basic in character.

(c) Halides:

All the elements of this group react with halogens to form the trihalides. B-halides are covalent due to its small size and high charge density.

The fluorides of other elements of the group are ionic and have high melting points while the other halides are covalent when anhydrous. For example, anhydrous $AlCl_3$ is covalent but in water it is hydrolyzed to give Al^{3+}(aq) ions. This is due to the high hydration energy of Al^{3+} ions.

The normal trihalides are planar triangular in shape (sp^2 hybridization). One vacant unhybridised p-orbital is present in the central atom of these halides which can accommodate one electron pair from the donor molecules or ligands, thus acting as Lewis acids. Boron trihalides have strong tendency to form complexes of BX_3L type where L is a neutral molecule or anionic donor (i.e. ligand). These complexes are tetrahedral with three normal and one coordinate bonds.

Boron trihalides exist as discrete molecules while trihalides of other elements exist as dimers both in vapour state and in non-polar solvents making use of vacant p-orbital.

(d) Hydrides:

These elements do not react directly with hydrogen to form hydrides. Howener, hydrides of all these elements have been prepared by indirect methods. Boron forms a large number of covalent polymeric hydrides called boranes. Aluminium forms only one high molecular weight polymeric hydride, $(AlH_3)_n$ containing Al-atoms octahedrally surrounded by six H-atoms. Gallium gives only one volatile and unstable liquid hydride-gallane (Ga_2H_6). Indium forms polymerized solid hydride, $(InH_3)_n$ but Tl hydrides are unstable. These elements also form the complex anionic hydrides with alkali metal hydrides like $Li^+[BH_4]^-$, $Li^+[AlH_4]^-$ etc. where H^- ion acts as electron pair donor. These complex hydrides are used as reducing agents.

Uses of Group 13 elements:

Boron and aluminium are more commonly used elements.

(i) Boron is used as deoxidiser, in the casting of copper, for making boron steels which being very hard are employed as control rods in atomic reactors, in the manufacture of thermo regulators etc.

(ii) Its hydrides are used as fuels for rockets, borides and boron carbide are used as abrasives.

(iii) Boric acid is used in antiseptics and eye lotions etc.

(iv) Aluminium-alloys find extensive use in industry, Al itself for making utensils, frames, coils for motors and cable wire for electrical transmission, in the extraction of chromium and manganese.

(v) Aluminium-powder is used in making silvery white paints, in fireworks, flash light powders and thermite welding.

(vi) Ga, In and Tl elements do not find important applications but their salts are sometimes used for various purposes.

9.4 HYDRIDES OF BORON: DIBORANE AND BORAZINE

Boron forms a large number of polymeric hydrides called boranes, e.g. B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} etc. Diborane (B_2H_6) is an import member of this series.

9.4.1 Preparation of diborane (B_2H_6):

Diborane can be prepared by the following methods:

(i) By the action of ionic hydrides like NaH or CaH_2 on BCl_3

$$6NaH + 3BCl_3 \longrightarrow B_2H_6 + 6NaCl$$

$$3CaH_2 + 2BCl_3 \longrightarrow B_2H_6 + 3CaCl_2$$

(ii) By the reduction of BF_3 with Li H, Li (BH_4) or Na (BH_4)

$$8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$$

$$BF_3 + 3Na(BH_4) \longrightarrow 2B_2H_6 + 3Na\,F$$

(iii) By the reduction of BCl_3 with Li [AlH_4]

$$4BCl_3 + 3Li(AlH_4) \longrightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$$

(iv) By the reduction BCl_3 vapours with molecular hydroge.

$$2BCl_3 \text{ (vapours)} + 6H_2 \longrightarrow B_2H_6 + 6HCl$$

Properties:

It is an inflammable colourless gas, extremely toxic and reactive and stable only at low temperatures in absence of moisture.

(A) Decomposition:

(i) By heat:

When heated between 100^0C and 250^0C, it changes into a number of boranes:

$$2B_2H_6 \xrightarrow{100^0C} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow{100^0C} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow{105^0C} 2B_5H_{11} + 4H_2$$

$$5B_2H_6 \xrightarrow[120mm]{250^0C} B_5H_9 + B_5H_{11} + 5H_2$$

(ii) By water:

B_2H_6 is readily decomposed (hydrolysed) by water into boric acid and H_2.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2O$$

(iii) By aquous alkalies:

On passing B_2H_6 into an aq. solution of alkalies, e.g. KOH, at 0^0C, potassium hypoborate, $K_2[B_2H_6O_2]$, is obtained solution.

$$B_2 H_6 + 2KOH \xrightarrow{0^0C} K_2[B_2 H_6O_2] \text{ (pot. hypoborate)}$$

On diluting this solution, potassium metaborate is formed.

$$K_2[B_2H_6O_2] + 2H_2O \longrightarrow 2KBO_2 + 5H_2$$

Evolution of H_2 in alkaline medium makes it a useful reducing agent.

(B) Combustion:

B_2H_6 is an extremely reactive gas hence under controlled conditions, if reacted with O_2, gives large amount of energy at room temperature.

$$B_2H_6 + 3O_2 \xrightarrow{25^0C} B_2O_3 + 3H_2O + \text{Energy (Rocket fuel)}$$

(C) Action of halogens and halogen acids:

Under different conditions it reacts with halogens (except iodine) and halogen acids.

$$B_2H_6 + 6Cl_2 \xrightarrow[100^0C]{25^0C} 2BCl_3 + 6HCl \text{ (vigorous reaction)}$$

$$B_2H_6 + Br_2 \longrightarrow B_2H_5Br + HBr \text{ (slow reaction)}$$

$$B_2\,H_6 + HX \xrightarrow[\text{catalyst}]{\text{temp.}} B_2H_5\,X\ (X = Cl, Br, I) + H_2.$$

(D) Reaction with alkali metal hydrides:

Alkali hydrides suspended in ether react with diborane and give alkali metal borohydrides which are used as reducing agents.

$$B_2H_6 + 2LiH \longrightarrow 2Li[BH_4]$$

$$B_2H_6 + 2NaH \longrightarrow 2Na[BH_4]$$

(E) Reaction with ammonia:

Under different experimental conditions, diborane reacts with ammonia giving various products:

(i) At low temperature of about 120^0C, excess of ammonia gives an addition compound, diammoniate of diborane.

$$B_2 + H_6 + 2NH_3 \xrightarrow{\text{low tem.}} B_2H_6.2NH_3 \text{ (white non-volatile solid)}$$

(ii) At high temperature, it reacts with excess of ammonia forming boron ritride.

$$nB_2H_6 + 2nNH_3 \xrightarrow{\text{high temp.}} 2(BN)_n + 6nH_2$$

(iii) At high temperature, B_2H_6 and NH_3 in 1:2 ratio, react together to form borazine (or borazole), $B_3N_3H_6$.

$$3B_2H_6 + 6NH_3 \xrightarrow{\text{high temp.}} 2B_3N_3H_6 + 12H_2$$

Structure of diborane:

The electron diffraction and infra-red spectroscopic studies of B_2H_6 molecule have shown that this molecule has hydrogen bridge structure (**Fig. 9.1a**) in which two irregular BH_4 tetrahedra have one edge in common and thus two B atoms (B^1 and B^2) and four terminal H-atoms (H_t) are coplanar (lie in the same plane) while remaining two bridging H-atoms (H_b) are located at the centre above and below the plane, the two planes are perpendicular to each other.

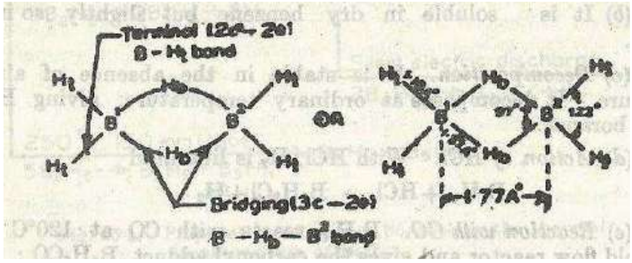


Fig 9.1a Bridged structure of diborane

From the figure it is clear that the B_2H_6 molecule possesses four B-H_t bonds, two bonds attached with each B atom with the bond distance = 1.19Å (2c-2e bonds), two bridging B^1-H_b-B^2 bonds with bond length of B^1 - H_b= 1.37Å. The B^1-B^2 distance is 1.77Å. The bond angles between H_t atoms and each B atom = 122^0 and that between H_b atoms and each B atom = 97^0, Both the B-H_b-B bonds are bridging bonds (3c-2e type).

The formation of the bridging (3c-2e) B^1-H_b-B and terminal (2c-2e) B-H_t bonds in this molecule may also be explained on the basis of hydrisation. According to this concept each B atom is sp^3 hybridization thereby giving four hybrid orbitals one of which is vacant and the other three are singly filled (B has $ns^2p^1 \longrightarrow ns^1px^1Py^1P_z^0$ configuration in the ground and excited states).

The formation of four terminal normal (2c-2e) covalent bonds, two each by both B atoms, occurs by the overlapping of two singly-filled sp^3 hybrid orbitals on each B atom with half-filled orbitals of four H_t atoms (two each with each B atom). Thus these are sp^3-s type bonds.

Each B atom is now left with one singly-filled and one vacant sp^3 hybrid orbitals which participate in the formation of the bridging bonds. One half-filled sp^3 hybrid orbital on B^1 atom and one vacant sp^3 hybrid orbital on B^2 atom then overlap jointly with half-filled 1s-orbital on one H_b atom to form a B^1-H_b-B^2 bridging bond. Another such bond is formed by overlapping of vacant sp^3 orbital on B^1atom, half-filled sp^3 hybrid orbital on B^2 atom and half-filled 1s-robital on another H_b atom. These two bonds are called 3 centre-2electon (3c-2e) bonds because 2 electrons hold 3 centres together (**Fig. 9.1b**)

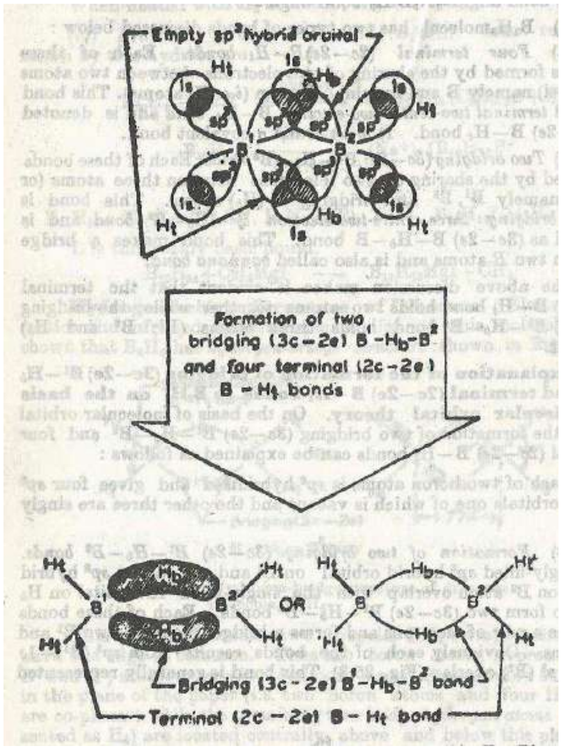


Fig. 9.1b Formation of 3c -2e bonds

9.4.2 Borazine or borazole ($B_3N_3H_6$):

This compound is also sometimes known as inorganic benzene and is isoelectronic with benzene.

Preparation:

(i) Heating a mixture of B_2H_6 and NH_3:

As has been given earlier in the properties of diborane, this compound is formed when diborane and ammonia are reacted at high temperature in 1:2 molar ratio.

$$3B_2H_6 + 6NH_3 \xrightarrow{\text{high temp.}} 2B_3N_3H_6 + 12H_2$$

Diammoriate of diborane formed at low temperature by mixing B_2H_6 and NH_3 may also be converted to borazine by heating at high temperature.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{low temp.}} B_2H_6.2NH_3$$

$$3(B_2 H_6.2NH_3 \xrightarrow{\text{high temp.}} 2B_3N_3H_6 + 12H_2$$

(ii) Reaction of Li [BH_4] on NH_4Cl:

This reaction is carried at high temperature.

$$3NH_4Cl + 3Li[BH_4] \longrightarrow B_3N_3H_6 + 3LiCl + 9H_2$$

(iii) Heating BCl_3 with NH_4Cl:

When BCl_3 is heated with NH_4Cl in chlorobenzene (C_6H_5Cl) in presence of a catalyst (e.g. Fe, Ni, Co etc) at 133^0C, trichloroborazine is obtained which on being reduced by $Li[BH_4]$ in polyether gives borazine (yield by this method is about 50-60%).

$$3BCl_3 + 3NH_4Cl \xrightarrow[\text{(Fe cata.)}]{\Delta,\ C_6H_5Cl} Cl_3B_3N_3H_3 + 9HCl$$

$$2Cl_3B_3N_3H_3 + 6Li[BH_4] \xrightarrow{\text{Redu.}} 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

Properties:

Borazine is a colourless and volatile liquid. Its important chemical properties are;

A. Hydrolysis:

(i) It is slowly hydrolysed by water to produce boric acid, H_3BO_3, ammonia and H_2 which is favoured by increasing temperature.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$$

(ii) It has also been reported that under certain conditions, borazine reacts with three molecules of water to produce tri-hydroxylbora-zine, $(OH)_3B_3N_3H_3$, in which OH groups are attached with B-atoms.

$$B_3N_3H_6 + 3H_2O \longrightarrow B_3N_3H_3(OH)_3 + 3H_2$$

B. Addition reactions:

(i) It has been found that one molecule of borazine adds three molecules of H_2O, CH_3OH, CH_3I, HCl or HBr in the cold without a catalyst. Since B-atom is less electronegative than nitrogen atom in B-N bond, more negative groups or atoms of these molecules are generally attached with boron. HCl derivative of this compound when heated at $50\text{-}100^0C$, loses H_2 molecules to gives B-trichloro borazine (Cl-atoms attached to B-atoms).

$$\overset{\Delta}{B_3N_3H_6 + 3HCl} \longrightarrow B_3N_3H_9Cl_3 \xrightarrow[-3H_2]{} B_3N_3H_3Cl_3$$

(ii) One molecule of borazine also adds three molecules of Br_2 at 0^0C giving B-tribromo-N-tribromoborazine which on heating at 60^0C, loses three molecules of HBr to form B-tribrimoborazine.

$$B_3N_3H_6 \xrightarrow{+3Br_2} B_3N_3H_6Br_6 \xrightarrow{60^0C} B_3N_3H_3Br_3 + 3HBr$$

0^0C

C. Hydrogenation:

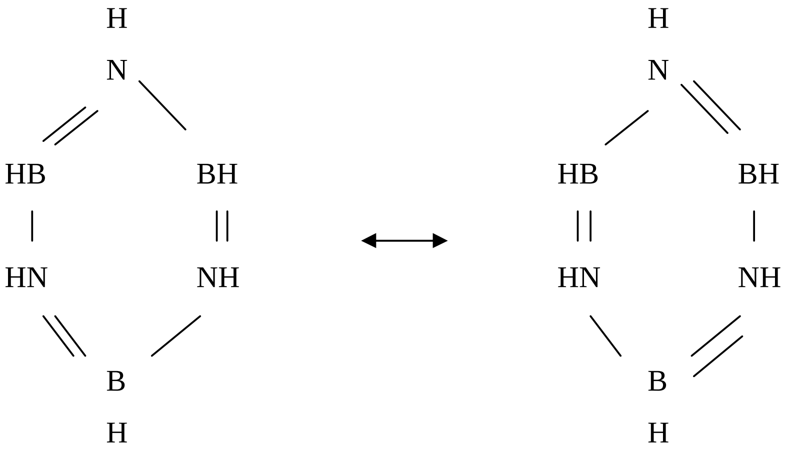
Borazine can be converted to cyclotriborazine, $B_3N_3H_{12}$ as shown below:

$$B_3N_3H_6 \xrightarrow{+3HCl} B_3N_3H_9Cl_3 \xrightarrow{+3NaBH_4} B_3N_3H_{12} + 3/_2B_2H_6 + 3NaCl$$

Cyclotriborazine

Structure:

Electron diffraction studies and various chemical reactions of this compound have shown that this is isoelectronic with benzene and its structure is similar to that of benzene. It has a planar hexagonal structure containing six-membered ring with alternate B and N atoms, i.e.-BH-and -NH groups.



Each of B-N bond distances is 1.44Å which is approximate average of single B-N (1.54Å) and double B-N (1.36Å) bond distances. All the angles are equal to 120^0. Like benzene, this compound is also said to have aromatic π electron cloud which is delocalized over the atoms of the ring. The B-N bonds are polar with π-cloud localized more on N- atoms. This weakens the π-bonding in the ring and hence polar species like HCl can attack this double bond between B and N and the molecule can undergo addition reactions readily.

All the B and N atoms in the ring presumably use sp^2 hybrid orbitals to form three B-N σ bonds and B-N π- bonds arise from the sideways overlapping of the unhybridised p-orbitals of B and N atoms which are at right angles to the plane of the ring and π-electrons are not derived from all the six atoms of the ring but from the three N-atoms only.

9.5 HALIDES OF BORON AND ALUMINIUM

9.5.1 Boron trihalides, BX_3 (X = F, Cl, Br, I)

Boron reacts with halogens and forms all the trihalides, BX_3 where X = F, Cl, Br, I.

Preparation of BX_3 (halides):

All the trihalides of boron, with the exception of trifluoride, can be prepared by the treatment of a mixture of B_2O_3 and carbon with the appropriate halogen at higher temperatures.

$$B_2O_2 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO \text{ (X = Cl, Br, I)}$$

The trifluoride has been prepared by the treatment of H_2SO_4 on the mixture of calcium fluoride and boron oxide.

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O + 2BF_3$$

Or by the action of HF on B_2O_3.

$$B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O$$

Properties:

BF_3 and BCl_3 are gases, BBr_3 is a liquid and BI_3 is a solid at room temperature.

(i) Covalent character:

All the boron trihalides are covalent in character due to the small size and high charge density of B^{3+} ion. As liquids they do not conduct electricity. i.e. are non-electrolytes. They exist as discrete molecular species and have very low boiling points.

(ii) Geometry and formation of complex halides:

They all have planar triangular geometry resulting from sp^2 hybridisation of B-atoms. One p-orbital in B-atom remains unhybridised which can accept a lone pair of electrons. Hence the trifluorides are strong electron acceptors or Lewis acids and are capable of complex ion formation, e.g. $[BF_4]^-$ with coordination number 4 but not beyond 4 due to non-availability of d-orbitals in its valence shell. $BF_3 + F^- \longrightarrow [F_3B \leftarrow F^-]$

(iii) Addition compounds-electron-acceptor property:

Due to the availability of vacant p-orbital on B-atoms, all the trihalides act as electron-acceptors because they are electron-deficient (two electrons short of an octet). They can accept an electron pair from the donor atoms of the molecules having lone pair (s) of electrons like N in NH_3, O in H_2O, P in PH_3 etc. to form adducts or addition compounds in the way as they form complex halides (given above)

$$BF_3 + :NH_3 \longrightarrow BF_3.NH_3 \quad = \quad [F_3B \leftarrow NH_3]$$

$$BF_3 + :OH_2 \longrightarrow BF_3.OH_2 \quad = \quad [F_3B \leftarrow OH_2]$$

This property of BF_3 makes it an extremely useful catalyst in organic chemistry.

Though BX_3 molecules have plane triangular geometry, the addition compounds attain tetrahedral shape, the central atom using all its orbitals in the valence shell, three half-filled and one vacant and undergoing sp^3 hybridisation.

The order of electron-acceptor ability of boron trihalides is $BF_3 < BCl_3 < BBr_3 < BI_3$ due to pπ-pπ back bonding in the molecules which decreases in the order: $BF_3 > BCl_3 > BBr_3 > BI_3$ with increasing atomic size of halogen atoms.

(iv) Hydrolysis:

B-trihalides are easily hydrolysed to form boric acid.

$$BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX \quad (X = Cl, Br, I)$$

BF_3, however, gives fluoroboric acid which is resulted by the combination of H^+ion and BF_4^- ions.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

$$[HF \longrightarrow H^+ + F^-] \times 3$$

$$[BF_3 + F^- \longrightarrow BF_4^-] \times 3$$

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3H^+ + 3BF_4^-$$

Or $$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HBF_4$$

BCl_3, BBr_3 and BI_3 are more readily hydrolysed by H_2O than BF_3 showing that they are stronger Lewis acids than BF_3 itself.

9.5.2 Aluminium halides:

Aluminium forms all the halides. AlF_3 is ionic while other halides are covalent when anhydrous. $AlCl_3$ is the most important of all the halides which will be discussed here.

Preparation of $AlCl_3$:

(i) When aluminum metal or its hydroxide is treated with HCl, solution of hydrated aluminum chloride is obtained.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

On evaporating the solution, crystals of $AlCl_3.6H_2O$ are obtained.

(ii) Anhydrous $AlCl_3$ is prepared as follows:

(a) By passing dry chlorine or HCl gas over heated Al-powder.

$AlCl_3$ vapours are condensed to get $AlCl_3$.

$$2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$$

$$2Al + 6HCl \xrightarrow{\Delta} 2AlCl_3 + 3H_2\uparrow$$

(b) By heating a mixture of alumina and coke in a current of chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3 + 3CO\uparrow$$

(c) By heating alumina in a current of S_2Cl_2 vapour and Cl_2.

This method is used for its **commercial preparation**

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 \xrightarrow{\Delta} 8AlCl_3 + 6SO_2$$

(d) $AlCl_3$ can also be obtained by heating alumina in a current of carbonyl chloride ($COCl_2$)

$$Al_2O_3 + 3COCl_2 \xrightarrow{\Delta} 2AlCl_3 + 3CO_2\uparrow$$

Propertius of Aluminium chloride:

Anhydrous salt is a white crystalline solid, is hygroscopic and fumes in moist air, it sublimes at ~ 180^0C below its melting point (193^0C at 2atm. pressure). It is a typical covalent compound soluble in organic solvents like C_6H_6, CS_2 etc. and shows poor conductivity in the fused state.

(i) **Hydrolysis:**

It undergoes hydrolysis in water to give an acidic solution due to the liberation of HCl.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

Similar reaction occurs in moist air to give fumes of HCl.

(iii) Its solution gives white precipitate of Al (OH)$_3$ with NH$_4$ OH.

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{ppt}{Al(OH)_3\downarrow} + 3NH_4Cl$$

(iii) With excess of NaOH, the salt solution gives soluble meta aluminate, NaAlO$_2$.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl$$

ppt

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

(iv) It forms adducts or addition compounds with a number of donor molecules like NH$_3$, PH$_3$, COCl$_2$ etc.

$$AlCl_3 + 6NH_3 \longrightarrow AlCl_3.6NH_3 \text{ (hexa ammoniate of Al Cl}_3\text{)}$$

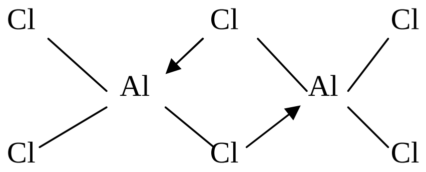
Uses:

It is used in organic chemistry as a catalyst in friedel-Crafts reaction and manufacture of dyes, drugs and perfumes.

Structure

In solution and at very high temperature of 750 – 800^{0}C, it has mono meric formula, AlCl$_3$ but at 350 - 400^{0}C, its vapour density corresponds to the dimeric formula, Al$_2$Cl$_6$. In the dimer, the halogen atoms are tetrahedrally arranged around the Al-atoms.

The dimeric formula is retained when it is dissolved in non-polar solvents like benzene.



Dimeric AlCl$_3$

9.6 OXIDE OF BORON AND BORATES

9.6.1 Oxide of boron (B$_2$ O$_3$):

Preparation:

When boron is heated in presence of oxygen, B_2O_3 is formed

$$4B + 3O_2 \xrightarrow{700^0C} 2B_2O_3$$

Properties of B_2O_3:

B_2O_3 is a solid of high melting point.

(i) Acidic character:

Its acidic character is revealed by the fact that it reacts with strong alkalies or fused metal oxides to give metaborates.

$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$

$$B_2O_3 + MO \longrightarrow M(BO_2)_2 \qquad \text{(MO = metal oxide)}$$

(ii) Feeble basic character:

It is also very weakly basic in nature since it also reacts with HF. This method is sometimes used to prepare BF_3.

$$B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O$$

It also reacts with HCl forming BCl_3.

$$B_2O_3 + 6HCl \longrightarrow 2BCl_3 + 3H_2O$$

(iii) Hydrolysis:

When treated with water, it undergoes hydrolysis to produce boric acid.

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

(iv) Reduction:

It is reduced by Mg or alkali metals to the free state.

$$B_2O_3 + 3Mg \longrightarrow 3MgO + 2B$$

$$B_2O_3 + 6K \longrightarrow 2B + 3K_2O$$

(v) Formation of carbide:

On heating with carbon in an electric furnace, it gives boron carbide.

$$2B_2O_3 + 7C \xrightarrow{\Delta} B_4C + 6CO$$

(vi) Reaction with Cl_2:

When B_2O_3 is heated with carbon in a current of dry Cl_2, BCl_3 is formed.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

9.6.2 Borates:

Borates are the salts of weak boric acids, *viz*. orthoboric acid (H_3BO_3), metaboric acid (HBO_2), pyroboric acid ($H_6B_4O_9$) and tetraboric acid ($H_2B_4O_7$) and are named on the basis of the name of the acid, e.g. orthoborates, metaborates, tetraborates etc.

The most important borate, known as sodium tetraborate or **Borax,** is being discussed here.

Borax or sodium tetraborate ($Na_2B_4O_7$):

This compound is the sodium salt of tetraboric acid.

Preparation:

It occurs naturally as well as can be prepared artificially.

It can be prepared by the action of sodium carbonate or alkalies on boric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

$$4H_3BO_3 + 2NaOH \longrightarrow Na_2B_4O_7 + 7H_2O$$

Properties:

Borax exists in three forms: (a) ordinary or prismatic borax which is decahydrate, $Na_2B_4O_7.10H_2O$. It is obtained when a solution of the salt is crystallized at room temperature,. (b) Octahedral or Jeweller's borax which is pentahydrate, $Na_2B_4O_7.5H_2O$ and is obtained when the solution is crystallized above 60^0C. (c) Borax glass is the anhydrous from $Na_2B_4O_7$ and is obtained by heating the ordinary borax above its melting point until all of lattice water is given off.

(i) Basic nature:

Though this compound is sparingly soluble in cold water, yet is fairly soluble in hot water and the solution is alkaline because borax is hydrolyzed to give NaOH and H_3BO_3.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 4H_3BO_3 + 2NaOH$$

(ii) **Action of heat:**

On heating above its melting point, it loses its lattice water and swells up to a white porous mass. On further heating, it melts to a liquid which then solidifies to a transparent glassy mass consisting of $NaBO_2$ and B_2O_3.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

(iii) Action of Acids:

Being basic in nature it reacts with conc. acids to form boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

(iv) Action of NH_4Cl:

When heated with NH_4Cl, it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2BN + 2NaCl + B_2O_3 + 4H_2O$$

Uses:

Borax is used

(i) In borax bead test for the detection of basic radicals.

(ii) In the manufacture of enamels and glazes for pottery.

(iii) In making borosilicate glassware.

(iv) As a preservative for food.

9.7 ANOMALOUS BEHAVIOUR OF BORON

Boron, the first element of Group 13 (or IIIA), though shows similarity in some of its properties with other members of the group, yet there are dissimilarities also among them. These dissimilarities in the properties of boron from other member of its group are attributed to (i) its small size, (ii) high charge density, (iii) high electronegativity and (iv) non-availability of the d-orbitals in the ultimate shell of boron. The main points of difference among these elements are:

(i) All the compounds of boron are covalent while other elements give covalent as well as electrovalent compounds.

(ii) Maximum covalency of boron is 4 while other elements may have covalency higher than this. i.e. 6 or more due to the availability of vacant d-orbitals in their ultimate shell.

(iii) Electron accepting power, i.e. Lewis acid character of boron compounds is higher than those of other elements.

(iv) It does not exhibit inert pair effect at all while the elements beyond Ga show this property.

Both boron and aluninium are closer in some of their properties but the higher members have distinctly different behaviour.

Diagonal Relationship between B and Si

Boron resembles silicon, the element of higher group and higher period in many of its properties to which it is diagonally related. These are:

(i) Both the elements can be prepared by reducing their oxides with Mg metal.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

(ii) Both the elements are not attacked by water but dissolve in alkalies (in fused state) forming metaborate and metasilicate liberating H_2.

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2\uparrow$$

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2\uparrow$$

(iii) Both the elements do not occur in free state, are typical non-metals hence bad conductors of heat and electricity and exist in two allotropic forms, *viz*. amorphous and crystalline.

(iv) Both of them have almost the same density, ionization potential electronegativity and boiling point but differ in their melting points.

(v) Both the elements are inert at ordinary temperature but reactivity increases with rise in temperature and both form mainly covalent compounds like hydrides, halides, oxides etc. The oxides have macromolecular structure.

(vi) Both the metals combine with metals like Mg forming borides and silicides respectively

$$2B + 3Mg \longrightarrow Mg_3B_2 \text{ (boride)}$$

$$Si + 2Mg \longrightarrow Mg_2Si \text{ (Silicide)}$$

These products when treated with HCl give hydrides.

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6 + \text{higher boranes}$$

$$Mg_2\,Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4 + \text{higher silanes}$$

9.8. SUMMARY

The text of this unit comprises of the general characteristics of the elements of Group 13 (or IIIA). i.e. boron group and their gradation such as their electronic configuration, ionisation energy, oxidation state, electropositive character, oxidation potential and action of various reagents and nature of compounds. Hydrides of boron specifically diborane and borazine have been discussed in detail in terms of their preparation, properties and structure. The halides of boron and aluminium, the oxides of boron, borates and anomalous behaviour of B in the group and its diagonal relationship with silicon, the element of next higher period and higher group have been taken in detail.

9.9. TERMINAL QUESTIONS

i. Which element has the highest ionisation energy?

(a) Boron

(b) Aluminium

(c) Galium

(d) Thaleum

ii. In Tl, the last element, + 1 oxidation state is

(a) Less stable than + 3 state

(b) More stable than + 3 state

(c) Equally stable to + 3 state

(d) None of the above.

iii. The electron-acceptor capacity of boron trihalides is

(a) $BF_3 < BCl_3 < BBr_3 < BI_3$

(b) $BF_3 < BCl_3 > BBr_3 < BI_3$

(c) $BF_3 > BCl_3 > BBr_3 > BI_3$

(d) $BF_3 > BCl_3 > BBr_3 < BI_3$

iv. Boron shows diagonal relationship with

(a) Aluminium

(b) Beryllium

(c) Silicon

(d) Lithium

v. Discuss the structure of boron trihalides

vi. What happens when boron is heated?

9.10 . ANSWERS

i. (a)

ii. (b)

iii. (a)

iv. (c)

v. & vi. For their answers please refer to the text.

UNIT 10: ELEMENTS OF GROUP -14

CONTENTS:

10.1. OBJECTIVE

The objective of writing the course material of this unit, i.e. on the elements of Group 14 or group IVA of the periodic table, is to make the readers to understand their various aspects such as their general characteristics and uses, the oxides of carbon and silicon, halides of carbon, organo-silicon compounds-an important class of useful compounds and anomalous behaviour of carbon in contrast to that of other members of carbon family.

10.2. INTRODUCTION

Group 14 (or Group IVA) of the long form of periodic table containe five elements, *viz.* carbon (C_6), silicon (Si_{14}), germanium (Ge_{32}), tin (Sn_{50}) and lead (Pb_{32}). This group is also known as carbon group. All these elements belong to p-block of elements as the last electron in the atoms of these elements enters the p-subshell of the valence or ultimate shell. The first element carbon is distinctly non-metal, Si is non-metal with the characteristics of a semi-metal, Ge is a semimetal. The last two elements, Sn and Pb, are distinctly metals. Carbon occurs upto 0.1% in the earth's crust. However, combined with oxygen and hydrogen it occurs in all living tissues of plant or animal kingdom and also in petroleum and coal deposits. Silicon is the most abundant element, next to oxygen, in earth's crust (~28%) present as silica and silicates.

10.3. GENERAL CHARACTERISTICS

These elements have been included in the same group of the periodic table and this is justified by the following general characteristics of these elements. There occurs an appreciable extent of variation also in their properties.

(i) Electronic configuration:

The atoms of these elements have four electrons in their valence or ultimate shell, two of which are in s-orbital while the remaining two are in p-orbitals with ns^2np^2 type configuration, n being the principal quantum number (the valence shell). Like the elements of Group 13, atoms of these elements also have different arrangements of electrons in the penultimate shells, i.e. varying from inert gas to pseudo-inert gas configuration. Thus carbon has helium configuration (i.e. $1s^2$), silicon has an octet (i.e. $2s^2p^6$) and rest of the elements from Ge to Pb have (n-1) $s^2p^6d^{10}$ type arrangement of electrons in their respective penultimate shells. This difference in the configuration in the last but one shell, though the valence shells have the same configuration, is responsible for the variation in the properties of these elements. Thus carbon differs from Si and these two (i.e. C & Si) from other members of the group.

(ii) Occurrence:

Only Carbon occurs in the free state as diamond, graphite and coal. In the combined state it occurs as hydrocarbons, carbohydrates and carbon dioxide (in the atmosphere). Silicon is a major constituent of rocks. Germanium is a rare element. Tin is found as tin stone, SnO_2 while lead is present in nature as galena (PbS).

(iii) Density, atomic and ionic radii, atomic volume:

The density, atomic radii and atomic volumes of these elements show a regular increasing trend as usual. The ionic radii (of the ions with similar charge) also show the same trend as other physical properties given above.

(iv) Melting and boiling points

These properties generally decrease down the group though the trend is not regular. These values for C and Si are high because of their tendencies to form giant molecules.

(v) Metallic and non-matallic character:

The best illustration of the change from non-metallic to metallic character with increasing atomic number is provided by this group. The first two elements are non-metals, though Si shows some properties of metalloids, Ge is a semi-metal and the last two elements are metals.

(vi) Ionisation energy and electronegativity:

As expected, the ionisation energy values decrease down the group from C to Pb, though in an irregular manner. This is due to the presence of d-orbitals in case of Ge and Sn and f-orbitals in Pb in the penultimate shell which are not able to screen the valence electrons effectively in these elements.

The electronegativity also shows the same trend but the change is abrupt in the first two elements and then only a slight change is observed among other elements.

(vii) Valency and oxidation state:

All the elements show a covalency of 4 and are tetra covalent involving sp^3 hybridisation. Due to high ionisation energy values, the existence of simple M^{4+} ions is unlikely. Their low electronegatity also makes them unavailable for the formation of M^{4-} ions. The elements, C and Si, being non-metals do not have the tendency to form electrovalent compounds but Ge, Sn and Pb, the higher congeners of these elements, exhibit tetra and bi-electrovalency forming both M^{2+} and M^{4+} ions. Thus the oxidation state of +2 and + 4 is shown by them in their compounds. The stability of tetravalent ions (+4 oxidation state) goes on decreasing from Ge to Pb. i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$ and that of +2 oxidation state (bivalent ions) increases down the group, i.e. $Ge^{2+} < Sn^{2+} <$ Pb2+. This behaviour of the ions of Ge, Sn and Pb is attributed to the inert pair effect which is more prevalent in the heavier p-block elements, i.e. maximum for Pb in this group. That is why Sn (II) salts are used as reducing agents while Pb (IV) salts are strong oxidising agents, i.e. $Sn^{2+} < Sn^{4+}$and $Pb^{2+} > Pb^{4+}$.

The nature of the compounds of M^{2+} and M^{4+} cations can be predicted by Fajan’s rules, according to which the smaller cations cause more polarization of anions and make the compounds more covalent in nature. For example, Sn^{4+} ion is smaller than Sn^{2+} ion, hence Sn (IV) compounds are covalent while Sn (II) compounds are ionic in nature, similarly Pb (IV) compounds are covalent and those of Pb (II) are ionic.

(viii) Catenation or Self-linkage:

This depends on the tendency of the elements to form homo-chains. The atoms of all the elements of this group have this tendency of linking with themselves to form long chains called homo-chains. This property of the elements is known as catenation or self-linkage which decreases down the group from C to Pb. Thus carbon has maximum property of catenation while tin and lead hardly show this tendency, i.e. C > Si > Ge > Sn > Pb. This is because of decreasing M-M bond energy values for these elements (C= 348 $kJmol^{-1}$, Pb = 155 $kJmol^{-1}$). The result is that it is easy to prepare compounds centaining C-C chains up to twenty or even more carbon atoms while for Si and Ge, it is not possible to extend Si-Si or Ge-Ge chains beyond six units. For Sn and Pb, the Sn-Sn or Pb-Pb chain can not be extended beyond two units.

(ix) Allotropy:

All the elements, except Pb, of this group show allotropy, i.e. exist in different forms, e.g. carbon exists in the two forms: crystalline-diamond and graphite, and amorphous- coal, coke, charcoal etc. Silicon and Ge also exist in two forms: crystalline and amorphous. Tin has three allotropic forms: white tin, grey tin and rhombic tin.

(x) Formation of oxides:

These elements form three types of oxides, *viz.* mon-oxides (MO type), dioxides (MO_2 type) and other oxides such as C_3O_2, Pb_3O_4, Pb_2O_3 etc.

(xi) Formation of hydrides:

All the dements of this group form hydrides which are covalent in nature though the number of stable hydrides and the ease with which these are formed decreases as we move from C to Pb. The MH_4 type hydrides (monomers) are in the gaseous state. The thermal stability of these hydrides decreases steadily from CH_4 to PbH_4, as is evident from their decomposition temperature: $CH_4 = 800^0C$, $SiH_4 = 450^0C$, $GeH_4 = 285^0C$, $SnH_4 = 150^0C$ and $PbH_4 = 0^0C$ and decreasing M-H bond energy. This infers that the hydrides of higher elements are thermally unstable.

(xii) Formation of halides and halo complexes:

All the members of this group form halides either of simple type, MX_4 (e.g. CCl_4, $SiCl_4$ etc.) or MX_2 (e.g. $SiCl_2$, SiI_2 etc.) or those in which H-atoms are also present, MH_3X (e.g. CH_3Cl), MHX_3 (e.g. $CHCl_3$, $SiHF_3$ etc.) or catenated type halides (e.g. $Si_{10}Cl_{22}$).

The tetra halides of these elements can be prepared by a common method which employs the heating of element with appropriate halogen. These trahalides are having decreasing thermal stability down the group, i.e. CX_4 is most stable and PbX_4 is least stable. The tetra halides, MX_4 of Si, Ge, Sn and Pb when reacted with X^- ions, form the hexahalo complex ions, e.g.

$$SiF_4 + 2F^- \longrightarrow [Si\ F_6]^{2-}$$

Other examples are: $[GeX_6]^{2-}$, X = F, Cl; $[Sn\ X_6]^{2-}$, X = F, Cl, Br, I and $[Pb\ Cl_6]^{2-}$

(xiii) Acid formation:

All the elements give acids of H_2MO_3 type whose sodium salts are stable. The elements, Carbon and Silicon also form acids of $(MOH)_2$ type, e.g. $(COOH)_2$: oxalic acid, $(SiOOH)_2$: silico oxalic acid.

Uses of group 14 elements:

(a) Carbon is an essential element of the plant and animal kingdom. All fuels also contain carbon. SiC is an important compound of C used as an abrasive and B_4C is the hardest artificially made abrasive used for cutting diamonds.

(b) Si and Ge containing an impurity of Group 13 or Group 15 elements are used as the semi conductors. Silica (SiO_2) is an assential material for glass industry. Silicones are important polymers.

(c) Sn is used in the preparation of a number of useful alloys, in tin plating of iron sheets and tin amalgam for making mirrors.

(d) Pb is used for making cable covering, protective sheets for roofs and drains, water pipes and lining of the chambers in sulphuric acid manufacture and many important compounds, alloys etc.

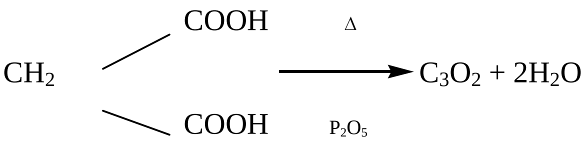
10.4 OXIDES OF CARBON AND SILICON

10.4.1 Oxides of carbon:

Three oxides of carbon are known, e.g. carbon monoxides (CO), carbon dioxide (CO_2) and carbon suboxide (C_3O_2).

(a) **Carbon Suboxide (C_3O_2):**

This oxide of carbon is formed by heating malonic acid with phosphorous pentoxide.



$$CH_2(COOH)_2 \xrightarrow[P_2O_5]{\Delta} C_3O_2 + 2H_2O$$

Thus, this oxide is the anhydride of malonic acid and exists as a gas. It is stable at room temperature and polymerises on warming. It explodes when sparked with oxygen.

This oxides has linear structure, i.e. O = C = C = C = O with each carbon atom undergoing sp hybridesation and each C = O and C = C double bond involving one σ and one π bond due to axial and lateral overlapping of orbitals of carbon and oxygen atoms.

(b) **Carbon monoxide (CO):**

Preparation:

(i) This oxide is obtained when formic acid or oxalic acid is dehydrated using H_2SO_4.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

$$(COOH)_2 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$$

(CO_2 is removed by NaOH or KOH solution)

(iii) Reduction of carbon dioxide or heavy metal oxides with carbon, gives CO.

$$CO_2 + C \xrightleftharpoons{\Delta} 2CO$$ (impurity of CO_2 is removed by caustic soda solution)

$$ZnO + C \xrightarrow{\Delta} Zn + CO$$

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

(iv) The action of steam on red hot coke also gives CO.

$$\text{C (hot)} + H_2O \text{ (vapours)} \longrightarrow CO + H_2 \text{ (water gas)}$$

CO is separated by liquefaction. The mixture is used as water gas. This method is used for large scale production of CO and H_2.

Properties:

It is only slightly soluble in water. It is highly poisonous, to such an extent that one part of the gas in 500 parts of air produces unconsciousness in about an hour and one part in 100parts causes death in a few minutes. It liquefies at (-)191.5^{0}C and solidifies at (-)200^{0}C.

(i) It is an unsaturated compound and hence forms addition products with H_2, O_2, Cl_2, S etc. to give various useful products under specific conditions.

$$CO + 2H_2 \xrightarrow{ZnO\text{-}Cr_2O_3} CH_3OH \text{ (methanol)}$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$CO + Cl_2 \xrightarrow{1:1 \text{ volume}} COCl_2 \text{ (phosgene)}$$

$$CO + S \text{ (vap)} \xrightarrow{\Delta} COS \text{ (carbonyl sulphide)}$$

(ii) CO is absorbed in NaOH solution under pressure to give sodium formate.

$$CO + Na\,OH \longrightarrow HCOONa \text{ (sod. formate)}$$

(iii) It combines with many metals such as Fe, Co, Ni, Cr etc. to form carbonyls, e.g.

$$Ni + 4\,CO \xrightarrow{50^0C} Ni(CO)_4$$

(iv) It is a good reducing agent and is used in metallurgical processes to reduce metal oxides to free metals.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

Uses:

(a) It is used as an essential constituent of fuel gases like water gas, producer gas etc. because on burning in air it forms CO_2 and evolves a large amount of heat.

(b) It is used in the manufacture of methanol by its reaction with hydrogen at300^{0}C and 300 atm. pressure in presence of a catalyst ($ZnO + Cr_2O_3$).

$$CO + H_2 \xrightarrow{300^0C} CH_3OH$$

300 atm.

(c) It is used in the reduction of metallic oxides in metallurgy.

(d) It is used in Mond's process for the refining of nickel.

Structure:

The carbon atom involves sp hybridization, one hybrid orbital containing a single electron which forms σ bond with O-atom and another hybrid orbital having an electron pair remains unbonded. There is one normal π-bond formed between C and O-atoms. The empty orbital of C-atom overlaps with a paired orbital O-atom forming a dative type π bond (O→C). Thus a triple bond exists in the molecule. The structure is : C ≡ O:

(c) **Carbon dioxide (CO_2):**

It occurs free in atmosphere up to 0.03 – 0.05 % and in minerals as carbonates like dolomite, limestone, etc.

Preparation:

Carbon dioxide may be prepared by the complete combustion of coke or by the action of heat or dilute acids on carbonates and bicarbonates.

$$C + O_2 \longrightarrow CO_2$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

Laboratory preparation:

In the laboratory, CO_2 gas is prepared by the action of cold and dilute HCl on marble ($CaCO_3$).

$$Ca\,CO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

Manufacture of CO_2:

(i) From combustion gases:

Large amount of it is produced during the combustion of coal or coke along with N_2, CO, O_2, other gases and vapours. This mixture on passing through a tower (packed with coke) upwards which is being sprayed with a solution of potassium carbonate downwards, CO_2 gets absorbed in solution.

$$K_2CO_3 + CO_2 + H_2O \longrightarrow 2KHCO_3$$

The solution is boiled when CO_2 is liberated

$$2KH\,CO_3 \xrightarrow{\Delta} K_2CO_3 + H_2O + CO_2$$

The solution containing K_2CO_3 can be used again for absorbing more CO_2.

(iii) **From Lime-Kilns:**

CO_2 is also obtained as a by-product in the calcination of lime stone in the manufacture of lime (CaO).

$$Ca\,CO_3 \longrightarrow CaO + CO_2$$

The gas can be purified by absorbing in a solution of potassium carbonate as above.

(iv) **From fermentation industries:**

Large amount of this gas is also obtained as a by-product during the fermentation of starch or sugar in the manufacture of alcohol.

Properties:

This gas is only slightly soluble in water under ordinary pressure but at high pressure the solubility increases appreciably. It can be liquefied by cooling at 20^0C and 56 atmospheric pressure.

(i) Acidic Character:

CO_2whendissolves in water gives carbonic acid which forms salts with alkalies.

$$CO_2 + H_2O \rightleftharpoons H_2\,CO_3$$

$$H_2CO_3 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

With excess of CO_2, the carbonate is converted to bicarbonate.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

(ii) **Action on lime water:**

It gives a white precipitate of insoluble $CaCO_3$ hence turns lime water milky. On passing more quantity of the gas, the white ppt. dissolves.

$$Ca\,(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca\,CO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Cal. bicarbonate}}{Ca\,(HCO_3)_2} \text{ (soluble)}$$

(iii) **Decomposition:**

CO_2 is neither combustible nor a supporter of combustion and thus a burning splinter gets extinguished when introduced into the gas. But burning Mg, Na or K continues to burn in the gas decomposing the gas into carbon.

$$CO_2 + 2Mg \longrightarrow 2MgO + C$$

$$CO_2 + 4Na \longrightarrow 2Na_2O + C$$

$$Na_2O + CO_2 \longrightarrow Na_2CO_3$$

(iv) **Reduction:**

When heated with red hot charcoal, it is reduced to CO.

$$CO_2 + C \longrightarrow 2CO$$

(v) **Photosynthesis:**

CO_2 is converted into starch and other carbohydrates by plants in presence of chlorophyll and sunlight liberating oxygen.

$$6nCO_2 + 5nH_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} \underset{\text{starch}}{(C_6H_{10}O_5)_n} + 6nO_2$$

Uses:

(a) CO_2 is used as fire extinguisher.
(b) It is used in aerated water due to its increased solubility under pressure.
(c) Solid carbon dioxide (dry ice) is used in freezing mixture to produce low temperature.
(d) It is used as a germicide and for artificial respiration.

Structure:

CO_2 has linear structure with C-O double bonds. C-atom in excited state has four unpaired electrons and undergoes sp hybridization forming two σ bonds with two O-atoms by axial overlapping. Two π bonds are formed between C and O atoms by lateral overlapping. Its structure can be shown as

$$O \overset{\pi}{\underset{\sigma}{=}} C \overset{\pi}{\underset{\sigma}{=}} O$$

Solid carbon dioxide: Dry Ice:

Dry ice is the solid carbon dioxide. It changes directly into the gaseous state at atmospheric pressure. It can be obtained by cooling the gaseous CO_2 at ordinary pressures. If the gas is compressed to a pressure of ~70 atmospheres, it condenses to the liquid state. This liquid is released through a jet into an evaporator at ~35 atms. and remains in liquid state. This liquid is introduced through a jet into press chamber kept at 5.2 atm. pressure. Here the liquid solidifies giving dry ice. Any gaseous CO_2 left in the evaporator or press chamber is drawn back and passed through the compressor at ~70 atms. to change it into the liquid state. The process is repeated to get more and more dry ice which is collected as the block and then cut into small cubes and transferred to a cold storage.

It is used as a refrigerant, as a substitute of ice in cold drinks and in the preparation of ice-cream. Mixed with ether or acetone, it provides freezing mixture of very low temperature. It is extensively used in the transport of parishable food-stuffs as it kills undesirable bacteria.

10.4.2 Silicon Oxide (SiO_2):

Silicon forms two oxides, SiO (monoxide) and SiO_2 (dioxide) SiO_2 is more important and is known as silica. Quartz is the most common naturally occurring form of silica.

Preparation:

Pure silica, in the amorphous form, can be prepared as a white powder by the action of water on $SiCl_4$ or Si F_4.

$$SiCl_4 + 4H_2O \xrightarrow{-4HCl} Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$$

Properties:

Silica is an inert substance and gives only a few reactions.

(i) Silica is insoluble in water and in all acids except hydrofluoric acid with which it forms tetrafluoride.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

(iii) It dissolves in hot conc. alkalies forming sodium silicate.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

On adding HCl to this mixture, hydrated gelatinous silica is reprecipitated which is separated from NaCl by washing with water.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SiO_2$$

(iv) It is non-volatile substance hence on heating with acid salts it displaces volatile acids from them.

$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$

(v) At very high temp; it reacts with coke to give SiC, a refractory material.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Uses:

(a) Transparent quartz is used in making optical instruments and lenses.

(b) The coloured varieties of quartz are used as gems.

(c) The opaque quartz is used in making acid and alkali resistant vessels and apparatus which are used in place of glass.

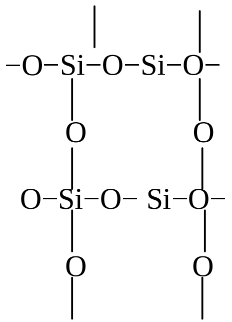
(d) Silica is used in making refractory bricks for furnace linings.

(e) Sand is used in the manufacture of glass, mortar and porcelain and is also an important construction material when mixed with lime or cement.

Structure:

It does not exist as discrete molecules like CO_2, rather it forms giant molecules by linking together a number of tetrahedra in which each Si atom is bonded to four oxygen atoms as is revealed by X-ray study of its crystal structure.

This is due to the fact that carbon has the properly of multiple bond formation but Si does not. It forms four single bonds with four o-atoms arranged tetrahedrally around it and various tetrahedra so formed are linked together by sharing of the O-atoms between two adjacent tetrahedra thereby forming a giant molecule with a three dimensional structure (**Fig 10.1**). This structure of silica is highly stable and explains its hardness and high melting point.



(**Fig. 10.1** Structure of silica)

10.5. HALIDES OF CARBON

Carbon forms a number of halides with various halogens but mostly these are the derivatives or substitution products of hydrocarbons. The tetra halides of carbon may be prepared either by heating the element with the appropriate halogen or by passing dry halogen over a heated mixture of the dioxide and carbon.

$$C + 2X_2 \xrightarrow{\Delta} CX_4$$

$$CO_2 + 2C + 2X_2 \xrightarrow{\Delta} CX_4 + 2CO$$

These tetrahalides are thermally stable and thermal stability and volatility of various tetrahalides decrease from F^- to I^-, Thus:

$CF_4 > CCl_4 > CBr_4 > CI_4 \longrightarrow$ Thermal stability decreasing.

The fluorides are, therefore, most stable and inert. The tetrahalides of carbon are not hydrolysed. This is because C, being a member of second period of the periodic table, does not have d-orbitals in the valence shell and is unable to accommodate the lone pair of electrons donated by the O-atom of water molecule to form the unstable intermediate compound as is done by higher members of this family. Thus there is no action of water molecules on these halides.

However, if sufficient energy is provided for the reaction to occur, CCl_4 undergoes hydrolysis when treated with superheated steam.

$$CCl_4 + H_2O \text{ (steam)} \xrightarrow{\Delta} COCl_2 + 2HCl$$

The reactions and properties of carbon halides are studied in organic chemistry hence can be discarded.

Fluorocarbons:

These are the derivatives of the hydrocarbons obtained as a result of substitution of H-atoms by F-atoms, i.e. fluorination. Fluorine reacts explosively with hydrocarbons and gives rise the complex mixture of fluorinated hydrocarbons called fluorocarbons, e.g. CH_3F, CH_2F_2, CHF_3, CF_4, C_2F_6 etc. Therefore, the formation of fluorocarbons is carried out by using fluorine diluted with nitrogen. Under controlled conditions these can be synthesised by:

(i) The replacement of halogen (other than F) in alkyl halides by F atom using a metal fluoride. This can be shown as:

$$RCl + AgF \longrightarrow AgCl + RF$$

(iii) The stepwise replacement of halogen atom by F-atom in anhydrous HF.

$$CCl_4 + HF \longrightarrow CCl_3F \xrightarrow[-HCl]{+HF} CCl_2F_2 \xrightarrow{+HF} CClF_3 \xrightarrow{+HF} CF_4 \text{ (Mixture of freons)}$$

$$CHCl_3 + 2HF \longrightarrow CHClF_2 + 2HCl$$

The Chlorofluorocarbons obtained from CCl_4 are called freons. The above reactions can be activated by using $SbCl_5$ as catalyst at high pressure and high temperature.

(iv) Electrolytic fluorination of organic compounds.

Organic compounds in liquid HF, if electrolysed in steel cells using Ni-anode and steel cathode, fluorination takes place at anode. This method has been used in laboratory and also as an industrial method.

$$(C_2H_5)_2O \longrightarrow (C_2F_5)_2O$$

$$CH_3COOH \longrightarrow CF_3COOF \xrightarrow{H_2O} CF_3COOH$$

(v) Direct replacement of H_2 by F_2.

The mixture of reacting compound and F_2 is subjected to electrolysis in nitrogen atmosphere. Cu-gauze or CsF or CoF_3 is used as catalyst.

$$C_6H_6 + 9F_2 \xrightarrow[\text{temp.}]{\text{Cu-gauze}} C_6F_{12} + 6HF$$

Properties and uses:

(a) The freons are used as non-toxic and non-corrosive inert refrigerants, aerosol bomb propellants and heat transfer and fire extinguishing agents. Freons are chemically inert. This property makes them useful solvents, lubricants and insulators.

Being non-toxic, Freon-12 (dichlorodifluoromethane, CCl_2F_2) is used in refrigeration and air conditioning. It is also used as a solvent for D.D.T. and other insecticides.

(b) Like ethylene, tetrafluoroethylene, C_2F_4, can be polymerized to form poly tetrafluoroethylene, $(C_2F_4)_n$. This polymer is called Teflon and is a plastic like inert material, insoluble in any solvent and unaffected by strong acids, alkalies and oxidising agents. Hence, it is used in the construction of chemical plants and as an insulating material in cables.

10.6. ORGANOSILICON COMPOUNDS: SILICONES

An important and useful class of organosilicon compounds is the organosilicon polymers known as silicones. These are synthetic polymeric materials containing-Si-O-Si-O-Si--- linkages along with C-C linkages present as the side chains.

When $SiCl_4$ is subjected to the Grignard reaction under suitable conditions, Cl-atoms in $SiCl_4$ are substituted by alkyl or aryl groups (R) and give mono-($RSiCl_3$), di (R_2SiCl_2) or tri substituted (R_3SiCl) chlorosilanes.

$$SiCl_4 + 3RMgX \xrightarrow{Ether} R_3SiCl + 3\ MgClX$$ (X is mainly Cl or Br and R = alkyl or aryl)

$$SiCl_4 + 2RMg\ X \xrightarrow{Ether} R_2SiCl_2 + 2\ MgClX$$

$$SiCl_4 + RMgX \xrightarrow{Ether} RSiCl_3 + MgClX$$

These mono, di or tri, alkyl or aryl substituted chlorosilanes when subjected to hydrolysis followed by condensation, result in the formation of either long-chain (linear) or cyclic or cross linked three dimensional polymeric materials called silicones. The nature of silicone depends on the type of substituted chlorosilane. Accordingly, the silicones are of the following type:

(a) Long chain (linear) silicones

(b) Cyclic silicones

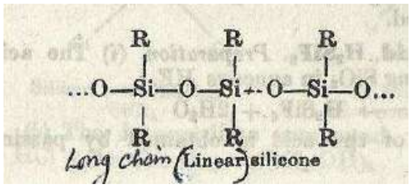
(c) Three dimensional (cross-linked) silicones.

(a) Linear (long chain) silicones:

These silicones are obtained as a result of hydrolysis and subsequent condensation of dialkyl or diaryldichlorosilane, R_2SiCl_2. This occurs in the following steps:

$$R_2SiCl_2 + 2H_2O \xrightarrow{Hydrolysis} R_2Si(OH)_2 + 2HCl$$ (R= alkyl or aryl group)

$$R_2Si(OH)_2 + R_2Si(OH)_2 + R_2Si(OH)_2 + ---- \xrightarrow{Condensation} \text{linear long chain polymer}$$



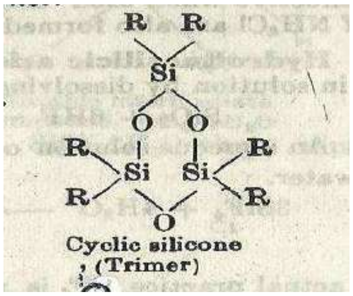
Thus the length of the chain can be increased to any extent.

(b) Cyclic silicones:

These silicones are also obtained from di-substituted chlorosilanes, first hydrdysing and then condensing them.

$$R_2\,SiCl_2 + 2H_2O \xrightarrow{\text{Hydrolysis}} R_2Si(OH)_2$$

The silicol molecules on condensation give cyclic polymers.

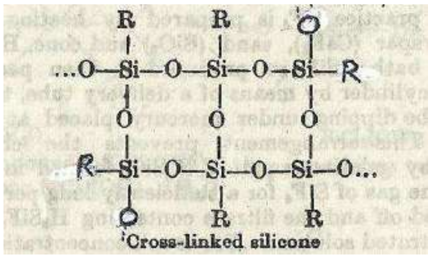


(c) Cross-linked silicones:

The hydrolysis of mono alkyl or aryl trichlorosilane, $RSiCl_3$ and subsequent condensation of silicol molecules gives a complex three dimensional, cross linked polymer involving the following steps.

$$RSiCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} RSi(OH)_3 + 3HCl$$

$RSi(OH)_3 + RSi(OH)_3 + RSi(OH)_3 +$ ----- $\xrightarrow{\text{Condensation}}$ complex three dimensional cross linked polymer. Evidently the structure can be extended in two dimension to any length and in any manner.



'Cross-linked silicone

However it is to be noted that tri substituted chlorosilane. R_3SiCl, on hydrolysis and condensation produces only dimer.

$$R_3SiCl + H_2O \xrightarrow{\text{Hydrolysis}} R_3SiOH + HCl$$

$$R_3SiOH + HOSiR_3 \longrightarrow R_3Si\text{-}O\text{-}SiR_3 + H_2O$$

Properties:

The peculiar property of silicon to hold three hydroxyl groups in the compound $RSi(OH)_3$ or two hydroxyl groups in $R_2Si(OH)_2$ in contrary to carbon atom which cannot hold more than one OH group, makes the formation of organosilicon polymers possible. Depending on the length of the chain and the nature of groups attached to the silicon atom, they can be obtained in the form of oils, viscous fluids, resins or even rubber like solids.

Thus the lower silicones are only liquids but the higher members containing long chains or ring (cross linking) structures are waxy and rubbery solids. These are thermally stable, chemically inert, non-toxic and not wetted by water. Silicone oils remain unaffected at high and low temperatures, i.e. their viscosity does not change on increasing or lowering the temperature.

Uses:

(a) Being non-volatile and highly stable at high temperature, silicone oils are used for high temperature oil baths, high vacuum pumps etc.
(b) There is no effect of cooling on the oils, hence they are used for low temperature lubrication.
(c) They are also used in making vaseline like greases which are used as lubricants in aeroplanes.
(d) Being water-repellents, they are used in making water proof cloth and paper by exposing the object to silicone vapours.
(e) They are also used as insulating materials for electric motors and other electrical appliances.

(f) They are mixed in paints and enamels to make them resistant to the effects of high temperatures, heat, sunlight and chemicals and damp.

10.7. ANOMALOUS BEHAVIOUR OF CARBON

Carbon, the first element of the group 14 (or IVA), shows some properties which are close to those of silicon but most of its properties differ from the rest of the members of its family. This is attributed, as usual, to its small size, high electronegativity, non-availability of d-orbitals in the valence shell etc. Some of its properties in contrast to other members of this group are summarised here:

(a) Though all the elements have four electrons (ns^2p^2) in the valence or ultimate shell, only carbon has helium configuration in its penultimate shell. Si has 8 and others have 18 electrons in their penultimate shells.

(b) Only carbon is distinctly non-metal, Si, though non-metal, has electrical conductivity like semi-metals (Ge). Other elements are distinctly metals.

(c) Carbon, like silicon, shows tetracovalency but does not form M^{4+} ions. Other elements (except Si) form M^{2+} and M^{4+} type ions.

(d) Carbon has a great tendency of catenation (self-linkage). Si shows catenation property to some extent but other elements do not have this property.

(e) Dioxides of carbon and silicon are acidic but those of other elements are amphoteric.

(f) Carbon forms a large number of hydrides, Si forms less number of hydrides while other elements give only a few hydrides.

(g) The tetrahalides of carbon are not hydrolysed by water but those of higher members get readily hydrolyse due to the availability of vacant d-orbitals in their valence shells and ability to form unstable intermediate compound with water which then eliminates HX molecules and forms hydroxide.

$$CX_4 + 4H_2O \longrightarrow \text{no action.}$$

$$MX_4 + 4H_2O. \longrightarrow MX_4\ 4H_2O \longrightarrow M\ (OH)_4 + 4HX$$

(h) Carbon is not attacked by caustic alkalies while all others are attacked and evolve hydrogen gas.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2\uparrow$$

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + H_2\uparrow$$

10.8. SUMMARY

The course material on the elements of Group 14 contains the introduction, the general characteristics of the elements like electronic configuration, occurrence, atomic and ionic radii, melting and boiling points, metallic and non-metallic character, ionisation energy and electronegativity, valency and oxidation state, catenation, allotropy, formation of oxides, halides, hydrides, acids and halo complexes etc. Also the oxides of carbon and silicon, halides of carbon and organo- silicon compounds have been discussed in detail. At the end, the anomalous behaviour of carbon in contrast to other members of this family has been taken into account.

10.9 TERMINAL QUESTIONS

i. Graphite is a form of

(a) Carbon

(b) Silicon

(c) Tin

(d) Lead

ii. The metallic character of the elements of Group 14

(a) Increases down the group

(b) Decreases down the group

(c) Remain the same in the group

(d) First decreases and the increases

iii. The stability of M^{2+} ions decreases in the order

(a) $Pb^{2+} > Sn^{2+} < Ge^{2+}$

(b) $Pb^{2+} < Sn^{2+} < Ge^{2+}$

(c) $Pb^{2+} > Sn^{2+} > Ge^{2+}$

(d) $Pb^{2+} < Sn^{2+} > Ge^{2+}$

iv. The gas used as fire extinguisher is

(a) N_2 + Co mixture

(b) CO

(c) $CO + CO_2$ mixture

(d) CO_2

v. How are crosslimked three dimensional silicon polymers prepared?

vi. White a note on use of CO_2 in photosynthesis

vii. SiO_2 exists as a giant molecule, explain.

viii. Give the uses of Freon-12.

10.10. ANSWERS

i. (a)

ii. (a)

iii. (c)

iv. (d)

v. to viii. Please refer to the text of the unit.

UNIT 11: ELEMENTS OF GROUP -15

CONTENTS:

11.1. OBJECTIVES

The objective of the preparation of the study material of this unit, i.e. on the elements of Group 15 (group VA) of the periodic table, is to provide the reader, the subject matter which they can easily understand and become acquainted with the various aspects of their general characteristics and uses, the study of their hydrides, halides, properties and structure of oxides and oxoacids and also the anomalous behavior of nitrogen in contrast to that of other members of nitrogen family.

11.2. INTRODUCTION

The group 15 (group VA) of the extended or long form of periodic table contains five elements, namely nitrogen (N_7), phosphorous (P_{15}), arsenic (As_{33}), antimony(Sb_{51}) and bismuth (Bi_{83}). This group is also known as nitrogen group. All the elements of this group belong to p- block due to the filling of p- orbital (or subshell) of the valance shell by the last electron of the atoms of these elements.

The first two elements (N and P) are distinctly non metals.

The next two elements (As and Sb) are semi- metals and the last element Bi, is metallic in nature.

These elements, except phosphorous, do not occur very abundantly in nature. Nitrogen constitutes only about 0.0045%, phosphorous 0.116%, As, Sb and Bi nearly 10^{-4} % of the rocks of earth. The phosphorous ranks tenth in abundance among all the elements known, nitrogen constitutes nearly 78 percent by volume of the atmosphere.

11.3. GENERAL CHARACTERISTICS

The inclusion of nitrogen group elements in the same group of modern periodic table is justified by the following general characterstics of these elements. These elements furnish another example in which there is a systematic gradation of properties and there is a change of character from a true non metal like nitrogen to a nearly true metal, e.g. bismuth.

11.3.1 . Electronic configuration.

There are five electrons in the valance or ultimate shell of the atoms of these elements, i.e. ns^2p^3 where n is the principal quantum number of the valance shell. Two of these electrons are in the s- subshell and the rest three are occupying the p- subshell according to the Hund's rule among the three p- orbitals. Because of exactly half- filled orbitals, the elements are fairly stable and not so reactive. The penultimate shells have variation in the number of electrons. The first element, N, has helium configuration s^2, P has inert gas octet s^2p^6 and other elements have pseudo inert gas, $s^2p^6d^{10}$, configurations, respectively in the penultimate shells of their atoms. This variation in the configuration is responsible for gradation of properties in the group.

11.3.2 Occurrence:

Nitrogen occurs in the free State as the diatomic gas in nature while all the remaining elements occur in the combined state. In the combined state it occurs mainly as nitrates. Being very reactive, phosphorous does not occur in the native state, rather it occurs as phosphates in its ores. As, Sb and Bi are less abundant and occur chiefly as sulphide ores.

11.3.3Physical state and elemental structure:

Nitrogen is a gas, phosphorous is a soft, lustreless solid, others are hard solids, Sb and Bi having characteristic metallic lustre. Nitrogen gas exists as a diatomic molecule, N_2 while P, As and Sb exist as tetratomic molecules, P_4, As_4 and Sb_4. These are not capable of forming diatomic molecules like N_2 because they do not form $p\pi$ - $p\pi$ bonds as their larger atoms cannot come closer to each other to form such bonds as well as due to the increased repulsions from the non bonding electrons of penultimate shell. The repulsion from the electrons of penultimate shell, $1s^2$, in nitrogen atoms is not appreciable. Further, formation of π bonds in the N_2 molecule satisfies the valency requirements of N- atoms while non formation of such bonds in other elements compels them to join with more atoms hence M_4 molecules are formed. These elements thus form giant lattices in which the bonding changes from covalent to metallic from P to Bi.

11.3.4 Metallic and non-metallic character:

The change from non- metallic to metallic character with increasing atomic number in the same group, exhibited by group 14, is observed equally well in this group also, the only metallic element being Bi, the last element of the family which has the lowest value of ionization energy. This is revealed by the variation in the properties both physical and chemical.

11.3.5 Density, hardness, atomic radius, and atomic volume:

On going from P to Bi (N- being a gas excluded) these properties increase regularly and markedly. The atomic radius and atomic volume also increase down the group with the exception of atomic volume of As which has low value.

11.3.6 Ionization energy, electro negativity and heat of atomization:

With increasing size from N to Bi, the values of first ionization energies decrease on descending the group. Similar is the trend in the electro negativity and heat of atomization. This gradation confirms the gradual increasing metallic character of the elements.

11.3.7 Melting and boiling points:

The melting points (expect for Sb and Bi) and the boiling points both increase with increasing atomic number. The melting point of Bi is unusually low perhaps because of non-availability of ns^2 electron pair for bonding in the metallic crystal. The elements of this group are more volatile than their immediate neighbours of group14.

11.3.8 Oxidation states:

(i) Formation of M^{5+} and M^{3+} cations

M^{5+} cations are formed when all the valance electrons, ns^2p^3, are used by the elements for bonding. N and P cannot lose all the five valance electrons due to prohibited energy considerations, i.e. because they have high ionization energies and electronegativities and hence do not form M^{5+} ions. These elements also do not form M^{3+} ions as such but these oxidation states, i.e.+3 and +5 can be assigned to them arbitrarily in their compounds with more electronegative elements, *viz*. O and F if formed. M^{3+} cations are formed by the elements if they lose only p- electrons from ns^2p^3 configuration of the valence shell and ns^2 electron pair remains inert (inert pair effect). Since this effect increases down the group, the heavier elements, *viz*. Sb and Bi are expected to form M^{3+} ions by losing three p- electrons only and retaining the ns^2 electron pair, though they can form M^{5+} ions as well. Thus only As and Sb will give salt with +5 and +3 oxidation states and Bi gives only Bi^{3+} ions.

(ii) Formation of M^{3-} anions

In order to achieve noble gas configuration, these elements accept three electrons from electropositive elements and form M^{3-} ions, e.g. N in NH_3 has -3 oxidation state. As the size of the atoms increases on moving down the group, the ionization energy and electronegativity values decrease and hence the attraction of the nucleus for the newly added electrons decreases. Thus the tendency of the elements to give M^{3-} ions also decreases. In fact, N-atom, being smallest in size, has strongest tendency to form N^{3-} ion, P forms P^{3-} ions less readily and Bi, the last member of the group, hardly exhibits negative oxidation state.

(iii) Covalency of 3 and 5

Each of these elements has two paired s- electrons and three unpaired p- electrons in the valence shell. If these elements form three covalent bonds using only the p- electrons, they attain the noble gas configuration (ns^2p^6). This gives the covalency of 3 to these elements. Except nitrogen, these elements also have vacant d- orbitals in the valence shell. Under suitable conditions of energy, one of the electrons of s level may be promoted to the vacant d–orbital, thus possessing five unpaired electrons. These five unpaired electrons may be used to form five covalent bonds, thereby giving the covalency of 5 to these elements. This covalency is common among P, As and Sb. That is why N forms only trihalide and other elements form tri as well as pentahalides.

11.3.9 Electron donor – acceptor properties:

All the elements in the trivalent state have a tendency to act as electron pair donors. Nitrogen having this tendency to the maximum extent. For example NH_3 and PH_3 molecules act as Lewis bases towards H^+ to form NH_4^+, PH_4^+ etc. due to presence of lone pair of electrons on N and P- atoms, thereby N showing a maximum covalency of 4, P, As and Sb show a covalency of 6 in $[PCl_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ complex ions in which their salts act as electron pair acceptors.

$$PCl_5 + Cl^- \longrightarrow [PCl_6]^-$$

11.3.10 Allotropy:

All the elements, except Bi, show allotropy. Nitrogen in solid state exists in two allotropic forms *viz.* α-nitrogen and β – nitrogen. Phosphorous exists in various forms such as white, red, scarlet, α–black, β–black and violet. Arsenic exists in grey, yellow and black allotropic forms while antimony in the forms as yellow, black, β- and explosive.

11.3.11 Catenation (Self linkage):

Although the catenation is considered to be a property peculiar to carbon, yet it is shown to some extent, by the elements lying close to carbon in the periodic table. The elements of this group have been found to show this property but to a much smaller extent than carbon. Thus, unstable compounds containing chains of upto eight N- atoms have been prepared but stable azide ion has a chain of three N- atoms, i.e. $(N\text{-}N\text{-}N)^-$ skeleton and $H_2N–NH_2$ has two N-atoms. In case of phosphorous, P-P links are limited to two atoms (e.g.P_2H_4). Other elements of the group have no tendency of self linkage. Thus tendency for catenation decreases on moving down the group because of gradual decrease in bond energies of M-M bonds.

11.3.12 Electrical and thermal conductivity:

Both these properties increase as we move down the group because of increased delocalization of electron from nitrogen to bismuth (with a metallic crystal lattice). Thus N and P are non conductors, As is a poor conductor, Sb is a good conductor and Bi is an excellent conductor.

11.3.13 Combination with active metals:

All these elements form compounds with metals, e.g. N forms nitrides: LiN, Mg_3N_2 etc; phosphorous forms phosphide Ca_3P_2 etc., Arsenic gives arsenides Na_3As etc. , Sb gives antimonides Mg_3Sb_2 and Bi forms bismuthides Mg_3Bi_2 etc. The nitrides among these compounds are most stable. The last two types of compounds are rare and Sb and Bi, infact, form alloys on combining with metals.

11.3.14 Chemical reactivity:

These elements differ from one another appreciably in their chemical reactivity. Nitrogen is chemically non–reactive. It does not combine under ordinary conditions. It combines with elements such as Li, Al, Ca, Mg etc to form nitrides at high temperature only and combines with oxygen only when heated in an electric arc to a temperature of the order of 2500^0C and above forming nitric oxide. On the other hand white phosphorous, an allotropic form of P, is extremely reactive. It burns readily in oxygen forming oxides of phosphorous. The heavier elements, *viz*. As, Sb, Bi burn only when heated in air or oxygen, to form oxides. This can be attributed largely to difference in the electro negativities of the five elements.

Uses:

(i) Nitrogen is an essential element for the growth of plants. It is generally added to the soil in the form of the fertilizers (compounds of Nitrogen) or atmospheric nitrogen is fixed by nature and this is absorbed by soil. From the soil it goes to the plants and then to the animals.

(ii) Red variety of P being non-poisonous is mostly used in match industry.

(iii) Phosphorous is also used as rat poison and in the manufacture of tracer bullets as well as in producing smoke screens.

(iv) As-Pb alloy is used in making lead shots.

(v) Antimony is mainly used in the manufacture of lead storage batteries as it is harder and acid resistant.

(vi) Bi-alloys have low melting points and are called fusible alloys. These are used in making automatic electrical fuses, fire alarms, sprinklers, safety plugs on boilers etc.

11.4 HYDRIDES OF ELEMENTS

All the elements of this group form hydrides of the type MH_3 : ammonia (NH_3), phosphine (PH_3), arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3). N and P also form dihydrides of the type M_2H_4 : hydrazine (N_2H_4) and phosphorous dihydride (P_2H_4). In addition to these, N also forms a third hydride of M_3H type : hydrazoic acid, N_3H.

11.4.1 Preparation:

The MH_3 type hydrides of these elements are prepared by the action of water or dilute acid on the binary metallic compounds such as Mg_3N_2, Ca_3P_2 , Zn_3As_2, Mg_3Bi_2 etc.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3\uparrow$$

$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3\uparrow$$

$$Mg_3Bi_2 + 6HCl \longrightarrow 3MgCl_2 + 2BiH_3\uparrow$$

Hydrazine, N_2H_4 , is prepared by the oxidation of excess ammonia in NaOH solution by sodium hypochlorite at 80 -90^{0}C. The reaction take place in two stages.

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

$$NH_4Cl + NH_3 + OH^- \longrightarrow H_2N - NH_2 + Cl^- + H_2O$$

The reaction is catalysed and side reaction between NH_4Cl and N_2H_4 formed is inhibited by adding glue or gelatin.

P_2H_4 is formed together with phosphine in the hydrolysis of impure calcium phosphide which contains Ca_2P_2

$$Ca_2P_2 + H_2O \longrightarrow 2Ca(OH)_2 + P_2H_4$$

Hydrazoic acid, N_3H, is obtained by the distillation of an acidified solution of sodium azide which is formed during the oxidation of molten sodamide with powdered sodium nitrate at 175^0C.

$$3NaN_2 + NaNO_3 \longrightarrow NaN_3 + 3NaOH + NH_3$$

$$2NaN_3 + H_2SO_4 \longrightarrow 2N_3H + Na_2SO_4$$

11.4.2 Properties:

All the trihydrides of these elements are colourless gases with specific odour. Ammonia has characterstic odour, phosphine has rotting fish odour and arsine and stibine both have garlic-like odours. The gradation in the electrochemical character of these elements is evidenced by the properties of their gaseous hydrides.

(i) Basic character:

The basic character, i.e. the ability to act as electron pair donor, decreases from NH_3 to BiH_3. Ammonia (NH_3) is distinctly a base and readily coordinates with H^+ ions to give a stable cation, NH_4^+. It also readily forms salts with acids both weak and strong, *viz.* $(NH_4)_2CO_3$, NH_4Cl etc. PH_3 is also a base but much weaker than ammonia and forms less stable PH_4^+ ions. Still it is strong enough to form halides called phosphonium halides, PH_4X which are readily decomposed by water. The MH_4^+ ions for As, Sb and Bi elements do not exist meaning thereby that these have no basic character, rather the last hydride, BiH_3, has feebly acidic character and dissolves in strong alkalies. It has been noticed that the electron donor ability of the hydrides is increased by the replacement of H–atoms by alkyl groups. Thus $P(CH_3)_3$ shows stronger basic character, than PH_3.

NH_3 is the strongest electron pair donor because N – atom has the smallest size and the electron density of the lone pair of electrons present in one of the four sp^3 hybrid orbitals of this atom is concentrated over a small region. As we move down the group, the increasing atomic size of the central atom causes the electron density of the lone pair to diffuse over the large region and thus the ability to donate the electron pair and hence the basic character decreases.

N_2H_4 is a colourless liquid, less volatile than phosphine due to H – bonding. It is a weak base and gives weakly alkaline solution with water.

$$N_2H_4 + H_2O \longrightarrow N_2H_5^+ + OH^-$$

Perhaps the hydrogen bonding between the $N_2H_5^+$ + OH^- ions decreases the alkalinity of the aqueous solution. P_2H_4 does not show basic properties. N_3H is a colourless liquid having melting point of 236K. It is freely soluble in water forming an acidic solution.

$$N_3H + H_2O \longrightarrow H_3O^+ + N_3^-$$

(ii) Thermal Stability:

The thermal stability of the MH_3 hydrides decreases gradually from NH_3 to BiH_3 with increasing size of the central atom. This is evident from the decreasing temperature of their decomposition into their elements, i.e. NH_3 (500^0C) > PH_3 (440^0C) > AsH_3 (280^0C) > SbH_3 (270^0C) > BiH_3 (very unstable). The least stable nature of BiH_3 (half life period = 20 minutes under normal conditions) confirms the fact that only trace quantities of this hydride have been prepared and identified. Thus we infer that the strength of M-H bond goes on decreasing as the thermal stability decreases from NH_3 to BiH_3. N_2H_4 and N_3H both are fairly stable towards mild heating but P_2H_4 is highly unstable and is spontaneously inflammable.

(iii) Reducing properties:

All the MH_3 type hydrides are reducing agents and with the progressive fall in stability, the reducing character of these hydrides goes on increasing due to the weakening of M – H bonds and increasing ease of their decomposition. Thus NH_3 is a mild reducing agent and is not oxidized readily, if oxidized, the product is usually nitrogen, e.g. when NH_3 burns in oxygen, it gives N_2 and water but if heated with oxygen in the presence of a Pt – catalyst, NO is formed.

$$4NH_3 + 3O_2 \xrightarrow{2N_2} + 6H_2O$$

$$4NH_3 + 5O_2 \quad , \xrightarrow{\Delta \ Pt} 4NO + 6H_2O$$

Phosphine, PH_3, is stronger reducing agent than NH_3 and is much more easily oxidized, i.e. when ignited in air, it gives phosphorous pentoxide.

$$4PH_3 + 8O_2 \xrightarrow{\Delta} P_4O_{10} \text{ (or } 2P_2O_5) + 6H_2O$$

SbH_3 and BiH_3 are powerful reducing agents and are oxidized very easily.

Anhydrous N_2H_4 burns readily in oxygen or air forming N_2.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

Aqueous hydrazine can act both as reducing and oxidizing agent.

As reducing agent**:** Alkaline solution: $N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-$

Acidic solution: $N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^-$

As oxidising agent: Alkaline solution: $N_2H_4 + 2H_2O + 2e^- \longrightarrow 2NH_3 + 2OH^-$

Acidic solution: $N_2H_5^+ + 3H^+ + 2e^- \longrightarrow 2NH_4^+$

P_2H_4 is a powerful reducing agent and is instantaneously oxidised in air or O_2:

$$P_2H_4 + 7O2 \longrightarrow P_4O_{10} + 4H_2O$$

Aqueous hydrazoic acid can act either as a reducing agent or as an oxidizing agent.

As a reducing agent: Alkaline solution: $2N_3^- \longrightarrow 3N_2 + 2e^-$

Acidic solution: $2HN_3 \longrightarrow 3N_2 + 2H^+ + 2e^-$

As oxidizing agent: Alkaline solution: $N_3^- + 7H_2O + 6e^- \longrightarrow N_2H_4 + NH_3 + 7OH^-$

Acidic solution: $HN_3 + 3H^+ + 2e^- \longrightarrow NH_4^+ + N_2$

(iv) Covalent character:

The NH_3 molecule has more ionic character than PH_3 ($NH_3 > PH_3$) due to more electronegativity difference between N and H than between P and H. Similarly, it can be shown that the ionic character of MH_3 molecules decreases and covalent character increases down the group from NH_3 to BiH_3.

(v) Shape of hydride molecules and H-M-H bond angles:

The shape of MH_3 type of hydrides is trigonal pyramidal. This shape may be regarded as tetrahedral shape having one lone pair of electrons occupying one of the four tetrahedral positions (involving sp^3 hybridisation of the central atom). The HMH bond angle in all the four MH_3 hydrides (M = N, P, As, Sb) is never equal to ideal tetrahedral angle of 109.5^0 but less than this value due to low electronegativities of the central atoms. N_3H is the linear molecule:

$H - N \leftarrow N \equiv N$. Actually it is a resonance hybrid or two canonical forms.

(vi) Hydrogen bonding:

Ammonia is least volatile among the MH_3 hydrides because in ammonia, intermolecular hydrogen bonding occurs resulting in the formation of cluster of molecules. This happens due to the development of strong polarity in the bonds of the NH_3 molecules and association of molecules (dipole – dipole type interaction).

11.5 HALIDES OF NITROGEN GROUP ELEMENTS

The elements of nitrogen group form two types of halides namely trihalides, MX_3 and pentahalides, MX_5 . All these halides have been given in table 11.1.

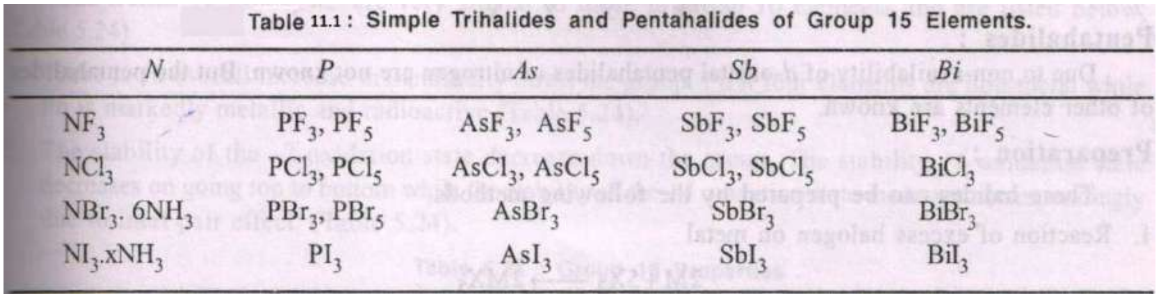


Table 11.1 : Simple Trihalides and Pentahalides of Group 15 Elements.

N	*P*	*As*	*Sb*	*Bi*
NF_3	PF_3, PF_5	AsF_3, AsF_5	SbF_3, SbF_5	BiF_3, BiF_5
NCl_3	PCl_3, PCl_5	$AsCl_3$, $AsCl_5$	$SbCl_3$, $SbCl_5$	$BiCl_3$
$NBr_3 . 6NH_3$	PBr_3, PBr_5	$AsBr_3$	$SbBr_3$	$BiBr_3$
$NI_3 . xNH_3$	PI_3	AsI_3	SbI_3	BiI_3

11.5.1 Preparation:

The trihalides are formed by all the elements and prepared by the two methods:

(a) By the reaction of excess element with halogen (except nitrogen)

$$2M + 3X_2 \longrightarrow 2MX_3 \text{ (M = As, Sb, Bi and X = Cl, Br, I)}$$

(b) By the reaction of hydrogen halide with the trioxide of the element.

$$M_2O_3 + 6HX \longrightarrow 3H_2O + 2MX_3$$

The pentahalides of nitrogen are not known due to the non availability of d- orbitals in its atom but all other elements, except Bi, form pentahalides which are prepared as follows:

(a) By the reaction of excess halogen with the element.

$$2M + 5X_2 \longrightarrow 2MX_5$$

(b) By the reaction of halogen on the trihalide.

$$MX_3 + X_2 \longrightarrow MX_5$$

In Bi, the ns^2 electron pair is inert (inert pair effect) and does not participate in bond formation, Therefore, BiX_5 compounds if formed, immediately converted to BiX_3 by decomposition and these are said to be non- existent.

11.5.2 Properties:

The trihalides of nitrogen are least stable except NF_3 which has strong N – F bond due to the small size of both N and F atoms. With the exception of BiF_3, all other trihalides have covalent character which decreases as we descend the group. Except NF_3 and BiF_3, all other trihalides are readily hydrolysed by water.

NCl_3 is an explosive compound and NBr_3 as well as NI_3 exist only as ammoniates. The explosive nature of these compounds is due to much lower stability or bond energy of N - Cl, N - Br, and N – I bonds.

(i) NX_3 (X= Ci, Br, I) trihalides are completely hydrolysed by water giving NH_3 and HOX (hypohalous acid)

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

For PX_3, AsX_3 and SbX_3, the ease and extent of hydrolysis generally increase with decreasing eletronegativity of halogen atom (I to F) and decrease with increasing metallic character of the central atom (P to Bi). Different chlorides on hydrolysis give different products.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$2AsCl_3 + 3H_2O \longrightarrow As_2O_3 + 6HCl$$

Sb and Bi trichlorides are only partly and reversibly hydrolysed.

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

(ii)All trihalides except NX_3 and PF_3, can act as Lewis acid.

$$SbF_3 + F^- \longrightarrow SbF_4^- \qquad SbF_4^- \equiv [SbF_3 \leftarrow F]^-$$

But PF_3 acts as Lewis base, e.g.

$$Ni(CO)_4 + PF_3 \longrightarrow (CO)_4Ni \leftarrow PF_3$$

NX_3, except NF_3 molecules are strong Lewis bases.

(iii) N– trihalides are not oxidized at all but the trihalides of other elements are oxidized and the ease of oxidation decreases down the group, i.e. P > As > Sb > Bi.

Properties of pentahalides:

(a) Pentahalides dissociate into MX_3 and X_2, the tendency of dissociation decreases in the order of M and X: P > Sb > As > Bi and F > Cl > Br

(b) These halides are hydrolised to give the acid of the M element or hydrated oxides along with HX mineral acid.

$$PX_5 + H_2O \longrightarrow POX_3 + 2HX$$

$$\underline{POX_3 + 3H_2O \longrightarrow H_3PO_4 + 3HX}$$

$$PX_5 + 4H_2O \longrightarrow H_3PO_4 + 5HX$$

$$2SbX_5 + 7H_2O \longrightarrow Sb_2O_5.2H_2O + 10\,HX$$

Except BiF_5 all are Lewis acids.

$$PF_5 + F^- \longrightarrow PF_6^- \equiv [PF_5 \leftarrow F]^-$$

11.5.3 Structure:

The structure of MX_3 trihalides is similar to that of NH_3 in gas phase, i.e. central atom is sp^3 hybridised, one of the sp^3 hybrid orbitals contains a lone pair of electrons (bonded pairs=

3, lone pair = 1) and molecules attain a trigonal pyramidal shape, i.e. distorted form of tetrahedral geometry.

X–Ray studies of MX_5 halides in the liquid and gaseous phases have revealed that these molecules possess trigonal bipyramidal shape (resulting from sp^3d hybridization of the central M-atoms (postulated by VBT). In solid state these are ionic and exist as $[PCl_4]^+$ $[PCl_6]^-$, $[PBr_4]^+$ Br^- etc. The shape of $[PX_4]^-$ ion is tetrahedral and that of $[PX_6]^-$ ion is octahedral. But different solid pentahalides have different structures. PI_5 does not exist due to large size of iodine atom.

11.6 OXIDES AND OXO ACIDS OF ELEMENTS

Almost all the elements of this group form oxides and oxo (oxygen containing) acids. More important oxides are trioxides (M_2O_3), tetraoxides (MO_2 or M_2O_4) and pentoxides (M_2O_5). In addition to these, nitrogen also gives nitrous oxide (N_2O) and nitric oxide (NO). Bismuth also forms bismuth monoxide (BiO). All these oxides are shown in Table 11.2

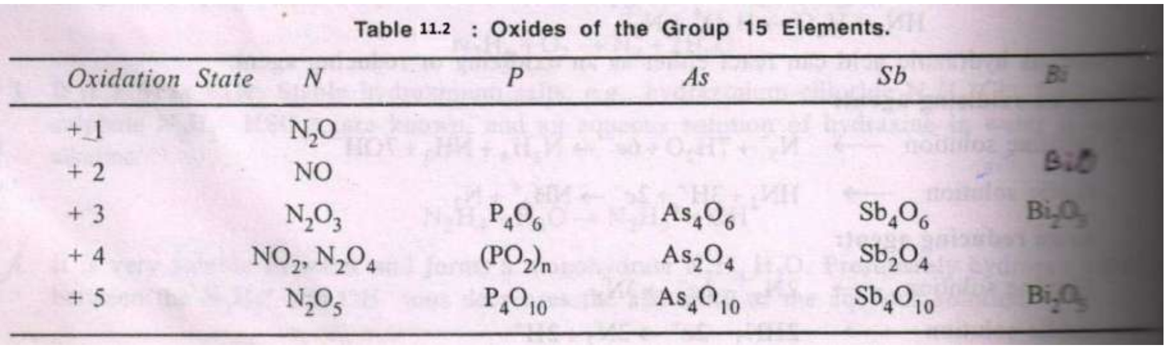


Table 11.2 : Oxides of the Group 15 Elements.

Oxidation State	N	P	As	Sb	Bi
+ 1	N_2O				
+ 2	NO				BiO
+ 3	N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
+ 4	NO_2, N_2O_4	$(PO_2)_n$	As_2O_4	Sb_2O_4	
+ 5	N_2O_5	P_4O_{10}	As_4O_{10}	Sb_4O_{10}	Bi_2O_5

11.6.1 Properties and structures of oxides:

All the oxides of nitrogen are thermodynamically unstable because compounds containing single N–O bonds tend to be dissociated because of low N–O bond enthalpy. Thermal stability and acidic character of M_2O_3 type oxides (trioxides) decreases from N_2O_3 to Bi_2O_3. Thus N_2O_3 and P_2O_3 are completely acidic and give nitrous and Phosphorous or phosphoric acids with water.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

$$P_2O_3 + 3H_2O \text{ (cold)} \longrightarrow 2H_3PO_3$$

$$2P_2O_3 + 6\ H_2O \text{ (hot)} \longrightarrow 3H_3PO_4 + PH_3$$

As_2O_3 and Sb_2O_3 are amphoteric and form salts with acids as well as alkalies.

$As_2O_3 + 6HCl \longrightarrow 2AsCl3 + 3H2O$

$As_2O_3 + 6NaOH \longrightarrow \underset{\text{Sod.arsenite}}{2Na_3AsO_3} + 3H_2O$

(Similar reactions are given by Sb_2O_3 also.)

Bi_2O_3 is predominantly basic and forms salts with acids. It also shows feebly acidic character since it dissolves in conc. alkalies due to the formation of bismuthites.

$Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O$

$Bi_2O_3 + 2NaOH \longrightarrow \underset{\text{sod. bismuthite}}{2NaBiO_2} + H_2O$

The decreasing acidic character from N_2O_3 to Bi_2O_3 is due to larger extent of interaction between smaller N^{3+} ion and H_2O thereby giving acidic N_2O_3 as compared to that between larger Bi^{3+} ion and water giving basic Bi_2O_3.

The reason of an oxide in lower oxidation state being less acidic than that in higher oxidation state can also be explained on the same ground that smaller ion with higher oxidation state interacts more strongly with water to give stronger acid. For example, N_2O (oxidation state of N= +1) is neutral while N_2O_4 (oxidation State of N= +4) is acidic. The decreasing acidic character from N_2O_3 to Bi_2O_3 is also consistent with the increasing metallic character of the elements on passing from nitrogen to bismuth.

P_2O_3 is readily oxidised to P_2O_5 ($P_2O_3 + O_2 \longrightarrow P_2O_5$) while the trioxides of other elements are rather stable towards oxidation to pentoxides. Bi_2O_3 shows maximum stability towards oxidation.

All the Pentoxides (M_2O_5) are acidic but the acidic character decreases from N_2O_5 to Bi_2O_5 with increasing atomic mass of the element M. Thus N_2O_5 is the strongest acidic oxide and Bi_2O_5 is the weakest. N_2O_5, P_2O_5 and As_2O_5 are exclusively acidic and react with water or alkalies to form oxo acids or their salts.

$N_2O_5 + H_2O \longrightarrow 2HNO_3$

$P_2O_5 + H_2O\text{(cold)} \longrightarrow 2HPO_3$

$P_2O_5 + 3H_2O\text{ (hot)} \longrightarrow 2H_3PO_4$

Sb_2O_5 is less acidic but forms salts called antimonates. Bi_2O_5 is only feebly acidic and forms salts when fused with alkalies called bismuthates.

$Bi_2O_5 + 6NaOH \xrightarrow{\Delta} 2Na_3BiO_4 + 3H_2O$

Sod. bisluthate

The decreasing acidic character from N_2O_5 to Bi_2O_5 is due to increasing size of M^{5+} ion from N^{5+} to Bi^{5+} and also due to increasing metallic character of the elements from N to Bi. The first three pentoxides, *viz*. N_2O_5, P_2O_5 and As_2O_5 are readily soluble in water and form acids while Sb_2O_5 and Bi_2O_5 are relatively insoluble. Thus the solubility of these oxides decreases from N_2O_5 to Bi_2O_5.

N_2O_5 is thermally least stable and gets dissociated into nitrogen dioxide (NO_2) and O_2 even at room temperature. P_2O_5 is stable but sublimes on heating. As_2O_5 decomposes into trioxide (As_2O_3) and O_2 at red heat.

Sb_2O_5 is less stable and decomposes into Sb_2O_3 and O_2 above 450^0C.

N_2O_5 is the strongest oxidising agent among the pentoxides which, except P_2O_5, show oxidising property.

The properties of some other oxides of nitrogen have been given below along with P_4O_8 (=$2P_2O_4$).

(i) **Nitrous oxide9N_2O):**

(a) It is slightly soluble in water, has faint sweet smell and is inert at 25^0c but decomposes at higher temperature to N_2 and O_2. Therefore, it is better oxidising agent than oxygen itself.

$$2N_2O \longrightarrow 2N_2 + O_2$$

(b) It does not react with water, acids and alkalies.

(ii) **Nitric oxide(NO):**

(a) It is sparingly soluble in water. It quickly reacts with oxygen to form the brown coloured gas NO_2

$$2NO + O_2 \longrightarrow 2NO_2$$

(b) It reacts vigorously with burning phosphorous and boiling sulphur.

$$S + 2NO \longrightarrow SO_2 + N_2$$

(c) On heating nitric oxide decomposes to N_2 and O_2

$$2NO \longrightarrow N_2 + O_2$$

(d) **Reducing Nature:**

It reduces O_2, Cl_2 and acidified potassium permanganate as follows:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO + Cl_2 \longrightarrow 2NOCl_2$$

$$2MnO4^- + 4H^+ + 5NO \longrightarrow 3Mn^{2+} + 5NO_3^- + 2H_2O$$

(e) Oxidising nature:

It acts as oxidising agent and is reduced to nitrogen and ammonia.

$$2NO + 2H_2 \xrightarrow{\text{sparking}} N_2 + 2H_2O$$

$$2NO + 5H_2 \xrightarrow{\text{Pt –black}} 2NH_3 + 2H_2O$$

(f) It forms dark brown nitrosyl complex with $FeSO_4$ solution, $[Fe(NO)(H_2O)_5]^{2+}$.

(iii) **Nitrogen dioxide ($N_2O_4 \rightleftharpoons 2NO_2$):**

(a) It is soluble in water, highly poisonous, has pungent smell and corrodes the skin.

(b) It changes its colour and physical state with temperature.

$$2NO_2 \overset{140^0C}{\rightleftharpoons} 2NO_2 \overset{26^0C}{\rightleftharpoons} N_2O_4 \overset{-57^0C}{\rightleftharpoons} N_2O_4$$

reddish	pale coloured	yellow	colourless
brown gas	gas	liquid	solid

(c) Acidic nature:

NO_2 is acidic towards litmus and neutralises alkalies to form nitrates and nitrites.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$2OH^- + 2NO_2 \longrightarrow NO^-_2 + NO^-_3 + H_2O$$

(d) Oxidising nature

Some oxidising reactions of NO_2 are as follows:

$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO4)_3 + NO + H_2O$$

$$2I^- + H_2O + NO_2 \longrightarrow I_2 + 2OH^- + NO$$

$$2MnO_4^- + 2H_2O + 10NO_2 \longrightarrow 2Mn^{2+} + 4H^+ + 10NO^-_3$$

(iv) **$P_4O_8 \rightleftharpoons 2P_2O_4$**

It reacts with water to produce H_3PO_4 and H_3PO_3

$$P_2O_4 + 3H_2O \longrightarrow \underset{(ic)}{H_3PO_4} + \underset{(ous)}{H_3PO_3}$$

Structure of oxides:

N_2O

It is isoelectronic with CO_2 and is almost linear. **Fig 11.1 (a)**

NO

It is an odd electron molecule with a total of 11 electrons. The unpaired electron is delocalised (paramagnetic). Has linear structure. **Fig 11.1 (b)**

NO_2

It has two normal bonds (1 σ and 1 π) and one coordinate bond and also an unpaired electron (paramagnetic). Has bent structure. The diner has planar structure. **Fig 11.1 (c)**

N_2O_5. In vapour phase it has a symmetrical structure. **Fig 11.1 (d)**

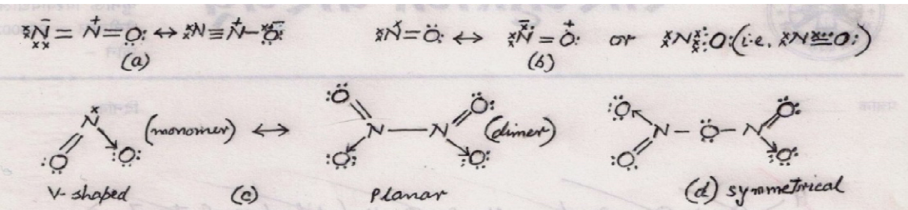


Fig. 11.1 (a) Linear structure of N_2O (b) Linear structure of NO
(c) V-shaped structure of NO_2 and planar structure of N_2O_4 (dimer)
(d) Symmetrical structure of N_2O_5.

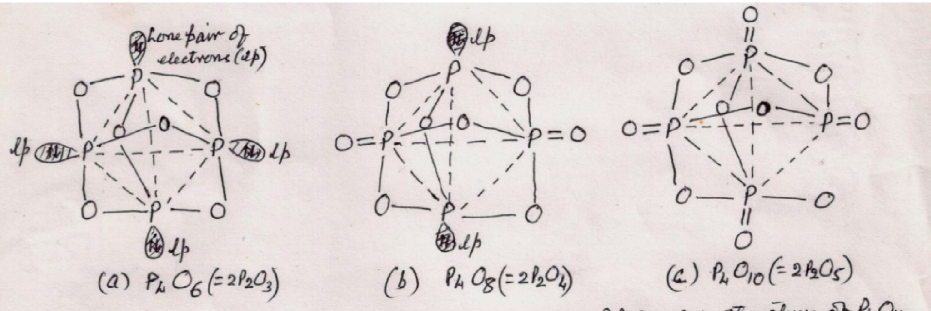
P_4O_6 ⇌ $2P_2O_3$

It has a tetrahedral structure with four P-atoms lying at the corners of a tetrahedron and six O-atoms along the edges, P-O bond length being between a single and a double bond due to considerable double bond character formed as O →P: p_π-d_π dative bond. **Fig 11.2 (a)**

P_4O_8 ⇌ $2P_2O_4$

It has two additional oxygen atoms as compared to P_4O_6 which are attached to two P-atoms. Structure is similar to that of P_4O_6. **Fig 11.2 (b)**.

P_4O_{10} ⇌ $2P_2O_5$. Each P atom of this molecule forms a double bond with terminal O-atom (p_π-d_π) and three single bonds with three bridged O-atoms. The structure is similar to those of P_4O_6 and P_4O_8. **Fig 11.2 (c)**



(a) P_4O_6 (= $2P_2O_3$) (b) P_4O_8 (= $2P_2O_4$) (c) P_4O_{10} (= $2P_2O_5$)

Fig. 11.2 (a) Structure of P_4O_6 (b) Structure of P_4O_8 (c) Structure of P_4O_{10}.

The structure of As_2O_5, Sb_2O_5 and Bi_2O_5 are not known.

11.6.2 Oxoacids:

Nitrogen forms four oxo acids, *viz*. Hyponitrous acid ($H_2N_2O_2$), nitrous acid (HNO_2), nitric acid (HNO_3) and pernitric acid (HNO_4). Phosphorous forms a number of oxo acids which can be classified according to formal charge of the phosphorous atom. The oxo acids of other elements (H_3AsO_3& H_3AsO_4, H_2SbO_3 (unstable), $HBiO_3$ etc.) are, perhaps, not so important and their details do not appear in the literature.

Properties:

(i) **$H_2N_2O_2$**

(a) On exposing to air, the acid decomposes slowly giving HNO_2 and HNO_3 but aqueous solution of the acid decomposes on heating to give N_2O.

$$2H_2N_2O_2 + 3O_2 \longrightarrow 2HNO_2 + 2HNO_3$$

$$H_2N_2O_2(aq.) \longrightarrow N_2O + H_2O$$

(b) It is a weak dibasic acid, soluble in water and organic solvents. It acts as a reducing agent and is oxidised by acidified $KMnO_4$ to nitrate.

$$5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 \longrightarrow 8MnSO_4 + 10HNO_3 + 4K_2SO_4 + 12H_2O$$

(ii) **HNO_2** (the readers have studied this acid in detail earlier, hence only a short account is being given here)

(a) It is also a weak acid, unstable and even in cold undergoes auto decomposition. At higher temperature, it decomposes into NO and NO_2.

$$3HNO_2 \xrightarrow[\Delta]{} HNO_3 + 2NO + H_2O$$

$$2HNO_2 \longrightarrow H_2O + N_2O_3 \rightleftharpoons NO + NO_2$$

(b) It is a good oxidising agent due to liberation of O-atom.

$$2\ HNO_2 \longrightarrow 2NO + H_2O + O$$

It oxidises $H_2S \rightarrow S$, $KI \rightarrow I_2$, $SnCl_2 \rightarrow SnCl_4$, $SO_2 \rightarrow H_2SO_4$,

$FeSO_4 \rightarrow Fe_2(SO_4)_3$, $AsO_3^{3-} \rightarrow AsO_4^{-}$ etc.

(c) It also acts as a reducing agent due to its easy oxidation to HNO_3

$$HNO_2 + O \quad HNO_3 \longrightarrow$$

It reduces $X_2 \rightarrow X^-$ (X=Br, I), $H_2O_2 \rightarrow H_2O$, $MnO_4^- \rightarrow Mn^{2+}$ (acid), $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (acid) etc.

(iii) **HNO_3** (The details of this acid have been studied by the readers in previous classes, hence only a short description will be given here.)

(a) Nitric acid is a strong oxidising agent because of its easy decomposition to give nascent oxygen.

$2HNO_3 \rightarrow 2NO_2 + H_2O + O$

Thus non-metals, e.g. S, I_2, C, P etc, metalloid (As etc.) are converted to acids, most of the metals except Au, Pt etc, are attacked by HNO_3. Some of them like Sn and Sb give oxides and others form nitrates. During the reaction, depending on the concentration of the acid, temperature and nature of the metal, various by-products such as NO, NO_2, N_2O, NH_2OH or even NH_3 are obtained.

(b) Mg and Mn are the only metals which liberate H_2 from dilute HNO_3.

$Mg + 2HNO_3 \text{ (dilute)} \longrightarrow Mg(NO_3)_2 + H_2\uparrow$

(c) 1 part of conc. HNO_3 and 3 part of conc. HCl is known as aqua regia dissolves even the noble metals, *viz*. Au, Pt etc due to the action of nascent chlorine on the metals.

$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl$ (nascent chlorine)

(d) It produces NO_2^+ ions (nitronium) in presence of conc. H_2SO_4 which cause nitration of organic compounds by replacing hydrogen.

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

$C_6H_6 + NO_2^+ + HSO_4^- \longrightarrow C_6H_5NO_2 + H_2SO_4$

$HSO_4^- + H_3O^+ \longrightarrow H_2SO_4 + H_2O$

$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

(e) HNO_3 shows strong acidic property: $HNO_3 \rightleftharpoons NO_3^- + H^+$.

Thus it reacts with metal salts forming metal nitrates**.**

(iv) **Hypophosphorous acid** (H_3PO_2), a mono basic acid ($H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$) and ortho phosphorous acid (H_3PO_3), a dibasic acid ($H_3PO_3 \rightleftharpoons 2H^+ + HPO_3^{2-}$) show similar properties, i.e. on heating give PH_3 and are reducing agents:

$2H_3PO_2 \longrightarrow PH_3 + H_3PO_4$

$4H_3PO_3 \xrightarrow{200^0C} 2H_3PO_4 \underset{\Delta}{+} PH_3$

$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$

$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H$

(liberation of H makes them strong reducing agents).

(v) Hypophosphoric acid ($H_4P_2O_6$) is a tetra basic acid ($H_4P_2O_6 \rightleftharpoons 4H^+ + P_2O_6^{4-}$) and decomposes to H_3PO_3 and HPO_3 on heating above its melting point.

$H_4P_2O_6 \longrightarrow H_3PO_3 + HPO_3$

But when heated at 180^0C gives PH_3 along with acids.

$4H_4P_2O_6 \longrightarrow 2H_3PO_4 + 4HPO_3 + PH_3$

On hydrolysing it gives H_3PO_4 and H_3PO_3.

(vi) **Ortho phosphoric acid (H_3PO_4)** is a tri basic acid ($H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$) and is an important member of acid series of P.

(a) Action of heat. When heated strongly it gives a series of products as given below:

$$2H_3PO_4 \xrightarrow[-H_2O]{250^{0}C} H_4P_2O_7 \xrightarrow[-H_2O]{320^{0}C} 2HPO_3 \xrightarrow[\text{red heat, }-H_2O]{600\text{-}700^{0}C} P_2O_5$$

(b) Reaction with alkalies. It forms three series of salts with alkalies.

$$H_3PO_4 \xrightarrow[-H_2O]{+NaOH} \underset{\text{primary}}{NaH_2PO_4} \xrightarrow[-H_2O]{+NaOH} \underset{\text{secondary}}{Na_2HPO_4} \xrightarrow[-H_2O]{+NaOH} \underset{\text{tertiary sod. phosphate}}{Na_3PO_4}$$

(b) Reaction with magnesia mixture. It reacts with magnesia mixture ($MgCl_2 + NH_4OH$) to produce a white ppt. of NH_4MgPO_4 (ammonium magnesium phosphate).

$$H_3PO_4 + MgCl_2 + NH_4OH \longrightarrow NH_4Mg\,PO_4 + 2HCl + H_2O.$$

(c) Reaction with ammonium molybdate. When phosphoric acid and phosphates are treated with conc. HNO_3 and ammonium molybdate, a canary yellow ppt. of ammonium phosphomolybdate is obtained on warning $\triangle$ to about $57^{0}C$.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{yellow ppt.}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

(vii) Pyrophosphoric acid ($H_4P_2O_7$) is a tetra basic acid ($H_4P_2O_7 \rightleftharpoons 4H^+ + P_2O_7^{4}$) but forms only two types of salts, i.e. $M_4P_2O_7$ and $M_2P_2O_7$ type. On heating it gives metaphosphoric acid (HPO_3).

$$H_4P_2O_7 \xrightarrow{217^{0}C} 2HPO_3 + H_2O$$

(viii) Meta phosphoric acid (HPO_3) is also known as glacial phosphoric acid. Its aqueous solution is gradually converted into H_3PO_4 on standing.

$$H_3PO_4 + H_2O \longrightarrow H_3PO_4 \text{ (ortho acid)}$$

(ix) Peroxy phosphoric acids are the derivatives of H_2O_2, i.e. H_3PO_5 and $H_4P_2O_8$.

Structures of oxo acids:

$H_2N_2O_3$. This acid is said to contain an azo group, -N=N- and assigned the structure, HO –N=N-OH. Because of the double bond, *cis-trans* isomerism may be there. But experimental evidences support the *trans*-structure of the acid. **Fig 11.3 (a)**

HNO_2. The infra- red study of the acid vapour has proposed the *trans* structure for the acid. Raman and X-ray study of crystalline salts of the acid have shown that NO^{-}_{2} ion has an angular structure as shown below: **Fig 11.3 (b)**

HNO_3. It is a mono basic acid, i.e. has replaceable hydrogen attached to N-atom through oxygen. The electron diffraction studies have indicated a planner structure to the acid in vapour state as shown here. NO_3^- ion has trigonal planner geometry (sp^2 hybridisation) postulated by VBT. **Fig 11.3 (c)**

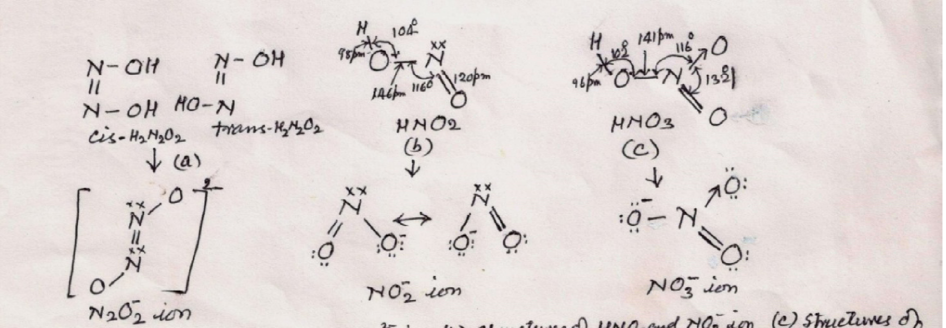


Fig. 11.3 (a) structures of $H_2N_2O_2$ and $N_2O_2^-$ ion (b) Structures of HNO_2 and NO_2^- ion (c) Structures of HNO_3 and NO_3^- ion.

Oxo acids of phosphorous :

The structure of various oxo acids of phosphorous have been shown in Fig. 11.4. In general various atoms or groups are arranged tetrahedrally around P atom (s) of the acids, i.e. there is no direct link between adjacent P-atoms.

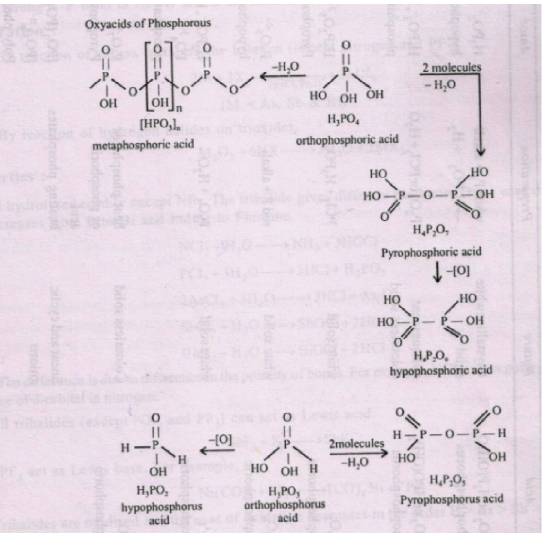


Fig. 11.4 Structures of oxoacids of phosphorus.

11.7 ANOMALOUS BEHAVIOUR OF NITROGEN

Nitrogen, the first element of the group VA, differs considerably, like other first elements of the respective earlier groups, from other elements of its group. This is, as stated earlier also, because of the inherent properties of nitrogen, i.e. its small size, high electro-negativity and non-availability of d-orbitals in the valence shell.

The main points of difference are:

(i) Nitrogen is a gas while other dements are solids.

(ii) Nitrogen molecule is diatomic (N_2) while other molecules are to tetra-atomic (P_4, As4, Sb_4 etc). This is due to the formation of p_π-p_π bond in nitrogen.

(iii) All the elements except N and Bi show allotropy.

(iv) Nitrogen occurs in free state in nature but other elements occur as ores.

(v) Nitrogen behaves as an inert (non-reactive) element but other elements are fairly reactive. This is because N≡N bond is present in N_2 and other elements have low M-M bond energy.

(vi) Nitrogen shows a large number of oxidation states, e.g. -3(NH_3), -2(N_2H_4), -1(NH_2OH), +1(N_2O), +2(NO), +3(N_2O_3), +4(NO_2) and +5(N_2O_5). Other elements do not show such a variety of oxidation states.

(vii) Its trihydride, NH_3, is highly stable and non-poisonous while the trihydrides of the other elements are progressively less stable and poisonous. Also, hydrogen bonding occurs only in NH_3 and not in other MH_3 compounds.

(viii) NCl_3 is explosive, highly reactive and unstable while the trichlorides of the remaining elements are more stable and less reactive. N does not form pentahalides but other elements except Bi form such halides because N cannot expand its octet due to the non-availability of d-orbitals in the valence shell.

(ix) Maximum coordination number of nitrogen is 4 and that for other elements is 6, e.g. $[M F_6]^-$

11.8. SUMMARY

The text of the study material of this unit contains the introductory part along with a detailed account of the general characteristics of the nitrogen group elements such as their electronic configuration, occurrence, physical state, elemental structure, metallic and non-metallic character, hardness, atomic radius and atomic volume, ionisation energy, electronegativity, heat of atomisation, melting and boiling points, oxidation states, electron donor- acceptor properties, allotropy, catenation, electrical and thermal conductivity, chemical reactivity etc. The preparation and properties of hydrides and halides of these elements have been given in detail along with their structural aspects. The properties and structure of oxides and oxo acids have been discussed elaborately with examples. At the end, the points of anomalous behaviour of nitrogen in contrast to other elements of its family have been mentioned.

11.9 TERMINAL QUESTIONS

i. The penultimate shell of phosphorous has

(a) $1s^2$ configuration

(b) $2s^2p^6$ configuration

(c) $3s^2p^6d^{10}$ configuration

(d) $2s^2p^6d^{10}$ configuration

ii. The elements that do not form pentahalides are:

(a) N and P

(b) N and As

(c) P and As

(d) N and Bi

iii. Hydrazoic acid is a hydride of

(a) N

(b) P

(c) As

(d) Sb

iv. Among the pentoxides, the strongest oxidising agent is

(a) N_2O_5

(b) P_2O_5

(c) As_2O_5

(d) Sb_2O_5

v. The only metals which liberate H_2 on reacting with dilute HNO_3 are

(a) Zn and Sn

(b) Mn and Sn

(c) Cu and Zn

(d) Mg and Mn

11.10 ANSWERS

i. (b)

ii. (d)

iii. (a)

iv. (a)

v. (d)

Literature Consulted (List of Books)

1. *Principles of Inorganic Chemistry* : B.R. Puri, L.R. Sharma and K.C. Kalia, Milestone publishers and Distributers, Meerut (2013)
2. *Advanced Inorganic Chemistry* : Satya Prakash, G.D. Tuli, S.K. Basu and R.D. Madan, Vol I, 17Ath Edn., S. Chand & Co. Ltd., New Delhi (1998)
3. *Comprehensive Inorganic Chemistry* : Sulekh Chandra, NewAge International (P) Ltd., Publishers, New Delhi (2004)
4. *Satya Prakash's Modern* : R.D. Madan, S. Chand & *Inorganic Chemistry* Company Ltd., New Delhi (1997)

UNIT 12: ELEMENTS OF GROUP - 16

CONTENTS:

12.1 OBJECTIVES

This unit will help readers to answer the following questions:

(a) What are Chalcogens?

(b) How elements of 16-group are useful?

(c) What is dπ-pπ bonding?

(d) What are the structures of oxides and oxoacides of 16-group elements?

(e) How oxygen is different from other elements in the group?

12.2 INTRODUCTION

In continuation of group-15 elements, within this unit you will learn about general properties, structure and uses of 16-group elements. There are five elements in this group, of which the first four are non-metals. All the elements of this group are solid except oxygen. Oxygen, sulphur and selenium are non-metals, tellurium metalloid while polonium is metallic in nature. These are also called as chalcogens. Chalcogens means ore-forming elements, as a large number of metal ores are oxides or sulphides.

Several reagents of this group element are commercially important. Sulphuric acid (H_2SO_4), sodium sulphite (Na_2SO_3) and hydrogen peroxide (H_2O_2) are some of them. The elements can be divided into metal (polonium, Po) and non-metals (oxygen, sulphur, selenium and tellurium; O, S, Se and Te).

Oxygen shows different properties from the other members of this family because oxygen has strong tendency to form π bond while sulfur has greater tendency to form chains and rings. Selenium, tellurium and polonium form toxic compounds which should be handled with great care.

12.3 GENERAL CHARACTERISTICS AND USES

Atomic radius, density and metallic character increase from oxygen to polonium while ionization potential decreases from oxygen to polonium. Oxygen is a diatomic gas while sulphur, selenium and tellurium are octa-atomic S_8, Se_8 and Te_8. Electronic configurations of each element of this group are given below. All elements except oxygen exhibit –2, +2, +4 and +6 oxidation states. All the elements of 16th group exhibits allotropy. Se, S, Te, Po and oxygen have 6, 4, 2, 2 and 2 allotropes, respectively. Out of 6 allotropes of Se, three are red non metallic, one amorphous red and two grey metallic forms. Allotropes of sulphur are α–(rhombic or octahedral sulphur), β-(monoclinic or prismatic sulphur), γ-(monoclinic sulphur) and λ– (plastic) sulphur. Te has one metallic and one non-metallic allotrope while Po has 2 allotropes; one α–cubic and the other β–rhombohedral. The two allotropes of oxygen are O_2 (oxygen) and O_3 (ozone). Elements of group 16 form a number of binary and ternary compounds. Among binary compounds; hydrides, halides and oxides are the main compounds.

Sixteenth group elements (VIA group) form H_2M type hydrides. All hydrides are covalent in nature.. All hydrides are poisonous gases with unpleasant and foul smell. Group 16 elements form monohalides (M_2X_2 type), dihalides (MX_2 type), tetrahalides (MX_4 type) and hexahalides (MX_6 type) where M is an element of 16th group and X may be F, Cl, Br or I. The oxides formed by group 16 elements are dioxides (MO_2 type) and trioxides (MO_3 type). Other important ternary complexes formed by elements of 16th group are oxoacids (-ous and -ic acids) such as sulphurous (H_2SO_3) and sulphuric (H_2SO_4) acids, sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) etc.

Electronic configuration of 16 group elements

Oxygen (O) – $1s^2 2s^2 2p^4$

Sulphur (S) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Selenium (Se) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

Tellurium (Te) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^4$

Polonium (Po) - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^4$

We know that dioxygen (O_2) is used in respiration by both plants and animals. Besides this, it is also used in steel plants. Along with air, dioxygen is used in blast furnaces for the reduction of iron-oxides to impure pig iron by coke. Dioxygen is also used in oxy-acetylene welding, metal cutting, manufacture of HNO_3 from NH_3 and ethylene oxide from ethane. Titanium dioxide is used as a white pigment in paint and paper and as filler in plastics. Dioxygen is also used as oxidant in rockets. Sulphur is the minor constituent of certain amino acids such as cystine, cysteine and methionine. Sulphuric acid (H_2SO_4) is used for making fertilizers while sulphite (SO_3^{2-}), hydrogen sulphites (HSO_3^-) and sulphur dioxide (SO_2) are used in bleaching. Sulphur is also used in the manufacture of carbon disulphide (CS_2), rubber, fungicides, insecticides and an explosive–gunpowder. Both sulphur and selenium dehydrogenate saturated hydrocarbons. Selenium metal (Se) is used to decolorize glass. Photoreceptors of photocopiers are made up of selenium. Selenium is an essential trace element and a component of many enzymes such as glutathione and peroxidase. When taken in larger quantity, it becomes toxic to the human beings. Tellurium (Te) is used in the manufacture of steel and non-ferrous alloys. Selenium and tellurium when absorbed in human body, excreted as foul smelling organic compounds along with breath and sweat. Polonium (Po) is a radioactive element.

12.4 OXIDES OF SULPHUR

Sulphur mainly forms dioxides (SO_2), trioxide (SO_3) and sesquioxide (S_2O_3).

12.4.1 Sulphur dioxide (SO_2).

12.4.1.1 Preparation:

Sulphur dioxide can be prepared by

(i) Burning sulphur (S) or sulphide ores in excess of air. This is the **commercial process** of SO_2 production.

$S + O_2 \rightarrow SO_2$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

(iii) Reaction of concentrated H_2SO_4 with Cu turnings, S, charcoal, Ag and Hg (**Laboratory method**)

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2\ 2H_2O$

(iii) Large amount of SO_2 is produced as a waste product during coal and/or other fossil fuel burning. This SO_2 is harmful for environment.

12.4.1.2 Properties:

Physical properties

Sulphur dioxide is a colourless gas with suffocating smell. It solidified at –76ºC and liquefied to a colorless liquid at –10ºC.

Chemical properties

The different chemical properties of SO_2 are given below:

(i) At 1200ºC, it decomposes into SO_3 and S.

$3S + O_2 \rightarrow 2SO_3 + S$ (at 1200^0C)

(ii) SO_2 is an **acidic oxide**. In aqueous solution, it shows acidic properties.

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulphurous acid)

Due to its acidic nature, it also reacts with basic oxides to form sulphides.

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

$SO_2 + CaO \longrightarrow CaSO_3$

(iii) Formation of addition compounds

As maximum covalency of sulphur atom is six, SO_2 (with four covalency), can form addition compound with O_2, Cl_2, PbO_2 and BaO_2 to attain maximum covalency of six.

$$SO_2 + O_2 \xrightleftharpoons{Pt\ or\ V_2O_5} 2SO_3$$

$$SO_2 + Cl_2 \xrightleftharpoons[or\ camphor]{Sunlight} SO_2Cl_2$$

$$SO_2 + PbO_2 \xrightleftharpoons{\Delta} PbSO_4$$

(iv) **Oxidizing properties**

SO_2 (S = +4) acts as a good oxidizing agent with strong reducing agents and reduces itself to S (S = 0).

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

$$SO_2 + 2CO \longrightarrow 2CO + S$$

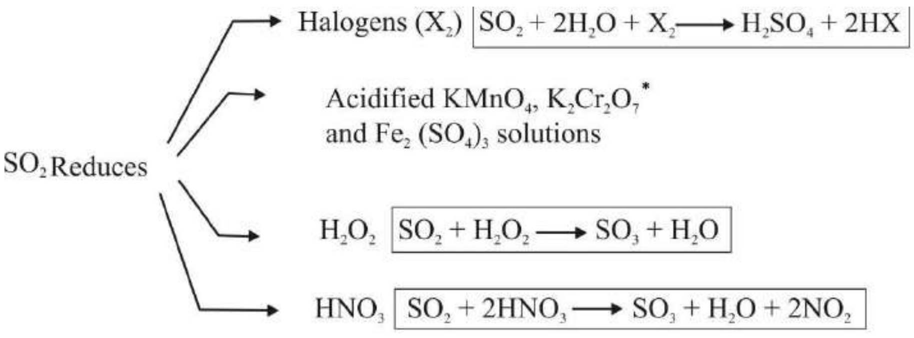
$$SO_2 + 4HCl + 2SnCl_2 \longrightarrow 2SnCl_4 + 2H_2O + S$$

(v) **Reducing properties**

In presence of moisture, SO_2 can act as reducing agent as it liberates nascent hydrogen on reaction with moisture (The nascent hydrogen acts as a reducing agent).

$$\underset{(moisture)}{SO_2 + H_2O} \longrightarrow SO_3 + 2H$$

During reduction process, SO_2 get oxidized to SO_3 or H_2SO_4.



$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$3SO_2 + K_2CrO_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO4)_3 + H_2O$$

$$SO_2 + 2H_2O + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 \quad 2H_2SO_4$$

12.4.1.3 Uses:

(i) SO_2 is used for the production of other chemicals such as $NaHSO_3$, Na_2CO_3 and $Na_2S_2O_3$

$$2SO_2 + Na_2CO_3 + H_2O \longrightarrow \underset{\substack{\text{Sodium bisulphite}\\ \text{(sodium hydrogen sulphite)}}}{2NaHSO_3} + CO_2$$

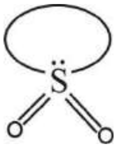
$$2NaHSO_3 + Na_2CO_3 \longrightarrow \underset{\text{Sodium sulphite}}{2Na_2SO_3} + H_2O + CO_2$$

$$Na_2SO_3 + S \xrightarrow{\text{heat}} \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

(ii) SO_2 is also used as a non-aqueous solvent. Liquid SO_2 is a useful solvent as a number of inorganic and organic compounds are soluble in this solvent.

12.4.1.4 Structure:

In the first excited state, sulphur attains $3s^2 3p^3 3d^1$ valence shell configuration. Then it undergoes sp^2 hybridization. Sulphur forms two bonds two σ bonds (p□ –p□ , p□ –d□) with oxygen atoms. The bond angle is 119º30’. Due to the presence of one lone pair of electyrons on S atom, its geometry became V-shaped.



12.4.2 Sulphur trioxide (SO_3):

12.4.2.1 Preparation

Sulphur trioxide can be prepared by the following methods:

(i) Oxidation of SO_2

$$2SO_2 + O_2 \xrightleftharpoons[400^o\text{-}450^o]{Pt} 2SO_3$$

$$SO_2 + H_2O_2 \longrightarrow SO_3 + H_2O$$

(ii) By the reaction of HNO_3 with SO_2

$$SO_2 + 2HNO_3 \longrightarrow 2NO_2 + SO_3 + H_2O$$

(iii) By the reaction of NO_2 with SO_2

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

(iv) By heating pyrosulphuric acid

$$H_2S_2O_7 + H_2O \xrightarrow{\Delta} H_2SO_4 + SO_3$$

12.4.2.2 Properties

(i) Physical properties

SO_3 exists in three following allotropic forms:

(a) α-form : chemically active form, ice-like transparent crystals with m.p. 17ºC

(b) β-form: Needle-like white crystals, above 50ºC. This form changes to α-form. The m. p. is 32.5ºC.

(c) γ–form: like β-form and obtained by complete drying of β-form. Its m.p. is 62.2ºC at 2 atm. pressure.

(ii) Acidic nature

In aqueous solution, it shows acidic properties, hence, acidic in nature.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

SO_3 also reacts with basic oxides to form corresponding sulphates

$$BaO + SO_3 \longrightarrow BaSO_4$$

(iii) Dissociation

SO_3 dissociates into SO_2 and O_2 at 1000ºC.

$$2SO_3 \longrightarrow 2SO_2 + O_2$$

(iv) Reaction with H_2SO_4

With conc. H_2SO_4, SO_3 forms pyrosulphuric acid (fuming sulphuric acid / oleum)

$$SO_3 + \text{conc. } H_2SO_4 \longrightarrow \underset{\text{Pyrosulphuric acid}}{H_2S_2O_7}$$

(v) Oxidizing property

Sulphur trioxide is a good oxidizing agent. During oxidation, SO_3 reduces to SO_2.

$$5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$$
$$SO_3 + 2HBr \longrightarrow SO_2 + Br_2 + H_2$$
$$SO_3 + PCl_3 \longrightarrow SO_2 + Cl_2 + POCl_3$$

(vi) Reaction with H_2O_2

SO_3 reacts with H_2O_2 to form per-oxy monosulphuric acid (H_2SO_5)

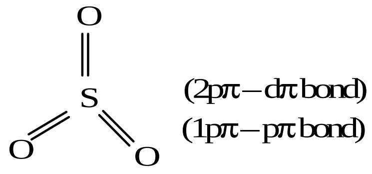
$$SO_3 + H_2O_2\ (\text{anhydreres}) \longrightarrow \underset{\text{Peroxy monosulphuric acid}}{H_2SO_5}$$

12.4.2.3 Uses:

SO_3 is used in manufacture of H_2SO_4 and $H_2S_2O_7$ and also as drying agent of gases.

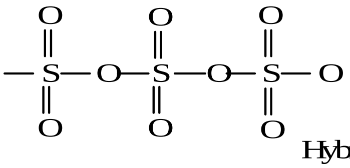
12.4.2.4 Structure of SO_3.

SO_3 molecule in gaseous state exists as monomer with trigonal planar geometry. In solid state, α-form exists as a trimer $(SO_3)_3$ having ring structure; β and γ-forms are dimeric, $(SO_3)_2$ with linear layer structure. In SO_3 molecule, sulphur is sp^2 hybridized.



Hybridization on sulphur is sp^2

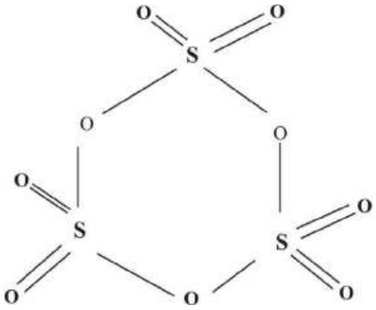
Trigonal planar geometry of gaseous SO_3 molecule



$$-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O$$

Hybridization on sulphur is sp^2

Structure of β & γ-forms of SO_3 (Linear layer structure)



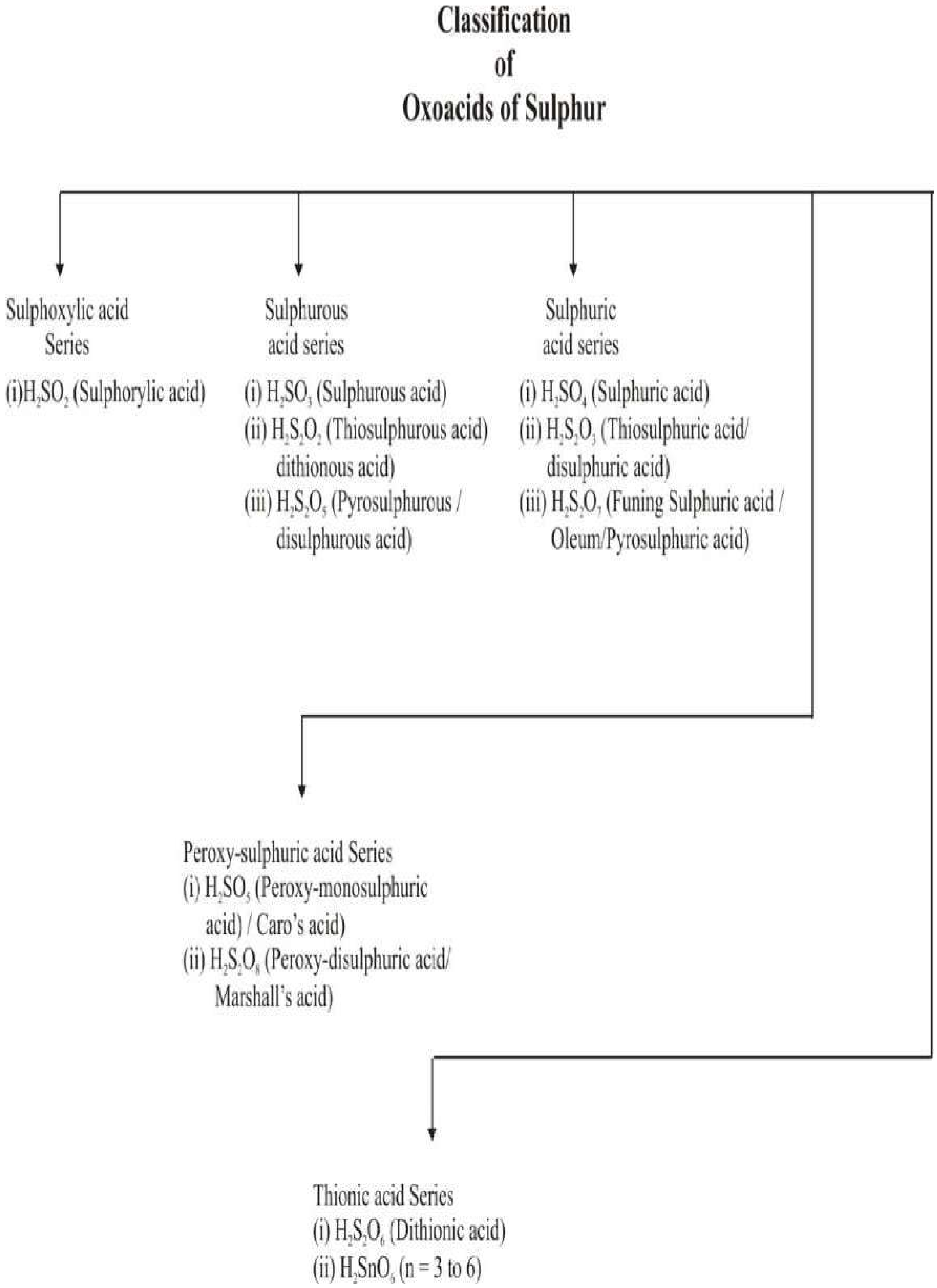
(Hybridization on sulphur is SP^3
Structure of α - form of SO_3
(cyclic trimer)

The other oxides formed by sulphur are S_2O, S_2O_3, S_6O to $S_{10}O$. The oxides from S_6O to $S_{10}O$ can be prepared by dissolving the cyclo forms of S_6, S_7, S_8, S_9 and S_{10} in CS_2 or CH_2Cl_2 and oxidizing with trifluoroperoxoacetic acid (CF_3COOOH) at –10ºC to –30ºC.

These compounds are orange-yellow in colour and have original rings of S-atoms. One oxygen atom attached via a double bond to one of the ring S-atom.

12.5 OXOACIDS OF SULPHUR.

Sulphur forms a number of oxoacids. The acids exist either in free State or in the form of their solutions or salts. Sulphur forms mainly four series of oxoacids as shown in the following flow chart (Flow chart 12.1)



Flow chart 12.1 Classification of oxoacids of sulphur

Polythionic acids include $H_2S_3O_6$ (trithionic acid), $H_2S_4O_6$ (Tetrathionic acid), $H_2S_5O_6$ (Pentathionic acid) and $H_2S_6O_6$ (hexathionic acid).

12.5.1 Sulphurous acid series:

This series includes sulphurous acid (H_2SO_3), thiosulphurous acid ($H_2S_2O_2$), pyrosulphurous acid or disulphurous acid ($H_2S_2O_5$) and hyposulphuric acid ($H_2S_2O_4$).

12.5.1.1 Sulphurous acid (H_2SO_3)

This acid is unstable and is known only in solution.

(a) Preparation:

(i) SO_2 on dissolution in water, forms sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

(ii) Reaction of thionyl chloride ($SOCl_2$) with water generates H_2SO_3.

$$SOCl_2 + 2H_2O \longrightarrow H_2SO_3 + 2\,HCl$$

(b) Properties:

(i) Acidic nature:

H_2SO_3 is dibasic in nature. It ionizes in two stages :-

$$H_2SO_3^- \rightleftharpoons H^+ + HSO_3 \text{ (Bisulphite ion)}$$

$$HSO_3^- \rightleftharpoons H^+ + HSO_3^{2-} \text{ (Sulphite ion)}$$

Thus, sulphurous acid forms two types of salts, namely bisulphites and sulphites.

(ii) Decomposition:

The solution of H_2SO_3 decomposes at 150ºC to form H_2SO_4.

$$3H_2SO_3 \xrightarrow{\triangle} 2H_2SO_4 + H_2O + S$$

(iii) Oxidising properties:

During oxidation of other substances, it reduces itself into sulphur.

$$H_2SO_3 + 2H_2S \longrightarrow 3S + 3H_2O$$

$$H_2SO_3 + 2SnCl_2 + 4HCl \longrightarrow S + 3H_2O + 2SnCl_4$$

$$H_2SO_3 + 2Hg_2Cl_2 + 4HCl \longrightarrow S + 3H_2O + 4HgCl_2$$

$$H_2SO_3 + 2CO \longrightarrow S + H_2O + CO_2$$

$$H_2SO_3 + 3Mg \longrightarrow 2MgO + MgS + H_2O$$

$$H_2SO_3 + 3Fe \longrightarrow 2FeO + FeS + H_2O$$

$$H_2SO_3 + 4HI \longrightarrow S + 3H_2O + 2I_2$$

(iv) Reducing properties:

H_2SO_3 also acts as reducing agent and during reduction of certain substances, it is oxidized to H_2SO_4.

$$H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$$

$$H_2SO_3 + H_2O + \underline{X_2} \longrightarrow H_2SO_4 + \underline{2HX}$$

$$5H_2SO_3 + 2K\underline{Mn}O_4 \longrightarrow K_2SO_4 + 2\underline{Mn}SO_4 + 2H_2SO_4 + 3H_2O$$

$$3H_2SO_3 + K_2\underline{Cr_2}O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underline{2Cr}\,(SO_4)_3 + 4H_2O$$

$$H_2SO_3 + H_2O + \underline{Fe}_2\,(SO_4)_3 \longrightarrow 2H_2SO_4 + \underline{2Fe}SO_4$$

$$5H_2SO_3 + 2KIO_3 \longrightarrow 4H_2SO_4 + K_2SO_4 + H_2O + I_2$$

(v) Bleaching properties:

Nascent hydrogen liberated during oxidation of certain substances by H_2SO_3, changes coloured matter to colourless matter. Hence, H_2SO_3 can acts as a bleaching agent.

$$H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$$

Coloured matter + H ⟶ Colourless matter

The bleaching action of H_2SO_3 is temporary, as colourless matter can again regains its colour when exposed to air.

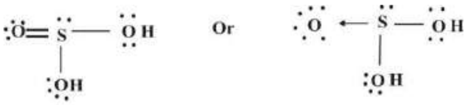
$$\text{Colourless matter} + \underset{\text{(air)}}{\text{O}} \longrightarrow \text{Coloured matter}$$

(c) Uses:

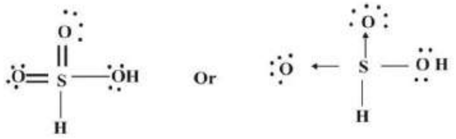
H_2SO_3 is used as an oxidizing agent and reducing agent in many reduction and oxidation reaction.

(d) Structure of H_2SO_3:

Two structures have been proposed for sulphurous acid.



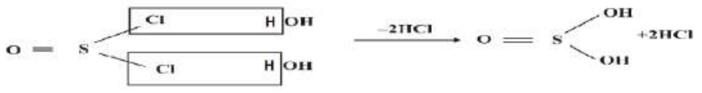
I Structure



II Structure

Support for structure I

(i) H_2SO_3 is prepared by the hydrolysis of $SOCl_2$ which is symmetrical.

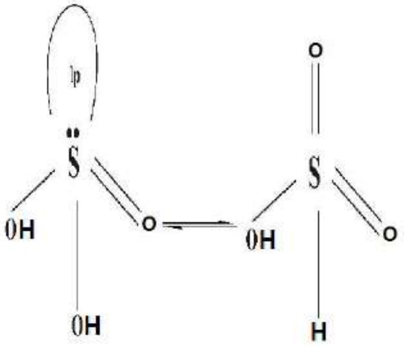


(ii) H_2SO_3 is a dibasic acid and this indicates symmetrical structure for H_2SO_3.

Support for structure II

Reaction of $NaHSO_3$ with KOH forms $NaKSO_3$ while of $KHSO_3$, with NaOH form $KNaSO_3$. Both $NaKSO_3$ and $KNaSO_3$ have different structures. If H_2SO_3 has symmetrical structure, $NaKSO_3$ and $KNaSO_3$ should have the same structures. Thus H_2SO_3 is unsymmetrical in shape.

You can see that the above reactions support both symmetrical and asymmetrical structures. Hence, the actual structure of H_2SO_3 is the tautomeric mixture of these two structures.

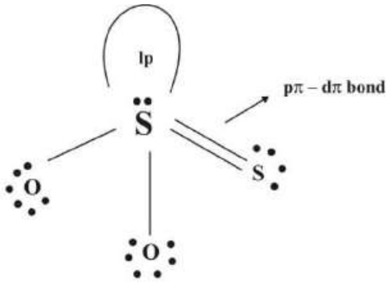


Trigonal pyramidal Tetrahedral

12.5.1.2 Thiosulphurous acid ($H_2S_2O_2$):

When one oxygen is replaced by sulphur in H_2SO_3, it is known as thiosulphuric acid. It is a dibasic acid

$H_2S_2O_2$ is trigonal pyramidal in shape and hybridization on sulphur is sp^3.



Structure of $S_2O_2^{2}$ ion (thiosulphite ion)

12.5.1.3 Hyposulphurous acid ($H_2S_2O_4$):

It is also called as dithionous acid.

(a) Preparation:

Zinc hyposulphite on reaction with $Ca(OH)_2$ and oxalic acid ($H_2C_2O_4$) forms hyposulphurous acid.

$$ZnS_2O_4\,(aq) + Ca\,(OH)_2 \longrightarrow CaS_2O_4\,(solution) + Zn(OH)_2\,ppt$$

$$CaS_2O_4 + H_2C_2O_4 \longrightarrow CaC_2O_4 + H_2S_2O_4\,(\text{Hyposulphurous acid})$$

(b) Properties:

(i) Acidic nature:

It is a dibasic acid and gives only one type of salts with $S_2O_4^{2-}$ ions.

(ii) Decomposition:

Hyposulphurous acid decomposes on heating to sulphurous acid.

$$2H_2S_2O_4 \xrightarrow{\triangle} 2H_2S_2O_3$$

$$H_2S_2O_3 \longrightarrow H_2SO_3 + S$$

(iii) Reducing properties:

This acid is strong reducing agent. During reduction of the other substances, they themselves oxidize to sulphite or bisulphite.

$$H_2S_2O_4 + 2H_2\,O \longrightarrow 2H_2SO_3 + 2H$$

$$H_2S_2O_4 + 2H_2\,O \longrightarrow 2HSO_3^- + 2H^+ + 2e^-$$

(iv) Oxidation:

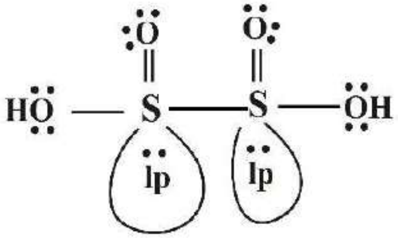
$H_2S_2O_4$ solution easily oxidized in presence of air to $H_2S_2O_5$.

$$2H_2S_2O_4 + O_2 \longrightarrow 2H_2S_2O_5$$

(c) Uses: The acid is used as reducing agent.

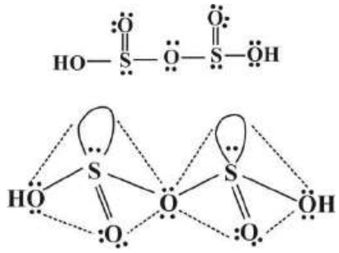
(d) Structure of $H_2S_2O_4$:

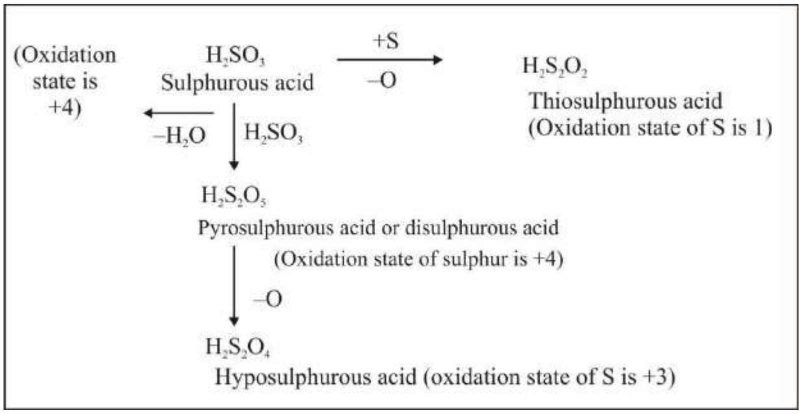
Each sulphur atom in hyposulphurous acid is sp^3 hybridised.



12.5.1.4 Pyrosulphurous acid ($H_2S_2O_5$):

This acid is also called as disulphrous acid. It is also a dibasic acid. Each sulphur atom is sp^3 hybridised and consists of two SO_3 molecules joined together through oxygen atom (Flow chart 12.2).





Flow chart 12.2 Flow chart to learn sulphurous acid series

12.5.2 Sulphuric acid series:

12.5.2.1 Sulphuric acid

It is also known as oil of vitriol and formula is H_2SO_4.

(a) Preparation:

(i) Lead chamber process:

Mixture of SO_2, air and NO is treated with steam to form H_2SO_4. Nitric oxide (NO) acts as a catalyst in this process.

$$2SO_2 + O_2 + 2H_2O + [NO] \longrightarrow 2H_2SO_4 + [NO]$$

(ii) Contact process:

This is a four step process. In the first step, SO_2 is prepared, in the second step, SO_3 is formed, in third step, $H_2S_2O_7$ and in the last step, H_2SO_4 is formed.

$$S + O_2 \longrightarrow SO_2 \text{ .... Step 1}$$

$$SO_2 + O_2 \xrightleftharpoons{V_2O_5} 2SO_3 \text{ .... Step 2}$$

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ .... Step 3}$$

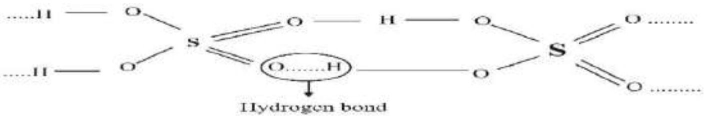
Oleum/Fuming
Sulphuric acid

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

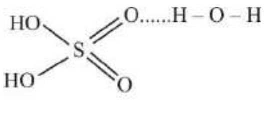
Sulphuric
acid

(b) Properties:

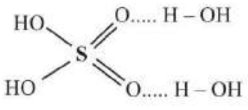
(i) Pure H_2SO_4 is a colourless liquid and forms a constant boiling mixture with water. Its boiling point is very high (340ºC) and this is due to the hydrogen bond between its molecules.



(ii) H_2SO_4 is soluble in water and this is an exothermic reaction. Heat is produced during dilution and may be due to the formation of hydrates like H_2SO_4, H_2O, H_2SO_4. $2H_2O$.



$H_2SO_4.H_2O$



$H_2SO_4.2H_2O$

$$2H_2SO_4 + Ca_3(PO_4)_2 + 5H_2O \longrightarrow [Ca\,(H_2PO_4).\,H_2O + 2\,(Ca\,SO_4.2H_2O)]$$

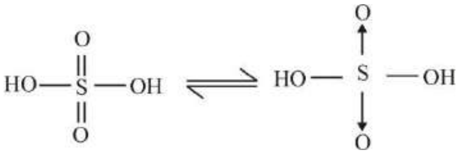
Superphosphate of lime

(c) Uses

H_2SO_4 is used in manufacturing of fertilizer, explosives, many chemicals like Na_2CO_3, alums, metal sulphates etc., in storage batteries, as laboratory regent and an oxidizing and dehydrating agents.

(d) Structure of H_2SO_4:

Actual structure of H_2SO_4 is the resonance hybrid of the following two structures:



In these structures, S is sp^3 hybridized and the geometry is tetrahedral.

12.5.2.2 Thiosulphuric acid ($H_2S_2O_3$):

(a) Preparation:

Thiosulphuric acid is stable at –78ºC but unstable at ordinary temperature. It is prepared by the reaction of SO_3 with H_2S.

$$SO_3 + H_2S \longrightarrow H_2S_2O_3$$

(b) Properties:

The acid is unstable, hence, decomposes easily to give SO_2 and sulphur.

$$H_2S_2O_3 \longrightarrow S + SO_2 + H_2O$$

or

$$S + H_2SO_3$$

(iii) Acidic nature:

It is a dibasic acid and forms bisulphate ion (HSO_4^-) and sulphate ion (SO_4^{2-}) when dissolved in water. It reacts with alkali to form salt and water.

(ii) Oxidising properties:

Hot concentrated sulphuric acid is a powerful oxidizing agent and reduces itself to SO_2 when reacts with reducing agents.

$$2H_2SO_4 + C \longrightarrow 2H_2O + 2SO_2 + CO_2$$
$$5H_2SO_4 + 2P \longrightarrow 2H_3PO_4 + 5SO_2$$
$$2H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2 + 2H_2O$$
$$2H_2SO_4 + Zn \longrightarrow ZnSO_4 + SO_2 + 2H_2O$$
$$H_2SO_4 + 2HBr \longrightarrow SO_2 + 2H_2O + Br_2$$
$$H_2SO_4 + H_2 \longrightarrow 2H_2O + SO_2$$
$$5H_2SO_4 + 8KI \longrightarrow H_2S + 4K_2SO_4 + 4H_2O + 4I_2$$

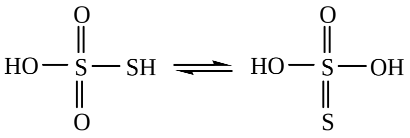
Besides these properties, H_2SO_4 can react with Ba (+2) and Pb (+2) salts to form insoluble sulphates, with SO_2 to form oleum and also used in the manufacturing different types of fertilizers like superphosphate of lime and ammoniated phosphate sulphate.

$$H_2SO_4 + 3NH_3 + H_3PO_4 \longrightarrow (NH_4)(H_2PO_4).$$
$$(NH_4)_2SO_4$$

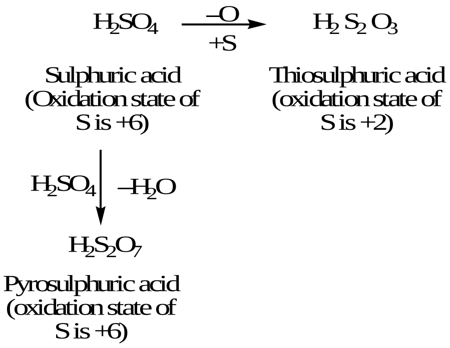
Ammonated phosphate sulphate

(d) Structure of $H_2S_2O_3$:

It is a dibasic acid and the actual structure is resonance hybrid of the following two structures.



In both the structures, central sulphur atom is sp^3 hybridized and hence, the geometry is tetrahedral.



Flow chart 12.3 Flow chart to learn sulphuric acid series

12.5.2.3 Pyrosulphuric acid, $H_2S_2O_7$:

It is also known as disulphuric acid or oleum.

(a) Preparation:

(i) It can be prepared by the reaction of SO_3 with conc. H_2SO_4.

$$SO_3 + \text{Conc. } H_2SO_4 \longrightarrow H_2S_2O_7$$

(b) Properties:

(i) Oleum is a brown oily liquid.

(ii) It is called as fuming sulphuric acid because it gives fumes in air.

(iii) It is dibasic and on warming, changes into H_2SO_4.

$$H_2S_2O_7 \xrightarrow{\text{Warm}} H_2SO_4 + SO_3$$

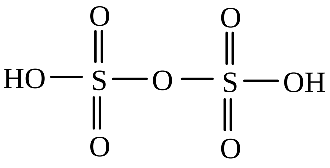
(iv) Pyrosulphuric acid solidifies on cooling below 0ºC. It is used in the preparation of dyes and explosives.

(c) Uses:

Oleum is used in the manufacture of explosives, drugs and dyes.

(d) Structure:

The acid is dibasic and each sulphur atom is sp^3 hybridised.



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

Structure of oleum

12.5.3 Peroxysulphuric acid series:

12.5.3.1 Peroxymonosulphuric acid) H_2SO_5):

This acid is also called as **Caro’s acid**.

(a) Preparation:

(i) By Caro's method (Reaction of potassium peroxydisulphate; $K_2S_2O_8$ with conc. H_2SO_4)

$$K_2S_2O_8 + H_2O \xrightarrow{\text{Conc. } H_2SO_4} K_2SO_4 + H_2SO_5$$

(ii) Ahrle's method (Reaction of SO_3 or Conc. H_2SO_4 on very concentrated H_2O_2).

$$SO_3 + H_2O_2 \longrightarrow H_2SO_5$$

$$\text{Conc. } H_2SO_4 + H_2O_2 \longrightarrow H_2SO_5 + H_2O$$

(iii) d'Ans and Friedrich method (Reaction of anhydrous H_2O_2 with chlorosulphuric acid, SO_2 (OH) Cl.

$$(OH)SO_2Cl + H_2O_2 \xrightarrow{-HCl} H_2SO_5 + HCl$$

(b) Properties:

(i) It is a white crystalline hydroscopic solid and its melting point is 45ºC.

(ii) It reacts with H_2O_2 and release O_2.

$$H_2SO_5 + H_2O_2 \xrightarrow{\triangle} H_2SO_4 + H_2O + O_2$$

(iii) With dil. H_2SO_4, H_2O_2 is obtained.

$$H_2SO_5 + H_2O \xrightarrow{\text{dil } H_2SO_4} H_2SO_4 + H_2O_2$$

(iv) Oxidizing properties

During oxidation of other substances, it reduces to sulphate. Nascent oxygen is responsible for its oxidizing action.

$$H_2SO_5 + 2FeSO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$H_2SO_5 + KX \longrightarrow K_2SO_4 + H_2O + X_2$$

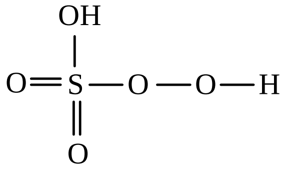
$$H_2SO_5 + Zn \longrightarrow ZnSO_4 + H_2O$$

(c) Uses:

Caro's acid is used for preparation of dyes, oxidation of olefins to glycols, oxidation of ketones to lactones or esters and in bleaching compositions.

(d) Structure:

H_2SO_5 is a mono basic acid. Sulphur atom is sp^3 hybridised. The two π–bonds (S = O) are pπ – dπ bonds.



$$O=\overset{\displaystyle OH}{\overset{|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-O-O-H$$

Structure of H_2SO_5

12.5.3.2 Peroxydisulphuric acid ($H_2S_2O_8$):

It is also called as Marshall's acid.

(a) Preparation

(i) Berthelot's method:

Reaction of SO_2, O_2, and H_2SO_4 give peroxydisulphuric acid.

$$SO_2 + O_2 + H_2SO_4 \longrightarrow H_2S_2O_8$$

(ii) Electrolysis of $(NH_4)_2SO_4$ aqueous solution containing H_2SO_4.

Aqueous solution of $(NH_4)_2SO_4$ in presence of H_2SO_4 forms peroxydisulphuric acid. Platinun is used as anode and graphite as cathode.

$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow 2NH_4HSO_4$$

$$NH_4HSO_4 \rightleftharpoons H^+ + [(NH_4)\ SO_4]^-$$

$$2\ [(NH_4)\ SO_4]^- \longrightarrow (NH_4)_2\ S_2O_8 + 2e^-\ \text{(anode)}$$

$$2H^+ + 2e^- \longrightarrow H_2(g)\ \text{(cathode)}$$

$(NH_4)_2\ S_2O_8$ quickly distilled with H_2SO_4 to obtain $H_2S_2O_8$.

$$(NH_4)_2\ S_2O_8 + H_2SO_4 \longrightarrow (NH_4)_2\ SO_4 + H_2S_2O_8$$

(iii) Eletrolysis of H_2SO_4 solution

Electrolysis of 50-60 % H_2SO_4 solution forms $H_2S_2O_8$ at anode. The anode is made up of platinum wire while cathode of copper wire.

$$H_2SO_4 \rightleftharpoons 2H^+ + 2HSO_4^-$$

$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^- \text{ (anode)}$$

$$2H^+ + 2e^- \longrightarrow H_2(g) \text{ (cathode)}$$

(iv) d'Ans and Friedrich method

Pure $H_2S_2O_8$ is formed by the reaction of H_2O_2 with chlorosulphuric acid.

$$\underset{\text{Chlorosulphuric acid}}{2(OH)SO_2Cl} + H_2O_2 \xrightarrow{-2HCl} \underset{\text{Peroxydisulphuric acid}}{(HO)\ SO_2 - O - O - SO_2\ (OH)}$$

(b) Properties:

(i) Peroxydisulphuric acid is a colourless, crystalline solid with melting point = 65ºC.

(ii) On heating, it releases O_2 and SO_3.

$$2H_2S_2O_8 \xrightarrow{\triangle} 2H_2SO_4 + 2SO_3 + O_2$$

(iii) It is used to prepare 30% H_2O_2. When $H_2S_2O_8$ is distilled with dil H_2SO_4, H_2O_2 yielded.

$$H_2S_2O_8 + H_2O \xrightarrow{\text{dil } H_2SO_4} 2H_2SO_4 + H_2O_2$$

(iv)On standing the aqueous solution of $H_2S_2O_8$ for some time, it gets hydrolysed into H_2SO_4 and H_2SO_5.

$$H_2S_2O_8 + H_2O \xrightarrow{\text{On standing}} H_2SO_4 + \underset{\text{Peroxy monosulphuric acid}}{H_2SO_5}$$

(v) Oxidizing properties

During oxidation of certain species, perdisulphuric acid reduces itself to SO_4^{2-}/HSO_4^-.

$$H_2S_2O_8 + FeSO_4 \longrightarrow Fe_2(SO_4)_3 + H_2SO_4$$

$$H_2S_2O_8 + Mn(OH)_2 \longrightarrow MnO_2 + 2H_2SO_4$$

Salt of perdisulphuric acid ($K_2S_2O_8$) oxidizes $AgNO_3$ to AgO, Cr to CrO_4^{2-}, I_2 to IO_3^- and KI to I_2.

$$K_2\,S_2\,O_8 + AgNO_3 \longrightarrow 2AgO + 2KHSO_4 + 2HNO_3 + + 2H_2O$$

$$\begin{aligned} 2K_2S_2O_8 + Cr + 4H_2O \longrightarrow\ & H_2CrO_4 + 3K_2SO_4 \\ & + 3H_2SO_4 \end{aligned}$$

$$5K_2S_2O_8 + I_2 + +6H_2O \longrightarrow 2HIO_3 + 5K_2SO_4 + 5H_2\,SO_4$$

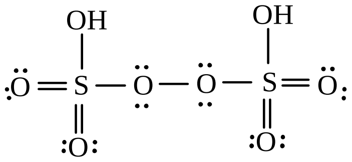
$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

(c) Uses:

Peroxydisulphuric acid is used as oxidizing and bleaching agent as it oxidizes aniline to aniline black and bleaches in indigo. It is also used in the preparation of H_2O_2 and photography.

(d) Structure:

Peroxydisulphuric acid is dibasic in nature and the two sulphur atoms are SP^3 hybridized. All the (S – O) π bonds are pπ – dπ bonds. The structure is



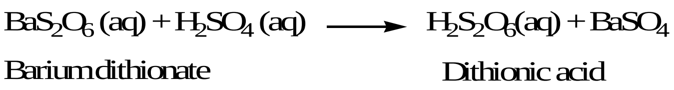
12.5.4 Thionic acid series:

12.5.4.1. Dithionic acid

This acid is present in solution. Its formula is $H_2S_2O_6$.

(a) Preparation:

Reaction of barium dithionate with weighed amount of H_2SO_4 produce dithionic acid.



$$\underset{\text{Barium dithionate}}{BaS_2O_6\,(aq)} + H_2SO_4\,(aq) \longrightarrow \underset{\text{Dithionic acid}}{H_2S_2O_6(aq)} + BaSO_4$$

(b) Properties:

The acid is stable only in solution and when we concentrate the solution; it decomposes to SO_2 and H_2SO_4.

$$H_2S_2O_6 \longrightarrow SO_2 + H_2SO_4$$

On hydrolysis, the acid gives H_2SO_4 and H_2SO_3.

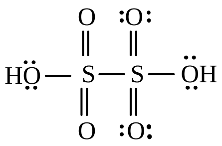
$$H_2S_2O_6 + H_2O \longrightarrow H_2SO_4 + H_2SO_3$$

(c) Uses:

Dithionates are good reducing agents

(d) Structure:

Dithionic acid is a dibasic acid. The two sulphur atoms are sp^3 hybridised and each of the π–bonds (S = O) is pπ – dπ bond. The two SO_3 units are joined via S – S bond to give $H_2S_2O_6$.



12.5.4.2 Polythionic acids ($H_2S_nO_6$; n = 3 to 6):

(a) Preparation:

(i) Direct hydrolysis of sulphur monochloride (S_2Cl_2): By this method, small quantities of $H_2S_3O_6$, $H_2S_4O_6$ and $H_2S_5O_6$ are obtained.

$$S_2Cl_2 + 3H_2O \rightarrow H_2SO_3 + H_2S + 2HCl$$

Sulphur monochloride

$$6H_2SO_3 + 2H_2S \rightarrow H_2S_3O_6 + H_2S_5O_6 + 6H_2O$$

$$3H_2 SO_3 + H_2 S \rightarrow H_2S_4O_6 + 3H_2O$$

(ii) Electrolytic oxidation of thiosulphate by H_2O_2, SO_2, I_2, $FeCl_3$ or electricity yields individual polythionates.

$$Na_2S_2O_3 + 3SO_2 \rightarrow 2Na_3 S_2O_6 + S$$

$$2Na_2S_2O_3 + 4H_2O_2 \xrightarrow{NaOH} Na_2S_3O_6 + 4H_2O + Na_2 SO_4$$

Cold solution)

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

$$2Na_2S_2O_3 + 2FeCl_3 \rightarrow Na_2S_4O_6 + 2FeCl_2 + 2NaCl$$

$$2S_2O_3^{2-} \xrightarrow[\text{oxidation}]{\text{Electrolytic}} S_4O_6^{2-} + 2e^-$$

(b) Properties:

(i) Solutions of different polythionates get decomposed on heating to SO_2 and S.

$$S_3O_6^{2-} \xrightarrow{\triangle} SO_4^{2-} + SO_2 + S$$

$$S_4O_6^{2-} \xrightarrow{\triangle} SO_4^{2-} + SO_2 + 2S$$

$$S_5O_6^{2-} \xrightarrow{\triangle} SO_4^{2-} + SO_2 + 3S$$

(ii) With sodium amalgam, $S_3O_6^{2-}$ form $S_2O_3^{2-}$ and SO_3^{2-}; $S_4O_6^{2-}$ yields only $S_2O_3^{2-}$ while with potassium amalgam, $S_5O_6^{2-}$ gives $S_2O_3^{2-}$ and S^{2-}.

$$S_3O_6^{2-} + 2Na \xrightarrow{Na/Hg} S_2O_3^{2-} + 2Na^+ + SO_3^{2-}$$

$$S_4O_6^{2-} + 2Na \xrightarrow{Na/Hg} S_2O_3^{2-} + 2Na^+$$

$$S_5O_6^{2-} + 4K \rightarrow 2S_2O_3^{2-} + S^{2-} + 4K^+$$

(iii) On reaction with S^{2-} (sulphide), $S_3O_6^{2-}$ gives only $S_2O_6^{2-}$ while $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ give a mixture of $S_2O_3^{2-}$ and sulphur.

$S_3O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-}$

$S_4O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + S$

$S_5O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + 2S$

$S_6O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + 3S$

(iv) On reaction with SO_3^{2-} (sulphite), $S_3O_6^{2-}$ gives no reaction while $S_4O_6^{2-}$, $S_5O_6^{2}$ and $S_6O_6^{2}$ give $S_2O_3^{2-}$ and lower polythionates

$$S_3O_6^{2-} \xrightarrow{SO_3^{2-}} \text{No reaction}$$

$$S_4O_6^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-} + S_3O_6^{2-}$$

$$S_5O_6^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-} + S_4O_6^{2-}$$

$$S_6O_6^{2-} + SO_3^{2-} \longrightarrow S_2O_3^{2-} + S_5O_6^{2-}$$

(v) **Reducing properties**

$S_3O_6^{2-}$ and $S_4O_6^{2-}$ get easily oxidized to SO_4^{2-} and H_2SO_4 in the presence of an oxidizing agent.

$4O + 2H_2O + S_3O_6^{2-} \rightarrow SO_4^{2-} + 2H_2SO_4$

$S_4O_6^{2-} + 3H_2O + 7O \rightarrow SO_4^{2-} + H_2SO_4$

Trithionic acid ($H_3S_3O_6$)

(a) Preparation:

(i) Trithionic acid is prepared by the action of sulphur monochloride with water.

$S_2Cl_2 + 3H_2O \rightarrow H_2SO_3 + H_2S + 2HCl$

$6H_2SO_3 + 2H_2S \rightarrow H_2S_3O_6 + H_2S_5O_6 + 6H_2O$

(ii) Reaction of potassium trithionate ($K_2S_3O_6$) with hydrofluosilic acid acid, H_2SiF_6.

$K_2S_3O_6 + H_2SiF_6 \rightarrow H_2S_3O_6 + K_2SiF_6$

(b) Properties:

(i) Trithionic acid decomposes on standing.

$$H_2S_3O_6 \rightarrow S + SO_2 + H_2SO_4$$

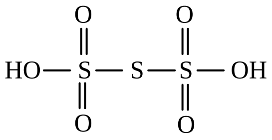
(ii) Trithionic acid does not react with $BaCl_2$ solution.

(iii) $H_2S_3O_6$ on reaction with $AgNO_3$ forms yellow precipitate of $Ag_2S_3O_6$

$$H_2S_3O_6 + 2AgNO_3 \rightarrow Ag_2S_3O_6 + 2HNO_3$$

(c) Structure:

In trithionic acid two sulphonic acid group (HSO_3) joined together via –S– link. The each sulphur atom of sulphonic acid is sp^3 hybridised and it is a dibasic acid. All the double bonds are $p\pi - d\pi$ type.



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Structure of trithionic acid

Tetrathionic acid ($H_2S_4O_6$)

(a) Preparation:

(i) Tetrathionic acid is also prepared by hydrolysis of S_2Cl_2.

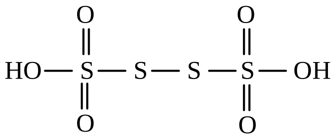
$$S_2Cl_2 + 3H_2O \rightarrow H_2SO_3 + H_2S + 2HCl$$

(ii) Tetrathionic acid is also prepared by the reaction of barium or lead tetrathinonate with measured quantity of dil H_2SO_4.

$$MS_4O_6 + H_2SO_4\ (dil) \rightarrow H_2S_4O_6 + MSO_4\downarrow \quad \text{where } M = Ba \text{ or } Pb$$

(c) Structure:

Tetrathionic acid is also a dibasic acid and here the two sulphonic acid units (HSO_3) are joined via – S – S – bond. The two sulphur atoms of sulphonic acid are sp^3 hybridised and all the π bonds are $p\pi - d\pi$ bonds.



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}S{-}S{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH}$$

Properties:

$H_2S_4O_6$ solution (aqueous solution) is stable, but it decomposes on heating.

$$H_2S_4O_6 \rightarrow H_2SO_4 + SO_2 + 2S$$

Pentathionic acid ($H_2S_5O_6$)

(a) Preparation:

Pentathionic acid is prepared by the reaction of H_2S with H_2SO_3 in solution.

$$5H_2S + 10H_2SO_3 \rightarrow 3H_2S_5O_6 + 12H_2O$$

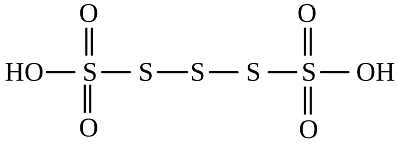
(b) Properties:

Pentathionic acid is stable in solution but decomposes on heating.

$$H_2S_5O_6 \rightarrow H_2SO_4 + SO_2 + 3S$$

(c) Structure:

Pentathionic acid is a dibasic acid. Two sulphonic acid (HSO_3) units are joined via –S–S–S– linkage. Each sulphur atom in sulphonic acid unit is sp^3 hybridised and all double bonds are $p\pi - d\pi$ bonds.



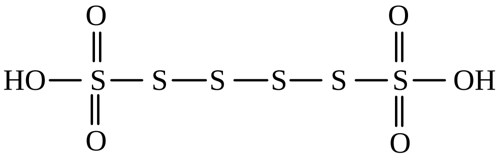
$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}S{-}S{-}S{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH}$$

Hexathionic acid ($H_2S_6O_6$)

This acid is also stable in solution. Its salt potassium haxathionate ($K_2S_6O_6$) is an important salt which is stable in the solid state.

Structure:

Hexathionic acid is a dibasic acid and two sulphonic acid units (HSO_3) are joined together by –S–S–S–S– unit to form hexathionic acid. The two sulphur atoms of sulphonic acid are units are sp^3 hybridized and all the π–bonds are pπ – dπ types.



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Structure of hexathionic acid

12.6 HALIDES OF SULPHUR

Halides of Sulphur

Sulphur forms the following type of halides with different molecular formula.

	MX_6	MX_4	MX_2	M_2X_2	$(MX_5)_2$
S	SF_6	SF_4 SCl_4	SF_2 SCl_2	S_2F_2 S_2Cl_2 S_2Br_2	$(SF_5)_2$

12.6.1 Preparation, Properties and structure of sulphur halides:

12.6.1.1 Dibalide (MX_2)

Sulphur form dihalides like SCl_2 and SF_2.

(a) Preparation:

Dihalides of sulphur can be prepared from sulphur monochloride

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

(b) Properties:

(i) Hydrolysis

SCl_2 is readily hydrolysed by H_2O.

$$2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$$

Or

$$2SCl_2 + 3H_2O \rightarrow S + H_2SO_3 + 4HCl$$

(ii) Action of NaF

SF_4 is obtained when SCl_2 is treated with NaF.

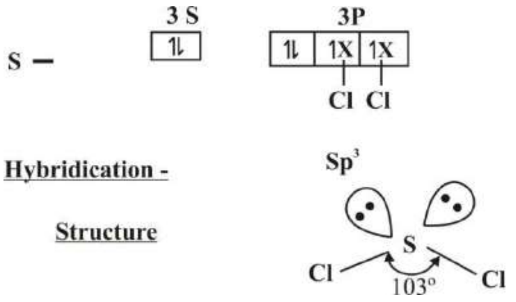
$$3SCl_2 + 4\ NaF \xrightarrow{75^oC} SF_4 + Na\ Cl + S_2\ Cl_2$$

(c) Stability

It is very unstable and decomposes easily.

(d) Structure

SCl_2 has angular structure (V–shaped) like H_2O with two lone pairs of electrons where the central atom, S is having sp^3 hybridization.



12.6.1.2 Tetrahalide (MX_4):

Sulphur forms tetrahalides like SF_4, SCl_4 but does not form SBr_4, SI_4.

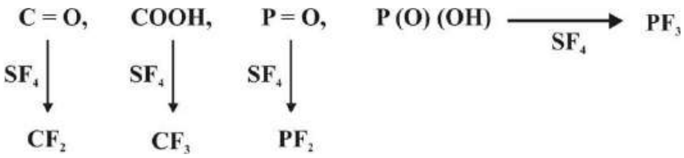
(a) Preparation:

$$S + 2Cl_2 \rightarrow SCl_4$$

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_4$$

(b) Properties:

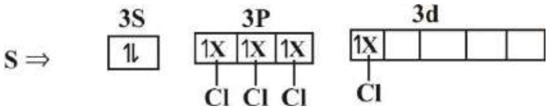
SF_4 is gaseous in nature. SF_4 is used as fluorinating agent.

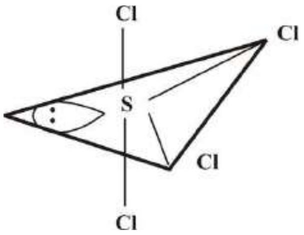


SCl_4 forms addition compounds with metal chlorides e.g. SCl_4, $AlCl_3$, SCl_4.

(c) Structure:

All the tetrahadides (MX_4) possess see saw geometry.The central atom S, undergoes sp^3d hybridization.





12.6.1.3 M_2X_2 Dimeric monohalide:

Sulphur can form M_2X_2 type halides e.g. S_2F_2, S_2Cl_2, S_2Br_2.

(a) Preparation:

$2AgF + 3S \text{ (Molten)} \rightarrow Ag_2S + S_2F_2$

$2S \text{ (fused)} + Cl_2 \rightarrow S_2Cl_2$

$3S + 2SOCl_2 \rightarrow 2S_2Cl_2 + SO_2$

$2S + SO_2Cl_2 \rightarrow S_2Cl_2 + SO_2$

$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ (Liquid mixture)

$2S + Br_2 \rightarrow S_2Br_2$

(b) Properties:

S_2F_2 is a gas while all other monahalides are liquids. On hydrolysis, S_2X_2 reduced to sulphur.

$$2S_2X_2 + 3H_2O \rightarrow 3S + H_2SO_3 + 4HX$$

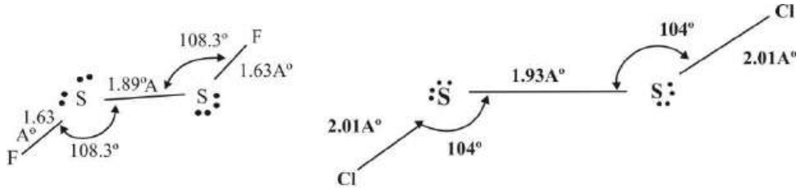
$$2S_2X_2 + 2H_2O \rightarrow 3S + SO_2 + 4HX$$

With chlorine, S_2Cl_2 forms SCl_2.

$$S_2Cl_2 + Cl_2 \xrightarrow{20^{\circ}C} 2SCl_2$$

(e) Structure:

These halides are like H_2O_2 in geometry having non-linear and non-planner structure.



Hybridisation of S ⇒ SP³

12.6.1.4 Hexahalide (MF_6):

Sulphur also forms SF_6.

(a) Preparation:

Sulphur hexafluoride can be prepared by the following reaction:

$$S + 3F_2 \rightarrow SF_6$$

(b) Properties:

SF_6 is extremely stable and chemically inert.

Covalent character

These fluorides have low boiling points and high volatility which indicates that these are highly covalent compounds.

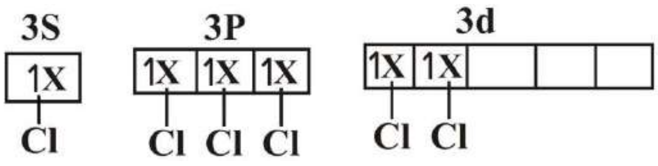
Action of boiling sodium

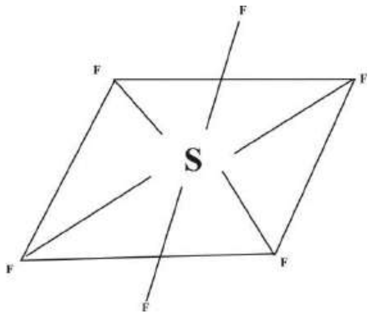
SF_6 gets decomposed, when it is passed through boiling sodium.

$SF_6 + 8Na \rightarrow Na_2S + 6NaF$

(c) Structure:

SF_6 has regular octahedron geometry





12.6.1.5 Dimeric sulphur pentafluoride $(SF_5)_2$ on S_2F_{10}

Only sulphur petafluroride is known and it is dimeric S_2F_{10}.

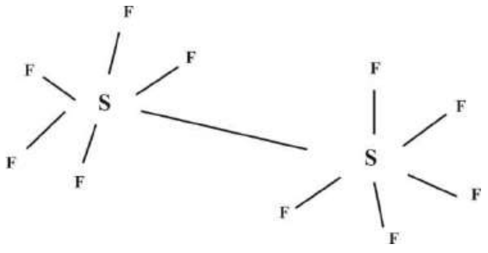
(a) Preparation:

It is obtained in traces along with SF_6 when sulphur is directly fluorinated.

(b) Properties:

It is dimeric liquid and is stable compound.

(c) Structure:



Structure of halides of sulphur at a glance

Type of (Formula)	**Name**	**Shape**	**Hybridization**
M_2X_2	Dimeric monohalide	Non-planner	sp^3
MX_2	Dihalide	V-Shaped	sp^3
MX_4	Tetrahalide	See-Saw	sp^3d
MX_6	Hexahalide	Octahedral	sp^3d^2
$(MX_5)_2$ or M_2X_{10}	Dimeric sulphur petafluoride	Dimer	sp^3d^2

12.7 *ANOMALOUS BEHAVIOUR OF OXYGEN*

Oxygen shows anomalous behaviour means, it is different from its other family members such as S, Te, Se and Po due to its small size, high electronegativity and ionization potential and absence of d-subshell in its valence shell. Generally all the first members of the p-block elements show anomalous behaviour due to the same reasons.

It is different from other family members in the following ways:

(a) Physical state-Oxygen is a diatomic gas while its other group members are polyatomic solids at room temperature.

(b) Oxidation state-The most stable oxidation state is -2, sometimes +2 (F_2O) and -1 (H_2O_2 or other peroxides) but not more than 2. The other family member elements show oxidation state beyond 2 (+4 or +6) due to the presence of vacant d-orbitals.

(c) Maximum covalency-Maximum covalency of oxygen is 2 while other elements have 6 covalency due to the presence of vacant d-orbitals.

(d) Magnetic behavior-Except oxygen, all the other member of this family are diamagnetic in nature. Oxygen is paramagnetic due to the presence of unpaired electrons in its antibonding molecular orbitals.

(e) Nature of compounds formed-Oxygen forms more ionic and polar covalent compounds as compared to the other members due to its high electronegativity. R–O–H, R–COOH, RCOR are polar in nature.

(f) Hydrogen bonding-Due to high electronegativity, it can form hydrogen bonds while the other elements cannot form hydrogen bond due to their large size. Hence, compounds of oxygen like H_2O, R-OH etc. have hydrogen bonding while compounds like H_2S and H_2Se are liquid and solid, respectively due to absence of hydrogen bond.

(g) Nature of bond-Oxygen has a tendency to form $p\pi$–$p\pi$ multiple bonding while other members have tendency to form $p\pi$–$d\pi$ bond.

12.8 SUMMARY

Sixteenth group has five elements naming, oxygen (O), sulphur (O), selenium (Se), tellurium (Te) and polonium (Po). These are p-block elements. These are also called as chalcogens (ore-forming). The periodic properties such as atomic radius, density and metallic character increases as we go from oxygen to polonium while the reverse was true for ionization potential. Sulphur, selenium and tellurium are octa-atomic (S_8, Se_8 and Te_8) while oxygen is a diatomic gas (O_2). Except oxygen, all the elements exhibit –2, +2, +4 and +6 oxidation states. All the elements of 16th group show allotropy. The 16th group elements form hydrides (H_2M), halides (M_2X_2, MX_2, MX_4 and MX_6). They have a tendency to form oxides of MO_2 and MO_3 type. These are the binary compounds formed by 16th group elements. The ternary compounds such as H_2SO_3, H_2SO_4 and $Na_2S_2O_3$, $5H_2O$ are also formed by these elements. The 16th group elements are very useful to various biological systems as;

i. O_2 is used in respiration by both plants and animals.

ii. Commercially, it is also used in steel plants, blast furnaces, welding, metal cutting, manufacture of HNO_3 and ethylene oxide, as oxidant in rockets.

iii. Sulphur is a minor constituent of certain amino acids such as cystine, cysteine and methionine. It is also used in manufacturing carbon disulphide, rubber, fungicides, insecticides and explosives.

iv. Selenium is also an essential trace element but becomes toxic to the human beings when taken in large quantities. It is an active part of many enzymes such as glutathione and peroxidase.

v. Selenium is useful for making red and pink coloured glass and photoreceptors for photocopiers.

vi. Tellurium is useful in the manufacturing of steel and non-ferrous alloys.

vii. Polonium is a radioactive in nature.

12.9 TERMINAL QUESTIONS.

A) State True (T) or False (F)

i. Chalcogens means ore-forming elements.

ii. Oxygen has strong tendency to form π bond while sulfur has greater tendency to form chains and rings.

iii. Oxygen is an octa-atomic gas.

iv. The two allotropes of oxygen are O_2 (oxygen) and O_3 (ozone).

v. Electronic configuration of tellurium (Te) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^4$.

vi. Oxygen is the minor constituent of certain amino acids such as cystine, cysteine and methionine.

vii. Sulphur is a radioactive element.

viii. Sulphur has a tendency to form addition compounds.

ix. During oxidation process, SO_2 reduces itself into sulphur.

x. SO_2 is trigonal planar in shape as sulphur atom is sp^2 hybridized.

xi. SO_3 is prepared by thermolysis of pyrosulphuric acid.

xii. SO_3 is used as drying agent of gases.

xiii. $SO_3\alpha$-form exists as linear layer structure.

xiv. Polythionic acids include $H_2S_3O_6$ (trithionic acid), $H_2S_4O_6$ (Tetrathionic acid), $H_2S_5O_6$ (Pentathionic acid) and $H_2S_6O_6$ (hexathionic acid).

xv. Sulphuric and sulphurous acids are dibasic acids.

xvi. H_2SO_3 oxidizes to H_2SO_4 during reduction of other substances.

xvii. H_2SO_3 has a strong bleaching action.

xviii. Thiosulphuric acid is trigonal pyramidal in shape and hybridization on sulphur is sp^3.

xix. Hyposulphurous acid is $H_2S_2O_4$.

xx. Oleum is fuming sulphuric acid.

xxi. Marshall’s acid is also called as peroxydisulphuric acid.

xxii. Oxidation state of sulphur in peroxysulphuric acid is 6.

xxiii. Trithionic acid is $H_3S_3O_7$.

xxiv. Sulphur pentafluoride is trimeric in nature.

B) Fill in the blanks

i. Allotropes of sulphur are ………………………………………………..

ii. ……………….. is also used in oxy-acetylene welding, metal cutting manufacture of HNO_3 from NH_3 and ethylene oxide from ethane.

iii. ……………… is used in the manufacture of steel and non-ferrous alloys.

iv. SO_3 reacts with H_2O_2 to form per-oxy ……………………………

v. $3H_2SO_3 + K_2\underline{Cr}_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underline{2C}r\,(SO_4)_3 + 4H_2O$ reaction shows …………………. property of sulphurous acid.

vi. ……………………… is also called as dithionous acid.

vii. Very high boiling point (340ºC) of sulphuric acid is due to the ………………………… between its molecules.

viii. …………………. acid is also called as Caro’s acid.

ix. Salt of perdisulphuric acid ($K_2S_2O_8$) oxidizes $AgNO_3$ to ………, Cr to ………, I_2 to …………. and KI to ………….

x. Dihalides of sulphur can be prepared from ………………………….

xi. Sulphur tetrafluoride possess ………………… geometry.

xii. Oxygen shows anomalous behaviour is due to its…………….., high ……………….. , …………….. and absence of ………………. in its valence shell.

C) Long answer questions

i. Write a note on general characteristics and uses of 16th group elements.

ii. How sulphur dioxide prepared? Give reactions.

iii. Describe in detail the structure of sulphur trioxide.

iv. Discuss oxoacids of sulphur in detail.

v. What are thionic acids. Write down it detail.

vi. Classify halides of 16th group elements with examples.

vii. Give in detail, preparation, properties and structure of sulphur halides.

viii. Oxygen is different from other members of the group. Explain.

12.10 ANSWERS

A) State True or False

i. T
ii. T
iii. F
iv. T
v. T
vi. F
vii. F
viii. T
ix. T
x. F
xi. T
xii. T
xiii. F
xiv. T
xv. T
xvi. T
xvii. T
xviii. F
xix. T
xx. T
xxi. T
xxii. T
xxiii. T
xxiv. F

B) Fill in the blanks

i. α–(rhombic or octahedral sulphur), β-(monoclinic or prismatic sulphur), γ-(monoclinic sulphur) and λ– (plastic) sulphur
ii. Dioxygen
iii. Tellurium (Te)
iv. monosulphuric acid (H_2SO_5)

v. reducing
vi. Hyposulphurous acid/ $H_2S_2O_4$
vii. hydrogen bond
viii. Peroxymonosulphuric
ix. AgO, CrO_4^{2-}, IO_3^- and I_2
x. sulphur monochloride
xi. see saw
xii. small size, electronegativity, ionization potential and d-sub shell

Bibliography

a) Br. R. Puri, L. R. Sharma and K. C Kalia. *Principles of Inorganic Chemistry*, Milestone Publishers & Distributors, Meerut, 2013.
b) G. S. Sodhi, *Textbook of Inorganic Chemistry*, Viva Books Private Limited, New Delhi, 2013.
c) M. S. Yadav. *Quick Review in Inorganic Chemistry*, Anmol Publications Pvt. Ltd., New Delhi, 2004.
d) P. Mishra, *Advanced Inorganic Chemistry*, Jagdamba Publishing Compan, New Delhi, 2011.
e) R. L. Madan, *Chemistry for degree students, B.Sc. I year*, S. Chand & Company Ltd., New Delhi, 2011.
f) S. Prakash, G. D. Tuli, S. K. Basu, and R. D. Madan. *Advanced Inorganic Chemistry*, Vol. I, S. Chand & Company Ltd., New Delhi, 2007.
g) W. U. Malik, G. D. Tuli, and R. D. Madan. *Selected Topics in Inorganic Chemistry*, S. Chand Publication, Delhi, 2013.

UNIT 13: ELEMENTS OF GROUP- 17

CONTENTS:

13.9 Anomalous behavior of fluorine

13.10 Summary

13.11 Terminal questions

13.12 Answers

13.1 OBJECTIVES

You will be able to answer the following questions after reading this unit.

(a) What are halogens?

(b) What are the characteristics and uses of halogens?

(c) Acidic behaviour of oxides and oxoacids.

(d) How fluorine is different from other halogens?

(e) What are the basic properties of halogens?

13.2 INTRODUCTION

Halogens belong to VIIA/17th group of the periodic table. It consists of five elements *viz.* flourine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are non metallic elements and also called halogens. The term halogen is derived from the Greek halo (=salt) and gens (=born) meaning salt producers because most of the elements exist in sea water, such as chlorides. Halogens contain 7 (seven) electrons in their valence shell. Astatine is radioactive. Flourine is the most electronegative, highly reactive and is called as super halogen. Halogens are not found in free state because they are highly reactive. They are found in sea water in the form of halides.

Astatine is a radioactive element and formed artificially. General electronic configuration of VIIth group elements is ns^2 np^5. They are very reactive and found in diatomic form like F_2, Cl_2, Br_2, I_2 (**Table 13.1**).

Table 13.1 Electronic configuration of halogen family

Elements	**Atomic no.**	**Electronic Configuration**	**Noble gas with configuration**
Fluorine (F)	9	$1s^2 2s^2 2p^5$	(He) $2s^2 2p^5$
Chlorine (Cl)	17	$1s^2 2s^2 2p^8 3s^3 3p^5$	(Ne) $3s^2 3p^5$
Bromine (Br)	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	(Ar) $3d^{10} 4s^2 4p^5$

Iodine (I)	53	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$	(Kr) $4d^{10}\ 5s^2\ 5p^5$
Astatine (At)	85	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2\ 6p^5$	(Xe) $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$

13.3 GENERAL CHARACTERISTICS AND USES

13.3.1 Physical properties of halogens (Table 13.2 and Table 13.3)

Table 13.2 Atomic halogens

Properties	**F**	**Cl**	**Br**	**I**	**At**
Atomic number	9	17	35	53	85
Atomic mass	19	35.45	79.90	126.90	210
Covalent radii (Å)	0.64	0.99	1.14	1.33	–
Ionic radii (Å)	1.33	1.84	1.96	2.20	–
Ionic enthalpy (KJmole^{-1})	1680	1256	1142	1008	–
Electronegativity	4	3.2	3	2.7	2.2
Electron affinity (KJmole^{-1})	–333	–349	–325	–296	–270

Table 13.3 Molecular halogens

Properties	**F_2 gas**	**Cl_2 gas**	**Br_2 liquid**	**I_2 solid**
Colour	Yellow	Green Yellow	Red Brown	Deep Violet
Density g/cm^3 (Liquid form)	1.51	1.66	3.19	4.94
Melting point (^{0}C)	-219	-101	–7	114
Boiling Point (^{0}C)	-188	-35	60	185
Bond length(Å)	1.43	1.99	2.28	2.66
Bond Dissociation Enthalpy (KJmole^{-1})	158.5	242.6	192.8	151.1

13.3.1.1 Physical state:

All halogen are non polar solvent and diatomic molecules and their physical state are

F_2	Cl_2	Br_2	I_2
Gas	Gas	Liquid	Solid

Difference in the physical state depends upon their van der Waals force which further depends on their atomic size and molecular weight. Size and atomic weight of chlorine and fluorine are less and thus, the van der Waals forces are weak. Hence, Cl_2 and F_2 are in gases phase. Size of Br_2 is more than Cl_2 and F_2 which is liquid and I_2 is much higher in size and it forms in solid phase.

13.3.1.2 Melting and boiling points:

As size of the elements in group increases, van der Waals force also increases and thus, m.p. and b.p. of molecules also increases. The order of m.p. and b.p. of the halogens follow the order:

$F_2 < Cl_2 < Br_2 < I_2$

13.3.1.3 Ionization enthalpy or ionization potential:

Due to the small atomic size, halogens have higher ionization energy and less power to remove electron to form X^+ ion. Ionization enthalpy increases down words in a group because their size increase.

$F > Cl > Br > I$ (I.P.)

13.3.1.4 Electronegativity:

Group 16 elements have higher electronegativity because of small size of the atoms and fluorine is most electronegative element in the periodic table.

$F > Cl > Br > I$ (see table 13.2)

13.3.1.5 Electron affinity:

Electron affinity of halogens upto chlorine increases and after chlorine decreases. Flourine has lower electron affinity because of the small size of fluorine. The outer most shell has higher electron density and due to electron-electron repulsion, it cannot gain electron easily.

13.3.1.6 Odour:

All the halogens have very pungent odours. If inhaled, even in very small quantities, they cause inflammation of the mucous membrane of the throat and nose. Thus, responsible for irritation of respiratory duct. Large quantities may have fatal effect.

13.3.1.7 Non metallic character:

All halogens are non metallic. Downward in a group, their non metallic character decreases and metallic character increases and iodine shows some metallic properties such as:

(i) Iodine is solid (ii) Iodine has metallic luster (iii) Iodine can form cation.

13.3.1.8 Bond energy and reactivity:

Halogens are diatomic molecules and iodine has the least bond energy because as the size increases, nucleus will be far apart from outermost shell. Thus, the subshell has weaker over lapping tendency. Bond energy of fluorine is less than chlorine and bromine due to the size of fluorine and non bonding electron-electron repulsion in fluorine molecule.

$Cl_2 > Br_2 > F_2 > I_2$ (Order of bond energy)

13.3.1.9 Oxidation state:

Electronic configuration of halogen family is ns^2np^5. It can gain $1e^-$ to attain noble gas configuration. Except fluorine, other elements of the group have d orbitals. Hence, fluorine shows (–1) oxidation state only. Other elements show –1, +1, +3, +5, +7 oxidation states.

13.3.1.10 Solubility of halogens:

Halogens are nonpolar in nature, hence, are slightly soluble in water. Their solubility decreases from Cl to I. Flourine is not soluble as it decomposes with water librating O_2 and O_3.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$

The halogens are more soluble in organic solvents like CCl_4, $CHCl_3$, CS_2 and hydrocarbons. In organic solvents like $CHCl_3$ and CCl_4, Cl_2 gives yellow, Br_2 gives brown colour and I_2 gives violet colour. In the presence of sun light, they are decomposed. Cl_2 is more reactive than Br_2.

Sun light

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$Br_2 + H_2O \rightarrow HBr + HBrO$$

13.3.2 Chemical properties of halogens:

Halogens are chemically more reactive due to high electronegativity, high electron affinity and low dissociation energy. Among halogens, F is the most reactive element and reactivity decreases as : F > Cl > Br > I.

13.4 HALIDES AND HALOGEN OXIDES

13.4.1. Characteristics of hydrogen halides:

Halides are mainly of three types: (i) Ionic halides like LiF, CaF_2, SrF_2, BaF_2 (ii) Molecular or covalent halides ($OsCl_4$, $OsBr_4$, BCl_3, PCl_3, PCl_5, CCl_4 etc.) and (iii) Bridging halides ($AlCl_3$, BeF_2, $BeCl_2$, HbF_5, TaF_5 etc).

Hydrogen halides have general formula HX, where X is halogen (Cl, Br, I, F). Their aqueous solutions are called as hydrohalic acids or halogen acids. All the halogens react with hydrogen to form hydrides (HX). Reactivity of halogens toward hydrogen decreases down a group. Fluorine violently reacts with hydrogen. Hydrogen reacts with chlorine very slowly in the dark, faster in day light and explosively in sunlight. Reaction of hydrogen with iodine is very slow at room temperature.

The other characteristics of hydrogen halides are discussed in following section.

(a) **Physical state:** Except HF which is liquid at room temperature, other halogen halides are found in gas state. In liquid state of HF, due to the intermolecular hydrogen bonding, the HF molecules associate with each other to form liquid. The other halogens do not form hydrogen bond and hence, they are gases at room temperature.

$$\cdots\cdots\overset{+S}{H}-\overset{-S}{F}\cdots\cdots\overset{+S}{H}\cdots\cdots\overset{-S}{F}\cdots\cdots\overset{+S}{H}\cdots\cdots\overset{-S}{F}$$

Hydrogen bonding in HF molecule

(b) **Thermal stability:** Stability of halides decrease from HF to HI. HF is highly stable and HI is the least. From HF to HI, thermal stability decreases.

HF > HCl > HBr > HI

This trend is observed due to the hydrogen bonding in HF.

(c) **Acidic behaviour:** Downwards in the group, the acidic nature increases because size increases and release of hydrogen become more easy.

HF < HCl < HBr < HI

(d) Reducing properties: Downwards in a group, reducing properties increase because bond energy decreases.

$HF < HCl < H Br < HI$

Order of reducing property

13.4.2 Oxides of halogens:

The electronegativity difference between the halogens and oxygen is very small; hence, the bonds in halogen oxides are covalent. Most of the oxides of halogens are unstable and explosive in nature (when exposed to light or shock). The oxides of iodine are the more stable then the chlorine oxides. While the oxides of bromine are very unstable as they decompose below room temperature. Oxides with higher oxidation states are more stable as compared to lower states.

The different oxides formed by halogens are OF_2, O_2F_2, F_2O_4, Cl_2O, ClO_2, Cl_2O_7, Cl_2O_6, ClO_3, Br_2O, BrO_2, I_2O_5, I_4O_9 and I_2O_4. Among these, ClO_2, Cl_2O, I_2O_5 and OF_2 are the most useful. ClO_2 is used in paper industry, bleaching clothes and purification of water. OF_2 and $Cl_2O_7$are strong oxidizing agents. In this section, you will read detailed chemistry of some halogen oxides.

Oxygen difluoride (OF_2)

It is a pale yellow gas used as an oxidizing agent and rocket fuel. It vigorously reacts with metals, S, P and halogens to give fluorides and oxides. It has V-shaped geometry as in case of H_2O molecule.

Dioxygen difluoride (O_2F_2)

It is an unstable orange yellow solid with oxidizing and fluorinating properties. Structurally, it is similar to H_2O_2.

Dichlorine monoxide (Cl_2O)

It is a yellow brown gas used in the preparation of hypochlorites such as NaOCl, $Ca(OCl)_2$, chlorinated solvents and as bleaching agent. It is also V-shaped but the bond angles of the three oxides (F_2O, Cl_2O, Br_2O) increases in following order:

$F_2O < Cl_2O < Br_2O$

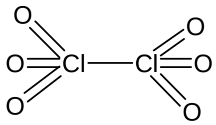
The different bond angles are due to the steric crowding of the larger halogen atoms.

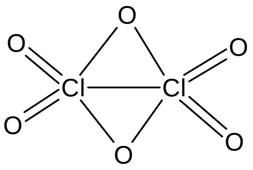
Chlorine dioxide (ClO_2)

It is a yellow gas and used for bleaching purpose, purifying drinking water and manufacturing $NaClO_2$. It is paramagnetic due to the presence of an odd electron. It does not dimerize because, the odd electron is delocalized.

Dichlorine hexaoxide (Cl_2O_6)

It is a dark red liquid and solidifies at –180ºC. It is a strong oxidizing agent and explodes when comes in contact with grease. The probable structure of Cl_2O_6 is–



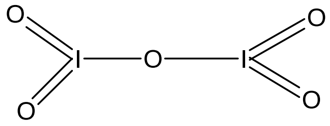


Dichlorine heptoxide (Cl_2O_7)

It is a colourless liquid and shock sensitive and less reactive than lower oxides.

Oxides of bromine are less important as those of chlorine. Br_2O is a dark brown liquid while BrO_2 is a pale yellow solid.

Oxides of iodine are more stable as compared the other halogen oxides. Iodine pentaoxide (I_2O_5) is useful in analyzing gases. I_2O_5 is having a three dimensional network.



The other iodine oxides are moderately or less stable.

13.5 OXOACIDS OF HALOGENS

The oxoacids formed by halogens are discussed in this section.

Halogen	Hypohalous acid	Halous acid	Halic Acid	Perhalic acid
	Oxidation No. +1	Oxidation No.+3	Oxidation No. +5	Oxidation No.+7
Chlorine (Cl)	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Bromine (Br)	HBrO	–	H BrO_3	$HBrO_4$
Iodine (I)	HIO	–	HIO_3	HIO_4

The above table shows that the oxidation number of the central atom is 1, 3, 5, 7 respectively. F is more electronegative than O atom and does not have orbital to receive the electron pair by back donation and it does not give any oxoacids.

13.5.1 Oxyacids of chlorine:

Hypochlorons acid (HClO)

The acid is known only in solution. HClO is prepared by

(i) Passing Cl_2 through H_2O or in to a suspension of $CaCO_3$

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$CaCO_3 + H_2O + 2Cl_2 \rightarrow CaCl_2 + CO_2 + 2HClO$$

(iii) The action of CO_2 with NaOCl

$$NaOCl + CO_2 + H_2O \rightarrow NaHCO_3 + HOCl$$

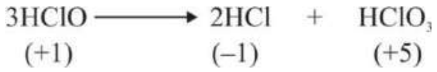
Properties:

(i) The concentrated solution of HClO is yellow, while the dilute solution is colourless. It is a weak acid.

(ii) Disproportion of the acid- the dilute solution of the acid is fairly stable in the dark but when concentrated solution exposed to light, it become unstable and disproportionate into Cl_2 and $HClO_3$.

$$5HClO \rightarrow 2Cl_2 + HClO_3 + 2H_2O$$

When aqueous solution of HClO is heated it undergoes disproportionation in to HCl and $HClO_3$.



$$\underset{(+1)}{3HClO} \longrightarrow \underset{(-1)}{2HCl} + \underset{(+5)}{HClO_3}$$

(iii) On distillation HClO decomposes into H_2O and Cl_2O.

$$2HClO \rightarrow Cl_2O + H_2O$$

(iv) Action on metals - it dissolves in Mg to give H_2

$$Mg + 2HClO \rightarrow Mg(OCl)_2 + H_2\uparrow$$

(v) Oxidizing and bleaching properties

The aqueous solution of HClO gives nascent oxygen [O] which shows oxidizing and bleaching properties.

$$HClO \xrightarrow{\text{Reduction}} HCl + O$$

(vi) Acidic nature

HClO is a monobasic in nature.

$$HClO\,(aq) \rightarrow H_{(aq)}^{+} + ClO_{(aq)}^{-}$$

$$NaOH + HClO \rightarrow NaOCl + H_2O$$

(vii) Action of $AgNO_3$

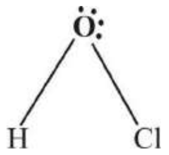
HClO reacts with $AgNO_3$ to give AgOCl which is unstable and give AgCl and $AgClO_3$.

$$HOCl + AgNO_3 \rightarrow AgOCl + HNO_3$$

$$3AgOCl \rightarrow AgCl + AgClO_3$$

Structure of HOCl:

It is V-shaped and oxygen is sp^3 hybridized.



Chlorous acid ($HClO_2$)

This acid is obtained in the aqueous solution by treating a suspension of barium chlorite with dilute H_2SO_4.

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow 2HClO_2 + BaSO_4\downarrow$$

$HClO_2$ can also be obtained when ClO_2 reacts with H_2O

$$2ClO_2 + H_2O \rightarrow 2HClO_2 + O_2$$

Properties:

(i) The freshly prepared solution of the acid is colourless but it soon decomposes into ClO_2.

(ii) It gives a violet colour with $FeSO_4$.

(iii) $HClO_2$ undergoes disproportionation on heating in an alkaline solution.

$5HClO_2 \rightarrow 4ClO_2 + NaCl$

(iv) $HClO_2$ shows oxidizing properties due to nascent oxygen.

$HClO_2 \rightarrow HCl + 2[O]$

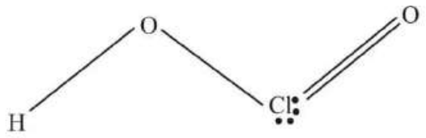
$HClO_2$ liberates I_2 from KI solution.

$HClO_2 + 2H_2O + 4KI \rightarrow 4KOH + HCl + I_2$

(v) In acid solution, $HClO_2$ rapidly decomposes as follows:

$4HClO_2 \rightarrow 2ClO_2 + HClO_3 + HCl + H_2O$

Structure:



Structure of $HClO_2$
(Chlorine is sp^3 hybridized with two lone pair of electrons)

13.5.1.3 Chloric acid ($HClO_3$):

This acid is the only oxoacid exists in solution. It can be prepared

(i) By the action of dil. H_2SO_4 on $Ba(ClO_3)_2$

$Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HClO_3$.

(ii) By the action of hydrofluosilicic acid (H_2SiF_6) on $KClO_3$

$2KClO_3 + H_2SiF_6 \rightarrow K_2SiF_6 + 2HClO_3$.

Properties:

(i) Concentrated solution of the acid is colourless and pungent smelling liquid.

(ii) It is stable in dark and in light, it decomposes and become yellow.

$3HClO_3 \xrightarrow{\Delta} 3HClO_4 + Cl_2 + 2O_2 + H_2O$

(iii) When organic substances like cotton, wool paper etc come in contact with the acid, they catch fire.

(iv) The acid is very powerful oxidizing and bleaching agent.

(v) When iodine is evaporated with $HClO_3$, iodic acid (HIO_3) is obtained.

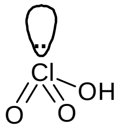
$2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$

This reaction is used for the preparation of HIO_3.

(vi) $HClO_3$ is a monobasic acid

$$HClO_3 \rightleftarrows H^+ + ClO_3^-$$

Structure of $HClO_3$:



Hybridization on chlorine is sp^3, with one lone pair of electron

13.5.1.4. Perchloric acid ($HClO_4$):

(i) It is prepared by heating $HClO_3$

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2 + 2O_2 + H_2O$$

(ii) Anhydrous acid is obtained by distilling a mixture of potassium per chlorate ($KClO_4$) with conc. H_2SO_4.

$$Ba(ClO_4)_2 + H_2SO_4 \rightarrow 2HClO_4 + BaSO_4\downarrow$$

Properties:

(i) Anhydrous $HClO_4$ is a colourless, mobile, hygroscopic and oily liquid. It fumes strongly in moist air and dissolves in water with a hissing sound due to the liberation of heat.

(ii) It forms hydrates with 1, 2, 2.5, 3 and 3.5 molecules of water as water of crystallization.

(iii) It is highly dangerous acid and produces wounds on the skin.

(iv) On dehydration with P_2O_5 at $-10^{\circ}C$, it gives Cl_2O_7.

(v) $HClO_4$ is the strongest acid among all the acids.

(vi) The metals like Zn, Fe etc dissolve in the aqueous $HClO_4$ solution and form the soluble per chlorates.

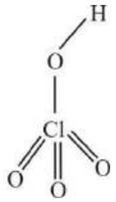
$$Zn + 2HClO_4 \rightarrow Zn(ClO_4)_2 + H_2\downarrow$$

(vii) The acid is not reduced by nascent hydrogen but get reduced to chlorine by the strong reducing agent like $SnCl_2$, $CrCl_2$ etc.

Uses:

The aqueous solution of the acid is used for the estimation of potassium grammatically.

Structure of $HClO_4$



In $HClO_4$, Chlorine atom is again sp^3 hybridized with three dπ-pπ

13.5.2 Oxoacids of bromine:

13.5.2.1. Hypobromous acid (HBrO):

Like HClO, HBrO is also known only in solution.

Preparation:

(i)It is prepared by shaking Br_2 water with freshly precipitated HgO or Ag_2O

$$2Br_2 + 2HgO + H_2O \rightarrow HgBr_2.\ HgO + 2HBrO$$

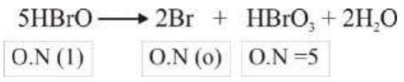
$$2Br_2 + Ag_2O + H_2O \rightarrow 2AgBr + 2HBrO$$

(ii)It is also obtained by distilling a mixture of Br_2 and concentrated $AgNO_3$ solution.

$$Br_2 + AgNO_3 + H_2O \rightarrow HBrO + HNO_3 + AgBr$$

Properties:

(i) The aqueous solution of the acid is starve-yellow in colour and is always contaminated with the products which are obtained due to the decomposition.



$$\underset{\boxed{O.N\ (1)}}{5HBrO} \longrightarrow \underset{\boxed{O.N\ (o)}}{2Br} + \underset{\boxed{O.N = 5}}{HBrO_3} + 2H_2O$$

(ii) HBrO is a strong oxidizing and bleaching agent. HBrO oxidizes H_2O_2 to O_2.

$HOBr + H_2O_2 \rightarrow H_2O + O_2 + HBr$

13.5.2.2. Bromic acid ($HBrO_3$):

Like $HClO_3$, $HBrO_3$ is also known in solution.

Preparation:

(i)By passing Cl_2 in bromine water.

$$Br_2 + 5Cl_2 + 6H_2O \rightarrow 2HBrO_3 + 10HCl$$

(ii)By shaking $AgBrO_3$ with bromine water

$$5AgBrO_3 + 3Br_2 + 3H_2O \rightarrow 5AgBr + 6HBrO_3$$

Properties:

(i) On evaporating the aqueous solution of the acid, it decomposes as follows :

$$4HBrO_3 \rightarrow 3Br_2 + 5O_2 + 2H_2O$$

(ii) The aqueous solution of $HBrO_3$ decomposes on heating and gives Br_2 and nascent oxygen (O) that acts as a good oxidizing agent.

$$2HBrO_3 \xrightarrow[\Delta]{\text{Reduction}} Br_2 + H_2O + 5\,(O)$$

Also reduces H_2S to sulphur.

$$2HBrO_3 + 5H_2S \rightarrow Br_2 + 6H_2O + 5(S)$$

Reduces SO_2 to H_2SO_4

$$2HBrO_3 + 5SO_2 + 4H_2O \rightarrow Br_2 + 5H_2SO_4$$

13.5.3 Oxoacids of iodine:

13.5.3.1 Hypoiodous acid (HIO):

It is also known only in solution like as HClO and HBrO.

Preparation:

It is prepared by shaking a solution of finally powdered iodine with freshly precipitated HgO

$$2I_2 + 2HgO + H_2O \rightarrow HgI_2.HgO + 2HIO$$

Properties:

It is the weakest acid of all the hypohalous acid. The acid acts as a very weak base, since it also gives OH^- ions

$$HIO \rightleftharpoons I^+ + O\overline{H}$$

Like HOCl and HOBr, HOI also undergo disproportionation forming I_2 and HIO_3.

$$5HIO \rightarrow 2I_2 + HIO_3 + 2H_2O$$

13.5.3.2 Iodic acid (HIO_3):

It is the most stable oxoacid of iodine.

Preparation:

(i) By oxidation of iodine with boiling conc. HNO_3.

$$I_2 + 10HNO_3 \rightarrow 3HIO_3 + 10NO_2 + 4H_2O$$

(ii) By passing Cl_2 into suspension of iodine in water.

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl.$$

(iii) By dissolving I_2O_4 in hot water.

$$5I_2O_4 + 4H_2O \rightarrow 8HIO_3 + I_2$$

Properties:

(i) It is colourless crystalline solid, very soluble in water but in soluble in alcohol.

(ii) **Action of heat:**

When heated at 240°C, it decomposes to give I_2O_5.

$$2HIO_3 \xrightarrow{240^\circ C} I_2O_5 + H_2O$$

(iii) **Action of metals:**

When reacts with Sn, Au, Pb or Zn, it evolves H_2 gas.

$$Zn + 2HIO_3 \rightarrow Zn(IO_3)_2 + H_2$$

(iv) **Oxidizing properties:**

Like $HBrO_3$, it also acts as a good oxidizing agent. During oxidation of other species, it itself reduced to I_2.

$$5H_2S + 2HIO_3 \rightarrow I_2 + 6H_2O + 5S$$

$$2HIO_3 + 5SO_2 + 4H_2O \rightarrow I_2 + 5H_2SO_4$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

(v) **Formation of salt:**

HIO_3 is a monobasic acid and it gives normal salt (e.g. KIO_3). On action of conc. H_2SO_4, I_2O_4 is obtained.

$$4HIO_3 + 2H_2SO_4 \rightarrow 2I_2O_4 + 2(H_2O)^+ HSO_4^- + O_2$$

13.5.3.3. Meta periodic acid (HIO_4):

Preparation:

It is obtained by heating para periodic acid (H_5IO_6).

$$H_5IO_6 \xrightarrow{100^0C} HIO_4 + 2H_2O$$

Properties:

i. It is a weak acid and dissociates as –

$$HIO_4 \rightleftharpoons H^+ + IO_4^-$$

ii. When dissolved in water, it changes back to H_5IO_6.

$$HIO_4 + 2H_2O \rightarrow H_5IO_6$$

iii. HIO_4 is a strong oxidizing agent in acidic medium and reduces itself to I_2.

$$2IO_4^- + 16H^+ + 14e^- \longrightarrow I_2 + 8H_2O$$

13.5.3.4. Paraperiodic acid ($HIO_4.2H_2O$ or H_5IO_6):

(i) It is obtained by decomposing silver mesoperiodate Ag_3IO_5 with Cl_2.

$$4Ag_3IO_5 + 6Cl_2 + 10H_2O \rightarrow 4H_5IO_6 + 12Ag\,Cl + 3O_2$$

(ii)By heating a suspension of I_2 in $HClO_4$.

$$2HClO_4 + I_2 \rightarrow 2H_5IO_6 + Cl_2$$

Properties:

i. It is a colourless crystalline solid and deliquescent in nature. It is soluble in water but slightly soluble in alcohol and ether.

ii. It is strong monobasic while weak dibasic acid in nature.

iii. When heated at 138ºC, it decomposes in to I_2O_5, H_2O and O_2.

$$2H_5IO_6 \xrightarrow{138^oC} I_2O_5 + 5H_2O + O_2$$

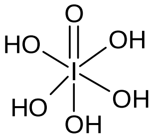
When heated in vacuum at 80ºC, $H_4I_2O_9$ is obtained. On further heating at 100ºC, HIO_4 is obtained and on heating at 140ºC, it gives HIO_3 and O_2.

$$2H_5IO_6 \xrightarrow[-3H_2O]{80^oC} H_4I_2O_9 \xrightarrow[-H_2O]{100^oC} 2HIO_4 \xrightarrow{140^oC} 2HIO_3 + O_2$$

iv. The acid is a very good oxidizing agent and liberates I_2 from KI in neutral and acidic medium.

$$H_5IO_6 + 7KI + 7HCl \rightarrow 4I_2 + 7KCl + 6H_2O$$

Structure of H_5IO_6



Octahedral structure of H_5IO_6

H_5IO_6 has octahedral structure due to sp^3d^2 hybridization of I atom.

13.6 INTERHALOGEN COMPOUNDS

Interhalogen compounds are the compounds of more than one halogen. General formula is AB_n, where A and B are halogens, A is heavier than B (n = 1, 3, 5, 7). Most of the interhalogen compounds are fluorides. They can be classified as:

i. Neutral – They are binary compounds such as BrF_3 or IF_7.
ii. Cations – They may be homonuclear I_2^+ or Cl_3^+ or heteronuclear $I_3Cl_2^+$.
iii. Anions – Polyhalide anion such as I_3^- or $IBrCl^-$.
iv. Covalent organic derivatives – $ArAF_n$ (Where Ar = arene; A = I or Br and n = 2 or 4).

13.6.1. General Properties:

(i) The interhalogen compounds are covalent diamagnetic molecules.
(ii) They are generally volatile solids or liquids except ClF which is a gas at 25ºC.

(iii) These are more reactive than parent halogens. All of them show halogenation reactions: (BrF_3, IF_5, ICl are good halogenating agents)

(iv) Interhalogens can be hydrolysed by water or alkali to produce halide ion of the lighter halogen.

$$AB + H_2O \rightarrow HB + HOA \text{ (AB type)}$$

(v) Interhalogens can add to alkenes (addition reaction)

$$H_2C = CH_2 + ICl \rightarrow ICH_2 – CH_2Cl$$

(vi) They are strong oxidants and can be used to halogenate metals and metal oxides.

(vii) They act as useful fluorinating agents. There reactivity order is as follows:

$$ClF_3 > BrF > BrF_5 > IF_7 > ClF > IF_5 > BrF$$

Thermal stability order of reactivity [(IF (1.5) > BrF (1.2) > ClF (1.0) > ICl (0.5) > IBr (0.3) > BrCl (0.2)]

(viii) These are used as non aqueous solvents.

(ix) They are polar in nature.

(x) Reactions with non-metallic and metallic oxides: when react with oxide, form corresponding fluorides

$$4BrF_3 + 3SiO_2 \rightarrow 3SiF_4 + 2Br_2 + 3O_2$$

(xi) Self ionization (halide ion transfer) – Show donor acceptor property (generally liquid interhalogens have this quality).

ICl, IBr, BrF_3, IF_5

13.6.2 Preparation:

(A) (AB type interhalogen) – (ClF, BrF, BrCl, ICl, IBr)

(i) Direct reaction of halogens

$$Cl_2 + F_2 \xrightarrow{225^0C} 2ClF$$

$$Br_2 + F_2 \xrightarrow{300^0C} 3BrF$$

$$I_2 + F_2 \xrightarrow{\text{Room Temp.}} 2IF$$

$$Cl_2 + ClF_3 \xrightarrow{300^0C} ClF$$

(ii) By direct reaction of halogens with interhalogen compounds

$$Br_2 + BrF_3 \longrightarrow 3BrF$$

(B) AB_3 type interhalogens

$$Cl_2 + 3F_2 \xrightarrow[\text{Cu or Ni}]{200\text{- }300^0C} 2ClF_3$$

$$ClF + F_2 \xrightarrow[\text{Cu or Ni}]{200\text{- }300^0C} ClF_3$$

$$Br_2 + 3F_2 \xrightarrow{\text{Room Temp}} 2BrF_3$$

$$BrF + F_2 \xrightarrow{\text{Room Temp}} BrF_3$$

$$F_2 + I_2 \xrightarrow{CCl_3F} 2IF_3$$

$$I_2 + 3XeF_2 \longrightarrow 2IF_3 + 3Xe$$

(C) AB_5 and AB_7 type interhalogens

$$Cl_2 + 5F_2 \xrightarrow{\text{Excess F2, }350^0C\text{ or }250^0\text{ atr.}} 2ClF_5$$

$$ClF_3 + F_2 \xrightarrow{\text{hv, room temp, 1 art}} ClF_5$$

$$I_2 + 5F_2 \xrightarrow{>150^0C} IF_5$$

$$I_2 + 5F_2 \xrightarrow{250^0\text{-}300^0C} IF_7$$

13.6.3 Chemical Properties:

(A) AB type is terhalogen compounds

i. **Halogenations reaction**

ClF is a good fluorinating agent and reacts with many metals or nonmetals either at room temperature or above and convert them to fluorides and liberate chlorine.

$W + ClF \rightarrow WF_6 + 3Cl_2$

$Se + 4ClF \rightarrow SeF_4 + 2Cl_2$

It can also act as a chlorofluorinating agent by addition across a multiple bond:

$$(CF_3)_2\,CO + ClF \xrightarrow{MF} (CF_3)_2\,CFOCl$$

$$CO + ClF \longrightarrow COFCl$$

$$5F_4 + ClF \xrightarrow{CSF} 5F_5\,Cl$$

$$\text{Reaction with water} \longleftarrow H_2O + 2ClF \longrightarrow 2HF + Cl_2O$$

$$HNO_3 + ClF \longrightarrow HF + ClONO_2$$

ii. **Donor acceptor property**

$BrF_3 + 2ClF \rightarrow [Cl_2F]^+ [BrF_4]^-$

iii. **As solvent system**

Both ICl and IBr partially dissociate into ions which gives rise to an electrical conductivity.

$ICl + MCl \rightarrow M^+ [ICl_2)^-$

$2ICl + AlCl_3 \rightarrow [I_2Cl]^+ [AlCl_4]^-$

$PCl_5 + ICl \rightarrow [PCl_4]^+ [ICl_2]^-$

$SbCl_5 + 2ICl \rightarrow [I_2Cl]^+ [SbCl_6]^-$

(B) AB_3 type interhalogen compounds

Properties:

ClF_3 and BrF_3 are volatile liquid whereas IF_3 and ICl_3 are solids. ClF_3 is the most reactive chemical compound. It reacts explosively with water and with most organic substances. BrF_3 is used for preparative work.

(i) Fluorinating agent

$2AgCl + ClF_3 \rightarrow 2AgF + Cl_2 + ClF$

$Co_3O_4 + 3ClF_3 \rightarrow 3CoF_3 + 3/2Cl_2 + 2O_2$

$NH_3 + 2ClF_3 \rightarrow 6HF + N_2 + Cl_2$

$U + 3\ ClF_3\ (l) \xrightarrow{50\text{-}90^\circ C} UF_6 + 3ClF$

$2ClF_3 \rightarrow (ClF_4)^- [Cl_2F]^+$

(ii) Donor acceptor property

$MF_5 + ClF_3 \rightarrow [ClF_2]^+ [MF_6]^-$ M = As, Sb or Pt

$MF + ClF_3 \rightarrow [ClF_4]^- [M]^+$ M = K, Rb or Cs

$BF_3 + ClF_3 \rightarrow (BF_4)^- [ClF_2]^+$

(iii) Self ionization

$2\ ClF_3 \rightleftharpoons ClF_2^+ + ClF_4^-$ (has high electrical conductivity)

BrF_3 is decomposed bigorously by water. It is very reactive and displaces oxygen from oxides such as B_2O_3, SiO_2, As_2O_3, CuO etc.

$4BrF_3 + 3SiO_2 \rightarrow 3SiF_4 + 2Br_2 + 3O_2$

(C) AB_5 and AB_7 type interhalogen compounds (ClF_5, BrF_5, IF_5 and IF_7)

Properties

All are colourless volatile liquids or gases at room temperature.

(i) Fluorinating agent

IF_7 is a stronger fluorinating agent than IF_5.

$IF_7 + H_2O \rightarrow IOF_5 + 2HF$ (Partial fluorination)

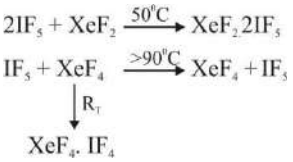
$IF_7 + 4H_2O \rightarrow HIO_4 + 7HF$

$2IF_7 + SiO_2 \rightarrow 2IOF_5 + SiF_4$

(ii) Donor acceptor property

$ClF_5 + A_5F_5 \rightarrow [ClF_4]^+ [AsF_6]^-$

$BrF_5 + 2SbF_5 \rightarrow [BrF_4]^+ [Sb_2F_{11}]^-$



$$2IF_5 + XeF_2 \xrightarrow{50^0C} XeF_2.2IF_5$$

$$IF_5 + XeF_4 \xrightarrow{>90^0C} XeF_4 + IF_5$$

$$IF_5 + XeF_4 \xrightarrow{R_T} XeF_4.\ IF_4$$

$IF_7 + A_5F_5 \rightarrow (IF_6)^+ [A_5F_6]^-$

(iii) As solvent

$IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

$KF + IF_5 \rightarrow KIF_6$

$NOF + IF_5 \rightarrow [NO]^+ [IF_6]^-$

$SbF_5 + IF_5 \rightarrow [IF_4]^+ [SbF_6]^-$

(iv) Reaction with water

Interhalogen compounds of this type react with water to from HF and corresponding halo acids.

$ClF_5 + 2H_2O \rightarrow FClO_2 + 4HF$

$BrF_5 + 3H_2O \rightarrow HBrO_3 + 5HF$

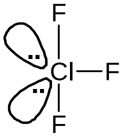
$IF_5 + 3H_2O \rightarrow HIO_3 + 5HF$

$IF_7 + 4H_2O \rightarrow HIO_4 + 7HF$

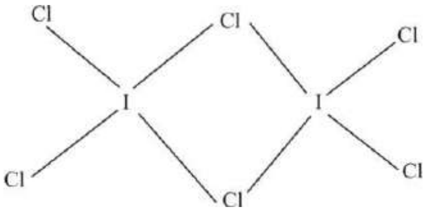
13.6.4. Structure of interhalogen compounds:

i. **AB type:** Linear geometry due to the presence of three lone pair of electrons on central atom.

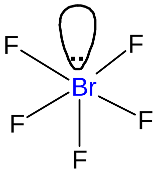
ii. **AB_3 type:** ClF_3 and BrF_3 are T-shaped due to the presence of two lone pair of electrons and the central atom is sp^3d hybridized.



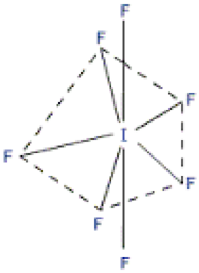
Structure of ICl_3 is entirely different, being comprised of planar I_2Cl_6 separated by normal van der Waals distances between Cl atoms. The terminal ICl distances are similar to those in ICl but bridging I-Cl distances are longer.



iii. **AB_5 type:** Square pyramidal geometry due to the presence of one lone pair electron with central atom. The central atom undergoes sp^3d^2 hybridization.



iv. **AB_7 type:** Example is IF_7, where iodine undergoes sp^3d^3 hybridization. The geometry of the molecule is pentagonal bipyramidal with bond angles 72^0 and 90^0.



13.6.5. Applications of interhalogen compounds:

i. ICl (Iodine monochloride) is used in the estimation of iodine number which is a measure of the unsaturation in acids and fats.

ii. Liquid BrF_3 and ClF_3 are used as fluorinating agents.

iii. BrF_5 is used as oxidizer for propellants.

13.7 POLYHALIDES

When halide ions associate with halogens or interhalogen, univalent ions are obtained and are called as polyhalide ions and the compound of these are known as polyhalides.

Examples of polyhalides containing polyhalide anions, are $K^+[Cl_3]^-$, $NH_4[I_5]^-$, $M^+[Cl_2]^-$ ($M^+ = K^+$, Rb^+, NH_4^+).

Examples of polyhalide cations are ICl_2^+, ClF_2^+, BrF_4^+, IF_6^+, BrF_6^+ etc.

Iodine has maximum tendency to form polyhalide ions. Cl, Br and I atoms can form triatomic anions Cl_3^-, Br_3^- and I_3^-. Fluorine atom ion not able to form F_3^- ion as it does not contain d orbitals in the valence shell.

13.7.1 Preparation:

General methods of preparation of polyhalides are:

(i) Polyhalides can be prepared by the action of halogen on metallic halides or another polyhalides.

$Cl_2 + KCl \rightarrow K[Cl_3]$

$Cl_2 + KI \rightarrow K[ICl_2]$

$I_2 + KI \rightarrow K[I_3]$

$2I_2 + NH_4I \rightarrow [NH_4]\, I_4$

The value of n has been found to depend on the amount of I_2 used in the reaction.

(ii) By the action of interhalogen on metals/metallic halides or other polyhaladies.

$4BrF_3 + 3K \rightarrow 3K[BrF_4]$

$16BrF_3 + 6Nb \rightarrow [6BrF_3]^+ [NbF_6]^- + 5Br_2$

$2F_2 + CsCl \rightarrow Cs^+[ClF_4]^-$

$ICl + KCl \rightarrow K^+[ICl_2]^-$

$ICl + KBr \rightarrow K[ICBrCl]$

(iii) Polyhalides can be converted in to the other type by the action of halogens or interhalogen on them.

$K[ICl_2] + Cl_2 \rightarrow K[ICl_4]$

$CsBr_3 + I_2 \rightarrow Cs[IBr_2] + IBr$

13.7.2. General properties:

i. All the polyhalides are coloured compound. The intensity of the compound increase with increased atomic number. Thus the bromo iodides are red while chloro iodides are yellow.

ii. Polyhalide compounds have low melting point.

iii. Polyhalides dissolved in liquid of high dielectric constant like water, acetone, alcohols etc.

13.7.3. Chemical properties:

i. These are ionic in nature. They tend to decompose on heating.

$$CsI_3 \xrightarrow{\text{Heal}} CsI_3 + I_2$$

$$RbICl_2 \xrightarrow{D} RbCl + ICl$$

ii. The polyhalides having ICl_4^- anion dissociate in aqueous solution to metal chlorides and ICl_3. The latter than hydrolyze to iodine and IO_3^-

$$M^+[ICl_4]^- \rightarrow MCl + ICl_3$$

$$5ICl_3 + 9H_2O \rightarrow 3HIO_3 + 15HCl + I_2$$

$$M^+[ICl_4] + 9H_2O \rightarrow 5MCl + 3HIO_3 + 15HCl + I_2$$

iii. **Formation of complexes:** Some of the polyhalides ions are able to form complexes with organic donor molecules. Some examples of such complex are LiI_3, $4C_6H_5CN$, MI_3. $3C_6HSCN$ (M = Na and K)

iv. **Replacement (substitution) properties**: Halogen in the polyhalides may be replaced by a more electronegative atom but the central metal is not replaceable. Chlorine cannot replace central iodine atom in IBr_2^- but replace bromine in IBr_2 to yield ICl_2^-

$$IBr_2^- + Cl_2 \rightarrow ICl_2^- + Br_2$$

- **Action of halogens:** A halogen may be directly added to the polyhalides. This behaviour is not exhibited by interhalogen compounds.

$$ICl_2^- + Cl_2 \rightarrow ICl_4^-$$

Structure and shapes of trihalide anions

Examples ICl_2^-, I_3^- IBr_2^-, IBF etc.

(i) Structure of ICl_2^-

This type of ion has symmetrical linear shape with sp^3d hybridization on Iodine atoms. Iodine atom can be considered as having eight electrons instead of seven electrons in the valence shell. In ICl_2^-, I atom is surrounded by two σ bond pair (bp) of electrons and the rest six electrons remain as three lone pair (lp) of electrons on Iodine atom 2bps + 3lps = 2 + 3 = 5 orbitals are sp^3d hybridized in ICl_2^- as shown below.

Ground state in I atom

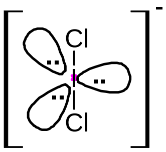
$^{53}I = 5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1,\ 5d^0$

Iodine atom gains $1e^-$

$5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d^1$ (sp^3d hybridization)

Liner shape of ICl_2^- ion with three blone pairs on a plane

(ii) Structure and shape of I_3^- ion is similar to that of ICl_2^- ion. I_3^- ion is also having liner shape as shown below.



13.8 BASIC PROPERTIES OF HALOGENS

In the periodic table, metallic or basic properties of elements increase on descending in a group and decrease in a period. In the group 4th, 5th, and 6thA, the first elements (C, N, O) are non metals where as the heavier members (Pb, Bi and Po) are metals. Similarly, one can expect the same trend for group 7thA. In 7thA group (that is 17th group);

i. Flourine is the most electronegative element of the periodic table and hence possessing no basic or metallic properties.
ii. Chlorine shows a slight basic character.
iii. Bromine shows comparatively high basic properties in its complexes.
iv. Iodine shows the highest basic character i.e. the tendency of iodine atom to form cation is easier.
v. Unfortunately, there is no evidence which may prove the basic character of astatine.

The basic character of I_2 is well established and a large number of compounds contain basic iodine.

13.8.1. Reasons for basic properties of iodine:

i. The electronegative character in halogens decreases from fluorine to iodine. Iodine is the least electronegative and exhibits electropositive character.

$F < Cl < Br < I$ (order of electropositive character)

ii. Low electronegativity

iii. Decrease in ionization potential. Iodine can remove electron easily to give positive iodine due to its lowest ionization potential.

iv. Size of the atoms increase from fluorine to iodine. Iodine has biggest size amongst active halogens.

$F < Cl < Br < I$ order of size

v. Ionic radii values from fluorine to iodine also increase. Therefore, the electrons loose easily to form unipositive I^+ ion or tripositive I^{3+}.

13.8.2. Evidence for I^+:

i. When the compound like ICl, IBr, ICN, INO and I_2SO_4 in their molten state or as their aqueous solutions are electrolyzed, iodine is liberated at cathode. The liberation of iodine at cathode proves the existence of cationic iodine in these compounds.

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$
$$ICN \rightleftharpoons I^+ + CN^-$$

ii. ICl acts as a strong electrophilic iodinating agent and converts salicylic acid into 3,5-di iodosalicylic acid.

iii. When I_2 dissolved in H_2O, a variety of reactions take place.

$$I_2 + 2H_2O \rightarrow [I(H_2O)]^+ + I^-$$

$$[I(H_2O)]^+ + H_2O \rightarrow [I(OH)]^0 + H_3O^+$$

13.8.3. Evidence for I_3^+:

i. Molten ICl_3 conduct electricity, liberating iodine and chlorine at both the electrodes. Thus, its ionization is probably as:

$$2ICl_3 \rightarrow ICl_2^+ + ICl_4^-$$

ii. If iodine is oxidized by fuming nitric acid in acetic anhydride, $I(CH_3COO)_3$ is obtained. It this is electrolyzed using silver electrodes, one equivalent of AgI is liberated at the cathode for the passage of 3 Faradays of electricity.

$$\mathrm{I\,(acetate)_3} \gtrsim \mathrm{I_3^+} + 3\,\mathrm{(acetate)}$$

iii. When iodine is dissolved in olium, I_3^+ ion is formed. If the olium is concentrated, I^- is formed.

iv. Aubke (1995) spectroscopically confirmed the existences of I^{+3} ion by the reaction of iodine with HSO_3F.

13.9 ANOMALOUS NATURE OF FLUORINE

Fluorine shows different behaviour with other elements of the group due to the following reasons.

(i) Small size
(ii) Lowest electronegativity
(iii) Low bond dissociation energy
(iv) Absence of d-orbitals in the valence shell

Low dissociation energy of fluorine is due to non-bonding electron repulsion and due to the small size (causes high electronegativity), it forms ionic bond easily as compared to the other elements. Consequently, ionic fluorides have larger negative free energies and enthalpies of formation.

The main differences between fluorine and other members are:

i. Fluorine is the most reactive element among all the halogens because of lower bond dissociation energy (F_2 =158; Cl_2 = 243; Br = 192 and I_2 = 151 KJ mol^{-1})

ii. Fluorine shows only one oxidation state i.e. –1 due to the highest electronegativity and due to the absence of d-orbitals in valence shell, does not show positive oxidation states. While, the other halogens can show positive oxidation states (+1, +3, +5 and +7).

iii. Its hydride shows strong hydrogen bonding due to its smallest size and high electronegativity.

iv. Due to the highest strength of H–F bond, HF is the weakest acid among all the halogen acids.

v. HF is liquid while the other halogen acids are gases at room temperature.

vi. Fluorides have the maximum ionic character. Other halides are covalent in nature.

vii. HF forms acid salts of the type KHF_2 due to the presence of H-bonding. On the other hand, HCl, HBr and HI do not form such salts.

viii. Fluorine has the highest positive reduction electrode potential among halogens. Hence, it is the strongest oxidizing agent.

ix. As HF reacts with silicates to form fluorosilicates, it cannot be stored in glass bottles.

$$Na_2SiO_3 + 6HF \rightarrow Na_2SiF_6 + 3H_2O$$

The other acids can be stored in glass bottles because they do not react with silicates.

i. Due to its ionic behaviour, AgF is soluble in water while AgCl, AgBr and AgI are insoluble in water. In contrast, CaF_2 is insoluble while $CaCl_2$, $CaBr_2$ and CaI_2 are soluble in water.

ii. Fluorine cannot form polyhalide ions due to the absence of d-orbitals in their valence shell while other halogens can form polyhalide ions.

3.10 SUMMARY

In 17th group of periodic table, five non-metallic elements known as halogens are present. The term ‘halogen’ means ‘salt former’ and thus the compounds of halogens are called ‘salts’. The halogens are diatomic and exist in all three states of matter at room temperature:

Iodine, Astatine are solid; Bromine is liquid; Chlorine and fluorine are gases

There are 7 electrons in the valence shell of all halogens which are responsible for an oxidation number of –1. Except for fluorine, all halogens also have +1, +3, +5 and +7 oxidation states. Due to the highest electronegativity of fluorine, extensive hydrogen bonding in HF molecule occurs. Therefore, HF exists as liquid and has high melting point and boiling point. You have also studied that all halogens are good oxidizing agents and among all halogens, fluorine is the strongest oxidizing agent. All halogens can form hydrogen halides (HX). Among halides, HI is the most acidic in nature. Halogens on reaction with other halogens form interhalogen compounds which are non reactive than elemental halogen except fluorine. Halogen also forms oxides with oxygen. Iodine forms the most stable oxides. Halogens form oxoacids of type HOX, HOX_2, HOX_3 (where X is halogen). Fluorine forms only oxoacid that is HOF.

Polyhalides is the other class of compound synthesized using halogens. Among all halogens, iodine has maximum tendency to form poly halides. Among halogens, iodine shows the most basic metallic character due to the lowest electronegative character.

13.11 TERMINAL QUESTION

13.11.1. State True (T) or False (F)

i. Halogens are present in VIIA / 17th group of the periodic table.
ii. Astatine is metallic in nature.
iii. Atomic number of iodine is 35.
iv. Cl_2 and F_2 are gases due to weak van der Waals forces.
v. The order of m.p. and b.p. of the halogens follow the order: $F_2 < Cl_2 < Br_2 < I_2$
vi. Among halogens, iodine shows some metallic character.
vii. Bond energy of fluorine is less than chlorine and bromine.
viii. Fluorine slowly reacts with hydrogen.
ix. Downwards in the group, the acidic nature of hydrogen halides increases.
x. OF_2 is V-shaped.
xi. In $HClO_2$, chlorine is sp^3 hybridized with one lone pair of electron.
xii. $HClO_4$ is the strongest acid among all oxoacids.
xiii. Chemical formula of para periodic acid is H_5IO_6.
xiv. Interhalogen compounds are chlorofluorinating agents.
xv. ClF_3 and BrF_3 are trigonal planar in shape due to the presence of two lone pair of electrons.
xvi. In ICl_2^-, iodine is sp^3d hybridized.
xvii. Iodine is acidic in nature.
xviii. Fluorine is the strongest oxidizing agent.
xix. Fluorine forms polyhalide ions.

13.11.2. Fill in the blanks.

i. Halogen consists of five elements ………….., …………………, ………………., ………….., ………………..
ii. Flourine is the most electronegative highly reactive and is called as………………
iii. Astatine is a ……………… element and formed artificially.

iv. Electronic configuration of iodine is ……………………………………………….

v. Physical state of F_2 and Cl_2 is …………., Br_2 …………….. and I_2 …………………….

vi. Melting point of halogens increases in order ……………………………………

vii. Halides are mainly of three types: a) …………………….., b) ……………………., c) ………………………….

viii. Stability of halides decrease from HF to …………...

ix. ClO_2 is used in ………………………….., ……………………………. and …………………...

x. …………………………… is a dark red liquid and solidifies at –180ºC.

xi. HClO disproportionate into ……………… and ……………….

xii. Anhydrous acid is obtained by distilling a mixture of ………………………………. with ……………………

xiii. The aqueous solution of …………….. decomposes on heating and gives Br_2 and nascent (O) that acts as a good oxidizing agent.

xiv. ………………. also undergo disproportionation forming I_2 and HIO_3.

xv. ……………….. is obtained by heating para periodic acid (H_5IO_6).

xvi. Paraperiodic acid is ………………..

xvii. Interhalogen compounds are the compounds of more than one …………….

xviii. Interhalogens can be hydrolysed by water or alkali to produce halide ion of the …………… halogen.

xix. ClF_3 and BrF_3 are ………………….. whereas IF_3 and ICl_3 are ……………….

xx. AB_3 type interhalogen compounds are ………….. shaped.

xxi. ………………. is used as oxidizer for propellants.

xxii. ……………………… has maximum tendency to form polyhalide ions.

13.11.3 Long questions

i. What are halogens? Discuss general characteristics and uses of halogens.

ii. Discuss characteristics of hydrogen halides.

iii. Give in detail preparation, properties, uses and structure of oxoacides of chlorine.

iv. Give in detail preparation, properties, uses and structure of oxoacides of bromine.

v. Give in detail preparation, properties, uses and structure of oxoacides of iodine.

vi. What are interhalogen compounds?

vii. Describe, in detail, the polyhalides.

viii. Iodine is basic in nature. Why?

ix. How fluorine is different from other elements of 17th group?

13.12. ANSWERS.

13.12.1. State True (T) or False (F)

i. True (T)
ii. False (F)
iii. False (F)
iv. True (T)
v. True (T)
vi. True (T)
vii. True (T)
viii. False (F)
ix. True (T)
x. True (T)
xi. False (F)
xii. True (T)
xiii. True (T)
xiv. True (T)
xv. False (F)
xvi. True (T)
xvii. False (F)
xviii. True (T)
xix. False (F)

13.12.2. Fill in the blanks:

i. Flourine (F), Chlorine (Cl), bromine (Br), iodine (I) and astatine (At)
ii. Super halogen
iii. Radioactive
iv. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$
v. Gas, liquid, solid

vi. $F_2 < Cl_2 < Br_2 < I_2$
vii. (a) Ionic halides (b) Molecular or covalent halides (c) Bridging halides
viii. HI
ix. Paper industry, bleaching clothes and purification of water
x. Dichorine hexaoxide (Cl_2O_6)
xi. Cl_2, $HClO_3$
xii. Potassium per chlorate ($KClO_4$) with conc. H_2SO_4
xiii. $HBrO_3$
xiv. HOI
xv. HIO_4
xvi. H_5IO_6
xvii. Halogen
xviii. Lighter
xix. Volatile liquid, solids
xx. T
xxi. BrF_5
xxii. Iodine

UNIT 14: CHEMISTRY OF NOBLE GASES

CONTENTS:

14.1 OBJECTIVES

After carefully reading this unit, you will be able to answer the following questions:

- What are noble gases?
- What are inert gases?
- What are the periodic properties of noble gases and how they vary in a periodic table?

- Why among noble gases, only xenon can form a number of compounds?
- What are the uses of noble gase compounds?
- What are the structures of different xenon compounds?

14.2 INTRODUCTION

Noble gases belong to the 18th group (VIIIA) in the periodic table. The noble gases are also called as 'inert gases' or 'rare gases'. Because, these gases are non reactive/unreactive, they are also called as inert or noble gases. Their shells and subshells are completely filled and thus, they have very stable configurations which can be related to their chemical inactivity. The noble gases are also considered as rare gases because they represent not more than 1% of air (<1%). Their electronic configurations are:

Element's symbol	**Atomic Number**	**Name of element**	**Electronic configuration**
He	2	Helium	IS^{2}
Ne	10	Neon	[He] $2s^{2}2p^{6}$
Ar	18	Argon	[Ne] $3s^{2}3p^{6}$
Kr	36	Krypton	[Ar] $3d^{10}4s^{2}4p^{6}$
Xe	54	Xenon	[Kr]$4d^{10}5s^{2}5p^{6}$
Rn	86	Radon	[Xe] $4f^{14}5d^{10}6s^{2}6p^{6}$

Among these gases, except radon (Rn), all exists in the atmosphere. Rn is an element generated through radioactive process and can be produced by the radioactive decay of radium and thorium minerals.

$${}^{226}_{88}\mathrm{Ra} \longrightarrow {}^{222}_{88}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

$^{222}_{88}$Rn is an α ray emitter.

Cavendish in 1784, for the first time separated a mixture of noble gases. Rayleigh in 1894 discovered argon and it was the first among the noble gases to be discovered. Neon, krypton and xenon were discovered in 1898 by fractional evaporation of argon under varying reduced pressure conditions. Radon was discovered by Dorn in 1902 as a radioactive disintegration product of radium. The name of noble gases derived from Greek words and\their meaning is:

He: Helios; Neon: New; Argon: Lazy or inert; Krypton: Hidden and Xenon: Stranger

Helium is present in the atmosphere at a concentration of 5ppm, and can be obtained from natural gas deposits. The most abundant noble gas is argon (Ar) (0.9% by volume in air). Argon is produced by electron capture (β decay) of potassium.

$$^{140}_{19}\text{K} + ^{0}_{-1}\text{e} \longrightarrow ^{140}_{18}\text{Ar}$$

Uses of noble gases/inert elements

As helium has the lowest boiling point (–269ºC) among noble gases, it is used as cooling gas in nuclear reactor and also as a carrier gas in gas-liquid chromatography. It is also used in cryoscopy. Helium is also preferable over hydrogen in airship due to inflammable nature of hydrogen. Helium is also preferably used to dilute oxygen in gas cylinders in place of nitrogen for divers. This is because helium is slightly soluble in blood while nitrogen gas is more soluble in blood at high pressure and causes painful condition in patients (nitrogen narcosis). Noble gases including neon are used in discharge tubes to give different colours (Ne gives orange colour in discharge tubes). Argon (Ar) is used in welding stainless steel, metallurgical processes of aluminum, magnesium and titanium. Argon is also used in electric bulbs, fluorescent lamps etc. Radon is used in the cancer treatment due to its radioactive nature.

14.3 GENERAL CHARACTERISTICS AND USES

At ordinary temperature and pressure, all noble gas elements are monoatomic gases except Radon. They are chemically inert but under certain conditions, they can form complexes. These gases are cololurless, odourless and tasteless. The other general properties are explained below:

(a) Atomic Radü:

Their atomic radii are very large because the radii are van der Waal or non-bonded radii. Atomic radii of elements increase from top to bottom in a group.

(b) Melting point (M.P.) and boiling point (B.P.):

Melting and boiling points of noble gases are very low because inter atomic forces are very weak in these gases.

(c) Electron affinity:

Due to completely filled electronic configuration, the electron affinity of these gases is zero.

(d) Enthalpy of vaporization:

Enthalpy of vaporization is very low because the forces between the atoms are very weak forces i.e. van der Waals forces.

(e) Ionisation energy:

Their ionisation energy is very high because they have very little tendency to accept or loose electrons.

Physical Properties:

Adsorption:

All noble gases can be adsorbed on charcoal (wood) at low temperature and the order of their adsorption is:

He < Ne < Ar < Kr < Xe

Diffusion:

All noble gases have a tendency to diffuse through glass, plastic and rubber materials. Therefore, it became difficult to work with them in the laboratory. The order of diffusion depends upon their size (gas with small size diffuse easily) which is as follows:

He > Ne > Ar > Kr > Xe

Electrical conductivity:

All noble gases have high electrical conductivity at low pressure and thus, can produce characteristic coloured light during electric discharge at low pressure.

Liquification:

Due to the van der Waal forces (weak forces), they can be easily liquefied. The liquefaction depends upon their atomic size (larger the size, more easily liquefiable gas). The order of ease of liquefaction of noble gases is

He < Ne < Ar < Kr < Xe

Solubility behavior:

All noble gases are less or sparingly soluble in water. The solubility is due to dipole-induced dipole interaction and increases from top to bottom with increase of the size of the atom. Therefore, the increasing order of their solubility is:

He < Ne < Ar < Kr < Xe

Abnormal behaviour of helium:

Among noble gases, helium shows abnormal behaviour. It has some different properties from other group members. Helium gas on cooling below (-)269^{0}C changes to liquid (He-I). He-I on further cooling at (-)271^{0}C and at 1 atmospheric pressure changes to a liquid (He-II) which has high thermal conductivity. Helium can be obtained in solid form under high pressure (about 25 atmospheric). While all the other noble gases solidify on cooling. He-II has a tendency to flow upwards. It acts as super-fluid.

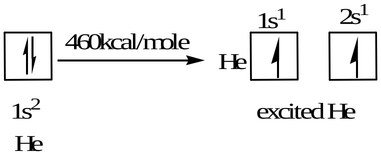
Chemical properties:

The atoms of inert gases have completely filled shells and, therefore, they are chemically inert. Under certain specified conditions, they combine and form some rare compounds.

14.4 COMPOUNDS OF NOBLE GASES

14.4.1 Compounds formation under excited state conditions (Helides)

These type of compounds are formed by helium. At low pressure, in the presence of mercury, tungsten etc., helium forms $HgHe_2$, $HgHe_{10}$ and WHe_2. One electron from1s orbital of He excite and go to 2s orbital. This excitation costs about 460 kcal/mole energy.



These compounds are called helides which can survive only for a moment and can be detected spectroscopically.

14.4.2 Compounds formation through coordination:

Noble gases have electron pairs in their valence orbitals. In the presence of strong electron deficient groups, noble gas compounds can be prepared through coordination (electron pairs of noble gases donated to empty orbitals of electron deficient groups). Among noble gases, argon (Ar) forms a number of unstable compounds of the type Ar.xBF_3 (X = 1, 2, 3, 4, 6, 8, 16), which can be easily dissociated at their M.P. (Figure 14.1).

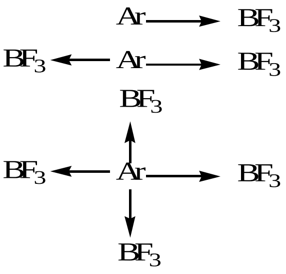


Figure 14.1. Different types of compounds formed through coordination

14.4.3 Compounds formation through dipole induced dipole interactions (Formation of hydrates):

The inert gases such as Ar, Kr and Xe can form compounds with water through dipole induced dipole interactions at low temperature and high pressure. These compounds are known as hydrates.

$Ar.6H_2O$.; $Kr.6H_2O$; $Xe.6H_2O$

14.4.4 Compounds formation through physical trapping (Clathrate compound):

The inert gases such as Ar, Kr and Xe can form solid compounds with certain organic molecules such as phenol and hydroquinone under a pressure of 10-40 atmosphere. In these compounds, the noble gases (Ar/Kr/Xe) are trapped into the crystal lattices or cavities formed by the organic molecules (Figure 14.2). The organic substances that form the cavities are called the host while the atom of noble gases entrapped or enclosed in it, is called the guest. Thus, it is also called as a guest host interaction.

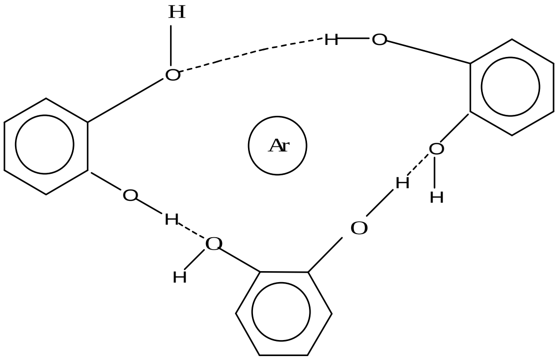


Figure 14.2. Clathrate compound of 1, 2 dihydroxy benzene and argon

In these compounds, the guest components are held together by van der Waals forces. Hence, there is no chemical bonding (only weak interactions) involved in these compounds. This is a kind of physical interaction. It is not necessary that all the cavities in the host lattice are filled. Thus, the clathrates are also called as non-stoichiometric compounds. These weak interactions can easily be broken and guest inert gas atom can escape from the host by simple heating the crystal or by dissolving them in a suitable solvent such as alcohol.

For example, clathrates can be prepared by crystallization of an aqueous solution of quinol (1,4-dihydroxybenzene) with Ar, Kr or Xe under a pressure of 10-40 atmosphere (quinol forms cavities with a diameter of about 4Å in which the inert gas atoms trapped).

The smaller noble gases like He and Ne do not have tendency to form clathrate compounds because they are too small to fit in the cavities and can easily escape from the cavities. Synthetic zeolites can also form cavities in which heavier noble gas elements can fit easily. Clathrates are very useful category of compounds because they can store radioactive Kr and Xe produced in nuclear reactors.

14.5 COMPOUNDS OF XENON

(a) Preparation:

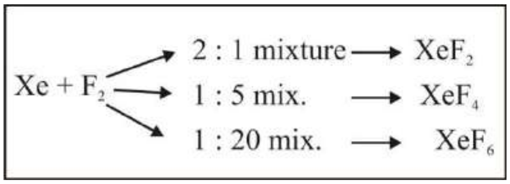
The first noble gas compound; $Xe[PtF_6]$ was prepared in 1962 by the reaction of PtF_6 with Xe in equal ratio at room temperature.

$$\underset{\text{(deep red)}}{PtF_6} + Xe \longrightarrow Xe[PtF_6]$$

$$Xe[PtF_6] + PtF_6 \xrightarrow{25^{\circ}C} [XeF]^+ [PtF_6]^-$$

$$[[XeF]^+ [PtF_6]^- + PtF_6 \xrightarrow{60^{\circ}C} [XeF]^+ [Pt_2F_{11}]^-$$

Xenon reacts directly only with F_2 to form xenon complexes. However, oxygen compounds can be prepared from the xenon fluorides. Xenon reacts directly with fluorine at 400ºC in a sealed nickel vessel, and the final products depend on the Xe/F ratio.



(b) Properties:

The compounds XeF_2, XeF_4 and XeF_6 are all white solids. They sublime at room temperature, and can be stored in nickel containers for a long time. The higher fluorides can be prepared from lower fluorides by heating with F_2 under pressure.

(i) All the xenon fluorides are strong oxidizing agents. On reaction with hydrogen, they reduce themselves to Xe.

$$XeF_2 + H_2 \rightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \rightarrow 4HF + Xe$$

$$XeF_6 + 3H_2 \rightarrow 6HF + Xe$$

In similar manner, they oxidize I^- to I_2, Cl^- to Cl_2 and Ce^{3+} to Ce^{4+} and reduce themselves to Xe.

$$XeF_2 + 2HCl \rightarrow 2HF + Xe + Cl_2$$

$$XeF_4 + 4\,KI \rightarrow 4KF + Xe + 2I_2$$

$$SO_4^{2-} + XeF_2 + Ce_2^{III}(SO_4)_3 \rightarrow 2Ce^{IV}(SO_4)_2 + Xe + F_2$$

(ii) All the xenon fluorides are strong fluorinating agents. They fluorinate the other elements.

$$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_6$$

$$XeF_4 + Pt \rightarrow Xe + PtF_4$$

In the above reactions, XeF_4 is fluorinating sulphur and platinum.

(iii) In organic synthesis

XeF_2 is commercially used in synthetic organic chemistry. It does not react with alkyl or aryl groups of organometallic compounds but attack / oxidize /fluorinate only the hetero atom in the organometallic compound.

$$CH_3I + XeF_2 \rightarrow CH_3IF_2 + Xe$$

$$C_5H_5I + XeF_2 \rightarrow C_6H_5IF_2 + Xe$$

$$(C_6H_5)_2S + XeF_2 \rightarrow (C_6H_5)_2SF_2 + Xe$$

In the presence of anhydrous HF, its reactivity increased and it may be due to the formation of XeF^+.

$$Pt + 3XeF_2 \xrightarrow{HF} PtF_6 + 3Xe$$

$$Mo\,(CO)_6 + 3XeF_2 \xrightarrow{HF} MoF_6 + 3Xe + 6CO$$

(iv) Reaction with water

All the fluorides have different reactivity with water. XeF_2 reacts slowly with water and reduce itself to Xe.

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

While XeF_4 violently reacts with water and form XeO_3.

$$3XeF_4 + 6H_2O \rightarrow 2Xe + 12HF + XeO_3 + 3/2O_2$$

XeF_6 also reacts with water violently. On reaction with atmospheric moisture, XeF_6 form highly explosive solid XeO_3.

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

XeF_6 on partial hydrolysis form colourless liquid $XeOF_4$.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

(v) Preparation of other Xenon compounds

Xenon trioxide (XeO_3) is an explosive white hydroscopic solid soluble in water. It reacts with XeF_6 and $XeOF_4$ to form $XeOF_4$ and XeO_2F_2, respectively.

$$XeO_3 + 2XeF_6 \rightarrow 3XeOF_4$$

$$XeO_3 + XeOF_4 \rightarrow 2XeO_2F_2$$

XeO_3 forms xenate $[HXeO_4]^-$ and perxenate ions $[XeO_6]^{4-}$ in alkaline solution (pH > 10.5).

$$XeO_3 + NaOH \longrightarrow \underset{\text{Xenate ion}}{Na^+[HXeO_4]^-}$$

$$2[HXeO_4]^- + 2OH^- \longrightarrow \underset{\text{Perxenate ion}}{[XeO6]^{4-}} + Xe + O_2 + 2H_2O$$

Perxenate ions also act as strong oxidizing agents and oxidize HCl to Cl_2, H_2O to O_2 and Mn^{2+} to MnO_4^-. Perxenate ions; $[XeO_6]^{4-}$ form volatile and explosive compound XeO_4 (xenon telraoxide) on reaction with concentrated H_2SO_4.

$$[XeO_6]^{4-} + H_2SO_4 \rightarrow XeO_4$$

(vi) Complex formation

XeF_2, XeF_4 and XeF_6 have tendency to form complexes with BF_3, GeF_4, SnF_4, PF_5, AsF_5, SbF_5, NbF_5, RuF_5, OsF_5, IrF_5 and PtF_5. In these complexes, fluorides act as fluoride donor.

The complexes of XeF_2, XeF_4 and XeF_6 are as follows:

$$XeF_2.\ MF_5 \rightarrow [XeF]^+[MF_6]^-$$

$$XeF_2.\ 2MF_5 \rightarrow [XeF]^+[M_2F_{11}]^-$$

$2XeF_2 . MF_5 \quad \rightarrow \quad [Xe_2F_3]^+ [MF_6]^-$

$XeF_4 . PF_5 \quad \rightarrow \quad [XeF_3]^+ [PF_5]^-$

Similar complexes are formed with AsF_5, SbF_5, BF_3 etc.

14.5 COMPOUNDS OF XENON

Xenon forms a large number of compounds as compared to the other noble gas elements because ionization potential decreases from He to Rn, among these, He, Ne and Ar are inert (due to high ionization potential) and Kr, Xe and Rn are noble. The structure and bonding in different xenon compounds is discussed in this section.

15.5.1 Structure and bonding in Xenon Compounds.

(A) XeF_2

XeF_2 is linear in shape having three lone pairs of electrons. In the atom of xenon, one pair of electrons of p orbital gets unpaired and one electron is promoted to d orbital. Then, central xenon atom undergoes sp^3d hybridization with trigonal bipyramidal orientation of five sp^3d hybrid orbitals. The hybrid orbitals with lone pair of electrons take equatorial position. The remaining two orbitals with single electron in each take axial position and overlap with p orbitals of fluorine atom. Due to the presence of lone pairs on a plane, its geometry appears and is linear. (Figure 14.3).

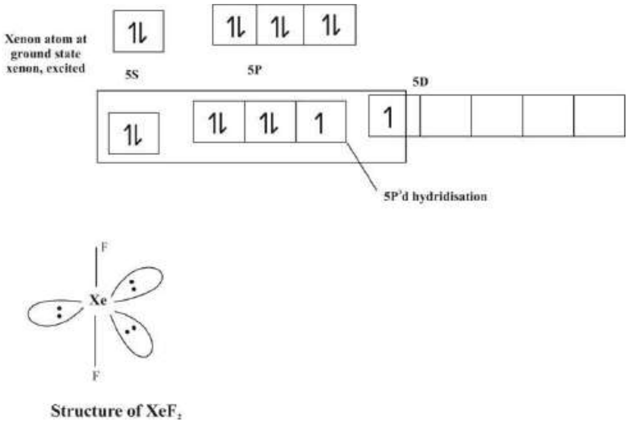


Figure 14.3. Structure of XeF_2

(B) XeF_4

In XeF_4, the central Xe atom is sp^3d^2 hybridized and the six sp^3d^2 orbitals should be present on the 6 corners of octahedral geometry. But due to the presence of two lone pairs of electrons at axial position, its actual geometry becomes square planar (Figure 14.4).

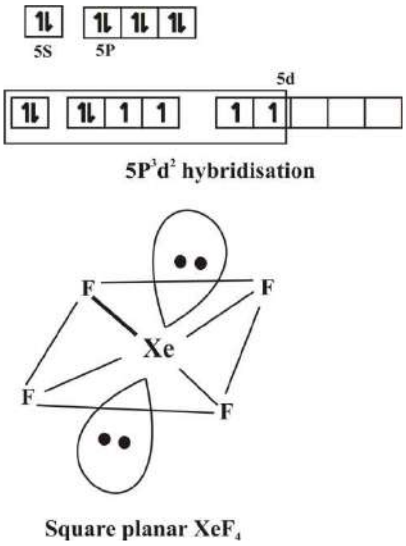
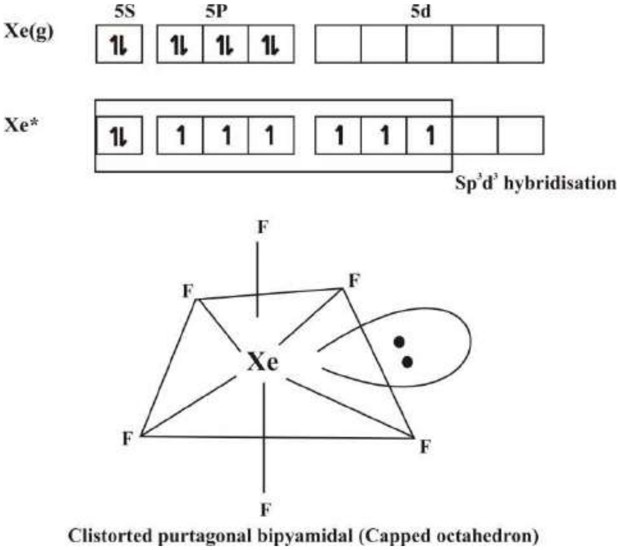


Figure 14.4. Geometry of XeF_4

(C) XeF_6

The central atom (Xe) in XeF_6 is sp^3d^3 hybridized and the geometry should be pentagonal bipyramidal. But due to the presence of one lone pair of electrons, its geometry become distorted pentagonal bipyramidal in which the lone pair of electron pointing through one of the faces of the octahedron (Figure 14.5).



Distorted pentagonal bipyramidal (Capped octahedron)

Figure 14.5. Geometry of XeF_6

(D) XeO_3

In XeO_3, the central atom (Xe) is sp^3 hybridized and due to the presence of one lone pair of electrons, its geometry becomes pyramidal instead of tetrahedral. The thre unpaired electron promoted to d orbitals, form three pπ–dπ bond with three oxygen atoms (Figure 14.6).

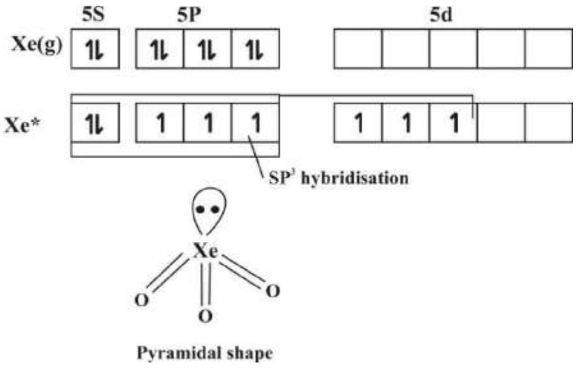


Figure 14.6. Geometry of XeO_3

(E) XeO_4

In XeO_4, the Xe atom is sp^3 hybridized and the geometry is regular tetrahedron. There are only bonded pairs of electrons and no lone pair of electrons present in the structure. All the Xe-O bonds are double bonds (pπ–dπ bonds) in XeO_4 molecule (Figure 14.7).

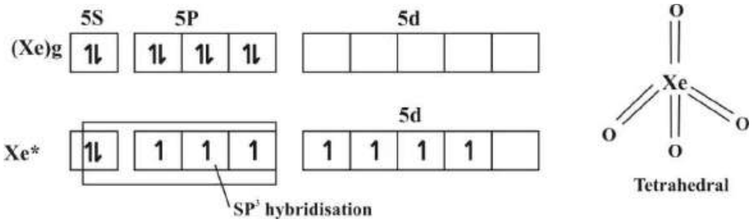


Figure 14.7. Geometry of XeO_4

(F) $XeOF_4$

In $XeOF_4$, Xe atom is sp^3d^2 hybridized and geometry of the molecule should be octahedral. But due to the presence of one lone pair of electrons, its geometry becomes square pyramidal. One Xe–O double bond is pπ–dπ type (Figure 14.8).

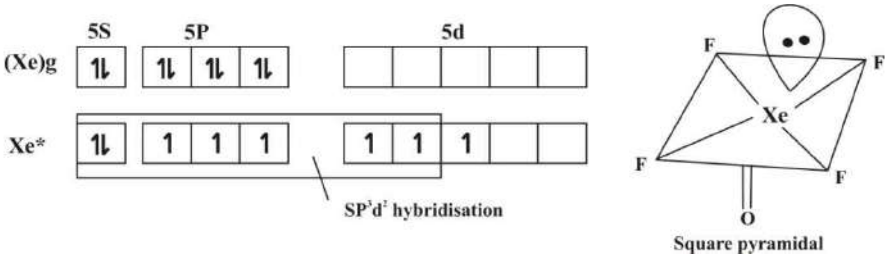


Figure 14.8. Geometry of $XeOF_4$

(G) XeO_2F_2

In XeO_2F_2, the central atom Xe is sp^3d hybridised and due to the presence of one lone pair of electrons at equatorial position, its geometry became butterfly shaped. The two Xe–O double bonds are pπ–dπ type (Figure 14.9).

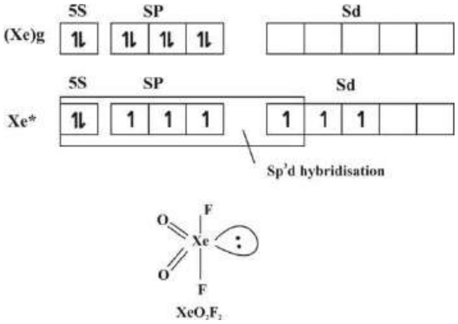


Figure 14.9. Geometry of XeO_2F_2

(H) $[XeO_6]^{4-}$ Perxenate ion

In perxenate ion, the central atom (Xe) is sp^3d^2 hybridized. Hence, the geometry is octahedral. The two Xe–O double bonds are pπ–dπ type (Figure 14.10).

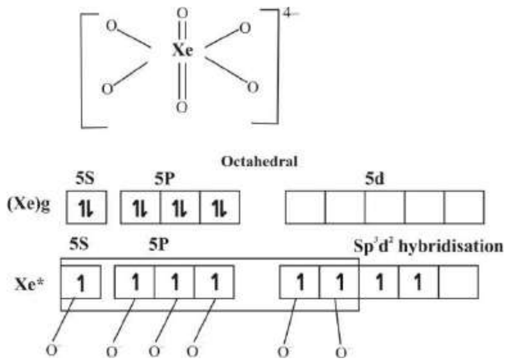


Figure 14.10. Geometry of [XeO$_6$]$^{4-}$

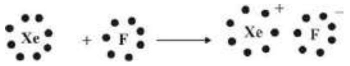
14.5.2 Theories of bonding in xenon compounds:

There are four theories for defining bonding in xenon compounds.

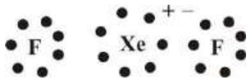
(i) Ionisation potential (IP) based theory (Ionic and covalent bond between Xe and F)

Element	IP (eV)
F	17.4
Xe	12.1

Hence, due to lower ionisation potential of F, it can attract an electron of Xe toward itself and form Xe$^+$F$^-$. Thus first bond is ionic in XeF$_2$.



Now, it become very difficult to attract second electron of Xe$^+$ because second IP of Xe is very high. Hence, the second bond will be covalent bond.



Hence, XeF$_2$ can show the two resonating structures.

F-Xe$^+$-F$^-$ ↔ F$^-$-Xe$^+$-F

(ii) Valence Band Theory (VBT)

According to VBT theory, there are two covalent bonds in XeF$_2$. The structures of oxygen containing xenon compounds can be correctly defined by VBT.

(iii) Molecular Orbital Theory (MOT)

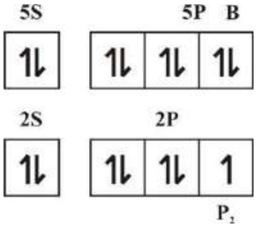
There are some limitations of VB structure for XeF_2. These are:

a) Due to the large size of 5d orbitals, overlapping is very weak.

b) According to valence bond theory, atomic orbitals of same energy can overlap. While in case of 5p and 5d orbitals of Xe, the energy difference is 960 KJ mol^{-1}. Hence, overlapping cannot occur easily.

However, MOT can easily explain polyatomic bonding in XeF_2 molecule. Three atomic orbitals (one of Xe and two of F (2p) orbitals) linearly combine to form three molecular orbitals (MOs).

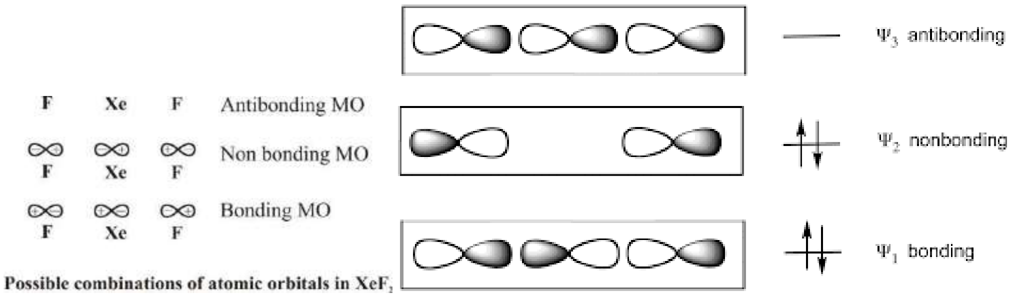
One Bonding MO; One Antibonding MO; One Nonbonding MO



Bonding involves the $2P_z$ orbital of two F atoms and the $5P_z$ orbitals of Xe atom because of bonding to occur, only orbitals with the same symmetry must overlap.

Out of the four electrons, the two electrons occupy bonding molecular orbitals (BMOs), and this pair of electrons is responsible for binding all the three atoms (Xe and 2F). The rest of the two electrons occupy the non-bonding MO (Figure 14.11). Because the non-bonding orbitals have more F character as compound to Xe character, these electrons are situated mainly on the F atoms. This type of bonding is 3-centre, 4-electron σ bonding (3c-4e).

The following linear arrangement of the atoms gives the best agreement with its observed structure.



Possible combinations of atomic orbitals in XeF_2

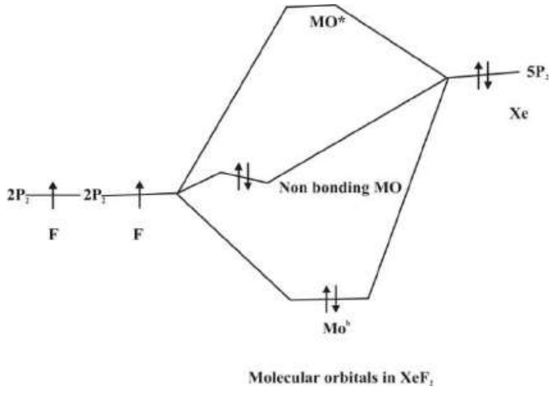


Figure 14.11. Molecular Orbital Diagram of XeF_4

The structure of XeF_4 can be understood in similar way to that of XeF_2. The $5p_x$ orbital of Xe forms a three-centre MO with $2p_z$ orbitals of two F atoms just as in XeF_2. The $4p_y$ orbital of Xe forms another three-centre MO involving the other F atoms. Thus, the two perpendicular three-centre MOs are formed, which give rise to square planar geometry to XeF_4 molecule.The MO theory cannot explain the structure of XeF_6 because, three-centre MO system that are perpendicular to each other would give a regular octahedral geometry. But, the shape of XeF_6 is capped octahedron.

14.6 *SUMMARY*

Now we can summarize that there are six noble gas elements found in group 18 of the periodic table.

i. These include helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) in order of increasing atomic weight.
ii. These elements are also called as inert gases, as they have full filled electronic configuration.
iii. All the noble gas elements are found in minute quantities in the atmosphere except Rn which is radioactive in nature, All the gases are monatomic. The boiling point of He is the lowest 4.2K (-269^0C).
iv. The 1st ionization energy decreases on descending the group and the first ionization energy of xenon is comparable with that of bromine. Hence, xenon can relatively easily forms compounds with oxygen and fluorine. The different compounds formed are XeF_2, XeF_4, XeF_6, XeO_3, $XeOF_2$, $XeOF_4$ etc. Xenon forms compounds with +2, +4, +6 and +8 oxidation states.

v. The Noble Gases have important industrial functions. Helium is used cryoscopy, airship and as carrier gas in Gas Chromatography. Helium-II has very high thermal conductivity (approximately 800 times of copper).

vi. Argon and neon are used in discharge tubes. Argon is used in metallurgical processes as well as welding of stainless steel. Radon is a radioactive element hence, is useful in the treatment of cancer.

vii. The compounds of xenon are also very useful in different areas. Xenon trioxide is about 22 times more powerful explosive as compared to trinitrotoluene.

viii. Clathrates of argon, krypton and xenon are useful in transporting and handling noble gases.

Compounds of Xenon at a glance

Compound	**Total electron pairs**	**Lone pairs**	**Hybridisation on xenon**	**Geometry of complexes**
XeF_2 Xenon difluoride	5	3	sp^3d	Linear
XeF_4 Xenon tetrafluoride	6	2	sp^3d^2	Square planar
XeF_6 Xenon hexafluoride	7	1	sp^3d^3	Capped octahedron or distorted pentagonal bipyramidal
XeO_3 Xenon trioxide	4	1	sp^3	Pyramidal
XeO_4 Xenon tetraoxide	4	NIL	sp^3	Tetrahedral
$XeOF_4$ Xenon	6	1	sp^3d^2	Square pyramidal

oxytetrafluoride				
XeO_2F_2 Xenon dioxydifluoride	5	1	sp^3d	Butterfly
$[XeO6]^{4-}$ Perxenate ion	6	NIL	sp^3d^2	Octahedral

14.7 TERMINAL QUESTIONS

14.7.1. Fill in the blanks:

i. Noble gases belongs to the …………..group in the periodic table.

ii. The noble gases are also called as ……………… or ……………….

iii. Their shells and subshells are ……………….. filled and thus, they have very ……………. configurations which can be related to their chemical inactivity.

iv. The electronic configuration of Xe is [Kr]………………….

v. The atomic number of Ar is ………

vi. The noble gas …………… is radioactive in nature.

vii. Rn is produced by radioactive decay of …………. and ……………. Minerals.

viii. ………………. in 1894 discovered argon.

ix. Radon was discovered by ………… in 1902 as a radioactive disintegration product of radium.

x. Krypton was derived from Greek word …………….

xi. Argon is produced by electron capture (□ decay) of ………………...

xii. ……………. is used as cooling gas in nuclear reactor and also as a carrier gas in gas-liquid chromatography.

xiii. …………….. are used in discharge tubes to give different colours.

xiv. …………….. is used in welding stainless steel, metallurgical processes of aluminum, magnesium and titanium.

xv. ……………. is used in the cancer treatment due to its radioactive nature.

xvi. Their atomic radii are very large because the radii are ……………. or ………….. radii.

xvii. Melting and boiling points of noble gases are very ……. because inter atomic forces are very weak in these gases.

xviii. The electron affinity of inert gases is …………

xix. Enthalpy of vaporization is very ……….. because the forces between the atoms are very weak forces.

xx. The ionization energy of inert gases is very ……….. because they have very little tendency to accept or donate electrons.

xxi. The order of adsorption of noble gases in wood charcoal is ………………………………………

xxii. All noble gases have ………….. electrical conductivity at low pressure.

xxiii. The order of ease of liquefaction of noble gases is ………………………………...

xxiv. The solubility of noble gases is due to ……………………………………………..

xxv. Compounds formation by noble gases under excited state conditions are called …………………………

xxvi. Helides can be formed by …………

xxvii. In the presence of strong electron deficient groups, noble gas compounds can be prepared through ………………..

xxviii. The inert gases such as Ar, Kr and Xe can form compounds with water through dipole induced dipole interactions at low temperature and high pressure. These compounds are known as ……………..

xxix. Compounds formation by noble gases through physical trapping are called as ……………………………………

xxx. Interaction in clathrate compounds is also called as ……………………… interaction.

xxxi. The smaller noble gases like ……… and …………… do not have tendency to form clathrate compounds because they are too small to fit in the cavities and can easily escape from the cavities.

xxxii. Clathrates store radioactive …………. and ………….. produced in nuclear reactors.

xxxiii. The first noble gas compound; ……………….. was prepared in 1962 by the reaction of PtF_6 with Xe in equal ratio at room temperature.

xxxiv. The compounds XeF_2, XeF_4 and XeF_6 sublime at room temperature, and can be stored in ………… containers for a long time.

xxxv. $SO_4^{2-} + XeF_2 + Ce_2^{III}(SO_4)_3 \rightarrow$ ……………………… $+ Xe + F_2$

xxxvi. $XeF_6 + 3H_2 \rightarrow 6HF$ + …………….

xxxvii. $XeF_2 + 2HCl \rightarrow 2HF + Xe$ + …………..

xxxviii. …………… + $Pt \rightarrow Xe + PtF_4$

xxxix. $(C_6H_5)_2S + XeF_2 \rightarrow$ ……………….. + Xe

xl. On reaction with atmospheric moisture, XeF_6 form highly explosive solid ……………………….

xli. XeF_6 on partial hydrolysis form colourless liquid ……………………..

xlii. $XeO_3 + XeOF_4 \rightarrow$ ………………………..

xliii. Perxenate ion is …………………….

xliv. Xenate ion is ………………..

xlv. Perxenate ions; $[XeO_6]^{4-}$ form volatile and explosive compound …………………………… on reaction with concentrated H_2SO_4.

xlvi. XeF_2 is ……………. in shape having ………… lone pairs of electrons.

xlvii. In XeF_4, the central Xe atom is ……………….. hybridized.

xlviii. The central atom (Xe) in XeF_6 is ……………… hybridized and the geometry is ………………..

xlix. In XeO_3, the central atom (Xe) is …………… hybridized and due to the presence of one lone pair of e^-, its geometry became ……………. There are ……………….. $p\pi$–$d\pi$ bonds in XeO_3 molecule.

l. In XeO_4, the Xe atom is ………. hybridized and the geometry is ………………………

li. In $XeOF_4$, Xe atom is ……………. hybridized.

lii. In XeO_2F_2, the central atom Xe is …………….. hybridized and due to the presence of one lone pair of e^- at equatorial position, its geometry became …………………. shaped.

liii. In perxenate ion, the central atom (Xe) is ……………. hybridized. Hence, the geometry is …………………..

14.7.2 State True (T) or False (F):

i. Noble gases belong to the group 18 (VIIIa) in the periodic table.

ii. The noble gases are reactive, hence, they are also called as inert or noble gases.

iii. The electronic configuration of Rn is [Kr] $4f^{14}5d^{10}6s^26p^6$.

iv. Neon, krypton and xenon were discovered in 1898 by fractional evaporation of argon under varying reduced pressure conditions.

v. Hydrogen is also preferable over helium in airship due to inflammable nature of helium.
vi. Xenon is used in the cancer treatment due to its radioactive nature.
vii. Atomic radii of noble gas elements increase from top to bottom in a group.
viii. Electron affinity of noble gases is one.
ix. Due to the van der Waal forces (weak forces), noble gases can be easily liquefiable.
x. The solubility of noble gases increases from top to bottom with increase of the size of the atom.
xi. He-II acts as super-fluid.
xii. $HgHe_2$, $HgHe_{10}$ and WHe_2 are helides.
xiii. In $Ar \rightarrow BF_3$, BF_3 is an electron deficient compound.
xiv. Formation of $Kr.6H_2O$ compound takes place through dipole induced dipole interaction.
xv. 1,2 Dihydroxy benzene form complex with argon through coordination.
xvi. Synthetic zeolites can also form cavities in which heavier noble gas elements can fit easily.
xvii. XeF_4 is prepared by reaction of two part of Xe and one part of F_2.
xviii. Xenon fluorides act as fluorinating agents.
xix. XeF_4 violently reacts with water to form XeO_4.
xx. Formula of perxenate ion is $[XeO_6]^{4-}$.
xxi. XeF_2. MF_5 and $[XeF]^+[MF_6]^-$ are the same.
xxii. In XeF_2. $2MF_5$, XeF_2 acts as fluoride donor.
xxiii. Hybridization on Xe in XeF_2 is sp type
xxiv. XeF_4 is tetrahedral in shape.
xxv. The shape of XeO_3 is trigonal planar.
xxvi. There are three pπ-dπ bonds in XeO_2F_2.

14.7.3 Answer the following questions:

i. Why the noble gases also called as inert and rare gases?
ii. Write down the electronic configuration of each noble gas.
iii. Show the reaction through which Rn prepared.
iv. In brief, note the uses of noble gases.
v. Write a note on the general characteristics of noble gases.
vi. How diffusion vary among noble gases?
vii. Define solubility behaviour of noble gases.
viii. How helium shows abnormal behaviour among noble gases?
ix. What are the different types of compounds prepared by noble gases?

x. Write short notes on

a. Host guest interactions

b. Structure of XeF_2 on the basis of VBT

c. Preparation of XeO_3

d. Reaction of xenon fluorides with hydrogen

e. Use of xenon compounds in organic synthesis

f. Structure of xenate ion

xi. Explain the structure of XeF_4, XeO_2F_2 and $XeOF_4$ on the basis of VBT.

xii. Describe ionization potential base theory for defining bonding in xenon compounds.

xiii. Use MOT to explain the structure of XeF_2.

14.8 ANSWERS

14.8.1 Fill in the blanks:

i. Group 18 (VIIIA)

ii. inert or rare gases

iii. completely, stable

iv. $4d^{10}5s^{2}5p^{6}$

v. 18

vi. Rn

vii. Radium and thorium minerals

viii. Rayleigh

ix. Dorn

x. Hidden

xi. ${}^{140}_{19}K$

xii. He

xiii. Ne

xiv. Ar

xv. Rn

xvi. van der Waal or non bonded radii.

xvii. low

xviii. zero

xix. low

xx. high
xxi. He < Ne < Ar < Kr < Xe
xxii. high
xxiii. He < Ne < Ar < Kr < Xe
xxiv. dipole induced dipole interaction
xxv. helides
xxvi. argon
xxvii. coordination
xxviii. hydrates
xxix. clathrates
xxx. guest host interaction.
xxxi. He and Ne
xxxii. Kr and Xe
xxxiii. $Xe[PtF_6]$
xxxiv. nickel
xxxv. $2Ce^{IV}(SO_4)_2$
xxxvi. Xe
xxxvii. Cl_2
xxxviii. XeF_4
xxxix. $(C_6H_5)_2SF_2$
xl. XeO_3
xli. $XeOF_4$
xlii. $2XeO_2F_2$
xliii. $[XeO_6]^{4-}$
xliv. $[HXeO_4]^-$
xlv. XeO_4.
xlvi. linear, three
xlvii. sp^3d^2
xlviii. sp^3d^3
xlix. sp^3, pyramidal, 3
l. sp^3, tetrahedral
li. sp^3d^2
lii. sp^3d, butterfly
liii. sp^3d^2, octahedral

14.8.2 State True (T) or False (F):

i. T
ii. F
iii. F
iv. T
v. F
vi. F
vii. T
viii. F
ix. T
x. T
xi. T
xii. T
xiii. T
xiv. T
xv. F
xvi. T
xvii. F
xviii. T
xix. F
xx. T
xxi. T
xxii. T
xxiii. F
xxiv. F
xxv. F
xxvi. F
xxvii.

References:

a. Br. R. Puri, L. R. Sharma and K. C Kalia. *Principles of Inorganic Chemistry*, Milestone Publishers & Distributors, Meerut, 2013.

b. G. S. Sodhi, *Textbook of Inorganic Chemistry*, Viva Books Private Limited, New Delhi, 2013.

c. M. S. Yadav. *Quick Review in Inorganic Chemistry*, Anmol Publications Pvt. Ltd., New Delhi, 2004.

d. P. Mishra, *Advanced Inorganic Chemistry*, Jagdamba Publishing Compan, New Delhi, 2011.

e. R. L. Madan, *Chemistry for degree students, B.Sc. I year*, S. Chand & Company Ltd., New Delhi, 2011.

f. S. Prakash, G. D. Tuli, S. K. Basu, and R. D. Madan. *Advanced Inorganic Chemistry*, Vol. I, S. Chand & Company Ltd., New Delhi, 2007.

g. W. U. Malik, G. D. Tuli, and R. D. Madan. *Selected Topics in Inorganic Chemistry*, S. Chand Publication, Delhi, 2013.

CONTENTS

BLOCK- 1 STRUCTURE OF ATOM AND PERIODIC PROPERTIES

BLOCK-2 CHEMICAL BONDING

BLOCK-3 s-BLOCK ELEMENTS

BLOCK- 4 p- BLOCK ELEMENTS